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Austenitic stainless steels
TAILORING THE MECHANICAL PROPERTIES THROUGH THE CONTROL OF HEAT TREATMENTS IN A PRECIPITATION HARDENING MESTABLE STAINLESS STEEL

Abstract

This research focuses on a complex precipitation (Ni₃(Ti,Al)) hardenable metastable stainless steel. Dual phase (austenite, γ/martensite, α’) and ultrafine grained austenitic microstructures obtained after applying isochronal heat treatments (0.1-10°C/s) to a cold-rolled (CR) metastable stainless steel have been microstructurally and mechanically characterized using different experimental techniques (Optical microscopy, SEM, TEM, magnetic measurements, tensile tests). A wide range of strength (2.1-1.1 GPa) and elongation (3-25%) values have been obtained using sub-size samples (7 mm in gauge length). The scientific aim is the understanding of those microstructural parameters and mechanisms that influence the achievement of ultra-fine microstructures and control or the mechanical behaviour of different complex microstructures in this type of steels. Whereas the industrial aim would be to expand the applicability of this steel and use this scientific knowledge to design steels with optimized microstructures and mechanical properties.

Keywords

Metastable stainless steel, ultrafine grained steel, austenite, martensite, precipitation, TRIP, mechanical testing.

1. Introduction

Precipitation hardening metastable austenitic stainless steel are good candidates for applications requiring corrosion resistance, high strength and ductility. In the annealed state (γ), they exhibit excellent ductility, ideal for forming into complex shapes. The hardening is achieved during the plastic deformation, due to the TRIP effect that induces the transformation into martensite (α’), and subsequent precipitation hardening treatment of nano-intermetallic phases [1,2]. As a means to expand the applicability and improve the mechanical properties of austenitic stainless steels grain refinement of CR materials through controlled annealing has been found to be a key method to develop high strength steels with good ductility [3,4]. In this work a detailed investigation has been carried out to achieved dual phase martensite/austenite (α’/γ) and fully ultrafine austenitic (γ) microstructures and investigate their corresponding mechanical properties. It will be shown that by controlling the processing (heating rate and temperature) applied an initial cold-rolled microstructure a wide range of mechanical properties can be obtained.
2. Materials and Experimental procedure

The base composition of the steel under investigation is Fe-12Cr-9Ni-4Mo-2Cu-1Ti-0.7Al and minor additions of Si and Mn. It has a very low amount of interstitials (C+N<0.01). The steel produced by a Sandvik AB has been received in the formed of cold-rolled thin sheets of 0.45 mm in thickness.

To determine the temperature dependence of the volume fraction of austenite/martensite during continuous heating (1-10 °C/s), selective heat treatments have been performed on samples with dimensions of 12 mm in height and 4 mm in width using the furnace of a high resolution dilatometer Adamel Lhomargy DT1000 (Fig. 1).

Besides, to study the mechanical behaviour of these dual phase partially (α’/γ) or fully (γ) reaustenized microstructures, sub-size samples having a gauge length of 7 mm have been employed. These samples have been heat treated using the furnace of an LK02 dilatometer. The tensile experiments were carried out until fracture in a universal tensile testing machine with a load cell of 10 kN at room temperature and applying a strain rate of $\dot{\varepsilon} = 5 \times 10^{-4} s^{-1}$.

The austenite/martensite volume fractions on heat treated samples and on tensile samples after fracture have been determined by magnetization saturation measurements employing a quantum design MPMS-XL SQUID magnetometer. By measuring the saturation magnetization the austenite volume fraction can be estimated from $f_\gamma = 1 - (M_{sat}/M_{sat}^\alpha)$, with $M_{sat}$ and $M_{sat}^\alpha$ the saturation magnetization of the sample and the saturation magnetization of a fully martensitic microstructure, respectively. The latter value has been estimated in a previous work (146 Am$^2$/Kg) [5].

For the optical and scanning electron microscopy imaging of the microstructure, the transversal section of the samples has been mounted in bakelite and prepared metallographically using standard procedures, finishing with 1 μm diamond paste (for optical) and with a colloidal silica solution (for electron microscopy). The initial microstructure has been revealed chemically using the hot (60 ºC) Lichtenegger-Blöch etching solution [6]. This solution colour etching solution is very sensitive to the etching temperature and time, giving a wide ranges of colours depending on this two etching parameters [7,8]. As it will be shown later, this solution unveils the presence of a chemical banding in the microstructure of this steel; in addition, χ-
phase precipitates [9] have been revealed as white spherical or elongated precipitates. The volume fraction of $\chi$-phase was measured on electron micrographs based on the contrast existing between the particle and matrix and using an image analyser. Two electron microscopes have been employed in this work, a FEG-SEM Hitachi S4800 and a FEG-SEM JEOL JSM 6500F. The chemical banding present in the initial microstructure has been analysed by Electron Probe Microanalysis (EPMA) using a JEOL JXA 8900 M microprobe with a wavelength dispersive spectrometer (WDS). Finally, transmission electron microscopy has been also used to unravel the nature and determine the size of strengthening nanoprecipitates formed during the reaustenization process. In this regard, Discs of 3 mm in diameter were machined from dilatometry specimens by wire erosion and thin foils (30 $\mu$m) were prepared from them by mechanical grinding. Electropolishing was done with a mixture of 10/90 of perchloric and acetic acid solution at RT and 38 V using a twin-jet Struers Tenupol-5. A TEM-JEM 2100 HT operating at 120 kV and a 200 kV high-resolution Philips Tecnai-G2-F20 FEI-TEM were used.

3. Results and discussion

Initial microstructure.

Fig. 2 shows the transversal section of the initial microstructure of a cold-rolled steel sheet. The microstructure has been etched with hot (60 °C) Lichtenegger-Blöch for 6 seconds. In a previous work it was already observed that the microstructure is composed by cold-rolled martensitic microstructure and residual phases (TiN, $\chi$-phae, $\delta$-ferrite and retained austenite) below a volume fraction of 0,02 [6]. The presence of some of these phases has been pinpointed in this optical micrograph by arrows ($\chi$-phase as precipitates of around 1-2 $\mu$m and TiN particles of around 5 $\mu$m). This etching solution reveals the presence of different bands in the rolling direction which may indirectly highlight the presence of inhomogeneities in the microstructure as a result of the solidification + hot-rolling + cold rolling process applied to the steel during its thermo-mechanical processing. In this regard, EPMA measurements have confirmed the presence of chemical inhomogeneities (chemical banding) that would explain the etching contrast unveiled. Fig. 3 shows to EPMA maps corresponding to nickel (Ni) and chromium (Cr) along with a composition line scan extracted from these EPMA maps. The composition in this line scan has been normalized (divided by the nominal value of the steel composition: 9 wt.% and 12 wt.% for Ni and Cr, respectively). The comparison of the optical micrograph and the EMPA maps shows that there seems to be a direct relationship between the bright white/yellow colours and the presence of Ni-rich bands in the microstructure. Besides, although it is not shown in this paper, copper and titanium show a similar segregation behaviour as Ni, which is contrary to the one observed for chromium (the line scan in Figure 3 clearly shows that almost every compositional peak for Ni is accompanied by a drop in the amount of Cr and viceversa). This behaviour has been observed in other commercial metastable austenitic stainless steels [10,11]. The presence of this chemical banding should be taken into account when investigating solid-solid phase transformations in this type of steels, as the thermal/mechanical stability of phases like austenite and martensite will be affected.
**Fig. 2** Transversal section of the initial microstructure of the cold-rolled steel sheet under investigation. The microstructure has been etched with hot (60 °C) Lichtenegger-Blöch for 6 seconds. The presence of some coarse second phase precipitates (TiN and χ-phase precipitates) has been pointed out by arrows.

**Fig. 3** To the left, two EPMA maps for chromium (Cr) and nickel (Ni) along the transversal section of the initial microstructure of the cold-rolled steel sheet. To the right, normalized (with respect to the average values) composition line scan along the transversal section of the steel sheet, for the same elements (Cr in blue and Ni in red). The dash line in the Ni-EMPA map represents the approximate location of the composition line scan.

**Austenite formation**

Fig. 4a shows the variation of the critical transformation temperatures that set the start (A$_S$) and end (A$_F$) of the martensite to austenite phase transformation during continuous isochronal heating, for different rates (0.1-10 °C/s). The areas where austenite and martensite coexist or are present independently have been shaded with different grey colours. As the heating rate is increased, the A$_S$ and A$_F$ temperatures shift to higher values, being the influence slightly more pronounced on the A$_F$ temperature. This behaviour is characteristic of diffusional transformations [12-14]. Fig. 4b shows the temperature evolution of the austenite volume fraction, estimated from magnetization measurements, during heating at three different rates.
(0.1; 1; 10 °C/s). The microstructure never reaches 100 % austenite because second phase precipitates, like the χ-phase, also form in the microstructure during heating. Although some small differences have been observed among heating rates, the transformation behaviour is quite similar for the three of them and it proceeds in two stages. These two transformation steps have been shaded with different grey colours: during the first 90 °C from the start of the transformation, the austenite volume fraction increases very fast up to values of around 0.6-0.7. Subsequently, the transformation proceeds slower and fully transforms 250-300 °C above the AS temperature. This transformation behaviour is a consequence of the chemical banding present in the initial microstructure; during the first 90 °C the transformation takes places in those bands which are rich in Ni and poorer in Cr, because Ni is an austenite stabilizer and would promote the formation of austenite.

![Fig. 4](image)

**Fig. 4** a) Evolution of the critical transformation temperatures that set the start (AS) and end (AF) of the martensite to austenite phase transformation during continuous isochronal heating, for different rates. Three shaded areas differentiate where austenite and martensite coexist or are present independently; b) Temperature evolution of the austenite volume fraction for four different heating rates taking as a reference the AS temperature. Two shaded areas separate regions where different transformation rates have been observed. The solid and dash lines have been drawn as a guide to the eye.

Fig. 5a shows a scanning electron image of the microstructure after heating at 0.1 °C/s, 40 °C above the AS temperature. At this temperature, an austenite volume fraction of around 0.1 has been formed. The presence of some coarse χ-phase precipitates (spherical/ellipsoidal coarse white phase) has been marked using arrows. These precipitates were already present in the initial cold-rolled microstructure and form during the process of casting and rolling. The austenite nuclei also appear in this image as white sub-micrometer size phases, but smaller than χ-phase precipitates. Due to the chemical banding, the austenite grains start nucleating in Ni-rich bands (it is evident from this image that the nuclei distribute along bands in the microstructure). The presence of some these austenite nuclei has been highlighted with arrows. In Fig. 5c a TEM bright field image accompanied by the selective area diffraction pattern of an austenite grain and the corresponding dark field image of the austenite, after heating at 0.1 °C/s to 650 °C, is shown. At this temperature, the microstructure is full of nanometer sized Ni₃(Ti,Al) precipitates that increase significantly the initial hardness of the martensite from 425 to above 575-625 Hv depending on the processing conditions [15, 16]. The presence of one of these precipitates and forest unrecovered dislocations in the martensite have been pinpointed and labelled (several additional precipitates are also visible in this image).
As the transformation goes on, the remaining untransformed martensite is richer in Cr; these regions are thermodynamically more stable and require higher temperatures to transform to austenite reason why the transformation extends to high temperatures until full austenitization is complete. Fig. 5b provides a scanning electron image of the microstructure close to full transformation (austenite volume fraction ~0.80). In this microstructure coarse spherical $\chi$-phase precipitates are present together with finer precipitates that have been formed during heating. These precipitates are a bit brighter that the austenite grains which appear as the light grey phase, with martensite being the darker matrix.

![Fig. 5a-b Scanning electron micrographs of the microstructures after heating at 0.1 °C/s up to two different austenization temperatures within the $A_S$ – $A_F$ phase field. In a)-b) the presence of $\chi$-phase has been highlighted with arrows. In a), examples of nuclei forming in the microstructure has been also pinpointed with arrows. In c) a TEM bright field image accompanied by the selective area diffraction pattern (SADP) of an austenite grain and the corresponding dark field image of the austenite, after heating at 0.1 °C/s to 650 °C, is shown. In this microstructure, the presence of $\text{Ni}_3(\text{Ti, Al})$ precipitates and forest dislocations in the martensite have been pinpointed and labelled.](image)

After the full austenitization of the initial martensitic microstructure, the austenite grain size is very small and remains in the sub-micrometer scale. Table 1 provides the austenite grain size (along with the standard deviation) measured using TEM images and EBSD maps as reported in previous paper [16]. As it would be expected, the lower the heating rate, the larger the average austenite grain is, as the austenite grains have more heating time to grow at slow
rates. It is interesting to note that even after increasing the heating rate two orders of magnitude from 0.1 to 10 °C/s, the austenite grain size does not grow much. This is partially due to the pinning effect subjected by the finer \(\chi\)-phase precipitates formed during heating. The volume fraction of this phase, measured on SEM micrographs, after heating to the As temperature is around 0.10 and 0.04 after heating at 0.1 and 10 °C/s to As, respectively. In addition, the strengthening Ni\(_3\)(Al,Ti) that form in the martensite during heating dissolve completely around 100 °C above the As temperature at which the austenite volume fraction is above 0.6-0.7. Thus, these latter precipitates would have a weaker effect if any.

**Table 1. Average austenite grain size at the As temperature after full austenitization [Mater Char 2016].**

<table>
<thead>
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<th>HR, °C/s</th>
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<tr>
<td>Grain size ((\gamma)), nm</td>
<td>440±240</td>
<td>430±260</td>
<td>360±200</td>
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</table>

**Mechanical behaviour: austenite stability and strengthening/ductility mechanisms.**

Fig. 6 shows the temperature evolution of the yield strength (\(R_{p0.2}\)), tensile strength (\(R_m\)), uniform elongation (\(\varepsilon_u\)) and total elongation (\(\varepsilon_t\)) estimated from engineering stress – engineering plastic strain plots obtained after performing tensile tests on partially (\(a'/\gamma\)) and fully (\(\gamma\)) reaustenitized sub-size samples for two different heating rates (0.1 and 10 °C). The As temperature has been taken as a reference for the origin of the heating temperature in the x-axis, similarly as in Fig. 4b.

![Fig. 6](image)

**Fig. 6** Temperature evolution of the yield strength (\(R_{p0.2}\)), tensile strength (\(R_m\)), uniform elongation (\(\varepsilon_u\)) and total elongation (\(\varepsilon_t\)) estimated from Fig. 6. The triangles represent the values obtained for the initial cold-rolled microstructure. The solid and dash lines have been drawn as a guide to the eye.

These results show that, initially, after heating above As, the strength increases significantly, being higher for 0.1 °C/s. This is due to the formation of strengthening nanoprecipitates of the type Ni\(_3\)(Ti,Al) in the martensite. The lower the heating rate, the larger the volume fraction of these precipitates in the microstructures and the higher the strength is. These precipitates grow along preferred directions, with their axial length parallel to the
<011> direction and may increase the strength of precipitation hardening steels significantly by applying ageing treatments between 300 and 600 °C [17]. The average equivalent circular diameter of these elongated precipitates, formed after heating to 650 °C at 0,1 °C/s (Fig.5c), has been estimated to be around 20±5 nm and remains fairly stable during the process of austenite formation until their spheroidization and dissolution when the austenite volume fraction reaches values around 0.7. Further continuous heating towards the A_F temperature decreases the strength and increases the elongation of the samples due to the recovery of the cold-rolled martensitic microstructure and to the increase in the volume fraction of the softer austenite phase. It is interesting to note that around 100-150 °C above the A_S, the tensile strength and the uniform/total elongation reach similar values regardless of the heating rate applied. From this point on, further heating decreases the tensile strength linearly and increases the uniform/total elongation also linearly. Besides, the yield strength drops significantly during these first 100-150 °C above A_S temperature and remains fairly constant upon further heating.

Thus, two different mechanical behaviours can be differentiated above and below A_S+100 °C. Below this temperature the mechanical behaviour of the microstructure is determined by the martensite phase and the amount of precipitation of intermetallic phases, Ni3(Ti,Al), in the microstructure, which depends on the heating rate. The decrease in strength and increase in ductility is influenced by the amount of retained austenite transformed and the recovery of the martensite matrix (which less pronounced for the lowest the heating rates because the microstructure contains a greater density of pinning precipitates). Above the threshold temperature (A_S+100 °C), the mechanical behaviour is mainly determined by the austenitic matrix which reaches a volume fraction of around 0.6-0.7 and becomes fairly independent of the heating rate. The yield strength is mainly determined by the average austenite grain size and, to a lesser extent, by the precipitation of the fine γ-phase precipitates. The tensile strength and the uniform/total elongation depends on the stability of the austenite and its transformation to martensite during straining (so-called TRIP effect), in addition to the remaining untransformed volume fraction of martensite which was present in the initial microstructure. The positive contribution to the tensile strength by the martensite that was present in the initial microstructure and which amount is reduced during heating is not compensated by the amount formed during TRIP resulting in a decrease of the tensile strength. The results in Fig. 6 show that the best combination of mechanical properties is obtained for a dual phase microstructure composed of an austenite volume fraction of around 0.7, which is achieved after heating at 0.1 °C/s, to around 100 °C above A_S, and at which a yield strength of R_p0.2=1.25 GPa, tensile strength of R_m=1.65 GPa and a uniform and total elongation of ε_u=0.10 ε_t=0.15, respectively, are obtained.

Regarding the mechanical stability of austenite and its influence on the mechanical behaviour, Fig. 7 represents the percentage of austenite transformed by straining, after fracture of the tensile samples, measured on the whole gauge length of the tensile samples, compared to the initial volume fraction of austenite after the heat treatments, i.e., the amount that was initially present in the tensile samples. These results show that as the volume fraction of austenite in the microstructure increases, the austenite transformed during straining also increases, enhancing significantly the total elongation. This behaviour is not influenced by the heating rate. It is clear that low volume fractions of austenite possess a greater the mechanical stability due to the smaller size of the grains and because they are contained in a hard martensitic matrix, reducing the load partitioning to the austenite. As the heating temperature increases, austenite grains grow and martensite becomes softer (recovery and dissolution of the Ni3(Ti,Al) leading to the decrease of the austenite stability. It should be also taken into account that the austenite grains that form first during heating have a higher Ni-content and, thus, a greater mechanical stability compare to those that transform at higher temperatures (close to A_F) and which are poorer in Ni and enriched in Cr.
Fig. 7 Percentage of austenite transformed by straining after fracture, measured on the whole gauge length of the tensile samples vs. the initial volume fraction of austenite after the heat treatments.

5. Conclusions

By controlling the processing conditions (heating rate and temperature) applied to a cold-rolled microstructure of precipitation hardening metastable austenitic stainless steel, a wide range of mechanical properties can be obtained.

It has been discussed that different factors may affect the stability of the microstructure and its mechanical behaviour: i) the volume fraction of austenite/martensite; ii) formation of intermetallic phases ($\chi$-phase, Ni$_3$(Ti,Al)); iii) chemical banding; iv) austenite grain size.

The best combination of mechanical properties is obtained for a dual phase microstructure composed of an austenite volume fraction of around 0.7 (achieved after heating at 0.1 °C/s, to around 100 °C above $A_S$), at which a yield strength of $R_{p0.2}$=1.25 GPa, tensile strength of $R_m$=1.65 GPa and a uniform and total elongation of $\varepsilon_u$=0.10 $\varepsilon_t$=0.15, respectively, are obtained.

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7. References

AN OVERVIEW OF MECHANICAL PROPERTIES OF TODAY’S GRAIN-REFINED AUSTENITIC STAINLESS STEELS

Abstract

Numerous studies have demonstrated that a short reversion annealing following cold rolling is an efficient method to refine the grain size of metastable austenitic stainless steels down to a micron-scale. Commercial grades such as AISI 301 (EN 1.4310) and 301LN (EN 1.4318), AISI 201L (EN 1.4371) have been found suitable for the treatment. Also, low cold rolling reductions have been shown to result in considerable refinement of the grain size enhancing the yield strength and high-cycle fatigue strength to be more than double compared to those of the commercial grades. Elongation is only slightly decreased. In spite of higher strength, stretchability is identical to that of the commercial annealed 301LN. The paper gives a short overview of the reversion process variables and the level of mechanical properties which have been achieved in numerous laboratory-scale studies.

Keywords

Austenitic stainless steel, cold rolling, reversion, grain size, tensile strength, elongation, fatigue strength, stretchability

1. Introduction

Austenitic stainless steels (ASSs) are presented as potential candidates for structural parts in transportation and construction industries due to their excellent formability, work hardening capability and weldability, together with good corrosion resistance. However, their yield strength (YS) is generally low (around 350 MPa for grade EN 1.4318/AISI 301LN), which limits their use for structural applications. Many grades are metastable, i.e. the austenite phase transforms to martensite under cold working, so that their excellent ductility and work hardening capability can be utilised to improve the strength by cold deformation. However, the disadvantage of strengthening by temper rolling is the formation of anisotropy in mechanical properties, the strength being different in different directions relative to the rolling direction [1,2]. Therefore, other strengthening methods are desirable.

The grain size (GS) of commercial ASSs is typically coarse, over 10 µm. GS refinement is an effective method for increasing the static strength properties of metals and alloys and also their fatigue performance, especially in the high-cycle fatigue regime. Even though the impact of GS on strength is not so high in ASSs as in ferritic steels, it has been shown that the refinement of GS can provide significant improvement in YS, e.g. [3–6]. The traditional hot rolling process or cold rolling and recrystallization annealing are not effective for GS refinement of the austenite phase, although GS of 2 µm has been obtained without martensite by using warm rolling and annealing [7]. The role of dynamic recrystallization in GS refinement has been reviewed by Zhao and Jiang [8], but it is not very efficient due to high temperatures required. However, the martensitic reversion treatment, in which deformation-induced α’-martensite (DIM) transforms back to austenite has been shown to refine the austenite GS even

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to submicron size. As a result, excellent combinations of YS and elongation are achievable, as reported in numerous studies during the last 30 years, e.g. [5,6,12–38]. (Note: the reference list is not all-encompassing due to the space limitation). The reversion process for austenitic Cr-Ni steels was already studied in 1970’s and 1980’s, [9], but in more detail in Japan in early 1990’s, e.g. [10,11], and later in several groups (Italy [12], Korea [13], France [7], India [14,15], China [16,17], Spain [18,19], Germany [20], Iran [21–29]) and extensively at the University of Oulu in Finland in collaboration with two American groups and a Czech one, e.g. [5,6,30–38], as supported by a local stainless steel company. In spite of extensive academic research, as far as the present authors know, there are only a couple of industrial companies utilizing the reversion-treatment for ASSs. In Japan, Nano grains Co. Ltd (Komatsuseiki Kosakusho Co., Ltd.) produces grain-refined 304, 316 and 301 foils (80–300 µm thick), with the GS less than 1 µm, using repeated reversion annealing. Especially the enhanced properties of micro-scale cutting and hole piercing are utilized in the manufacturing of orifices for electronic fuel injection [39]. Nippon Steel & Sumitomo Metal company lists in its product catalogue the fine-grained 304 (SUS304 BA19) and 301L (NSSMC-NAR-301L BA1) grades [40]. The feasibility of the process for an industrial manufacturing using a continuous annealing line has been demonstrated in one laboratory study [15]. In recent studies by Järvenpää et al. [37], a pilot induction heating line has been employed to simulate industrial conditions in reversion annealing of 301LN grade.

In order to highlight the advantages of grain-refined ASSs, in the following, the main variables in the reversion-treatment are discussed and the state of the art of mechanical properties of reversion-treated ultrafine-grained ASSs are briefly reviewed. The corrosion properties, weldability and medical applications also studied are not included in this survey.

2. Prior cold rolling

For the reversion treatment, a metastable austenitic steel must first be cold rolled to transform austenite to DIM. Highly-deformed cell-type DIM is preferable for a source of a large number of nucleation sites for new austenite grains to attain ultrafine (less than a micron) GS in the subsequent reversion annealing [3,5,6,11,21,23,31]. At low cold-rolling reductions, DIM formation remains partial and coarse-grained deformed austenite (DA) grains are retained in the structure. Further, the lath-type low-deformed DIM reverses into austenite with morphological characteristics of the parent phase. Accordingly, very high cold rolling reductions of 90–95% were recommended and applied in numerous works [11,21–29].

The susceptibility to DIM formation is affected by the chemical composition and GS of the steel as well as deformation conditions. Highly metastable grades are favourable. In Fig. 1 the DIM fractions formed during cold rolling are plotted as a function of the cold rolling thickness reduction for some Cr-Mn and Cr-Ni grades. In order to achieve a fully martensitic structure in 301LN, cold rolling reductions beyond 60% are required [5,6], but for 201 and 201L with a low N content, the reduction of 40% is enough [23,25]. If the pass reductions are large, adiabatic heating tends to reduce the DIM formation.

Concerning the actual deformation degree experienced by DIM, it is important to realize that the DIM formation proceeds gradually, as seen in Fig. 1. This means that at low rolling reductions, a significant fraction of DIM remains inevitably only “slightly-deformed” and the resultant lath martensite plays a significant role in the microstructure evolution. However, heavy cold rolling or complex processing routes are not desired in industrial practice. Promisingly, in 301LN steel, cold rolling reductions as low as 35–52% seem to result in excellent strength-ductility combinations (see Table 1 in Section 5.1), even though GS refinement is not most efficient and the GS obtained is not uniform [5–7,36–38]. Even very low
reductions of 10–40% have found to reduce significantly the average GS in 301LN in complete reversion [18,19]. It seems that low cold rolling reductions have not been applied to 201 and 201LN grades, but without doubt successful results can be expected.

Fig. 1. Formation of deformation-induced α’-martensite in 201, 201L and 301LN grades during cold rolling as using small or large passes.

3. Reversion annealing: Mechanism and kinetics

DIM reverses back to austenite during continuous heating or isothermal annealing at a proper temperature. The reversion of DIM to austenite can occur by two mechanisms, a diffusionless shear or diffusion-controlled one [5,11]. The shear phase reversion first involves transformation of DIM to austenite which contains traces of prior α’-martensite morphology, the same grain boundaries as those of original austenite and a high density of defects. After the fast phase transformation, with increase in annealing temperature or time, defect-free austenite subgrains are formed which coalesce to a structure resembling that of a recrystallized structure. On the contrary, the diffusional reversion is characterised by the nucleation and growth of randomly oriented equiaxed austenite grains [5,11]. The nucleation occurs on the cell or lath boundaries of the deformed DIM and austenitic grains grow in size with time but can stay in a nanometre or submicron range. Secondary phase precipitates such as chromium nitrides can also form in 301LN [5,30,31,38].

Concerning the GS refinement, the both mechanisms can readily lead to a micron-scale GS, but the diffusional reversion is more efficient. The chemical composition of the steel is an important factor affecting the type of the reversion mechanism [5,11]. For instance, AISI 301 reverses by the shear mechanisms above 670 °C [5,32], but the temperature of 900 °C is required for the recrystallization following the reversion. AISI 301LN usually exhibits the diffusion-driven transformation [5], although under certain conditions the both reversion mechanisms seem to be active in 301LN [36,38]. The diffusion-controlled reversion starts, depending on cold rolling reduction, around 650–700 °C and is complete within few seconds at 750–800 °C [5,30,36].

4. Reversion-annealed microstructures

After very high cold-rolling reductions, such as 90–95%, and at temperatures leading to complete reversion (850–900 °C), a highly refined GS is readily achieved, even a few tens of nanometres [21–27]. On the contrary, after a low cold rolling reduction, different deformation
states of DIM and the presence of retained DA tend to modify the microstructure, resulting in non-homogeneous GS distributions inherited from reversed DIM and DA [7,36].

In low-temperature (<800 °C) reversion structures, in addition to micron-scale grains and coarse DA grains, the presence of medium-sized (GS 3–10 μm) grains has been established in 301LN [6,36,38]. However, a wide GS distribution is not necessarily detrimental. A bimodal grain structure can be beneficial for mechanical properties, where softer grains (GS > 1 μm) among hard submicron-sized grains enhance the ductility of the structure and the retained strong phases, DIM and DA, enhance the strength. In Fig. 2, examples of different microstructures created in 301LN are shown: a homogeneous submicron-size grain structure obtained in annealing at 800°C after 63% cold rolling reduction, and after 45% cold rolling reduction a mixture of fine reversed grains and coarse recrystallized grains obtained at 900°C or a complex partially reversed structure formed very shortly in annealing at 750°C.

The grain growth tendency of very fine reversed grains is high. However, it is not any severe problem at low annealing temperatures, if a GS of around 1 μm is targeted [30,31], or it can also be restricted effectively by microalloying [26–28,34].

Fig. 2. Microstructures in 301LN after (a) 63% cold rolling reduction and annealing at 800°C for 1 s showing uniform reversed grain structure, (b) 45% cold rolling and annealing at 900°C for 1 s showing reversed fine grains with larger grains from recrystallized DA and (c) 45% cold rolling and annealing at 750°C for 0.1 s showing partially reversed structure consisting of fine- and medium-sized reversed grains, retained DIM (red grains) and non-recrystallized DA.

5. Properties of the reversion-treated structures

5.1. Tensile properties

A major target of the reversion treatment is to increase the YS of ASSs. Extensive data of the mechanical properties of reversion-treated ASSs were collected from the literature and they are listed in Table 1. In addition, the cold rolling reduction, annealing temperature and duration, and the (average) GS are given in most cases. The commercial steel grades mostly investigated are 201/201L, 301/301LN and 304/304L. Some data are also for a 204Cu steel and Ti or Nb microalloyed 201 and Nb microalloyed 204Cu.

It can be realized that there is no distinct difference between the Cr-Ni and Cr-Mn steels, i.e. identical properties seem to be achievable in metastable ASS grades, but the processing route required can be different. For instance, the less metastable 304 and 304L grades require a high cold rolling reduction at lowered temperatures. YS (proof stress, R_p0.2) values of the reversion-treated steels are generally over 700 MPa, i.e. at least double compared to the YS of the commercial annealed steels. The highest YS are above 1 GPa (for 201/201L), but it can be noticed that severe cold rolling reductions of 90–95% have been applied in those cases to obtain a GS of order of 50 nm. With cold rolling reductions of 60% or below, YS reported are in a wide range of 600–1000 MPa, depending on annealing temperature and duration.
## Table 1. Collected literature data for reversion-treated steels.

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<tr>
<th>Grade</th>
<th>CR [%]</th>
<th>$T_a$ [°C]</th>
<th>$t$ [s]</th>
<th>AGS [µm]</th>
<th>$R_{0.2}$ [MPa]</th>
<th>$R_m$ [%]</th>
<th>Tel [%]</th>
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<td>Rolling at 10 °C</td>
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CR, Cold rolling reduction; $T_a$, annealing temperature; $t$, holding time; AGS, average grain size; $R_{0.2}$, proof/yield stress; $R_m$, ultimate tensile strength; Tel, total elongation.
Especially the low-temperature reversed structures (800 °C and below) exhibit significantly enhanced YS and a slight upper yield point with discontinuous yielding compared to the structures created at temperatures of 900 °C or higher [6,36,38]. Importantly, the degree of the prior cold rolling reduction in the range of 32–63% does not affect the mechanical properties of the low-temperature reversed structures, for the larger, non-uniform GS will be balanced by retained strong phases, DIM and DA.

The tensile strength cannot be increased so significantly as the YS, typically about 200 MPa to 1.1 GPa. This is due to somewhat lower strain hardening rate and shorter elongation in reversed fine-grained structures. The elongation values are good in spite of high strength, though decreasing with increasing YS. Generally, the total elongation is in the range 30–40% even for the structures with the YS ≈ 1 GPa. It must, however, be noticed that many elongation values have been measured using non-standard tensile specimens with a short gauge length (15–25 mm).

In order to highlight the excellent strength-ductility combinations achieved with reversion-treated ASSs, YS vs. total elongation combinations for the steels listed in Table 1 are plotted in Fig. 3 together with few technical data for commercial temper-rolled steel. The data indicate that the combinations achieved by reversion treatments are generally better than obtained by temper-rolling. Furthermore, the directional anisotropy, present in temper-rolled grades, is found to be absent in completely reversed structures without DIM and DA [33,38]. This means that a steel with its YS of 700 MPa can be manufactured without the anisotropy.

![Fig. 3. Yield strength-elongation combinations for reversion-treated steels listed in Table 1 and typical values for temper-rolled 301LN and annealed 201L and 301LN.](image)

The background of high YS has been analysed in few papers. For instance, in completely reversed structures of 301LN, the contributions of solid solution strengthening, precipitation, dislocations and GS have been evaluated, the values being approximately 200, 120, 40, 250 MPa respectively (annealing at 800 °C for 1–10 s; GS ≈ 0.54–1 µm) [30]. Thus, the refined GS is an important strengthening factor. Also, Kisko et al. [34] estimated the amount of GS strengthening being about 300 MPa in a 204Cu as annealed at 900 °C for 10 s (GS 1.4–1.9 µm). In structures reversed at low temperatures, the amount of precipitation, the retained phases and their state are additional contributors, so that it is obvious that any simple relationship between the GS and YS cannot be expected for them. The non-uniform GS is a factor affecting the scatter, while the average GS cannot describe precisely the strength of the structure.
5.2. Fatigue strength

The effect of the GS refinement on fatigue strength has been studied extensively also for ASSs, e.g. [18–20, 42,43]. It has been shown that fine GS also improves fatigue resistance, especially in the high cycle fatigue regime. For instance, Hamada et al. [43] found a significant improvement in the fatigue life of a reversion-treated 301LN steel (63% cold rolling reduction, annealing at 800 °C for 1 s; average GS ~0.5 µm) under bending fatigue loading.

Fatigue strength of the reversion-treated 301LN is illustrated in Fig. 4 [38]. It is seen that in strain-controlled fatigue tests, low cycle fatigue life is not significantly affected by the microstructure. However, in a comparison based on mid-life stress amplitudes, the reversed structure is distinctly better. Fatigue strength, i.e. the stress amplitude level at $10^6$ cycles, is in the range of 460–570 MPa in the reversed structures (GS $\approx$ 0.6–3.4 µm), being even more than twice higher than the corresponding values of the annealed coarse-grained (~20 µm) structures. It was also found out that a low prior rolling reduction can lead to fatigue strength identical to that achieved after 63% reduction. Mateo et al. [18] reported that even a cold rolling reduction of 20% resulting in very non-homogeneous reversed structure (the mean GS below 3 µm) led to 36% improvement (100 MPa) in the fatigue limit compared to an annealed 301LN, although the fatigue limit remained lower than that of a 20% cold rolled sheet.

![Fig. 4. Fatigue life of reversion-treated 301LN in strain-controlled tests compared to annealed 301LN based on (a) strain amplitude and (b) mid-life stress amplitude. Data from [38,42].](image)

5.3. Stretch formability

The formability properties of the reversion-treated structures are not yet reported in the open literature. In austenitic stainless steels the tensile ductility remains high, so it can be expected that the formability could remain on a good level in spite of the GS refinement. The stretch formability of the reversion treated 3 mm sheets of 301LN with the YS in the range 682–998 MPa and that of temper-rolled structures of 301LN and 301 grades for reference, have been determined by the Erichsen cupping tests [44]. It was found that the stretch formability is identical or slightly better for the reversion-treated structures than that of the temper-rolled counterparts at a given YS level. Furthermore, the stretched cup surface of reversion-treated sheets is smoother than the surface of the cups of commercial temper-rolled sheets. This is in accordance with a technical data from Nippon Steel & Sumitomo Metal reporting excellent formability and surface condition for grain-refined thin sheets of AISI 304 (SUS304 BA1) and 301L (NSSMC-NAR-301L BA1) [40].
Conclusions

Numerous laboratory-scale experiments have demonstrated that commercial metastable austenitic stainless steel grades such as 201, 201L and 301LN can, even after a reasonably low cold rolling reduction ($\approx 30–50\%$), be reversion treated at 700–900 °C for a short desired duration resulting in an excellent yield strength-elongation combination and high fatigue strength (in sheet with the thickness of 3 mm at least). The mechanical properties surpass those of temper-rolled sheets. The robustness of the processing should be investigated.

Acknowledgements

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A. Kisko, L. Rovatti, I. Miettunen, L.P. Karjalainen and J. Talonen, Microstructure and anisotropy of mechanical properties in reversion-treated high-Mn type 204Cu and 201 stainless steels, Proceedings. The 7th European Stainless Steel Conference-Science and Market, Como, Italy (2011) No. 81


INFLUENCE OF HEAT TREATMENT AND THERMOCHEMICAL SURFACE ENGINEERING ON THE HIERARCHICAL MICROSTRUCTURES OF 3D PRINTED AUSTENITIC STAINLESS STEEL

Abstract

This research focuses on characterisation of the hierarchical microstructure of AM-manufactured austenitic stainless steel and the effect of post-processing. The austenitisation treatment is found to dissolve the cellular structure and to reduce hardness, particularly in the layer closest to the support structure. The effect of substrate on low temperature surface hardening (LSTH) is investigated. It is found that the prior annealing and homogenisation of the austenitised specimen change both the depth of expanded austenite formation and the hardness profile.

Keywords

Additive manufacturing, austenitic stainless steel, austenitisation, low temperature surface hardening, microstructure stability

1. Introduction

Since the emergence of Selective Laser Melting (SLM) as a prototyping technology in the early 2000s, it has gained interest and is now widely adopted in industry. This is due to its technological advances such as reduction in cost in the field of reliable industrial lasers, high performance computing software and hardware, and high quality feed stock. The advantages of SLM include geometrical freedom and the reduced need for specialised tooling, which enables low-volume production or even fully customised products [1]. The SLM process entails layer-based solidification, where metallic powder is melted by traversing a laser over the surface and locally raising the temperature above the melting point. As one layer is completed, the build platform is lowered and a new layer of powder is distributed and the scanning process is repeated [1]. Hence, the nature of the SLM process is rather complex and the resulting microstructures can be far from equilibrium due to local temperature gradients. One of the most commonly applied materials for SLM is the austenitic stainless steel AISI 316L. The microstructure of SLM fabricated AISI 316L steel was initially described by Yasa and Kruth as elongated austenite grains crossing several semi-circular melt pools and containing a fine, cellular subgrain network within the grains [2]. Recent research confirmed that the microstructure contains characteristic features which are a direct consequence of the manufacturing method [1, 3, 4, 5, 6]. The cellular walls are formed by a dislocation network...
and are enriched in Cr and Mo [3, 5]. Additionally, amorphous silicates are dispersed as nanosized inclusions and form as a result of residual oxygen in the chamber [5, 7].

The formation of non-equilibrium microstructures is determined by the local cooling conditions as defined by temperature gradients and solidification rate. For this reason the microstructure can significantly vary in different locations in the specimen. During printing, the part is surrounded by powder, which acts as a good insulator because the thermal conductivity through the gas between the particles is lower than that through a solid material. The formation of a different microstructure adjacent to the overhanging surfaces has so far not been reported for stainless steel.

Furthermore, few investigations published on the effect of annealing on SLM manufactured 316L reported that the cellular sub-grain structure dissolved at temperatures above approximately 900 °C [7, 8, 9]. The dissolution of the cellular subgrain structure is associated with a reduction of the hardness of the material [7, 8]. At temperatures in the 950-1100 °C range, δ-ferrite can be dissolved with sufficiently long exposure time [7]. However, heat treatment at a very high temperature, 1400 °C will result in further ferrite formation, nucleating on existing δ-ferrite [8].

Alloying austenitic stainless steels with nitrogen can be beneficial due to stabilisation of the austenite phase and increased strength without a reduction in ductility [10]. Nitriding at temperatures in the 490-950 °C range leads to poor corrosion performance due to massive formation of chromium nitrides that renders the material to be non-stainless. This can be circumvented by nitriding in a low temperature surface hardening (LTSH) process. This treatment results in the formation of a case consisting of a supersaturated solid solution of nitrogen in austenite, i.e. expanded austenite. The expanded austenite case is characterised by high hardness, large compressive residual surface stresses and excellent corrosion resistance [11]. This makes low temperature nitriding a promising technology to remedy some of the inherent shortcomings of SLM austenitic stainless steels. However, the LTSH processes have been developed for conventionally manufactured components and are therefore not optimised for additive manufacturing. It has previously been shown that LTSH on SLM 316L is possible, albeit this was only shown on austenitised and high temperature solution nitrided materials [12]; such treatment will homogenise the material by removing the cellular segregation network.

This present work deals with the response of low temperature nitriding on as-printed and austenitised 316L austenitic stainless steel manufactured using SLM. Additionally, the variation in microstructure in relation to the location in the as-printed and austenitised SLM manufactured AISI 316L samples is investigated here.

2. Experimental

2.1 Materials processing and heat treatment

Specimens were manufactured on a MCP Realizer SLM 250 using gas atomised AISI 316L stainless steel powder from SLM Solutions consisting of particles with a 35.5 µm mean diameter. The printing was done in shielding atmosphere of nitrogen gas. The chemical composition of the powder as obtained with EDS was validated to be within the tolerance range of AISI 316L (16-18 wt% Cr, 10-14 wt% Ni and 2-3 wt% Mo). The specimen geometry is illustrated in Fig. 1-a, and the specimens were printed onto a lattice-like support structure, applying an anti-parallel stripes pattern with a 90° rotation between consecutive layers (Fig. 1-b).
The most important build settings for the support and main specimen are given in Table 1.

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Austenitisation was carried out for 10 minutes at 1080 °C in a gas mixture of high purity argon and hydrogen in a 1:5 ratio. The average heating rate was 40 °C /min and the cooling rate was 60 °C /min.

The samples were subjected to low temperature gaseous nitriding treatment in a Netzsch STA449 F3 thermobalance. Prior to nitriding, a proprietary in-situ surface activation was performed. The LTSH treatment was carried out at 420 °C for a duration of 16 h in an atmosphere consisting of flowing NH3 gas. The effect of the substrate condition was investigated by subjecting one sample to austenitisation as described above prior to LTSH. The austenitised sample is designated AU+LTSH, while the as-printed sample is designated AP+LTSH.

2.2 Microstructure Characterization

Microstructural analysis was conducted primarily on cross-sections of the specimens. Standard metallographic preparation was used and the specimens were etched in a solution consisting of 1% HF and 4% HNO3 in water for 20 minutes by submersion. LOM was carried out on a Zeiss Axio Vert A1. Microhardness was measured on the polished specimens using a 200 g load. The hardness in the bottom of the specimen was measured at a location 200 μm from the edge. Microhardness profiles of the LTSH specimens were measured using a load of 10 g. The nitrogen content in the specimens was determined using a LECO TN500. Phases and texture were analysed using X-Ray diffraction (XRD) in a Bruker D8 Discovery diffractometer with CrKα radiation. A symmetric coupled 0-20 focusing principle was used to record diffractograms with a 0.04°2θ step size and a 7 s measurement time for each step. Scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) were conducted on unetched, electropolished specimens. SEM imaging was carried out using a Zeiss Supra 35 FEGSEM, while energy dispersive spectroscopy (EDS) was carried out using a JEOL JSM-5900 SEM. For texture analysis a 1 mm² area was covered by EBSD with a step size of 5 μm. For microstructural analysis a step size of 1 μm was used to cover 90 000 μm². Low angle boundaries (LABs) and high angle boundaries (HABs) were defined as those with 1.5-15° and >15° misorientations, respectively.
3. Results and Interpretation

3.1 Microstructure of as-printed material

The nitrogen content in the as-printed material was measured as 0.112±0.003 wt% and in the re-used powder 0.106 ±0.006 wt% N. Both nitrogen contents exceed the upper limit specified by the ASTM A240 standard for AISI 316L.

X-ray diffraction (not shown) confirmed that the as-printed specimens consist primarily of austenite, with a very small 110 ferrite peak observed in some measurements. This is interpreted as δ-ferrite that has formed during rapid solidification.

Fig. 2 presents LOM micrographs showing the microstructure of the as-printed specimens. The microstructure consists of elongated austenite grains aligned along the build direction. These austenite grains have grown across the semi-circular melt pool (Fig 2-a). The hierarchical microstructure becomes visible in Fig. 2-d with the austenite grains containing a cellular network crossing the melt pool boundaries. The cellular growth during solidification in the majority of the SLM 316L is due to a relatively steep temperature gradient combined with a slow growth rate. From the bottom the microstructure up to ~400 µm differs remarkably from the remainder of the specimen, see Fig. 2-a, -b and -c. Here, the austenite grains are not elongated, but equiaxed, dendritic and cellular microstructural morphologies are observed, as indicated by the arrows Fig. 2-b. The different microstructure in the bottom indicates that different cooling conditions applied near the support structure, leading to moderate temperature gradients. Porosity is observed in 2-d. A partially unmelted powder particle is present in the bottom of 2-c.

Backscatter electron (BSE) micrographs of the unetched as-printed and austenitised specimens are presented in Fig. 3. Elongated austenite grains are aligned approximately parallel to the build direction, i.e. the direction of the largest heat flux of the specimen, in the centre and top. In the as-printed specimen the cellular structure is visible as a network of bright cell walls, suggesting a local enrichment of relatively heavy elements, particularly Mo, within the cell walls (see Fig. 3). Furthermore, the as-printed specimen contains a uniform distribution of dark, nanoscale features, indicating that they have a lower density than the matrix. These features are not revealed with SE imaging, confirming that they are indeed particles and not porosities. As also observed with LOM, the microstructure in the bottom part of the specimens differs from the centre and top. The austenite grains are less elongated and not aligned with the build direction. Instead, more equiaxed austenite grains and annealing twins are present (Fig. 3-j). Fewer nanoscale particles are observed in the bottom than at other locations in the specimen.
Fig. 3: BSE micrographs of as-printed and austenitised specimens: a-d) Top; e-h) Centre; i-k) Bottom

As-printed

Austenised
The orientation micrographs determined with EBSD are given in Fig. 4. The top and centre locations in the as-printed specimen contain many LABs within the grains separated by HABs. The grain orientation differences between the top and centre (compare Fig. 4-a with 4-b) are a consequence of the limited area that is sampled in the images. The texture in the bottom equiaxed region is practically random, but changes gradually to a weak <100> texture at the top of the specimen. This transition was confirmed for two specimens. The equiaxed grains in the bottom contain no LABs and no gradual colour change occurs within the grains. It can be observed in Fig. 4-c) that equiaxed zone contains a range of grain sizes. Practically no twins formed in the centre and top of the specimen (~1%), while the bottom contained ~10% twin boundaries. This indicates that the bulk microstructure with elemental segregation supresses the formation of annealing twins.

The hardness in the bottom of the as-printed specimen is 336 HV and is appreciably higher than the hardness of 231 HV in the centre and top (Table 2).

**Table 2 Micro hardness compared in the centre/top and bottom of the specimens.**

<table>
<thead>
<tr>
<th>Micro hardness [HV0.2]</th>
<th>Centre/Top</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Std. deviation</td>
<td>Std. deviation</td>
</tr>
<tr>
<td>As-printed</td>
<td>234</td>
<td>5.3</td>
</tr>
<tr>
<td>Austenitised</td>
<td>195</td>
<td>8.1</td>
</tr>
</tbody>
</table>

---

**Fig. 4 a), b) and c) Top, Centre and Bottom of as-printed specimen. d), e) and f) Top, Centre and Bottom of austenitised specimen. HAB >15° (black) and LAB > 1.5° (white).**
3.2 The Effect of Austenitisation

BSE micrographs of the austenitised specimen are presented in Fig 3. At a low magnification (Figs. 3-c, -g and -k), the bulk microstructures in the centre and top of the specimens appear similar to the as-printed specimen. The cellular structure observed in the as-printed condition (Fig. 3-b and -f) has disappeared after austenitisation, see Fig.3b,d,f,h. Grain growth is observed in each location, but particularly in the bottom.

Comparing orientation micrographs for the as-printed condition with the austenitised condition (compare Figs. 4-a to -c with Figs. 4-d to -f), the most obvious differences are again observed in the bottom. The grains are notably larger in the austenitized condition than in the as-printed condition. Also, austenitisation increased the frequency of twin boundaries in the bottom of the specimen from about 10% to more than 50%, while no new twins were formed in the centre and top of the specimen upon annealing. This indicates a recrystallization due to plastic deformation due to the formation of annealing twins.

Austenitisation slightly reduces the hardness of the top/centre of the specimen, from 234 HV to 195 HV (Table 3). On the other hand, in the bottom a massive reduction from 332 HV to 169 HV is observed. Interestingly, the bottom hardness is lower than the top/core after austenitisation, while the bottom was significantly harder than the top/core in the as-printed condition.

3.3 The Effect of Low Temperature Surface Hardening

As seen in Fig. 5 a uniform case of expanded austenite was formed on both specimens. The case is visibly thicker in the AP+LTSH specimen. After etching, the melt pools and cellular network are also visible in the expanded austenite of AP+LTSH. Furthermore, as mentioned above, the austenitisation dissolved the cellular subgrain structure and removed the melt pools. The grains are however still elongated. In both specimens, the microstructure of the bulk (grain boundaries, melt pools and cells) continue into the expanded austenite, but appears fainter. This can be attributed to improved etching resistance of the expanded austenite, which could indicate an improved corrosion resistance as seen on conventional 316L [10].
The microhardness profiles, seen in Fig. 6, show differences between the two substrates. The immediate obvious difference is the case depth of the expanded austenite. The sharp hardness transition indicates the interface between bulk austenite and expanded austenite. For the AP+LTSH specimen the transition was located around 16 μm from the surface, while on the AU+LTSH specimen, this depth was reduced to approximately 10 μm. Both samples have a tail on the hardness profile into the austenite (more pronounced on the AU+LTSH specimen). Both samples have the same initial hardness of approximately 1160 HV near the surface, however the AR+LTSH sample has a pronounced hardness plateau through the expanded austenite as well as a second smaller plateau directly adjacent to the transition, while the AU+LTSH sample has a gradual hardness change through this zone. The bulk hardness of both samples is consistent with the results seen above, where the austenitisation treatment significantly lowers the hardness.

4. Discussion

The microstructure in the body of the SLM printed AISI 316L investigated in this study is in agreement with those described in the literature. However, the microstructure observed in the present study for the bottom ~0.4 mm zone has not been previously reported for AISI 316L stainless steel. The grains here are equiaxed, contain annealing twins and have no cellular subgrain structure. The grains in the bottom are finer and more equiaxed than the elongated austenite grains in centre and top and have no preferred orientation These fine grains do not appear to form any strong texture, which is similar to the observations made on Inconel 718 [13, 14]. As suggested for other SLM materials, this different microstructure in the initial layers closest to the support is most likely due to changes in the cooling conditions as a result of the lower thermal conductivity of the powder. Evidently, this has direct influence on the resulting microstructure after solidification.

This effect is potentially due to the heterogeneous distribution of the alloying elements in the as received condition, as it is not yet understood how the different elements affect the diffusion rate. Generally, Mo is influential for the high temperature stability of the expanded austenite case, while Cr is crucial in the formation of expanded austenite as it enhances the nitrogen content by short-range ordering.

The austenitised and as-printed substrate respond very differently to a subsequent low temperature nitriding as the AP+LTSH specimen creates a hardness plateau before the interface, while the AU+LTSH has a more gradual transition through the expanded austenite. It is hypothesised that this behaviour could be due to the formation of very small Cr-nitrides, which are diffracting coherently with the austenite or are present in a volume fraction too low for detection as no nitrides were observed using XRD. The second plateau could also be ascribed
to the cellular walls. The walls could potentially be ferritic as both Mo and Cr are known ferrite stabilisers and LTSH on ferritic materials have been shown to result in a more gradual hardness profile [15]. The behaviour of AR+LTSH could also be explained from the cellular walls providing austenitic areas with a high Mo and Cr content, which can be regarded as a different austenite, which behave differently when subjected to LTSH [16]. The tail on the hardness profiles is possibly a zone where the austenite is enriched in nitrogen, i.e. the equilibrium solubility in austenite, or carbon pushed inwards by nitrogen. The tail is more pronounced on the AU+LTSH, which, together with the smaller case depth, could indicate that the presence of the cellular sub-grain structure in the AP+LTSH sample promotes the growth of expanded austenite. The differences in case thickness is potentially due to the heterogeneous distribution of the alloying elements in the as received condition, as it is not yet understood how the different elements affect the diffusion rate. Generally, Mo is influential for the high temperature stability of the expanded austenite case, while Cr is crucial in the formation of expanded austenite as it enhances the nitrogen content by short-range ordering.

The hardness in the bottom part of the as-printed specimen is clearly higher than in the bulk, and the average grain size here is smaller. However, the centre and top contain a network of cells with a size about 500-700 nm, while the grains in the bottom have a size around 6-7 μm. The cellular subgrain microstructure has a higher hardness than the austenitised 316L in this research. The reason for the higher hardness in the bottom part is thought to be associated with plastic deformation during printing, which dramatically increases the hardness beyond the usual range of hardness for undeformed 316L. The changing temperature gradients during printing of the bottom adjacent to the support and the bulk could potentially result in thermally induced plastic deformation, which is indicated both by the formation of annealing twins in the bottom and the very high hardness in this region in the as-printed specimen. Upon austenitisation, the plastic deformation induces recrystallization and the formation of annealing twins in the bottom, as seen with EBSD. This will reduce the hardness much more severely than the bulk, which does not recrystallize. After austenitisation the bulk hardness is reduced as a result of the dissolution of the cellular network and reduction of the dislocation density. The nitrogen content in the specimen is above the tolerance range of AISI 316L, which will also provide solid solution strengthening. The austenitisation in a H2-containing atmosphere can remove the nitrogen from the bottom region as well.

5. Conclusions

The selective laser melting process of 316L creates a high heterogeneous, hierarchical microstructure, consisting of elongated austenite grains with a cellular subgrain structure in the bulk and an equiaxed, non-cellular microstructure. The bottom hardness is very high at 332 HV, potentially due to plastic deformation during printing as evidenced by the formation of annealing twins through recrystallization during annealing. Annealing also removes the cellular structure and causes grain growth in the bulk. LTSH is found to be high sensitive to the condition of the substrate as annealing both creates a gradual hardness change through the expanded austenite and reduces the case depth.

6. Acknowledgement

The authors would like to acknowledge the Danish Technological Institute for providing the tested specimens.
7. References

MONITORING THE SURFACE QUALITY OF STAINLESS STEEL SLABS WITH REVEAL CAST – FINDINGS AND SUBSEQUENT QUALITY IMPROVEMENTS

Abstract

Quality of stainless steel semi-products is important for the cost-efficient production of final products. Yield losses due to excessive grinding, losses due to the down-grading or scrapping the whole semi-finished product may impair the profitability of the production. By monitoring the surface quality of the hot slabs during the casting on line, it is possible to get valuable information for making improvements in caster condition and in composition of a steel grade to improve castability and surface quality. This research was concentrating on the monitoring of surface quality of stainless steel, but the same principles apply also for carbon steel.

This paper shows how Reveal CAST surface inspection system can be used to identify different types of defects from the hot surface of cast slabs. The paper also describes the relationship between the caster condition and the slab surface quality. As an example, using the reporting tools included in Reveal CAST together with automatic defect detection features, it was easy to find out that with Ti-alloyed austenitic stainless steel, the rate of the sticking defects was clearly higher during summer time compared to winter time. The reason for increased sticking defects during summer time is explained. The same phenomenon was also found earlier, but with much more time-consuming work. Similar studies are easy to do with Reveal CAST.

Using Reveal CAST also in the hot band inspection, it is possible to evaluate, which of the defects on the slab surface are causing the defects on the rolled strips. Grinding of the rolled strips is clearly more expensive than the grinding of slabs. Monitoring during grinding of the slabs ensures removal of defects without extensive grinding losses.

This paper shows that monitoring the surfaces of semi-products on line with Reveal CAST can result in cost savings and in quality improvements.

Keywords:
CONTINUOUS CASTING – SLABS – SURFACE QUALITY – AUTOMATIC DEFECT DETECTION – IMAGES

1. Introduction

Price of stainless steel is high because of expensive raw materials and high processing costs. So that is why especially with stainless steel any yield losses should be avoided. Slabs of some of stainless steel grades are not allowable to cool down after casting to avoid cracking. Increase of hot charging of slabs to walking beam furnace shorten throughput time, save energy and can in some cases also improve quality.
When new innovative stainless steel grades are processed in melting shop first time it is important to see quality of cast semis. And once again when tuning composition or casting parameters. There are many reasons to have monitoring of surfaces of cast semis straight after casting and have full documentation of images of cast semis.

To solve the causes of defects, it is essential to detect defects. To have covering information concerning different kind of defects it is needed to have images of every cast semis. Not to detect only single defects, but having statistic concerning appearance of defects in relation to different factors which can vary on time, maintenance timing, raw material changes etc. As example it is presented a study concerning seasonal variation of a defect.

Connecting images with measurements from caster system is first step to solve causes thought measurements are often giving indications not final root cause. In most difficult cases there is not only one root cause. Depending of dominating cause the appearance of the defect can vary. By dividing the types of defects with the aid of images into subtypes can help to find out the dominant cause in each case. This needs a collection of defects.

2. Slab surface quality monitoring - Reveal CAST

In this study, Reveal CAST, a slab surface quality monitoring solution, developed and sold by a Finnish company called Sapotech [1] was used as a basic tool to provide huge amount of continuous casting slab surface data to slab quality indicator and trend graph development. Reveal CAST has been built on top of IoT Reveal Technology Platform, combining the latest software, machine vision, high speed imaging and illumination technologies. The basic working principle of Reveal CAST is shortly described below.

Usual Reveal CAST installation comprises of top and bottom imaging of continuous casting slabs; however, it is possible to image all the surfaces or concentrate on the corners of the slabs. The basic set up of top and bottom Reveal CAST is presented in Fig.1. The imaging units (1 and 2) are installed to an optimal distance from the slab surface. The number of cameras in each surface depends on the required resolution. Laser illumination is used to illuminate the surface of the slabs (3). By using the laser illumination, the heat radiation from the high temperature slabs, which usually weakens the image quality, can be avoided. The control cabinet (4) takes care the overall control of the system, data acquisition and processing. It also provides electrical power to the rest of the system.
Fig.1 Reveal CAST installation at the exit of continuous casting line, after cutting of the slabs.

Reveal CAST provides accurate images from slab surface, which are stitched together as whole slabs for automatic defect detection and for manual defect marking in an extremely easy-to-use web-based browser interface. In addition, Reveal CAST can be equipped with 3D topographic measurement, full dimension profile measurements and infrared imaging, according to customer need.

Intensive work has been done to develop automatic defect detection in Reveal CAST. Customized algorithms, depending on the imaged surface, are used to automatically detect defects. Sticking defects are one of the most harmful defects on the slab surface to deteriorate the slab quality. Defect detection mechanism in Reveal CAST is based on reading combinations of shadows and lighter areas [2-4]. Based on the algorithmic defect detection, six different indicators, ranging from 0 to 1 are automatically created, each indicating different features of defects. These quality indicators are then displayed on the user interface (UI) of Reveal CAST (Fig.2). Those six quality indicators are shown on the left-hand side of the Reveal CAST UI for every slab. If Reveal CAST is integrated with the manufacturing execution system (MES), slab number and other related data concerning the slab can be displayed on Reveal CAST UI as well. This slab information is saved and can be revived at any time. [5]
3. Materials and methods

The material contains a huge number of images taken from the slabs by Reveal CAST. For each separate study selected images were visually inspected. In Reveal CAST there is a feature to set one or several types of defects to make search and get a list of slabs containing only those types of defects, as for example in this study to find only slabs with sticking defects among thousands of slabs.

Combining images of Reveal CAST and events from caster data

For this study it was chosen certain defects joined with rapid heat transfer change indicated with temperatures of thermocouples installed in the mould. Temperature behaviours of thermocouples and some other data was collected from the caster system. Images related to changes was searched.

Inner bow and outer bow defects

One feature to evaluate possible reasons for defects is to observe if defects are on both sides or only on one side of the slab. For example, a reason for longitudinal cracks can be subentry nozzle locating too near to the other side of the mould or there is something wrong with mould powder feeding. Scratches caused by stagnant rolls are typically only on the other side of the slab. Of the 4000 slabs, the search function in Reveal CAST was used to select slabs with a sticking defect. With images of found 80 slabs it was given index (0-5) for sticking defects [5].
**Seasons and sticking defects with Ti alloyed austenitic stainless steels**

Reveal Cast’s statistical tools were used to find defects. To find a seasonal effect on a defect, it was made search from every month using automatic defect detections. The search criteria were: time interval from beginning of the month to the end, steel grade and defect type.

**Trend graph**

Trend graphs can be produced from the defect information that is provided by Reveal CAST. Trends can be based on the found defect (e.g. sticking defects, transverse crack) or based on the automatically created slab quality indicators (six indicators described above) and they can be plotted against specific time period or a certain number of slabs produced or only for certain steel grades. Trend graph describing the level of defects over some specific time period is very useful to plan the maintenance or to follow when some parameter in the caster has been changed. Aim is to see easily that level of defects is not increasing but remains low [5].

**RESULTS AND DISCUSSION**

**Combining images of Reveal CAST and events from caster data**

In the figure 3 is shown defect and certain data from casting process. It can be seen, that there have been two sticking defects on a row only on the other side on the slab. On that side there have been rapid changes in the temperatures of thermocouples first in the 1.row, followed 2.row and finally 3.row with both defects. Sticking alarm has occurred in meters 199, steel level has risen, but prevention of break out was successful. Second sticking (or end of that defect) has happened with lowered casting speed.

Steel grade was Ti alloyed. On the outer bow side there was also defect but less serious. Ti in steel is reacting with liquid flux in mould reducing SiO$_2$ leading deteriorating of the lubrication. Inner bow side is worse because Ti containing inclusion are rising more to the liquid flux in the mould on inner bow side thus impairing lubrication on that side.

By combining defects found with the images to the events in the casting process, it is possible to take one step forward to find the root causes of the defects.

In the figure 3 arrow shows the casting direction and the dotted lines connect the defect and change in the temperatures of the thermocouples. Column 4 (c4) is in the middle area and column 2 (c2) near the corner of the slab.
**Defect occurrence in inner bow side versus outer bow side**

It is known that certain defects are not equally occurring on inner and outer bow sides with the bow type caster. When having images taken from both sides of the slabs it was possible to study the occurrence of sticking defects in inner and outer bow sides simultaneously.
Reveal CAST was put into service in two steps in the reference plant. In the first step the top surface of the slabs was imaged. When Reveal CAST was taken into use also on outer bow side, it was possible to make a comparison shown in the Fig.4. First, it shows the percentage of slabs with sticking defects for five different stainless steel grades, namely 304L, 304, 321, 316Ti and 316. It can be seen, that the least sensitive grade for sticking defects is AISI316. The highest sensitivity to sticking defects has the grades with Ti alloying (321,316Ti). That two grades have also the largest difference in the level of sticking defects between inner and outer bow side. In Ti alloyed grades there are clearly more inclusions (TiN), which are disturbing the performance of the casting powder [9], especially on inner bow side in the straight mould curved kind of caster machine. Principally that phenomenon is known, but with Reveal CAST images and automatic defect detection it was possible to prove.

![Graph](image)

**Fig.4** Steel grades and indexes of sticking defects on inner and outer bow side and shares of slabs with sticking defect.

As shown in Fig.5 (straight mould curved machine) sticking defects are very seldom only on outer bow side. Most often they are on both sides, but often more serious on inner bow side. Many defects are only on inner bow side, like trash, extra material or grease spots. So, having Reveal CAST only for inner bow side may be adequate starting point to improve the quality of the slabs as also the caster performance. In the curved mould type caster, the occurrence of the defects only on outer bow side is probably even less common than with straight mould curved machine. These results comparing inner versus outer bow side could be useful to consider if planning a new caster design. [5]
Fig 5 Steel grades and shares of sticking defects on inner versus outer bow sides on slabs.

Seasons and sticking defects with Ti alloyed austenitic stainless steels

In the figure 6 is shown monthly share of slabs with the sticking defect. There is a trend, that in summer was more sticking defects. During summer 2018 June and July were dry, but August was rainier which means higher humidity in air. That means higher risk to have higher hydrogen content in steel. In winter humidity of air is low because of low temperature (can be -25 °C).

This kind of statistical study would be without images very time consuming to do unless impossible. This result is one piece in a puzzle to find the root cause for defects.

Fig. 6 Share of sticking defects monthly.
**Trend graphs to evaluate the stability of the continuous casting**

Fig. 7 shows an example of a trend graph in which a share of slabs with sticking defects is depicted against sequential casting periods. Every period is at least 200 slabs. Some periods are consisting of thousands of slabs in cases of long periods with very low level of defects. After every maintenance stop (letter M in Fig. 7) it is possible to notice improvement in slab quality in terms of lower number of sticking defects. The only exception is the maintenance stop depicted with MX. It was revealed afterwards that there were difficulties to install the new mould to the caster; the mould was not fully aligned. It can be seen, that the level of sticking defects rose rapidly to undesired level [5].

Trend graph is useful use to check when new steel grade shall be cast and check defect index at that moment; when casting a new steel grade, it is good to check level of defect index. For example, if defect index level is at the point marked with △ in the figure 7, probability may be poor to wait good result.

![Trend graph showing the share of slabs with sticking defect in sequential casting periods](image)

**Fig. 7** Trend graph showing the share of slabs with sticking defect in sequential casting periods

**Conclusions**

Images of the cast semis are valuable material for many purposes.

- to study the appearance of defect and corresponding events found in the caster on line measurements
- to analyze differences with different steel grades
- when making first processing of a new steel grade to see condition of caster performance before casting
- to see changes in longer periods or as in a case presented seasonal effects

Aims are to improve quality, yield and for example speed up the production of new steel grades. When new grades are developed, Reveal CAST gives valuable information concerning possible problems with castability of the grade thereby supporting fast entry to market
References

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THE EFFECT OF HEAT TREATMENT AND SURFACE HARDENING OF 3D PRINTED AUSTENITIC STAINLESS STEEL AISI316L ON CORROSION AND WEAR PROPERTIES

Abstract

The present work focuses on the effect of heat treatment and surface hardening on the microstructure, wear characteristics and corrosion resistance, of 316L stainless steel produced by Selective Laser Melting (SLM). Specifically, the high temperature treatments austenitisation, high temperature solution nitriding (HTSN) and a new “active austenitisation” treatment, performed with a controlled low partial pressure of nitrogen, were investigated. Additionally, low temperature surface nitriding (LTSN) was investigated for surface hardening. Gaseous thermochemical treatments are well suited for SLM parts, as uniform hardening is achieved on all surfaces exposed to the reactive gas.

The wear resistance was tested in a pin-on-disc setup under dry conditions using an AISI 52100 ball as a counterpart, revealing significantly higher wear resistance after LTSN treatment, due to increased surface hardness, while a significant reduction in wear resistance was observed after HTSN treatment.

High temperature treatments resulted in the removal of both melt-pool and cellular structures, resulting in a more homogenous material. This lead to improved corrosion resistance as reflected by a lower current density in the passive region during cyclic potentiodynamic polarization testing (CPP) LTSN treatments lead to dramatically increased pitting potentials and improved repassivation characteristics.

Keywords

Selective Laser Melting, AISI 316L, corrosion, wear, heat treatment, gaseous nitriding

1. Introduction

Additive manufacturing (AM) of AISI 316L by Selective Laser Melting (SLM) is currently gaining more and more attention due to its broad application range combined with the high strength-ductility relation obtained by the unique hierarchical microstructure produced by SLM.[1] Due to the high cooling rates and layer by layer building characteristics of SLM, the as-fabricated parts can contain strongly inhomogeneous microstructures, porosities, rough surfaces and residual stresses.[2] For example, the as-fabricated microstructure of SLM 316L typically consists of austenite grains elongated in the build direction with an internal cellular substructure. The cell width is approximately 1µm and the cell boundaries are dislocation rich and can be enriched in Cr and Mo.[1]

Post-processing by heat treatment or surface finishing is often necessary in order to optimize the materials properties and performance. For austenitic stainless steel AISI 316L heat treatment has always been essential in order to obtain the desired corrosion performance. Conventionally, AISI 316L is austenitised in a hydrogen atmosphere or in high vacuum at a temperature in the range 1040-1120°C, to ensure a fully austenitic structure with optimal
corrosion resistance. In AM some producers prescribe nitrogen gas as the “inert” atmosphere for SLM of AISI316L. Nevertheless, nitrogen pick-up in the solid state occurs for temperatures above, say, 900 °C.[3] Such uncontrolled nitrogen dissolution in the stainless steel can have a positive or a negative effect on the electrochemical and mechanical properties. Hitherto, the effect of “nitrogen alloying” in printed parts has received little attention in the literature.

Dissolution of nitrogen in austenitic stainless steels can also be carried out as a deliberate surface treatment referred to as high temperature solution nitriding (HTSN). HTSN improves the corrosion resistance and moderately enhances the hardness by the addition of up to 0.7 wt% nitrogen, depending on the alloy composition. Low temperature surface nitriding (LTSN) dissolves much higher nitrogen contents in the surface of the stainless steel (even more than 8 wt%) and results in the formation of expanded austenite, which significantly increases the surface hardness (up to 1200-1400 HV).[4] Gaseous nitriding is an excellent match with the complex geometries SLM enables to manufacture, providing a uniform layer thickness on all surfaces exposed to the gas. Thus hardening of internal surfaces of geometrically complex parts is possible.

The corrosion resistance of SLM 316L has recently gained significant attention in the literature, showing a wide variation in corrosion performance when compared to wrought 316L specimens. Most of the literature reports improved corrosion resistance in SLM 316L tested in chloride solutions (see for example [5], [6]) due to absence of CrS inclusions and their associated Cr-depleted regions [7]. Also, improved barrier characteristics of the passive film in acidic and Cl-containing media [8] and in simulated body fluids [9] have been reported for SLM 316 in comparison to wrought 316L. Recently, Sun et al. showed a significant increase of the pitting potential in SLM 316L specimens with a uniquely textured microstructure [10]. Others found poorer corrosion resistance of SLM 316L as compared to wrought material, as evidenced by a higher anodic current density, which was attributed to the inhomogeneous distribution of solutes, most importantly Mo [11]. Man et al. showed that SLM 316L was more susceptible to sensitization compared to wrought 316L, which was explained from easier nucleation of alloying-element carbides onto sub-grain boundaries.[12] Sun et al. reported slightly increased susceptibility to pitting in chloride solution. They ascribed this deterioration to the presence of pores, and postulated that the corrosion resistance for fully dense SLM 316L would be comparable to conventional 316L[13]. In the same paper, the group reported reduced wear resistance on SLM 316L as compared to wrought 316L, due to fracture and non-oxidative wear as the most dominant wear mechanism.[13]

So far, the influence of heat treatment on the corrosion and wear resistance of SLM 316L has received little attention in the scientific literature. Etefag and Guo observed improved corrosion resistance by annealing the SLM 316L for 2 hours at 800 °C, which was explained from the elimination of stresses [14]. This present work aims at investigating the influence of high temperature heat treatments and thermochemical surface hardening on SLM 316L, focusing on the microstructural changes and on the concomitant effects on corrosion and wear resistance.

2. Experimental

3D printed 316L specimens were manufactured by Selective Laser Melting on a SLM Solutions Realizer 250 Gas atomized 316L powder (SLM solutions) with the composition specified in Table 1 and size range 10-45 µm was used. An Ø10x10 mm cylinder geometry was chosen, with an Ø3 x 6.5 mm deep hole in the centre. The specimens were built on
support structures, using antiparallel stripes scanning, with 90° rotation between layers, with the following parameters: 158.8 W laser power, 0.533 m/s scan speed, 80 µm hatch distance, 50 µm layer thickness, resulting in 74.4 J/mm³ energy density.

**Table 1 Chemical composition of AISI 316L powder, as certified by the supplier SLM solutions.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>N</th>
<th>C</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content [wt%]</td>
<td>Bal.</td>
<td>17.6</td>
<td>12.8</td>
<td>2.32</td>
<td>0.85</td>
<td>0.59</td>
<td>0.12</td>
<td>0.09</td>
<td>0.030</td>
<td>0.004</td>
</tr>
</tbody>
</table>

A continuous flow of nitrogen gas was employed during the SLM process to protect the powder from oxidation. Due to the risk of nitrogen pick-up during printing [15], the nitrogen content of the SLM 316L specimens was determined by instrumental gas analysis on a LECO TN500. The nitrogen content in the printed part was (0.098 ± 0.002) wt%.

An internal 4 mm thread was made in the specimens used for corrosion testing. All specimens were ground with P80 paper until flat, followed by stepwise grinding until P4000, yielding a well-defined surface finish.

Five different heat and/or surface treatments were performed on ground specimens: austenitization (aust.), active austenitization (act. aust.), high temperature solution nitriding (HTSN) and low temperature surface nitriding (LTSN) using either act. aust. or HTSN as pre-treatment. Aust. was performed for 15 min at 1080 °C in a horizontal tube furnace at atmospheric pressure, using a reducing atmosphere (500 ml H₂/min and 100 ml Ar/min). Act. aust. and HTSN were performed in a horizontal tube furnace equipped with pressure control. Act. aust. was accomplished by 15 min at 1080 °C in 0.045 bar N₂ pressure, corresponding to an equilibrium nitrogen content of 0.14 wt% (see Fig. 1). HTSN was done at 1150 °C for 2 hours at 0.5 bar N₂, corresponding to an equilibrium nitrogen content of approx. 0.32 wt%. LTSN was performed after either act. aust. or HTSN. After a proprietary in-situ activation process, LTSN was done in Netzsch STA449 thermobalance in a two-step process at 440 °C, consisting of a 1 h boost in a flow of 100 ml NH₃/min and 5 ml N₂/min followed by 15 hours in a flow of 80 ml H₂/min, 20 ml NH₃/min and 5 ml N₂/min.

![Fig. 1 Isopleth in the phase diagram for 316L corresponding to the composition provided by the powder supplier, showing the stability of the austenite phase with varying N contents in the temperature range of 900 – 1300 °C. Relevant N2 isobars are superimposed on the isopleth, with the two treatments employing a N2 partial pressure marking the corresponding equilibrium nitrogen content.](image-url)
X-ray diffraction (XRD) analysis was performed to identify the phases present in SLM 316L in the as printed condition and after heat or thermochemical treatment. X-ray diffractograms were recorded in a parallel beam geometry, using symmetrical θ-2θ scanning on a Bruker D8 Discovery, equipped with CrKα radiation. The hardness of the specimens was characterised by Vickers microhardness indentation in both cross-sections and on the surface of full size samples (ground and passivated (in 20 % HNO₃) for the as printed specimen, passivated for the heat treated or thermochemically modified specimens). Hardness profiles were measured using a Struers DuroScan 70-G5 hardness tester, using a load of 10 g with a dwell time of 10 s. Hardness profiles were obtained on cut, embedded, ground and polished (until OP-U) cross sections. Surface hardness was measured on a FM-700 hardness tester, using a load of 50 g with a dwell time of 10 s. The embedded cross sections were used for microstructural characterisation, by light optical microscopy (LOM) investigations after etching by immersion in a 1% HF and 4% HNO₃ solution for 1080 s.

The tribological performance of the as printed and heat or thermochemically treated SLM 316L was evaluated by rotational pin-on-disc wear test on a CSM Tribometer, according to ASTM-99. The diameter of the wear track was set to 7 mm, and a rotational speed of 2 cm/s was chosen with a total wear distance of 250 m. The tribological properties were measured against an Ø6 mm AISI 52100 bearing steel ball using a load of 5 N. The wear test was performed at room temperature in ambient atmosphere, under dry/unlubricated conditions, on full size samples. For the as printed samples the surface was ground and passivated; for the heat treated and thermochemically modified samples the surface was ground before heat and/or surface treated and passivated after treatment. The specimens were cleaned in ethanol and weighed with a precision balance (0.1 mg), before and after wear test to evaluate the wear rate. The wear tests were performed on two samples for each specimen type. The surface morphology of the wear scars was inspected by LOM on a Keyence VHX6000 digital microscope, which was also used to evaluate the depth of the wear scar. The wear scars were further inspected by Scanning Electron Microscopy (SEM) using a Gemini Supra 35 (Zeiss) equipped with a BSE detector and a ThermoFisher Scientific EDS.

The resistance against corrosion of the SLM 316L specimens was investigated with cyclic potentiodynamic polarization testing (CPP), performed at room temperature using a ACM potentiostat. The samples were ground to P4000 prior to heat or thermochemical treatment, while the as printed specimen was tested in the ground (and passivated) condition, as no thermal treatment was performed. All specimens were passivated for 10 min in a freshly mixed 20 % HNO₃ solution prior to CPP. During testing, the specimens were fully immersed in the naturally aerated 3.5 wt% NaCl solution; the thread end was protected by a flat gasket. The exposed surface area of the working electrode (sample) was measured prior to each test. The potential was measured through a saturated calomel electrode (+244 V vs. SHE), using a platinum mesh as counter electrode. The open circuit potential (OCP) was measured for 600 s, after which the cyclic sweep was started. The CPP was run at a scan rate of 0.5 mV/s from -100 mV to +1200 mV with respect to the measured OCP. A current limit of 5 mA was employed, reversing the CPP if reached, otherwise the scan was reversed at +1200 mV vs. OCP. The corroded surfaces were investigated with light optical microscopy after CPP.

3. Results and discussion

The microstructure of the as printed SLM 316L is shown in Fig. 2 a), exhibiting several features typical of SLM 316L, including elongated austenite grains, rounded melt-pools and a cellular substructure. The microstructure consists primarily of austenite, as confirmed by
XRD (Fig. 3 a); a small b.c.c. 110 peak was also observed, indicating the presence of a small amount of δ-ferrite in the as printed microstructure.

![Fig. 3 X-ray diffractograms of SLM 316L samples in the a) as printed, austenitised, actively austenitised and solution nitrided, and b) low temperature surface nitrided with either active austenitization or solution nitriding as pre-treatment. Intensities were normalized to ease comparison.](image)

A slight shift to lower 20 angles of the γ(111) peak can be observed in the x-ray diffractograms of the actively austenitised specimen, indicating a small nitrogen uptake at the surface of the act. aust. specimen, while a slight shift to higher 20 angles of the γ(111) peak can be observed for the austenitised specimen, indicating a slight decrease in nitrogen content.
in the aust. specimen. This is further supported by the slightly higher surface hardness of the act. aust. specimen, as shown in Fig. 4 a, while the bulk hardness of the two austenitization types, measured in the cross sections, is comparable, shown in Fig. 4 b. Note the difference in the hardness values obtained on the surface (50 g load) and in the cross sections (10 g load).

The effect of the solution nitriding treatment (HTSN) can be observed by both XRD and hardness. XRD (Fig. 3a) shows a shift of the γ(111) peak towards smaller 2θ values which is evidence for the uptake of nitrogen as it causes an expansion of the austenite lattice. The hardening effect can be evaluated by the micro-hardness profile, shown in Fig. 4b, giving a hardening depth of at least 0.5 mm. Both the cross sectional hardness close to the surface and the surface hardness are slightly higher than that of the as-printed specimen, and significantly higher than that of the austenitised specimens. Etching revealed slight grain boundary sensitisation in the surface region to a depth of around 100 µm after HTSN treatment, as shown in Fig. 2 d and f.

Fig. 4 a) Surface hardness of SLM 316L as-printed and after heat- or/and surface treatment (average of 10 measurements). b) micro-hardness profile of SLM 316L after HTSN (average of 5 measurements, sigmoidal profile fit); the hardness values of as-printed, austenitized and actively austenitized are indicated (average of 50 measurements).

After low-temperature surface nitriding (LTSN), the surface hardness had increased significantly to around 700 HV0.05, as shown in Fig. 4 a, with a slightly higher hardness using HTSN as pre-treatment. This phenomenon has previously been observed and is shortly discussed in [16]. Phase analysis of LTSN specimens, Fig. 3 b, confirmed the formation of expanded austenite, γN, in the surface-adjacent region. The formation of an expanded austenite zone is also evident from LOM, Fig. 2 e and f. The thickness of the expanded austenite layer is approximately 7.5 µm.

The wear resistance of the as printed, heat-treated and surface hardened SLM 316L specimens was tested using pin-on-disc, using a 52100 ball counterpart under dry/unlubricated conditions. The wear rate, calculated from the mass loss of the 316L sample, is shown in Fig. 5 a, together with examples of cross-sectional wear profiles for each specimen, Fig. 5 b.

It is clear, that neither of the high temperature treatments resulted in improved wear resistance, with the HTSN treatment significantly increasing the wear rate, cf. the deep wear scar for this sample. As expected, the LTSN treatments increased the wear resistance of the SLM 316L significantly, with both of the LTSN specimens having the lowest wear rate, Fig. 5 a, and practically no depth on the wear scar, see Fig. 5 b.
The comparable wear rates of the as-printed and austenitised specimens and the similar appearances of the wear scars on these specimens (Fig. 6a-c) as well as on the 100Cr6 counterparts (Fig. 7a-c) suggest that the same wear type applies. The large dark patches observed in the wear tracks of the as-printed and austenitised specimens indicate the presence of oxidized wear debris. This was confirmed using EDS (not shown) by increased O and decreased Cr and Ni contents compared to unworn surfaces. The results would be consistent with a combination of adhesive and oxidative wear. Oxidative wear is generally known to be responsible for the mild wear on steels [17]. The oxidative wear creates hard oxides, which in turn lead to wear on the 52100 ball counterpart. The scar on the counterpart is not circular, because the extent of wear depends strongly on the particles formed.

![Fig. 5](image-url)  
**Fig. 5** a) wear rate and b) cross-sectional wear profile of SLM 316L after different heat and surface treatments; dry rotating pin-on-disc wear test against a 100Cr6 ball.

![Fig. 6](image-url)  
**Fig. 6** Back scatter electron images of wear tracks of SLM 316L a) as printed and after different b-f) heat or thermochemical treatments; rotating pin-on-disc wear test against an AISI 52100 ball.

In contrast, the HTSN specimen does not contain dark areas in the wear scar, Fig. 6 d. The counterpart 52100 ball, Fig. 7 d, has a lens-shaped wear scar of limited size, indicating
abrasive wear to be the dominant mechanism, mainly affecting the soft HTSN 316L (AISI 52100 has a hardness of ~850 HV).

After the LTSN treatments, the limited wear on the specimens is mainly adhesive and oxidative, Fig. 6 e and f. Instead, a significant abrasive wear occurred on the softer 52100 ball, leaving behind a perfectly round wear scar shown in Fig. 7 e and f.

Fig. 7 LOM of wear scar on AISI 52100 ball after rotating pin on disc test of different SLM 316L specimens.

Cyclic potentiostatic polarization (CPP) testing of the SLM 316L specimens in both as-printed and heat or thermochemically treated conditions, resulted in the polarization curves shown in Fig. 8. The as-printed specimen exhibits relatively poor resistance against pitting, with a badly defined passive region and pitting potential, E_{pit}. The current density reaches its limit before +1200 mV vs. OCP. The fluctuating curve from 300 to 750 mV indicates a numerous metastable pits, with the peaks of high current density showing that the as-printed specimen has difficulties to re-passivate.

Fig. 8 Polarization curves of as printed and a) high temperature and b) low temperature treated 316L SLM specimens, measured in 3.5 % NaCl solution at RT. All samples were passivated prior to immersion.
After the austenitisation treatment, SLM 316L showed improved resistance against pitting as compared to the as-printed condition, and broad passive range from 200 to approx. 750 mV, a well-defined \( E_{\text{pit}} \), with a fairly unchanged corrosion potential, \( E_{\text{corr}} \) and corrosion current density, \( I_{\text{corr}} \). The improved pitting resistance could be explained from a more homogeneous elemental distribution after austenitisation and possibly the dissolution of \( \delta \)-ferrite.

Active austenitisation improved the corrosion resistance of SLM 316L further, as evidenced by a significant increase in \( E_{\text{corr}} \) and a decrease in \( I_{\text{cor}} \), indicating a more noble material and a reduced corrosion rate, respectively; this is most likely due to the higher nitrogen content in the surface. The corrosion potential of the HTSN specimen is again significantly higher than the as-printed and aust. specimens, and is a consequence of the nitrogen dissolved in the surface, making the material more noble. Apparently, the observed sensitization from LOM did not have a notable negative effect in the CPP test. A lower current density compared to as printed, aust. and act. aust. specimens, can be observed during reverse anodic polarization, representing a higher resistance towards localized corrosion.

Both LTSN specimens exhibit excellent resistance against pitting. Although the current density of the anodic curve starts higher than the as-printed specimen, it increases much slower with increasing potential, exhibiting very little metastable pitting and a large passive region (roughly from 300 to 1400 mV); no fast increase in current density associated with the breakdown of the passive film \( (E_{\text{pit}}) \) is observed. The act. aust. + LTNS specimen was more noble (higher \( E_{\text{corr}} \)) than the HTSN + LTSN specimen, and while a generally higher current was observed in both LTSN specimens, the current density of the act. aust. + LTSN specimen was the highest. The higher current indicates higher corrosion rates, but there is a possibility that it is an artefact from chemical side reactions happening during the CPP test. In fact, the LTSN specimens showed a weight increase, whereas all other specimens exhibited a mass loss, which can be attributed to active corrosion (results are not shown). While the act. aust. + LTSN specimen showed a lower current density than the as printed and austenitised specimens, during reverse polarisation, the HTSN + LTSN specimen exhibited negative hysteresis loop, showing highly improved repassivation abilities.

4. Conclusion

SLM 316L was subjected to different heat- and thermochemical treatments including a new active austenitization, adjusting the surface nitrogen content of the part. The treatment had a major impact on the resulting microstructure, in that the cell structure resulting after SLM printing was dissolved. The tribological properties of the SLM 316L were largely unchanged by both austenitisation and active austenitisation whereas a highly reduced wear resistance was observed after HTSN treatment. The LTSN treatments improved the wear resistance significantly. The wear rates and wear tracks indicate adhesive and oxidative wear for the austenitized, samples, while adhesive wear occurs for the LTSN treated specimens. The pitting corrosion resistance of SLM 316L was improved by both austenitisation, active austenitisation and HTSN. Both active austenitisation and HTSN gave rise to increased corrosion potentials (more noble). LTSN specimens showed excellent resistance against pitting, although an overall high current density could mean increased corrosion rate.

Acknowledgement

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References

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HIGH NITROGEN HIGH CARBON STAINLESS STEEL

Abstract

High strength medium carbon austenitic stainless steels have been developed through partial and total replacement of nickel by nitrogen. Stainless steels containing 0.4% carbon with different combinations of nickel and nitrogen were produced in 10kg induction furnace under different nitrogen pressures. The produced stainless steels were cast and hot forged and the total nitrogen was determined. Furthermore, the produced forged steels were subjected to either only solution treatment or solution treatment followed by ageing process.

Nonmetallic inclusions such as carbides and nitrides were separated by electrolytic dissolution. Nitrogen as nitrides was determined and soluble nitrogen was calculated. XRD technique was used to investigate the types of nonmetallic inclusions. The microstructure of produced stainless steels was observed and the grain size was measured. The tensile properties at room temperature were determined. The influence of grain size, total nitrogen, insoluble and soluble nitrogen on tensile strength was investigated. All produced stainless steels as-quenched were aged at temperatures range from 450 °C to 950 °C for different times. Hardness test was carried out for aged stainless steels and the optimum ageing conditions were determined.

After solution treatment of the investigated stainless steels at 1050°C, a great portion of alloy carbides and nitrides is observed to be taken into solution. Nitrogen in solid solution increases both yield and tensile strengths. At optimum ageing temperature, this portion in solution precipitates, mainly as Cr2N, was causing higher precipitation strengthening. The yield strength and ultimate tensile strength of the aged stainless steels were found to increase at average rates of 706 MPa/1 mass % nitrogen and 723 MPa/1 mass % nitrogen, respectively. On the other hand, the increase of nitrogen content deteriorates the steel ductility.

Keywords

Nitrogen, stainless, steel, nickel, and nitrides

1. Introduction

At last few decades, nitrogen is added to stainless steels instead of nickel to improve mechanical properties. The main problem of nitrogen steel is how to introduce nitrogen in molten metal and how keep on it during solidification. The solubility of nitrogen is controlled by types and amount of alloying elements, temperature of melting and nitrogen pressure of casting. Alloying is the easier way of enhancing the nitrogen solubility. By adding elements with a negative interaction parameter and avoiding those of positive sign the low nitrogen content of an iron melt may be raised by more than two orders of magnitude. In the order of Cu < Co < Ni < Al < Si < C < N alloying have increasing detrimental effect on nitrogen solubility, while in the order of W < Mo < Mn < Cr < Nb < V < Ti nitrogen is more and more attracted to the melt. Thus its activity is lowered and its solubility is raised[1-19].

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Nitrogen was found to improve to large extent the properties of stainless steel, especially austenitic stainless steels. Nitrogen is significantly useful in increasing the yield strength [20-22].

Although the basic solid solution hardening mechanism by nitrogen in austenitic stainless steels is still in dispute, some concepts are based on the classical Fleischer theory of solid solution hardening in fcc materials [23-26].

The role of precipitation hardening mechanism for the high nitrogen steels (HNS) with high nitrogen concentration is suggested to be due to Cr$_2$N precipitation [27-28]. This behavior will be studied in this article. The role of nitrogen and its effect on mechanical properties and the mechanisms of hardening will be investigated.

2. Experimental

Eight types of stainless steels with different contents from nickel and nitrogen were carried out in 10 kg induction furnace under different nitrogen pressures. The reference stainless steel was melted in induction furnace in open air. The cast ingots were recharged into reheating furnace. The forging process was started at 1150°C and was finished at 900°C. The forging process was followed by air cooling. The kjeldahl method was used to determine nitrogen content in the produced stainless steels. The heat treatment processes for investigated stainless steels were made as follows. The stainless steel samples were heated up to 1050°C, kept for one hour, at this temperature and followed by water quenching. One set of quenched stainless steels was subjected to ageing process for one, two and three hours at different temperatures. The ageing process was followed by normal air cooling to room temperature.

Samples from the investigated stainless steels were prepared for microscopic examination. The grain diameter was calculated from the number of boundaries intersecting a line of known length at a known magnification. Rockwell hardness (HRC) tests were carried out on polished stainless steel samples. The hardness for produced stainless steels was measured at different ageing temperatures and time. Tensile tests were carried out at room temperature for stainless steels as-quenched and as-aged.

3. Results

The produced stainless steels have chemical compositions as shown in Table 1. For forging stainless steels, solution treatment carried out at 1050°C for 1 hour, followed by water quenching. Ageing process carried out for all produced stainless steels. Non-metallic Inclusions (NMI) were isolated electrolytically as insoluble precipitates which are collected and analyzed by using XRD. Nitrogen (nitrides) in NMI was determined and soluble nitrogen contents after solution treatment were calculated as given in Table 2. The XRD structure analysis of NMI of different investigated as-quenched and as aged stainless steels is illustrated in Figs. (1-2). The microstructures of produced stainless steels containing nitrogen after solution treatment and ageing process are mainly austenitic structure with different grain size as illustrated in Fig. 3. The mechanical properties at room temperatures for produced stainless steels after quenching and ageing are given in Tables (3-4). Hardness of aged stainless steels after solution treatment at different temperatures & time are illustrated in Fig. 4.
Table 1: Chemical composition of investigated steels

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>C%</th>
<th>Si%</th>
<th>Mn%</th>
<th>Cr%</th>
<th>W%</th>
<th>Ni%</th>
<th>N%</th>
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<td>3.20</td>
<td>1.14</td>
<td>18.10</td>
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<td>3.07</td>
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<td>0.17</td>
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<td>17.80</td>
<td>1.22</td>
<td>0.13</td>
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<td>2.77</td>
<td>1.16</td>
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<td>3.71</td>
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<td>16.33</td>
<td>1.13</td>
<td>4.13</td>
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</table>

* The chemical composition according to standard exhausted austenitic stainless steel DIN 1,4873

Table 2: Percentage of soluble ($\% N_s$) and insoluble ($\% N_{ppt.}$) nitrogen in investigated steels after quenching and ageing.

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>After quenching</th>
<th>After ageing</th>
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<tbody>
<tr>
<td></td>
<td>%N$_{ppt.}$</td>
<td>N$_s$</td>
</tr>
<tr>
<td>2</td>
<td>63.4</td>
<td>36.6</td>
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<td>3</td>
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<td>69.5</td>
</tr>
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<td>34.7</td>
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<td>8</td>
<td>57.6</td>
<td>42.4</td>
</tr>
</tbody>
</table>

Fig.1: XRD of non-metallic precipitates of investigated stainless steels after quenching.
**Fig. 2:** XRD of non-metallic precipitates of investigated steels after ageing.

**Fig. 3:** Microstructure of investigated as quenched and corresponding aged steels (Q: Quenched steel, A: Aged steel).
Table 3: Mechanical properties of investigated steels after solution treatment

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>$R_{0.2}$ (MPa)</th>
<th>$R_m$ (MPa)</th>
<th>Elongation %</th>
<th>Reduction of area %</th>
</tr>
</thead>
<tbody>
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<td>977</td>
<td>13.1</td>
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<td>1028</td>
<td>25.8</td>
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<td>550</td>
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<td>972</td>
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<td>592</td>
<td>946</td>
<td>13.1</td>
<td>5.2</td>
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Table 4: Mechanical properties of investigated steels at room temperature after optimum ageing conditions.

<table>
<thead>
<tr>
<th>Steel No.</th>
<th>$R_{0.2}$ (MPa)</th>
<th>$R_m$ (MPa)</th>
<th>Elongation %</th>
<th>Reduction of Area %</th>
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<td>654</td>
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<td>1013</td>
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<td>489</td>
<td>978</td>
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<td>8</td>
<td>735</td>
<td>1411</td>
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Fig.4: Hardness of investigated stainless steels measured at different ageing temperature.
4. Discussion

The aim of this work is to develop new austenitic stainless steels through replacing nickel by nitrogen. Eight stainless steels were designed to cover partial and the complete replacement of nickel by nitrogen as given in Table 1. Microstructures illustrate that all the produced stainless steels have austenitic phase with different grain size depends on nitrogen contents as given in Fig. 3.

To distinguish between the roles of soluble and insoluble nitrogen on the grain refinement, precipitation strengthening and, hence, on mechanical properties, NMI's were isolated electrolytically as insoluble precipitates which were collected and analyzed. The XRD structure analysis of NMI of different investigated steels are illustrated in Figs. 1-2. It is clear from these figures the existence of different iron and chromium carbides (Fe₃C and Cr₂₃C₆) accompanied with different iron and chromium nitrides (Fe₃N, Fe₃Nₐ and Cr₂N). An intermetallic compound of Cr₁.₃₆Feₐ.₅₂ is also observed in stainless 5. Few contents of non-metallic inclusions such as Ni₉S₈, Cr₃S₄, FeS₂ and MnO₂ are also found in the different investigated stainless steels. The main detected precipitate Cr₂N was found in all investigated stainless steels except stainless steel 1, which has no added nitrogen.

Table 3 represents the average results of the room-temperature mechanical testing of investigated stainless steels after solution treatment at 1050°C for 1 hr. The yield strength, ultimate tensile strength, elongation and reduction of area %, are plotted as a function of total nitrogen content in stainless steels, Fig. 5. The results clarify the improving effect of nitrogen on both yield strength and ultimate tensile strength. The effect is more significant in respect to yield strength. The investigated high nitrogen-nickel free austenitic stainless steels (steels No. 2 and 4) exhibit 0.2% proof stress of 550-601 MPa which is more than double the yield strength of conventional Cr-Ni steels of below 300 MPa in the solution annealed state [29]. The high yield strength of investigated high N-austenitic stainless steels after solution treatment is also accompanied by high levels of ultimate tensile strength. An ultimate tensile strength of 972 MPa has been attained by alloying Cr-7.1%Ni with 0.25%N. Approximately the same level of ultimate tensile strength (977MPa) has been attained by total replacement of nickel by nitrogen (nickel free, 0.43%N). In contrast to the yield strength and ultimate tensile strength, there is an approximately linear decrease in elongation and reduction of area with increasing nitrogen content.

The average results of the room temperature mechanical properties of investigated stainless steels after optimum ageing conditions are given in Table 4. The data representing the 0.2% proof stress and ultimate tensile strength are plotted as a function of nitrogen content in Fig. 6. Examination of this figure reveals that there is a strong positive correlation between the nitrogen content of investigated steels and both yield and ultimate tensile strength. The yield strength was observed to increase at an average rate of 706 MPa /1mass % nitrogen according to the relation:

\[ R_y (MPa) = 339 + 706[N\%] \] (1)

and the ultimate tensile strength increases at an average rate of 723 MPa /1mass % nitrogen given by the relation:

\[ R_u (MPa) = 801 + 723[N\%] \] (2)

On the other hand, the increase of nitrogen content deteriorates the steel ductility. The contribution of nitrogen in yield strength, in both solution treatment and ageing treatment, reveals that the strength increment brought about by aging treatment is mainly due to nitrogen
compound precipitated. In high-nitrogen containing steel, a sufficient amount of nitrogen is taken in solution and becomes available for precipitation during ageing treatment. However, this strength increment due to nitrogen compound precipitates is accompanied by further deterioration of steel ductility.

The comparison between the data given in Tables (3-4) clarifies the effect of ageing process on the mechanical properties of investigated steels. Increments up to 33% and 56% in the yield tensile strength and ultimate tensile strength respectively could be obtained due to ageing process.

The effect of both soluble and insoluble nitrogen contents on grain size of investigated stainless steels are shown in Figs. (7-8) for both quenched and aged stainless steels. Both soluble and insoluble nitrogen contents have a significant positive effect on grain size. There is a linear relationship between both soluble and insoluble nitrogen and the reciprocal of the square root of grain size ($D^{-0.5}$). Thus, as either soluble or insoluble nitrogen increases, the reciprocal of the square root of grain size increases, i.e. the grain size decreases. This positive effect of both soluble and insoluble nitrogen on grain refinement could be reflected on the mechanical properties of investigated stainless steels.

![Fig. 5 Variation of mechanical properties at room temperature with nitrogen content for investigated steels, after solution treatment](image1)

![Fig 6 Variation of mechanical properties at room temperature with nitrogen content for investigated steels after ageing at optimum](image2)

![Fig. 7 Effect of soluble nitrogen on grain size for investigated steels as a - quenched b - aged](image3)

![Fig. 8 Effect of precipitated nitrogen (as nitrides) on grain size of the investigated steel in a - Quenched state, b - Aged state](image4)
The nitrogen contained in NMIs - nitrides (N\textsubscript{ppt.}) - was determined. It was possible to calculate the soluble nitrogen content by subtracting the nitrogen contained as nitride (N\textsubscript{T}) from the total nitrogen content (N\textsubscript{T}). Table 2 summarizes the soluble and insoluble nitrogen contents in investigated stainless steels after quenching and ageing processes. However, soluble and insoluble nitrogen contents have different effects on the mechanical properties of investigated stainless steels. Increasing the soluble nitrogen content is accompanied with some losses in strength (both yield stress and ultimate tensile strength) for quenched and aged stainless steels (Figs.9-10). On the other hand, increasing the insoluble nitrogen content has a significant strength increment (both yield stress and ultimate tensile strength) for quenched and aged stainless steels (Figs. 11-12).

By increasing the soluble nitrogen, the solid solution hardening increases. However, this strength increment seems to be lower than the losses in precipitation strengthening (due to decrease of nitrides precipitates) with the result of decrease in both yield and ultimate tensile strengths as the soluble nitrogen increases. Strength increment due to increase of insoluble (precipitated) nitrogen could be attributed to increase of precipitation hardening as a result of increasing the volume fraction of alloy nitrides precipitates. Increase of insoluble nitrogen would be accompanied by decreasing the soluble nitrogen with the result of decreasing the solid solution strengthening. However, it seems that the strength increment due to increase of precipitation hardening is higher than the strength decrement due to the losses in solid solution hardening resulting in net increases in yield and ultimate tensile strengths as the insoluble nitrogen content increases.

To investigate the contribution of total nitrogen and each of its existing forms, mobile and/or precipitated on the strengthening of the investigated stainless steels, steel samples were selected to a heat treatment cycle. The heat treatment cycle consists of reheating the samples to 1050 °C for one hour, then quenching in water followed by ageing. Fig. 4 illustrates the effect of tempering temperature and time on the hardness of investigated stainless steels. It is clear that, depending mainly on the composition, the maximum hardness was developed between 550 °C and 900 °C. The soaking time has a negligible effect on the secondary hardening. Fairly rapid decreasing of hardness is observed with increasing ageing temperature after reaching its maximum value. This result is in agreement with that obtained by Uggowitzer et al [24,30]. It could be concluded that the precipitate of Cr\textsubscript{2}N starts nearly at 600 °C. Increasing both nitrogen content and temperature accelerate the formation of nitrides, as the Cr-N contribution is governed by the inter-granular precipitation hardening (~N\textsubscript{T}).

![Fig. 9](image9.png)  
**Fig. 9** Effect of soluble nitrogen on mechanical properties of investigated steels in quenched state.

![Fig. 10](image10.png)  
**Fig. 10** Effect of soluble nitrogen on the mechanical properties of the investigated steels in aged state.
The maximum hardness for stainless steels 2 & 4, with high nitrogen content and no nickel was attained at 550 - 650 °C. This secondary hardening phenomenon may be attributed to the formation of fine precipitates, carbides and nitrides. This fine precipitates are often nucleated on dislocation [31].

On over-aging, after secondary hardening, the precipitates on dislocation begin to be coarse and become more widely spaced and so become less effective in locking the dislocations. Eventually, the dislocations must be able to free themselves from these precipitates so the recovery can begin. The combined loss of strength, by freeing dislocations from precipitates and the recovery of the dense dislocation, leads to marked softening [32-35]. This softening process continues when the precipitates become more coarser and the matrix re-crystallizes.

To explain the influence of steel composition on the maximum ageing temperature one would take into account the following:

- Nickel decreases the nitrogen solubility in steel and, hence, increases its activity.
- Nickel forms inter-metallic phases \( \delta, \chi \) and \( \mu \).
- Alloying with nitrogen suppresses the formation of \( \delta \) phase.
- The precipitation of \( \chi \) phase is shifted by nitrogen to longer times and the temperature range of occurrence becomes narrow.
- With increasing nitrogen content the \( \text{M}_{6}\text{C} \) carbide was observed to appear instead of the \( \chi \) phase.

So, in the absence of nickel, i.e. in the absence of \( \chi \) intermetallic phase, the precipitation of nitrides and carbides starts at low temperature 550 °C – 650 °C. The presence of \( \chi \) phase as a result of nickel content needs a higher temperature up to 900 °C to substitute this phase by \( \text{M}_{6}\text{C} \). So, the maximum ageing hardness shifts towards higher temperature.

5. Conclusions

This work has been carried out to investigate the effect of partial and total replacement of nickel by nitrogen on the phase stability and its effect on mechanical properties of new designed austenitic stainless steels. From the results, the following conclusions can be drawn:

- The microstructure of the produced stainless steels are mainly austenitic phase
The maximum hardness temperature depends mainly on the chemical composition of investigated stainless steels. So each group of steels (2,4), (6,8) and (3,5) have nearly the same behavior.

Nitrogen in solid solution increases both yield and ultimate tensile strengths but its effect on yield strength is more significant.

Maximum hardness values are obtained in ageing at 550 °C to 900 °C depending on the chemical composition of the stainless steel.

In aged stainless steels, the yield and ultimate tensile strengths increase with an average rate of 706 MPa / %N and 723 MPa / %N, respectively.

Nitrogen, either as soluble or insoluble form, is effective in grain refinement of both as-quenched and as-aged stainless steels.

In both quenched and aged stainless steels, whereas increase of insoluble nitrogen increases the strength significantly, higher soluble nitrogen results in a decrease in the insoluble nitrogen, and hence causes some loss in strength.

In quenched stainless steels, a great portion of alloy carbides and nitrides is taken in solution during solution treatment at 1050 °C. This portion precipitates during subsequent ageing process, causing higher precipitation strengthening.

References


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Martensitic stainless steels
FORMATION OF AUSTENITE DURING AGEING OF 17-4 PH PRECIPITATION HARDENING STAINLESS STEEL

Abstract

The 17-4 PH is a precipitation hardening stainless steel. Precipitation hardening steels are characterized by good mechanical properties and corrosion resistance. Mechanical properties are achieved by ageing heat treatments. The aging process is essentially the formation of Cu-rich precipitates that increase the steel hardness. However, eventually their coarsening causes a substantial drop in hardness. The isothermal aging also causes austenite formation. The evolution of the microstructure during ageing was investigated in order to explain the processes that have effect on formation of the reversed austenite. A dilatometer was used to observe the austenite formation, while the coarsening of Cu-rich precipitates was observed by transmission electron microscope. The amount of austenite was measured with X-ray diffraction. It was found that the amount of reverse austenite does not only depend on the amount of transformed austenite during ageing but also on its chemistry, as it dictates its ability to transform into martensite during cooling.

Keywords: precipitation hardening stainless steel, reverted austenite, dilatometry, Cu precipitates

1. Introduction

Austenitic stainless steels have poor tensile strength, hardness and wear resistance, so martensitic stainless steels have been increasingly applied in marine environments, power plants, and chemical industries because of their good corrosion resistance and mechanical properties, the 17-4 PH is a widely used steel grade with high strength, ductility and corrosion resistance[1-5]. The 17-4 PH steel contains approximately 3 wt. % copper [6,7]. It’s mechanical properties can be attributed to precipitation of copper rich spherical particles which strengthen the martensite matrix [3,8]. The copper rich precipitates are coherent with the martensite matrix and represent dislocations obstacles [9–13]. Upon thermal ageing, nearly all of the copper becomes incorporated into precipitates [10].

Heat treatment of 17-4 PH martensitic precipitation steel is comprised of three main steps, namely: solution annealing, quenching and ageing followed by air cooling. During aging the tempering of martensite and reverse austenite formation also take place [7,8,12,13].

Microstructural development during heat treatment is crucial for understanding of steel properties. In 17-4 PH steel the most important and complex changes in the microstructure occurs during ageing. Therefore, the aim of the present work is to investigate the microstructural changes during ageing of 17-4 PH steel.
2. Experimental

Rods of 17-4 PH martensitic precipitation hardening stainless steel with the diameter of 30 mm were used for the experiments (chemical analysis in table 1). Carbon and sulfur were analyzed with TOFMS (time-of-flight mass spectrometer) LECO CS600, nitrogen was analyzed by TOFMS LECO TC436, while other elements were analyzed by OES (optical emission spectroscopy) ARL 3460.

*Table 1: Chemical composition of the investigated steel*

<table>
<thead>
<tr>
<th>element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>Nb</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>0.03</td>
<td>0.50</td>
<td>0.26</td>
<td>0.026</td>
<td>0.001</td>
<td>15.53</td>
<td>4.32</td>
<td>0.15</td>
<td>3.27</td>
<td>0.27</td>
<td>0.031</td>
</tr>
</tbody>
</table>

Dilatometry was carried out on the TA Instruments 805A/D quenching dilatometer. The specimens were cylinders with the diameter of 4 mm and 10 mm length. All samples were firstly solution annealed for 1 h at 1040 °C in vacuum and cooled to room temperature at 1 °C/s. Then the samples were aged at different temperatures (table 2). The heating rate to the aging (annealing) temperature was 5 °C/s and the cooling rate was 1 °C/s. The dilatometry was done for experimental heat treatments.

The samples for optical microscopy were etched with picral and observed with Nikon Microphot FXA optical microscope with Hitachi HV-C20A 3CCD video camera. The sample hardness was measured Intron Tukon 2100B HV10 measurements. The reverted austenite content was measured with X-ray diffraction on XRD Bruker D8 Advance machine.

Transmission electron microscopy samples of experimental heat treatments were prepared using argon ion-slicing with JEOL EM-09100IS Ion Slicer. After the thin-foil preparations, the two aged specimens were examined with transmission electron microscope (JEOL JEM-2100).

The thermodynamic calculations were done with ThermoCalc software TCFE 8.0 database.

*Table 2: Experimental dilatometer annealing heat treatments*

<table>
<thead>
<tr>
<th>Solution annealing/1 h (°C)</th>
<th>1040</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing/4 h (°C)</td>
<td>RT</td>
</tr>
</tbody>
</table>

*RT room temperature

3. Results and discussion

The microstructures consist of lath martensite (Fig. 1). The hardness and the amount of reverse austenite in the specimens is shown in table 3, the quenched sample 0 has the highest hardness 370 HV10. During aging at low temperatures (below 500 °C) the hardness rises, due to the formation of copper rich zones, as they occur before the copper precipitation [14,15].
Table 3: Hardness and amount of austenite in the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>RT</th>
<th>590</th>
<th>600</th>
<th>610</th>
<th>620</th>
<th>630</th>
<th>640</th>
<th>650</th>
<th>660</th>
<th>670</th>
<th>680</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (%)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>13</td>
<td>10.5</td>
<td>12.6</td>
<td>15.2</td>
<td>11.7</td>
<td>5.7</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
<td>HV10</td>
<td>370</td>
<td>349</td>
<td>344</td>
<td>334</td>
<td>317</td>
<td>310</td>
<td>317</td>
<td>318</td>
<td>321</td>
<td>325</td>
<td>323</td>
</tr>
</tbody>
</table>

*RT room temperature

Fig. 1. Lath martensite microstructure of 17-4 PH sample annealed at 660 °C

Annealing at higher temperatures lowers the hardness mainly, due to precipitate coarsening and martensite tempering; however, at higher annealing temperatures also due to increasing amount of the austenite in the microstructure. The hardness of the samples is lowered by increasing the annealing temperatures up to 630 °C, but it starts to rise at annealing temperatures of 640 °C and above despite precipitate coarsening. The rise in hardness is attributed to newly formed martensite as can be confirmed by the dilatometry (Fig. 2).

Fig. 2. Dilatometric curves of the specimens during isothermal annealing (aging) a) detail for austenite formation, b) detail for martensite formation

After heat treatment the samples of 17-4 PH steel were investigated by transmission electron microscopy. The copper precipitates in the martensite matrix appeared to be cylinder shaped, their size ranged from the 50 µm long and 10 µm wide precipitates (Fig. 3a) in the
sample annealed at 590 °C to 100 µm long and 30 µm wide precipitates in the sample annealed at 680 °C (Fig. 3b).

**Fig. 3.** Transmission electron microscopy of samples a) annealed at 590 °C and b) 680 °C showing Cu precipitates.

ThermoCalc analysis in Fig. 4 shows the equilibrium amount of austenite (FCC_A1), ferrite (BCC_A2), copper precipitates (FCC_A1#2), Cr₂₃C₆ chromium carbides (M23C6) and MC niobium carbides (FCC_A1#3). The copper-rich precipitates are stable in the whole temperature range between 580 and 700 °C.

**Fig. 4:** Amount of stable phases in g per 100 g sample, temperature range from 580 to 700 °C.

The amount of stable austenite and its composition during the annealing temperatures were calculated by ThermoCalc, Table 4. With the higher annealing temperatures the portion of austenite increases. The ThermoCalc analysis shows that the austenite that is formed during the lower temperatures is richer in austenite stabilizing elements, like Ni and Mn than at higher temperatures.
Table 4: The amount of austenite and $\gamma$-stabilising elements at different aging temperatures calculated by ThermoCalc

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Fe</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>(Cu+Ni+Mn)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>680</td>
<td>77.19</td>
<td>0.86</td>
<td>13.96</td>
<td>6.14</td>
<td>1.26</td>
<td>8.26</td>
<td>54.4</td>
</tr>
<tr>
<td>670</td>
<td>76.75</td>
<td>0.96</td>
<td>13.77</td>
<td>6.67</td>
<td>1.25</td>
<td>8.88</td>
<td>46.4</td>
</tr>
<tr>
<td>660</td>
<td>76.21</td>
<td>1.08</td>
<td>13.60</td>
<td>7.27</td>
<td>1.24</td>
<td>9.59</td>
<td>39.0</td>
</tr>
<tr>
<td>650</td>
<td>75.57</td>
<td>1.22</td>
<td>13.43</td>
<td>7.93</td>
<td>1.24</td>
<td>10.39</td>
<td>32.6</td>
</tr>
<tr>
<td>640</td>
<td>74.84</td>
<td>1.39</td>
<td>13.27</td>
<td>8.65</td>
<td>1.24</td>
<td>11.28</td>
<td>27.2</td>
</tr>
<tr>
<td>630</td>
<td>74.02</td>
<td>1.58</td>
<td>13.11</td>
<td>9.42</td>
<td>1.25</td>
<td>12.25</td>
<td>22.6</td>
</tr>
<tr>
<td>620</td>
<td>73.12</td>
<td>1.80</td>
<td>12.93</td>
<td>10.26</td>
<td>1.27</td>
<td>13.33</td>
<td>18.7</td>
</tr>
<tr>
<td>610</td>
<td>72.13</td>
<td>2.05</td>
<td>12.74</td>
<td>11.15</td>
<td>1.29</td>
<td>14.49</td>
<td>15.6</td>
</tr>
<tr>
<td>600</td>
<td>71.05</td>
<td>2.33</td>
<td>12.53</td>
<td>12.11</td>
<td>1.33</td>
<td>15.77</td>
<td>13.0</td>
</tr>
<tr>
<td>590</td>
<td>69.88</td>
<td>2.66</td>
<td>12.30</td>
<td>13.15</td>
<td>1.37</td>
<td>17.18</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Since there was no austenite detectable by the X-ray diffraction analysis of sample aged at 590 °C, we can assume there was not enough time for formation of detectable amounts of austenite. Transmission electron microscopy analysis of the sample annealed at 590 °C in Fig. 5 revealed the presence of austenite through elemental mapping which is somewhat in accordance to ThermoCalc calculations presented in Fig. 4. Also, Bhambroo et al. [12] found reverted austenite formation when ageing at 580 °C for 4h.

Fig. 5. TEM EDS elemental mapping of sample annealed at 590 °C showing Ni enriched austenitic areas.

The dilatometry curves in Fig. 2a show that austenite forms during isothermal annealing at temperatures 610 °C and above show a decrease in sample length. This decrease in length is associated with austenite formation (as it has higher density due to fcc structure). Above 650 °C the decrease in length is even more prominent and during cooling the martensite
transformation curve is evident, although the first signs of martensite transformation can be seen in the sample annealed at 640 °C, Fig. 2b. This means that although there was more stable austenite during isothermal annealing at temperatures 650 °C and above, there is less austenite present at room temperature due to the martensite formation. Namely, the austenite formed at lower annealing temperatures is richer in austenite forming elements like Ni and Mn that lower Ms and Mf temperatures and does not completely transform to martensite during cooling, Table 4. Therefore the amount of austenite at room temperature is greater, Table 4.

4. Conclusions

Precipitation hardening martensitic stainless steel 17-4 PH was investigated. Solution annealed samples were isothermally aged at different temperatures. The aging process and resulting samples were investigated by dilatometry, transmission electron microscopy and ThermoCalc. The results are can be summarised as follows:

- The amount of austenite present in samples after isothermal depends not only on the amount of formed austenite, but mainly on the chemical composition of newly formed austenite.
- The chemical composition dictates the reverse austenite’s ability to form martensite during cooling. This means that part of the reverted austenite that forms during ageing is transformed back to martensite during cooling. The revert austenite with higher Ni and Mn contents will not harden.
- Higher amounts of austenite will have roughly the bulk chemical composition and will form martensite during cooling, this becomes evident when annealing at 650 °C and above for 2 h.

5. References

Duplex stainless steels
APPLICATIONS OF X-RAY DIFFRACTOMETRY ON PHASE QUANTIFICATION IN STAINLESS STEELS

Abstract

Performance of stainless steels (SS) is a direct function of the microstructure, and phase quantification is an important experimental procedure for microstructural characterization. X-ray diffractometry (XRD) is widely used in phase identification of SS, and analysis of the diffracted intensity peaks of the phases allows the determination of their volume fractions. X-ray diffraction patterns using copper or chromium X-ray sources were obtained for two different SS. The first group of samples are composed of a duplex stainless steel (DSS) solution-treated at three different temperatures, in order to obtain different ferrite-to-austenite volume fraction ratios. The other group was composed by quenched and tempered samples of a supermartensitic stainless steel (SMSS) with different amounts of retained and/or reversed austenite. It was found that XRD results using copper targets as source of X-rays lead to better quantification of phases for both SS studied. However, the technique was influenced by crystallographic texture in DSS phases quantification; in the absence of marked texture, XRD results in quantification similar to other techniques. Only SMSS samples with higher amounts of coarse reversed austenite (as in samples tempered for 2 h at 625 or 650 °C) could have austenite partially quantified, being magnetic measurements a better indirect technique for quantification of phases in SMSS.

Keywords


1. Introduction

Duplex Stainless Steels (DSS) are applied in situations where mechanical resistance, toughness and high corrosion resistance are needed. Their typical microstructure approximately equal amounts of ferrite and austenite, which can be obtained after solution heat treatment between 1000 and 1200 °C followed by fast cooling, usually in water. This processing route maintain DSS in a metastable equilibrium, and for this reason subsequent heating cycles could lead to the formation of undesirable phases, like sigma, chi or chromium nitrides [1,2].

Supermartensitic Stainless Steels (SMSS) belongs to another important class of materials, and were developed to provide the high mechanical resistance associated to martensitic structures, together to the ability of receiving welding procedures without a loss in corrosion resistance. The low content of carbon in SMSS allows the martensitic phase to have a body centered cubic (BCC) crystal structure, the same found in the ferrite phase. Martensite, in SMSS, is crystallographic equivalent to the ferrite phase, differing from this phase in the phase transformations that lead to its formation. Ni content of SMSS can lead to expressive amounts of retained austenite after quenching, and/or reversed austenite during tempering heat treatment. [3].

1 FEI University, 2 USP
Considering that desired properties of DSS and SMSS are close related to the amounts of ferrite and austenite (for DSS), or the amount of retained/reversed austenite in SMSS, this work will analyse the possibility of X-ray diffraction (XRD) as a technique for phases characterisation and quantification, comparing the quantification results by XRD to the quantification of ferrite and martensite performed by magnetic measurements using a ferritscope. A UNS S31803 DSS and an experimental SMSS alloy were used, both in different heat treatment conditions.

2. Experimental Procedures

Samples of UNS S31803 DSS were obtained from a 3 mm thickness sheet, and were solution-treated for 30 min at 1070, 1130 or 1180 °C and water quenched. Samples of an experimental SMSS were austenitized at 1050 °C, oil quenched and then tempered for 2 hours at 550, 575, 600, 625, 650 or 700 °C. Chemical compositions of both alloys are presented in Table 1.

| Table 1 – Chemical compositions (wt%) of the DSS and SMSS studied. |
|------------------|----|----|----|----|----|----|----|----|----|----|----|
|                  | Cr | Ni | Mo | N  | C  | Mn | Si | Nb | Ti | Cu | Fe |
| DSS              | 22.48 | 5.74 | 3.20 | 0.162 | 0.018 | 1.42 | -  | -  | 0.15 | bal. |
| SMSS             | 13.35 | 5.10 | 1.08 | 0.17  | 0.008 | 0.63 | 0.39 | 0.11| 0.008| -   |

Specimens are metallographic polished before X-ray diffraction analysis, which were performed in a Shimadzuy XRD-7000 diffractometer. Copper target X-ray source generated Cu Kα1 X-ray (λ = 0.15406 nm, using a monochromator crystal just before the X-ray detector) were used for XRD analysis, with scanning angle in the range of 40° < 2θ < 100° for the DSS and 40° < 2θ < 85° for the SMSS. Chromium target X-ray source generated Cr Kα1 X-ray (λ = 0.22897 nm, using a vanadium filter in the X-ray source) were also used in XRD analysis, with scanning angle in the range of 60° < 2θ < 160° for both steels. Independent of the X-ray source, a step of 0.02° and a scanning rate of 0.5 °/min were employed; acceleration voltage in source was 30 kV, and filament current was 30 mA, generating a 0.9 kW power X-ray beam.

For each sample, ten XRD patterns were obtained.

As described elsewhere [4, 5, 6], when only two phases are identified in XRD, the quantification of phases corresponding to the peaks found was possible through the use of Eq. (1), which relates the volumetric fraction (X), the integrated intensity (I) of the diffraction peak and the scattering factor (R) of the (n) peaks related to α' phase and (m) peaks related to γ phase.

\[
X_{\alpha'} = \frac{\frac{1}{n} \sum_{1}^{n} \frac{I_{\alpha'}}{R_{\alpha'}}}{\frac{1}{n} \sum_{1}^{n} \frac{I_{\alpha'}}{R_{\alpha'}} + \frac{1}{m} \sum_{1}^{m} \frac{I_{\gamma}}{R_{\gamma}}} \tag{1}
\]

Scattering factor (R) was calculated from Eq. (2) for each crystallographic (hkl) Miller index plane, knowing: i) structure factor (F), ii) the multiplicity factor (p) associated with the plane (hkl), iii) diffraction angle θ of the Bragg Law (Eq. 3), iv) Debye-Waller (DWF) temperature factor, and v) the volume of unit cell (V) of the phase. V was calculated using the
unit cell parameter \(a\) obtained for all \((hkl)\) plane spacing \(d\) using Eq. 4, since both phases are cubic crystal structures [4,5]. All \(d\) values obtained were used for the Nelson-Riley adjustment (eq. 5) [7], obtaining \(a\) in each XRD for both phases.

\[
R_{hkl} = \left(\frac{1}{V^2}\right)[F^2p\left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}\right)]DWF
\]

\(n\lambda = 2d_{(hkl)} \sin \theta\)

\(a = d_{(hkl)} \sqrt{h^2 + k^2 + l^2}\)

\[CP_{N-R} = \frac{1}{2} \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\vartheta}\right)\]

The DWF factor is a function of the diffraction angle \(\theta\) and the wavelength of the X-ray source (\(\lambda\)), and according to ASTM E 975-13 [8], DWF can be estimated by Eq. (6).

\[DWF_{(hkl)} = e^{-0.71\left(\frac{\sin \theta}{\lambda}\right)^2}\]

The structure factor \(F(hkl)\) is dependent on the atomic scattering factor \((f)\), determined by the mean influence of atomic species in a phase. With the weighted \((f)\), the value of structure \(F(hkl)\) is calculated using simplifications according to the type of structure, BCC or FCC in the case of this work [4, 5, 6].

After XRD analysis, the volume fraction of magnetic phase (ferrite in DSS and martensite in SMSS) were obtained with the aid of a ferritscope MP30 FISCHER, which was calibrated using standard samples containing 14.4 %, 30.7 %, 86.2 % or 100% of magnetic phase. In each sample, 10 to 30 measurements were taken, determining mean values and standard deviation.

3. Results and discussion

Typical XRD patterns for studied DSS and SMSS can be observed in Fig. 1. Quantification of the ferromagnetic martensite volume fraction (obtained in ferritscope measurements) compared to the martensite volume fraction (obtained by XRD analysis) are presented in Fig. 2. In a similar way, in Fig. 3 the ferromagnetic ferrite volume fraction is compared to ferrite volume fraction of the DSS samples.
Fig 1. Typical XRD patterns for (A) SMSS using Cu Kα1 radiation, (B) SMSS using Cr Kα1 radiation, (C) DSS using Cu Kα1 radiation, and (D) DSS using Cr Kα1 radiation. Crystallographic planes of the phases are identified in each XRD pattern.

Fig 2. Ferromagnetic martensite volume fraction (obtained in ferritscope measurements) compared to the martensite volume fraction (obtained by XRD analysis using Cu Kα1 or Cr Kα1 radiation) for the SMSS.
The SMSS only showed $\gamma$(200), $\gamma$(111) and $\gamma$(220) peaks for the samples tempered at 625 or 650°C, in both radiation sources (Fig. 1A and 1B). For this reason, only at those temperatures austenite was quantified through XRD (Fig. 2). For all other temperatures, XRD analysis showed only martensite. Those results are very different from ferritscope measurements, which demonstrates that there are retained and/or reversed austenite in all samples. One explanation for this occurrence is the probable morphology of the austenite in those samples.

Retained austenite (more prone to occur at lower tempering temperature) was retained between martensite laths. The small thickness of these interlath austenite did not provide a sufficient volume of FCC crystal to allow X-ray diffraction, and the intensity of the peaks related to FCC will be much smaller than the diffraction peak intensities for martensite.

At 625 or 650 °C tempered samples, as reported elsewhere [3] reverse austenite can be formed during tempering. Retained austenite from quenching, in those samples, act as nucleation sites for reversed austenite formation during tempering, allowing this phase to grow. Larger volume of austenite allow a more intense diffraction of specific austenite planes, allowing its detection and quantification. The volume fraction of austenite measured by XRD, however, are smaller than the volume fraction of austenite measured by ferritscope, indicating that part of the retained austenite remained thinner, or part of the reversed austenite was transformed into martensite during cooling after tempering. This is probably what was happened in the sample tempered at 700 °C: a higher reversed austenite volume fraction lead to higher martensite formed after tempering.

Quantification by XRD of retained/reversed austenite in samples tempered at 625 °C or 650 °C, however, are more closer to ferritscope results if Cr Kα1 radiation is employed. This could be a result of the better separation between $\gamma$(111) and $\alpha$(110) peaks when Cr radiation is used (Fig. 1A and 1B), making the definition of the integrated intensity (I) of the diffraction peaks more precise.

Analysis of the XRD patterns for the DSS (Fig. 1C and 1D) clearly shows that all austenite peaks have higher intensities when compared to the austenite peaks observed in the SMSS samples (Fig. 1A and 1B). This corroborates the previous idea: being austenite in DSS...
present in higher volume fractions, and in a more block morphology, its detection by XRD are facilitated. This lead to the closer results between XRD quantification using Cu Kα1 radiation and magnetic measurements for the DSS solution-treated at 1130 °C or 1180 °C (Fig. 3). However, results obtained from XRD patterns using Cr Kα1 radiation were almost the same for the three temperatures studied. Nine different diffraction peaks were found using Cu Kα1 radiation, while only six were found during Cr Kα1 radiation XRD. Using Cr source, the number of peaks were smaller, and the definition of area under peaks (or the integrated peak intensity I) is worse. This is probably caused by the use of a V filter instead of a monochromator crystal, which intensify the presence of background and noise in Cr source XRD. The better separation of γ(111) and α(110) peaks, which allowed a better quantification in SMSS, was not an advantage in DSS phase quantification: the lack of more well defined peaks was mandatory in this case.

At the lower solution-treatment temperature of DSS (1070 °C) XRD quantification of phases, even using a copper source, resulted in values different from ferritscope quantification. The microstructure of the sample solution treated for 30 min at 1070 °C (Fig. 4A) showed a heavily banded microstructure, which can be associated to a crystallographic texture of that sample. If this happened, the quantification by XRD (which suppose a non-oriented sample) was compromised.

Evaluation of the possible influence of texture in XRD quantification of phases, using a copper source, was done by treating another sample of DSS for 168 h at 1070 °C. Microstructure of this sample presented larger grain sizes for both phases, and the equiaxial grains were more randomly distributed in the microstructure (Fig. 4B), and this can be an indicaion of the reduction of the previous texture. Ferritscope analysis of that sample (Fig. 3) showed that this higher solution-treatment time did not altered the volume fraction of phases, confirming that both samples, treated for 30 min or 168 h, reached the equilibrium volume fraction of ferrite and austenite.

XRD quantification of phases in the 168h solution-treated sample showed that values of ferrite and austenite obtained by this method are equivalent to the ferritscope measurements, confirming the influence of microstructure in the XRD technique.

![Fig 4. Microstrutures of the DSS solution-treated at 1070 °C for (A) 30 min and (B) 168 h, after modified Beraha etching. Ferrite is the darker phase, austenite is the lighter.](image)

### 4. Conclusions

- Ferritscope analysis of SMSS showed that retained and/or reversed austenite is present in all tempering conditions. However, XRD quantification were only able to detect and
quantify austenite in samples where the morphology of austenite lead to a higher volume, enhancing austenite peaks intensity.

➢ For the SMSS, the better separation between $\gamma$(111) and $\alpha$(110) peaks when Cr K\alpha 1 radiation was used lead to a better quantification of the reversed austenite formed at 625 °C and 650 °C tempered samples. However, detection of thinner laths of retained austenite was not possible even using Cr K\alpha 1 radiation.

➢ For the DSS, quantification of phases by XRD was only possible using Cu K\alpha 1 radiation, and the samples can not present preferential orientation of phases.

References

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RELATION BETWEEN PITTING POTENTIAL AND PREN VALUES FOR FERRITE AND AUSTENITE IN DUPLEX STAINLESS STEELS

Abstract

This work aims to investigate the relation between PREN of ferrite and austenite and the pitting potential of UNS S31803 DSS. Samples were solution-treated between 1040 and 1150 °C generating different phase fractions and, consequently, different alloy element contents. ThermoCalc® thermodynamic simulations were performed to predict the chemical composition of each phase allowing the PREN calculations. Besides, potentiodynamic polarization tests were conducted in 0.6M NaCl solution at 70°C to correlate pitting potential (Epit) and PREN. Thermodynamic simulation reveals that PREN for ferrite is higher than austenite between 975 and 1300 °C. Nevertheless, the electrochemical results show a slight reduction of pitting potential with increasing ferrite content, probably related to the reduction of Cr and Mo contents in this phase. Pits were found preferably in ferrite and in ferrite/austenite interfaces. This behavior suggests that even with only a slight reduction of pitting potential and, consequently, a discrete corrosion resistance reduction, ferrite is more susceptible to pitting. No pits were found in austenite, suggesting that higher N contents are fundamental to maintain the corrosion resistance of this phase.

Keywords: Duplex. Pitting. Polarization. PREN.

1. Introduction

Duplex Stainless Steels (DSS) are composed by ferrite (α) and austenite (γ) in approximately equal amounts and have been used in applications where is required both high mechanical and corrosion resistances [1-3]. The higher N contents enhances both properties and also, its weldability [3], allowing its application in chemical, oil and gas, pulp and paper, food and energy industries. Thus, the microstructure and the alloy element additions as Cr, Mo and N [2] contribute to the DSS properties.

The Pitting Resistance Equivalent Number (PREN) [4-5] is widely used to categorize duplex steels as super duplex (above 40), standard duplex (between 30 and 40) and lean duplex (below 30), and is also used to rank this material on corrosion resistance using chemical composition (%wt) as presented in equation (1)

\[
\text{PREN} = \%\text{Cr} + 3.3 (\%\text{Mo} + 0.5\%\text{ W}) + 16 \%\text{N}
\] (1)

Nevertheless, the PREN do not consider microstructural effects as grain size, intermetallic and/or secondary phases, other non-homogeneities like inclusions, and the alloy element partition in duplex microstructure that may influence the electrochemical behaviour of this materials [4-5]. In DSS, ferrite contains the highest contents of Cr, Si and Mo. In contrast, Ni, Mn, Cu, C and N are preferably partitioned to austenite [1-2,6].

1 FEI University
Garfias-Mesias [7] suggest that the use of PREN to predict pitting corrosion resistance in DSS assumes that the steel production used the correct heat treatment to adjust the recommended ferrite and austenite volume fractions, the absence of intermetallic phases or precipitates, and the partition of alloy elements of the material. Furthermore, the quality control must ensure that P, S and C contents, and the nucleation sites for pitting formation, are maintained in low levels.

Not only the presence of alloy elements but also its partition between ferrite and austenite may influence the corrosion resistance of DSS. Magnabosco [8] found pitting corrosion in both ferrite and austenite phases. Nevertheless, austenite presents the high N contents suggesting high corrosion resistance of this phase. The evidences found in literature indicates that PREN may not be evaluated for the global chemical composition of DSS, but for each phase separately and then, the PREN to be considered for the material is the lower value found.

This work aims to investigate the relationship between PREN of ferrite and austenite, in UNS S31803 samples with different volume fractions, and the pitting potential registered to each sample condition. The chemical composition of ferrite and austenite with different volume fraction was determined by thermodynamic calculations.

2. Methodology

The studied material, an Outokumpu UNS S31803 DSS, has the chemical composition given in Table 1. The specimens were obtained from a 3 mm sheet with dimensions of approximately 30 mm width and 60 mm length with different solution heat treatments conditions.

Table 1. Chemical composition of UNS S31803 DSS (wt%)

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>N</th>
<th>C</th>
<th>Si</th>
<th>Cu</th>
<th>Co</th>
<th>P</th>
<th>S</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.48</td>
<td>5.74</td>
<td>3.20</td>
<td>1.42</td>
<td>0.162</td>
<td>0.018</td>
<td>0.35</td>
<td>0.15</td>
<td>0.07</td>
<td>0.019</td>
<td>0.001</td>
<td>0.006</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Heat-treated specimens were abraded to a 220-grit finish before mounting in thermosetting plastic, leaving an exposed surface area of approximately 0.5 cm², parallel to the rolling direction. The mounted samples were metallographic polished with final polishing provided by 1-µm diamond abrasive. The samples were etched with modified Beraha reagent (composed of 20 mL HCl, 80 mL distilled water and 1 g K₂S₂O₅; to this stock solution, 2 g of NH₄F.HF were added just before the etching) just before the metallographic characterization through optical microscopy.

Thermodynamic simulation using ThermoCalc® version 2018b software was performed using TCFE8 thermodynamic database. The PREN calculation was obtained from the simulated Cr, Mo, and N equilibrium contents and its relation to the pitting potential was determined through electrochemical tests.

Potentiodynamic polarization tests were conducted in 0.6M (3.5%wt) sodium chloride solution (pH=6.5) exposed to laboratory air, in a jacket cell at 75°C at a scan rate of 1 mV/s, beginning 200mV below the open circuit potential (OCP) measured after 5 min of immersion. The test cell had a platinum wire as counter electrode and Ag|AgCl (silver|silver chloride) as a reference electrode. Immediately after the polarization, sample surfaces were washed with distilled water and then with ethyl alcohol (C₂H₅OH), dried with hot blown air, and then analysed through OM.
3. Results and Discussion

The thermodynamic simulation using ThermoCalc® software with TCFE8 database is presented in Fig. 1, and shows that above 975°C only ferrite and austenite coexists in equilibrium. Both sigma and chromium nitride only appear below this temperature.

![Graph showing equilibrium phase volume percent of UNS S31806 DSS between 500 and 1500°C.](image)

**Fig.1.** Equilibrium phase volume percent of UNS S31806 DSS between 500 and 1500°C.

Cr, Mo and N contents estimated by ThermoCalc® software are shown in Fig. 2 (a-c), and are the base for PREN calculations showed in Fig. 2 (d). As expected, ferrite is richer in Cr and Mo and austenite in N. Nevertheless, analysing Fig 2 (d), PREN of ferrite (PREN α) is higher than PREN of austenite (PREN γ) in all temperature range between 500 and 1500°C, with an exception of the temperature of 1320°C where the PREN of ferrite and austenite are equal. Thus, considering only the chemical composition of the material, ferrite could be more corrosion resistant than austenite.

Figure 3 explore the metallographic analysis of the samples with different ferrite volume percent. The quantitative stereology of those samples for ferrite volume fraction determination allowed the prediction of the equilibrium temperature through ThermoCalc® software and the precise values of PREN of ferrite and austenite, as shown in Table 2.

**Table 2. UNS S31803 duplex stainless-steel sample characterization parameters.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>% ferrite</th>
<th>ThermoCalc® predicted equilibrium temperature (°C)</th>
<th>PREN(α)</th>
<th>PREN(γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>44.9 ± 2.8</td>
<td>1070</td>
<td>39.1</td>
<td>33.1</td>
</tr>
<tr>
<td>(b)</td>
<td>49.0 ± 3.8</td>
<td>1110</td>
<td>38.3</td>
<td>33.2</td>
</tr>
<tr>
<td>(c)</td>
<td>82.7 ± 1.9</td>
<td>1310</td>
<td>37.9</td>
<td>33.4</td>
</tr>
<tr>
<td>(d)</td>
<td>96.6 ± 1.4</td>
<td>1340</td>
<td>37.4</td>
<td>33.4</td>
</tr>
</tbody>
</table>
Fig. 2. Cr (a), Mo (b) and N (c) contents and PREN calculus (d) in ferrite and austenite as a function of solution-treatment temperature.

Analysing the Table 2 it is evident the PREN-α reduction with increasing ferrite volume fraction as PREN-γ remains almost constant. The partition of alloy elements on both phases suggests that as ferrite volume fraction increases, the ferrite corrosion resistance decreases as Cr and Mo contents also decreases.

Electrochemical tests through polarization curves were conducted in all the samples, and typical results are presented in Fig. 4. The pitting potential, from which a pit nucleates and growth in stable conditions, decreases as ferrite volume fraction increases, probably caused by Cr and Mo reduction in this phase leading to PREN-α reduction. This observation suggests that ferrite plays an important role in pitting corrosion resistance of the material.
**Fig. 3.** UNS S31803 duplex stainless steel with different ferrite (black) volume fraction: (a) 44.9±2.8%; (b) 49.0±3.8%; (c) 82.7±1.9%; (d) 96.6±1.4%. Modified Beraha etching.

**Fig. 4.** Potentiodynamic polarization curves of UNS S31803 duplex stainless steel in 0.6M NaCl solution at 75°C in samples with different ferrite fractions.
The analysis of both pitting potentials ($E_{\text{pit}}$) and the PREN for ferrite and austenite with increasing ferrite percent is necessary and presented in Figure 5. A light decrease in the medium pitting potential values with increasing ferrite percent (and reduction of PREN $\alpha$) is observed. The increase in ferrite percent leads to the decrease in Cr and Mo contents more sharply in ferrite if compared to austenite as previously seen in Figure 2 (a) and (b). This behaviour may be related to the slight decrease of pitting potential and in PREN $\alpha$ observed in Figure 5. Instead, the PREN $\gamma$ is almost constant even in different ferrite volume contents.

Fig. 5. Pitting potential ($E_{\text{pit}}$) and PREN as a function of ferrite percent.

Other evidences of this behaviour may be observed in the optical microscopy of the samples after polarization tests (Fig. 6). Pitting formation occurs preferably in ferrite and in ferrite/austenite interfaces. In the samples with a less ferrite volume fraction, pits were found preferably in ferrite/austenite interfaces as presented in Fig. 6 (a), but also some pits were present inside ferrite phase. As with low solution treatment temperatures leads to a higher number of interfaces, as shown in Fig. 3 (a), and knowing that pitting occurs preferably in non-homogeneities like grain boundaries, inclusions and interfaces, the occurrence of pitting in ferrite/austenite interfaces is justified.

However, in the samples where the ferrite volume percent is high (Fig. 3 c-d), pits are found in ferrite phase or in non-homogeneities like inclusions (Fig. 6 c-d). No pitting was found in austenite islands, showing that even PREN-$\alpha$ being higher PREN-$\gamma$, apparently ferrite is less pitting resistant than austenite in the tested conditions. Probably the explanation for this behaviour is not in Cr and Mo contents on both phases, but the presence of N in austenite. This result corroborates other authors conclusions [2,8] which stated that austenite phase is more corrosion resistant than ferrite in duplex steels. As reported in those publications, ammonia formation as the product of the reaction of N with H dissolved in the solution would raise locally the pH leading to the passivation of the materials surface, reducing the tendency to pitting occurrence [2,9].
Fig. 6. Optical micrography of UNS S31803 after potentiodynamic tests in 0.6M NaCl solution at 75°C etched with oxalic acid. Pits are indicated by red arrows.

Conclusions

Thermodynamic simulation reveals that, using Cr, Ni, Mo and N equilibrium contents, the PREN for ferrite is higher than austenite between 975 and 1300 °C. Nevertheless, the electrochemical results show a slight reduction of pitting potential with increasing ferrite content, probably related to the reduction of Cr and Mo contents in this phase. Pits were found preferably in ferrite and in ferrite/austenite interfaces. This behavior suggests that even with only a slight reduction of pitting potential and, consequently, a discrete corrosion resistance reduction, ferrite is more susceptible to pitting. No pits were found in austenite, suggesting that higher N contents are fundamental to maintain the corrosion resistance of this phase.

References

INFLUENCE OF THE PROCESS PARAMETERS ON THE TRANSFORMATION BEHAVIOR OF 2205 DURING LASER BEAM WELDING

Abstract

A continuously growing market for corrosion-resistant steels requires new, innovative and economical joining methods. For the laser beam welding of thin-walled structures joining technologies are required, which cause a minimal energy input into the component and thus reduce the thermally induced distortion. Highly brilliant beam sources that meet these requirements are suitable [1]. However, the heating and cooling rates increase with decreasing beam diameter in the welding process. This results in large temperature gradients and minimal hold times between heating and cooling. When welding "thin" duplex stainless steel sheets, this results in less austenite in the ferrite matrix. However, these ferritic-austenitic alloys require a balanced phase ratio of ferrite and austenite for optimum mechanical properties and corrosion resistance.

In the present investigations (laser-based), the aim was to consider the effect of varying laser parameters on the phase balance between austenite and ferrite on duplex stainless steels. For this purpose, experimental tests have been carried out on grade 2205 (EN 1.4462 / UNS S32205) with different beam diameters and beam profiles.

Keywords
duplex stainless steels, laser welding, cooling rate, microstructure

Introduction

The laser welding process is characterized by a high heating and cooling speed. Especially when welding thin-walled component structure of duplex stainless steels, this reduces the austenite content within the joining zone. However, for austenitic-ferritic steels, a balanced phase ratio of austenite and ferrite ensures high mechanical stability combined with high corrosion resistance. Duplex stainless steels undergo profound microstructural transformations in laser beam deep welding, which influence the distribution and the phase balance in the various areas of the weld seam area.

A possible solution to achieve this goal of a balanced phase distribution is the use of a welding filler, which is tailored to the welded duplex stainless steel [2]. Due to the increasing costs and the complexity of the plant, laser welding with filler material is often dispensed with in industrial applications. If work is carried out without additional material, the welding process is usually followed by a second process step, for example, a thermal aftertreatment [3, 4]. However, this aftertreatment is only feasible or economical with small component sizes or in a continuous furnace.

In the literature, in connection with the welding of duplex stainless steels, the $t_{8/5}$ and $t_{12/8}$ times are encountered. The reason for this is essentially that one can mathematically merge $t_{12/8}$ and $t_{8/5}$ [5]. Furthermore, the most important microstructural transformations take place in this temperature range for steels [6]. As a result, $t_{8/5}$ is widely used in welding metallurgy.

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While $t_{12/8}$ amounts to values between 1 s and 40 s for arc welding of duplex steels, values of significantly less than 1 s are characteristic of laser beam welding [7]. Considering that there are investigations, which resulted in optimal cooling times of 17 s, it becomes clear that in laser welding, especially thin-walled duplex steels, austenitic formation in the weld is much more problematic than with conventional welding processes and hybrid welding [7, 8]. For austenite formation in the joining zone and heat-affected zone, there are several models which allow an estimation of the amount of austenite in the seam area. For example, the model of Southwick and Hoejoycombe is based on the evaluation of isothermal anneals and follows the Johnson-Flour-Avarami equation [9]. Mundt and Hoffmeister described the transformation of ferrite into austenite on the basis of evaluations of the microstructure of welds and associated them with CCT (continuous cooling transformation) diagrams [10]. Atamert and King have developed a model for diffusion-controlled austenite growth that takes into account the chemical composition of the material [11,12]. Modern formulas such as those of Omura, have turned out to be limited, since the influence of the extremely high cooling rates for the cooling is too low [13]. The higher the cooling rate, the faster the conversion range is crossed and the less ferrite is converted to austenite. Furthermore, a three-dimensional heat flow is often the basis, but with thin-walled structures a two-dimensional heat influence is assumed.

Problems with laser beam welding of duplex stainless steels

As already described for austenite formation in several models exist. By evaluating the microstructure of laser welds on a 22Cr duplex steel, Omura et al. Experimentally, a formula (E2.1) for estimating the ferrite content in the weld seam [13].

$$V_\delta = 7.6 \cdot \log(v_{700}) + 75$$  \hspace{1cm} (E2.1)

$V_\delta$ is the ferrite content in the weld, $v_{700}$ is the cooling rate at 700°C. The cooling rate is given by the formula (E2.2), which was obtained after analyzing the approach of C. M Adams, Jr for arc processes [14].

$$v_{700} = \frac{2 \cdot \pi \cdot c_p \cdot \lambda_{th} \cdot \rho \cdot (h \cdot v)^2 \cdot (T - T_0)^3}{(P \cdot \eta_p)^2}$$  \hspace{1cm} (E2.2)

with $\eta_p$ - process efficiency, $h$ - sheet thickness, $P$, $v$ - process parameters, $c_p$, $\lambda_{th}$, $\rho$ - material characteristics. Since this relationship was developed empirically, the solution with $v_{700}$ must be accepted as given, even if the transformation kinetics essentially takes place between 1200°C and 800°C and thus already predominantly completed at 700°C. It can be seen that the temperature difference between the starting temperature of the workpiece (before welding) and the temperature at which the cooling rate is considered is critically important. This speaks for a preheating of the workpiece. Furthermore, the workpiece thickness and the introduced (laser) power are square in reciprocal relationship. The higher the power input, the lower the cooling rate. The thicker the workpiece, the faster it cools. Although this initially gives the impression that thinner workpieces cool down more slowly and thus significantly better ferrite-austenite conditions in the weld can be achieved, it is taken into account, however, the significantly lower power for the laser beam deep welding, which are now required for a through-welding, so this effect is compensated again. Furthermore, it should be considered that (E2.2) is based on a two-dimensional heat influence. Based on various laser parameters, the resulting austenite content in the weld was determined. From these it emerged that for austenite content for cooling rates above $v_{700} > 1947$ K/s the austenite content becomes negative. This is possible because, due to the high cooling rates (and the associated cooling
times of well below 1 s), the formation of other phases (such as the σ phase) can be neglected. However, Omura et al. have not defined a scope for their empirically developed formula.

The next 3 models consider the formation of austenite in the heat affected zone. Thus, the Southwick and Hoeycombe [9] model is based on the evaluation of isothermal anneals on a 26Cr; 5Ni DSS. As already mentioned above, the conversion behavior follows the Avarami equation (E2.3)

\[
\frac{V_y}{V(T)} = 1 - \exp\left(-k_i(T) \cdot t_{12/8}^{n(T)}\right)
\]

(E2.3)

where \(V_y\) is the austenite volume fraction at time \(t\), \(V\) the equilibrium austenite volume fraction, \(k\) is a constant which depends on the chem. Composition, \(n\) is an experimentally determined size and \(T\) is the temperature. In the early 1990s, both Lindblom and Hannerz (E2.4), as well as Atamer and King (E2.5), essentially introduced a similar relationship [11, 15].

\[
V_y = k_i \cdot \left(t_{12/8}\right)^n
\]

(E2.4)

and

\[
V_y = 213,5 - 12,54 \cdot (Cr_{\text{eq}} - Ni_{\text{eq}}) + 0,1259 \cdot \Delta t_{1250-800}
\]

(E2.5)

with \(t_{1250-800}\) as the cooling time from 1250°C to 800°C. Atamert et al. used a numerical model for austenite growth at various temperatures on a 25Cr; 7.5Ni-SDSS and considered both the cooling time and the chemical composition of the duplex steel by using the Cr-Ni equivalent. The suitability of these models, especially for laser beam deep welding of thin-walled structures, is also low, since the influence of the high cooling rates is limited, see Figure 1. Because the higher the cooling rates (above \(10^4 \text{ K/s}\)), the more the diffusion is suppressed and the less ferrite is converted to austenite. This means that there is no sufficient homogenization of the structure.

![Fig. 1: Calculated austenite content depending on the cooling time (based on [9,11,15])](image-url)
Experimental Procedure

The tested material was a cold rolled X2CrNiMoN22-5-3 with a sheet thickness $d \leq 1\ mm$ and the chemical composition given in Table 1. Due to the development of the fiber and disk lasers and the associated increase in the beam quality up to almost the diffraction limit, the use of beam sources with correspondingly high brilliance, which leads to an optimized energy input, is possible for laser beam welding [16].

Table 1: chemical composition

<table>
<thead>
<tr>
<th></th>
<th>C [wt%]</th>
<th>Si [wt%]</th>
<th>Mn [wt%]</th>
<th>P [wt%]</th>
<th>S [wt%]</th>
<th>Cr [wt%]</th>
<th>Mo [wt%]</th>
<th>Ni [wt%]</th>
<th>N [wt%]</th>
<th>Cu [wt%]</th>
<th>Nb [wt%]</th>
<th>Co [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIN EN 10088-3</td>
<td>≤0,030</td>
<td>≤1,00</td>
<td>≤2,00</td>
<td>≤0,035</td>
<td>≤0,015</td>
<td>21,00-23,00</td>
<td>2,50-3,50</td>
<td>4,50-6,50</td>
<td>0,10-0,22</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>actual</td>
<td>0,025</td>
<td>0,38</td>
<td>1,32</td>
<td>0,035</td>
<td>0,001</td>
<td>22,41</td>
<td>3,19</td>
<td>5,78</td>
<td>0,10</td>
<td>0,31</td>
<td>0,02</td>
<td>0,11</td>
</tr>
</tbody>
</table>

Fiber and disk lasers with single-mode and multimode beam qualities were available for the investigations. Single-mode lasers feature an approximately Gaussian intensity distribution in the radial direction (see Figure 2, left), while multi-mode lasers form an intensity distribution in the form of a top hat (see Figure 2, right). The achievable focus diameters (20-700 $\mu$m) differed considerably due to the different beam qualities and the available fiber diameters (11 $\mu$m, 18 $\mu$m, 50 $\mu$m and 200 $\mu$m). While laser beam sources with multi-mode beam quality are often used for welding due to their large focus diameter compared to a single-mode laser, recent studies [17] show that high-brilliance sources are also suitable. When defining the parameter space to be examined, two limits were defined. The lower limit is defined by process instabilities, which express themselves in the form of hole formation in the weld. This is due to the smaller the aspect ratio between material thickness and focus diameter. The upper limit, see Figure 3, has been defined as a defective penetration, which can be determined by an analytical description. The welding speed at the process limit can be set with the related power $P/d_f \cdot h$ in a relationship

$$v \approx 31,4 \cdot P/d_f \cdot h$$

(E3.1)

with $P$ – laser power, $v$ – welding speed and $d_f$ – focus diameter. This makes it possible for the investigated material to predict the process variables for the welding process at the process boundary. Nitrogen was used as protective gas and an Ar+2 % N\textsubscript{2} mixture, each with a volume flow of 15 l/min, as forming gas.

![Fig.2: Intensity distribution, left: Gaussian, right: Top-Hat](image-url)
Cross-section fabrication and metallographic etching is done using standard techniques with a final SiO₂ finish. Revealing the two phase components was done using a modified Beraha II etchant (60 ml H₂O + 30 ml HCl + 1 g K₂S₂O₅). The determination of the average proportion of ferrite in the weld took place by means of image-optical analysis with the software ImageJ on 5 subsections of the weld. To refer to the evaluation method, the ferrite content of selected samples was determined by X-ray diffractometry.

Fig. 3: schematized process window

Results

Regardless of the focus diameter, the test samples show an imbalance in the austenite-ferrite ratio, coarse-grained structure and central banding as signs of an inhomogeneous structure, which creates conditions in which corrosion resistance is reduced and therefore a tendency towards pitting corrosion. The response surface graph (Figure 4) demonstrates that the ferrite content falls with increasing focus diameter, which leads to an improvement in the material-related properties. The rise in the austenite content in the weld seam is the result of up to a threefold increase in energy input per unit length. In order to get a through-weld with larger focus diameters, the energy input into the workpiece must be increased. As a result, this means that the cooling rates drop and the seam becomes wider, which in turn leads to higher austenite content when cooling is decelerated gradually rather than sudden cooling.
If there is a rapid cooling (figure 5, $t_{12/8} = 0.027 \text{ s}$), the base material fine-grained joint of austenite and ferrite transformed into a joint comprising larger ferrite grains. That means, the smaller the focus diameter, the closer the grain orientation followed the heat dissipation in the surface layer and root. In the upper and lower seam area, there is three-dimensional heat transfer, which means that the energy input is dissipated quicker from the material. Central banding ran as large elongated ferritic grains in the middle of the weld seam. Due to the increase in nitrogen on the ferrite grain boundaries, the austenite tends to precipitate here in the form of thin grain boundary austenite. The primary ferritic solidification causes an accumulation of chromium in the centre of the grain, as well as an accumulation of nickel in the area near the grain boundary. Nickel is an austenite-stabilising element, which explains how the austenite comes to be secreted at the edges of the primary ferritic grain. According to Batahgy et al and Vrtochova et al, the narrow heat-affected zone leads to high toughness and ductility in the joint zone [18, 19].

Due to the increase in energy per unit length while the intensity remains the same, the result is considerable heat input into the material. As a result of this, the $t_{12/8}$ time increased by factor 3, and a broadening of the seam along the entire material thickness was recorded. In comparison to $t_{12/8} = 0.027 \text{ s}$, the austenite content increased by $\approx 9\%$ (see figure 6). The resulting joint chiefly comprises large ferrite grains with intergranular secreted austenite. However, the reduction in the cooling rate led to the central banding ran as a continuous grain
A large-grained ferritic mesh structure was now the result, which consists of intragranular austenite and grain boundary austenite. This grain boundary austenite grows analogous to the Widmanstätten mechanism, from the grain boundary into the inside of the ferrite grain. The concentrated heat input results in a reduction of the cooling speed, which promotes the growth of the Widmanstätten austenite. This finally led to a decrease in the toughness.

Fig. 6: left-overview, right-middle of the fusion zone (MM, $d_f=300 \, \mu m$, $t_{12/8}=0.095 \, s$, ferrite content $\approx 91 \%$)

Through reheating in a furnace, Zhang et al. identified the temperature ranges in which an optimal weld seam structure is created. Mainly Widmanstätten and grain boundary austenite are formed between 1020°C and 1050°C, as well as a small amount of finely-spattered intragranular austenite. At 1080°C, mainly spherical intragranular austenite is formed, which has a positive effect on the ductility. This can be attributed to the incoherent interfaces of the austenite with the ferrite matrix, and especially to the low-energy grain boundaries, as well as the simultaneous reduction of the Widmanstätten austenite. Above 1100°C, the spherical intragranular austenite particle density again falls, which results in a slight drop in the ductility [20].

Fig. 7: overview (MM, $d_f=700 \, \mu m$, $t_{12/8}=0.195 \, s$, ferrite content $\approx 20 \%$)

From the temperature measurements showed that the dwell time (at $d_f=700 \, \mu m$) between 900°C to 1150°C in comparison to the higher cooling rate by at least a factor of 3.5 was greater. Figure 7 shows that in addition to the austenite formation at the ferrite grain boundaries, mainly Widmanstätten and fine intragranular austenite formed in scattered form. Therefore, it is believed that ferrite to austenite conversion does not occur as Zhang et al. thermodynamically, but is dominated by the solid state transformation, i.e. metastable ferrite becomes austenite. By changing the focus diameter to 700 μm, this conversion behavior was achieved. However, this increase in the path energy often resulted in a lower aspect ratio and a lower welding speed. The weld is now comparable to arc welding. Furthermore, the thermally induced distortion during laser beam whitening and the resulting gap formation impaired the reproducibility of the welding process.
In summary, however, it was found that each test sample was characterized by an inhomogeneous structure and what could have led to pitting corrosion. It should not be forgotten that Mourad et al. found in their investigations, that the weld width is more important for both the corrosion properties and the mechanical properties of duplex steels than a balanced ferrite-austenite ratio in the weld [21]. Smaller weld seams here produce more favourable properties (ibidem).

Conclusions

In summary, the outstanding properties of duplex stainless steels are not automatically transferred to the corresponding welds. If no additional measures are taken, such as the use of over-alloyed welding consumables or the use of subsequent heat treatment, the austenite content in the weld is significantly lower than in the base material. This applies in particular to the use of laser beam welding, which is the medium of choice for thin-walled structures. Welding such structures eliminates the use of over-alloyed filler metals. A subsequent heat treatment is very time consuming and relatively expensive. In the tests carried out, it was possible to show that in the production of welds on thin-walled structures made of duplex steel, the focus diameter represents a decisive factor for the resulting austenite content in the weld seam. Already by a favorable coordination of welding speed and focus diameter, in connection with the used laser power, Austenitgehalte are achievable, which come close to the recommendations of the DVS as well as those of Robert Gunn. Both recommend an austenite content of 30% to 70% for the weld [22]. Furthermore, it could be determined that the model of Omura et al. for thin-walled structures is only conditionally meaningful, see Table 2 as an example.

<table>
<thead>
<tr>
<th>focus diameter [µm]</th>
<th>laser power [W]</th>
<th>welding speed [m/s]</th>
<th>sheet thickness [mm]</th>
<th>austenite content [%] at Omura measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1000</td>
<td>0,02</td>
<td>0,5</td>
<td>5 20</td>
</tr>
<tr>
<td>500</td>
<td>500</td>
<td>0,01</td>
<td>0,5</td>
<td>5 20</td>
</tr>
<tr>
<td>400</td>
<td>700</td>
<td>0,02</td>
<td>0,5</td>
<td>3 17</td>
</tr>
<tr>
<td>300</td>
<td>300</td>
<td>0,01</td>
<td>0,5</td>
<td>2 6</td>
</tr>
<tr>
<td>87</td>
<td>500</td>
<td>0,05</td>
<td>0,5</td>
<td>-5 5</td>
</tr>
<tr>
<td>42</td>
<td>300</td>
<td>0,03</td>
<td>0,5</td>
<td>-5 4</td>
</tr>
<tr>
<td>24</td>
<td>300</td>
<td>0,05</td>
<td>0,5</td>
<td>-9 1</td>
</tr>
</tbody>
</table>

In order to perform a satisfactory prognosis with a new model, further experimental data sets are needed. A negligent statement about austenite formation for a wide variety of cooling rates, focus diameters and other laser parameters is incessant. A sensitivity analysis shows the individual characteristics and their effect on the material-specific properties. As a result, this leads to a realistic model behavior, which is subsequently to be tested against by means of a robustness analysis with the material from the Lean group.
Acknowledgements

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References


INCLUSION OF FORTA FDX 27 (UNS S82031) INTO ASTM A1084

Abstract

The new duplex steel Forta FDX 27 (UNS S82031) should be implemented into relevant standards. As for other duplex stainless steel grades, correct solution annealing is one of the most critical aspects for achieving good material properties. Relevant acceptance tests/standards are of great importance to verify that delivered duplex stainless steels have the expected material properties. For lean duplex stainless steels, ASTM A1084 is the standard used for this purpose. Specifically, this standard focuses on properties affected by chromium carbides and nitrides that precipitate at too low solution annealing temperature or too slow cooling from annealing. In order to evaluate suitable acceptance standards, sheet material of Forta FDX 27 in different heat treatment conditions, and different isothermal sensitizations have been investigated. Local corrosion resistance and microstructure has then been examined according to ASTM A1084 method A and C. A modified test solution for method C has also been evaluated and is proposed as a more relevant solution for the inclusion of Forta FDX 27 and other mid-range duplexes into ASTM A1084. As reference measurement, testing according to ASTM G150 in 0.1M NaCl has been performed and a TTT-diagram has been compiled based on this is presented.

Keywords

ASTM A1084, Lean duplex, stainless, sensitisation, microstructure, CPT, ferric chloride, etching.

1. Introduction

UNS S82031 is a new lean duplex which utilizes TRIP (Transformation Induced Plasticity) for improved formability compared to other existing duplex grades. The aimed market is primarily in applications where high strength in combination with good corrosion resistance, as typical for duplex materials, is required with the additional benefit of improved formability similar to that of austenitic grades with an equivalent corrosion resistance. Giving that forming applications are the focused market, UNS S82031 is primarily available as thin sheet <3mm. Therefore properties such as impact toughness are not of great concern.

As for other duplex stainless steel grades, correct final solution annealing is one of the most critical aspects for achieving good material properties. Relevant acceptance tests are of great importance to verify that delivered duplex stainless steels have the expected material properties. For this purpose standard test methods exist with the purpose of allowing for the detection of detrimental phases to the extent that toughness or corrosion resistance is affected significantly.
For high alloyed duplex stainless steels (22%Cr and 25%Cr) a general test method for evaluating appropriate solution annealing has been ASTM A923. The test method in this standard focuses on the detection of detrimental levels of intermetallic phases which is commonly the primary concern for these grades. As highlighted in Fig 1, such intermetallic phases form most rapidly in and around 900°C for 22%Cr and 25% Cr grades. Intermetallic phases are readily visible in the microstructure and can degrade both impact strength and corrosion resistance. ASTM A923 uses optical metallography, Charpy impact testing, and a ferric chloride corrosion test to detect the presence of these undesirable intermetallic phases, see Table 1 for details.

![Fig 1 Typical TTT-diagram from Outokumpu handbook for conditions causing a reduction of 50% impact toughness, showing that lean duplexes are more sensitive to precipitations at lower (700°C) temperatures.](image)

Lean duplex grades are much less sensitive to intermetallic phase precipitation than duplex and super duplex grades. Rather, they are most sensitive to precipitation of chromium nitride, Cr2N, and chromium carbide, M23C6 which occurs at lower temperatures (around 700°C) than the precipitation of intermetallics, see Fig 1 and [1]. The microstructural changes associated with improper heat treatment of lean duplex grades are therefore hard to detect using the metallographic procedure described in ASTM A923. In addition, the corrosion test used in ASTM A923 (immersion in 6% ferritic chloride solution) is too harsh for the lean duplexes, as previously reported [2], and require sub-ambient test temperatures which in many instances is impractical to use. For the reason mentioned above ASTM A1084 was developed based on the work [2,3,4] with modified etching and corrosion testing procedures more suited for the lean duplex grades, see Table 1.
Table 1 Methods used for delivery testing of duplex stainless steels

<table>
<thead>
<tr>
<th>A: Metallography</th>
<th>Higher alloyed duplex stainless steels</th>
<th>Lean duplex stainless steels</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASTM A923</td>
<td>ASTM A1084</td>
</tr>
<tr>
<td>Screening*</td>
<td>Comparison images</td>
<td>Exploratory† Comparison images</td>
</tr>
<tr>
<td>B: Impact toughness</td>
<td>-40°C 54J: Base metal 34J: 2205 weld metal</td>
<td>RT 70J: LDX 2101 100J: 2304</td>
</tr>
<tr>
<td>C: Local Corrosion</td>
<td>6% FeCl₃ solution (10mdd) 25°C: 22Cr-type Base metal 22°C: 22Cr-type Weld metal 40°C: 25Cr-type Base metal</td>
<td>5% FeCl₃ + 1% NaNO₃ (10mdd) 25°C (all alloys)</td>
</tr>
</tbody>
</table>

*Optical images can approve but not fail a material, †Optical images can neither pass or fail a material

Table 2 shows the chemical analysis of some grades that exist in the different standards together with the new grade. ASTM A1084 states that the Mo content for lean duplexes is typically <1%. As can be seen the Mo content of UNS S82031 can be higher than 1%. Despite this, the PRE value is 27 which is a similar level to the other lean duplexes in this standard. Furthermore, UNS S82031 is essentially designed to be lean in order to have the TRIP effect. For these reasons, and from previous experience with testing lean duplexes according to ASTM A923, this work has focused on testing UNS S82031 for inclusion in ASTM A1084 as a lean duplex rather that in ASTM A923 as a standard duplex.

Table 2 Chemical analyses of duplex stainless steels

<table>
<thead>
<tr>
<th>Chemical analyses of duplex stainless steels</th>
<th>PRE</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Grade UNS</td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>S32750</td>
<td>0.02</td>
<td>0.27</td>
</tr>
<tr>
<td>S32205</td>
<td>0.02</td>
<td>0.17</td>
</tr>
<tr>
<td>S32304</td>
<td>0.02</td>
<td>0.10</td>
</tr>
<tr>
<td>S32101</td>
<td>0.03</td>
<td>0.22</td>
</tr>
<tr>
<td>S82031</td>
<td>0.02</td>
<td>0.20</td>
</tr>
</tbody>
</table>

2. Materials

The investigated material UNS S82031 with chemical composition and PRE as given in table 2. The material thickness was 2.6mm which is typical of thickness produced for this grade. Production as-received, laboratory annealed and water quenched and sensitized conditions have been tested and reported.
3. Experimental Procedures

Material Sensitization

Materials were tested after sensitization in an electrical furnace and GLEELEGLEEBLE equipment. For the ferric chloride test (in accordance with the ASTM A1084 standard) sensitization has been performed at 700°C as is typically the most critical temperature for precipitation in lean duplex grades. Exposure time has been from 1 minute up to 2 hours in an electric laboratory furnace with a ramp up time (time to reach within 10°C of the sensitization temperature) of approximately 2 mins.

For complementary CPT corrosion testing to create a TTT-diagram, sensitization has been performed in a GLEELEGLEEBLE with various sensitizing temperature and hold times, Table 3. The ramp up in this case was 25°C/s following by rapid quenching.

Table 3 Test matrix for GLEELEGLEEBLE sensitizations

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Hold time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>1065</td>
<td>X</td>
</tr>
<tr>
<td>1000</td>
<td>X</td>
</tr>
<tr>
<td>965</td>
<td></td>
</tr>
<tr>
<td>915</td>
<td>X</td>
</tr>
<tr>
<td>815</td>
<td>X</td>
</tr>
<tr>
<td>715</td>
<td></td>
</tr>
<tr>
<td>615</td>
<td></td>
</tr>
</tbody>
</table>

Metallographic Evaluation

Polished samples were electrolytically etched with oxalic acid solution (10% C₂H₂O₄ in water) at room temperature with a voltage of 6-7V for 10 seconds. This is in accordance with the procedure recommended in ASTM A1084.

Ferric Chloride Test

The inhibited test solution consisting of 5 wt% FeCl₃ + 1 wt% NaNO₃ was initially used following the procedure given in ASTM A1084. Thereafter, a modified version was tested consisting of 5 wt% FeCl₃ + 0.3 wt% NaNO₃ i.e. the inhibitor was reduced increasing the aggressiveness of the test somewhat. The procedure for testing was the same regardless of the test solution as described below.
Samples were cut to an approximate length and width of 50 x 25 mm. All surfaces were dry ground to a 120 grit finish followed by an acetone rinse. Samples were weighed to the nearest 0.001 g and the length, width, and thickness were measured.

Testing was performed in glass beakers with a minimum of 600 ml of test solution. The test temperature was controlled to ± 1 °C. Each test involved immersion for 24 hours, after which the exposed samples were cleaned, rinsed and dried. Samples were then weighed to the nearest 0.001 g and the corrosion rate calculated in units of mg/dm2/day (mdd).

Each condition was tested at various temperatures to determine the pitting temperature as a function of the ageing time. A corrosion rate greater than 10 mdd was used as a threshold for unacceptable performance. The critical pitting temperature was defined as the lowest temperature at which corrosion above 10 mdd was observed.

ASTM G150

The tests were performed in a flushed port cell with volume of 1000 ml and a test area of 10 cm2. The cell was filled with a pre-cooled solution of 0.1 M NaCl and was allowed to stabilize at 0°C. A platinum mesh counter electrode and a saturated calomel reference electrode (SCE) were used. A potential of 700 mVSCE was then applied and the temperature was increased with 1°C/minute. The CPT was defined as the temperature where the current density first exceeded 100 μA/cm2 and stayed above that level for at least 60 seconds.

Impact Toughness

Although impact toughness is included in the standard as a relevant test method for identifying sensitization, it has not been implemented in this work. UNS S82031 is not intended as a thick gauge material and therefore impact toughness is not generally an issue.

Results and Discussions

Metallography and Local Corrosion Tests

The microstructures of the materials sensitized at 700°C are given in Fig 2-Fig 89 for different holding times. The reference material and those sensitized up to at least 4 minutes show no, or very few indications and would normally be classed as unaffected according to the standards. At hold times of 8 minutes and longer, precipitates start to appear. After 8 minutes precipitates exist primarily in the ferrite-ferrite grains boundaries. After 30 minutes the degree of precipitates is more extensive and exist even in the phase boundaries. These would be classed as affected structures. In general there is a good correlation between the degree of precipitation and the sensitization time as normally observed in lean duplex grades as this temperature.
Fig 2 As-received microstructure

Fig 3 Sensitized for 1 minute at 700°C

Fig 4 Sensitized for 2 minutes at 700°C

Fig 5 Sensitized for 4 minutes at 700°C

Fig 6 Sensitized for 8 minutes at 700°C

Fig 7 Sensitized for 30 minutes at 700°C
The results for the ferric chloride tests are given in Fig 10 and Fig 11. When using the test solution with the 1% NaNO₃ inhibitor, a slight drop in failure temperature, from 55°C to 45°C-47.5°C at 4 minutes is observed. Thereafter, a similar pass/failure temperature exists up until a sensitization time of 1 hour at 700°C where a slight drop again, of 5-10°C, occurs. This trend is not directly reflected by the observed microstructures where evidence of sensitization was first observed at 8 mins, Fig 6, followed by a rather rapid increase in precipitations with longer sensitization. In general, a relatively high test temperature is required with this test solution and it is difficult to define a clear sensitization acceptance temperature.

In a similar way to ASTM A923 where the non-inhibited test solution has been proven to be too harsh for the lean duplexes, the 1% NaNO₃ inhibited solution, as used in ASTM A1084, could be considered as too mild for UNS S82031, in the sense that the test temperature needs to be relatively high, and that a clear acceptance test temperature cannot easily be determined. For this reason a modified solution was investigated.

When instead using a test solution with 0.3% NaNO₃ as an inhibitor, the results, Fig 11, show no indication of sensitization up to and including 4 minutes with a pass temperature of 27.5°C for all tests. A dramatic decrease down to 10°C is however observed after 8 minutes sensitization, which agrees well with the observed onset of grain boundary precipitations in Fig 6. Fig 12 combines the corrosion test results with the microstructures of the equivalent sensitization conditions to illustrate the correlation between microstructure and corrosion more clearly.
The results show that the 5 wt% FeCl₃ + 0.3 wt% NaNO₃ test solution provides for a better potential for determination of the presence of detrimental phases in UNS S82031. A suitable acceptance criteria could be made by testing at 20-25°C as with the other grades in ASTM A1084, which is also an ideal temperature for practical testing purposes.

Critical Pitting Temperature and TTT diagram

Sensitization was performed in a GLEEBLE according to Table 3 and the critical pitting temperature (CPT) was subsequently measured. CPT is a well-established test method for evaluating the corrosion resistance of stainless steels. Producing a TTT-diagram, using CPT together with the very accurate GLEEBLE heat treatments, to indicate the onset of sensitization is therefore a useful method for evaluating the validity of the proposed inhibited ferric chloride solution used in this work. The CPT results are given in Table 4. Selected microstructures are given in Fig 13 to Fig 15.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Hold time (minutes)</th>
<th>0.5</th>
<th>2</th>
<th>4</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1065</td>
<td></td>
<td>37.8</td>
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<td>1000</td>
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<td>37.7</td>
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<tr>
<td>915</td>
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<td>34.2</td>
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<td>715</td>
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<td>615</td>
<td></td>
<td>36.8</td>
<td>34.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig 13 Fine precipitates at 715°C 8mins

Fig 14 Coarser precipitates at 815°C 8mins.

Fig 15 No observed precipitations after Gleeble heat treatment at a) 615°C 8 mins, b) 715°C 4 and c) 915°C 8mins.

Grain boundary precipitates are only observed at high magnification after 8 minutes at 715°C and 815°C as shown in Fig 13 and Fig 134 respectively. Samples exposed to lower or higher temperatures for the same time period, Fig 15a, and Fig 15c, or for shorter times at same temperature Fig 15b, do not have grain boundary precipitations. In general, the precipitates observed in the 715°C 8 minute sample tend to be finer and exist more as a thin film in the grain boundaries, as illustrated by the insert in Fig 13. This in comparison to the 815°C sample where the precipitates are coarser and less densely distributed. It is suggested that the fine densely populated grain boundary precipitates has more of a negative impact on the CPT than coarser precipitates.

Comparing the CPT results together with microstructures, it can be determined that the only real significant reduction of CPT is noted after 8 minutes at 715°C. This corresponds to a CPT reduction of 5°C when taking 38°C as a reference non-sensitized value. Although further testing could be done at longer hold times to give a more complete picture, the results presented here do indicate that the onset of property degradation is close to 8 minutes at 715°C as proposed in the TTT-diagram in Fig 16. This proposed TTT based on CPT results also agrees well with the more classical TTT-diagram for other lean duplexes, such as LDX 2101, as given in Fig 1.
Of particular interest, this agrees well with the findings from the ferric chloride tests as given in Fig 12, both in terms of time to sensitization and also showing that the chosen temperature of 700°C was the most sensitive and therefore correct temperature to use for the evaluation of inclusion of UNS S82031 in ASTM A1084.

Fig 16 Proposed TTT-diagram based on initial reduction of CPT

Conclusions

- Steel grade UNS S82031 can be added to ASTM A1084 with a small modification to the used corrosion media.
- Method A etch in oxalic acid can be successfully used to observe the presence of detrimental phases.
- Method C using current inhibited solution (5% FeCl$_3$ + 1%NaNO$_3$) gives relatively high failure/pass temperatures and a clear sensitization acceptance temperature is difficult to determine.
- Using a new solution with less inhibitor (5% FeCl$_3$ + 0.3%NaNO$_3$) shifts the pass temperature towards preferred ambient conditions and a clear acceptance level can be identified.
- The proposed TTT-diagram based on the CPT results, confirm that the new adapted ferric chloride solution (5% FeCl$_3$ + 0.3%NaNO$_3$) gives as good response to the detection of detrimental phases.
- It is proposed that the adapted corrosion media of 5% FeCl$_3$ + 0.3%NaNO$_3$ with an acceptance test temperature of 20-25°C can be adopted into ASTM A1084 Method C for detection of detrimental phases in UNS S82031 and possibly other mid-range duplexes.

References

Abstract

Duplex stainless steels owe many of their attractive properties to the interaction between austenitic and ferritic regions in the microstructure. Austenite fraction and austenite region inter-spacing are two parameters known to have a strong influence on product properties such as tensile strength and impact toughness.

This study describes how to extract such conventional parameters, together with others that are more difficult to estimate with manual methods. A generalized austenite distance measurement valid also for non-lamellar structures is introduced, together with a serrated phase boundary index. Both are shown to have a strong correlation to impact toughness. In total, some 30 parameters were extracted automatically from a set of light optical micrographs. More than 1000 high resolution images could be processed in an overnight run on a standard office computer. These parameters were then correlated to product properties such as impact toughness. Parameters related to phase boundaries were found to have the strongest correlation.

Keywords

Duplex Stainless Steel, Light Optical Microscopy, Grain Size, Austenite Spacing, Microstructure, Impact Toughness, Image Analysis.

1. Introduction

Light optical microscopy of metals is a mature technique — it has been in successful use for more than 150 years and is essential to our understanding of polycrystalline materials. The technique is still developing, and faster computers in combination with improved microscopes give access to an even illumination and bit depths that were not within reach even a decade ago. The main advantage with light optical microscopy is speed. It is possible to record images in fractions of a second. Another important factor is the possibility to work at ambient conditions, which facilitates sample preparation and speed.

Although parameters such as phase fractions appear simple to quantify, it is still possible to find articles describing recent method development in the literature. One example is the amount of ferrite as a function of position in a duplex weld structure, which was studied in a recent paper by Balazs et al. [1]. Increasing computer power gives access to new image processing methods. Microstructures have been classified by data mining methods [2], deep learning algorithms [3], or more directly by feature extraction with subsequent correlation to different material properties [4]. For an introduction to the subject, the reader is referred to general textbooks, for example the recently updated Digital Image Processing by Gonzalez and Woods [5].

In the present paper, it is shown how different types of parameters can be extracted from light optical micrographs. This data is then correlated to impact toughness. When run over large data sets, several thousands of images from different positions in the material can be treated, enabling automated parameter extraction as an important tool for product as well as process development.
2. Experimental

2.1 Material

The samples were of grade Sandvik SAF 2507™ / EN 1.4410 and were taken from bars with diameters ranging from 80 to 240 mm. Cross sections were cut and polished to 1 µm mirror finish prior to etching. It should be noted that the material in this study was taken from intermediary production steps. Consequently, the microstructures depicted are not representative to what is expected after conditioning for final delivery.

2.2 Etching

The standard etch procedure consisted of two short dips in a NaOH electrolyte under 6 V bias. This gave a result where the austenite and ferrite regions were well separated in contrast.

For grain size estimates, a triple step methodology was used to develop grain boundaries. It consisted of sequential etching using:

1. 6.5 wt% oxalic acid (10 g (COOH)$_2$·2H$_2$O in 100 g H$_2$O) for 30s @ 3V
2. 21 wt% nitric acid (25 ml 65% HNO$_3$ + 75 ml H$_2$O) for 10s @3V
3. 29 wt% sodium hydroxide (40 g NaOH in 100 ml H$_2$O), for 3s @ 3V

This resulted in an image with clear boundaries, but also with a strong signature from nitrides. It should be stressed that this structure is not typical for as-delivered material. The to-be-delivered microstructure is cleaner and set in the final heat treatment process.

2.3 Light-Optical Microscopy

The Light Optical Microscopy (LOM) images were acquired using a Zeiss Axio Observer inverted Microscope, equipped with an Axiocam 503 color camera, rendering high resolution images with 1936×1460 pixels. This microscope has the advantage of giving an even illumination, which is essential for a consistent thresholding procedure. All micrographs were recorded with a nominal magnification of 100X. Calibration of the LOM was performed with a calibration scale dedicated to light-optical microscopy.

3. Image Processing Algorithms

The image processing algorithms were implemented in Matlab, release 2019a, together with the image processing toolbox. Detailed information on many of the extracted parameters

Fig. 1. Original image after gray scale conversion.
Fig. 2. Image after thresholding. The austenitic regions are colorized by size. Particles touching upper and right boundaries were removed to get a correct number estimate.

are available in the online Matlab manual [6]. All calculations were made on a standard 64-bit desktop PC running under Windows 10.

Common to all image processing in this paper was the thresholding procedure, which was used to obtain a binary image. The thresholding was performed using the Otsu method, which uses the center of gravity in the image histogram. It is described in detail in reference [5].

3.1. Parameters with a straight-forward extraction procedure

Particles are defined as components with a connection between pixels set to true (white) in the binary image. This function directly provides a set of parameters such as area, linearity, eccentricity etc. Some of these entities have a direct metallurgical interpretation: small round particles are secondary austenite and holes within an austenitic region are secondary ferrite. Others, such as rotational invariant moments, were included in the correlation exercise to determine whether they had an influence on macro properties. Table 1 lists parameters that were extracted for the correlation exercise.

Table 1. Parameters obtained with either a simple extraction procedure, or functionality provided by the connected components function.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Procedure</th>
</tr>
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<tbody>
<tr>
<td>Phase fraction</td>
<td>Fraction of bright contrast after thresholding</td>
</tr>
<tr>
<td>Number of austenite islands</td>
<td>Direct output from connected components</td>
</tr>
<tr>
<td>Austenite spacing</td>
<td>A grid is placed perpendicular to the rolling direction and the average distance between the austenite regions is calculated</td>
</tr>
</tbody>
</table>

Austenitic region properties

<table>
<thead>
<tr>
<th>Area</th>
<th>Number of pixels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perimeter</td>
<td>Number of true pixels with a false neighbor</td>
</tr>
<tr>
<td>Eccentricity</td>
<td>Line = 1, circle = 0</td>
</tr>
</tbody>
</table>

Rotational invariant moments up to the order of 3

<table>
<thead>
<tr>
<th>Rotational invariant moments up to the order of 3</th>
<th>See equation below</th>
</tr>
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</table>

Secondary austenite

| Secondary austenite | Connected components smaller than a certain threshold |

Secondary ferrite

| Secondary ferrite | Average number of large holes per austenite region |
Some parameters required a more complex extraction algorithm, such as grain boundaries, and some were designed with metallurgical savoir faire to reflect features in the image that were expected to have a good correlation to macro properties. Below follows a more detailed description of the serrated boundary index, a method to calculate a generalized austenite interspacing, as well as an algorithm for grain boundary extraction from heavily etched duplex microstructures. The grain size extraction process is not yet automated, some steps still require manual adjustment.

3.2. Serrated Boundary Index

A serrated boundary can be shaped as a saw-tooth, or it can have a smoother structure with extensions and indentations. To estimate the size of the inter-phase interface between the austenite and ferrite, the image was opened using a disc shaped structural element. The size of this element was set in relation to the average austenite domain size in the image. This results in a smoother edge of the austenite region (b). The serrated boundary index was then defined as the amount of area removed (c), over the total original area of the particle (a). The procedure is illustrated in Fig. 3. This gives the fraction of true pixels related to the phase boundaries. As an image is made up of several austenite regions, it was chosen to export the maximum and minimum values of the serrated boundary index for each image.

3.3. Complex Parameters: Austenite spacing on non-lamellar structures

Traditional austenite spacing methods require a lamellar structure to give consistent results. For structures with a less pronounced, or no directional preference, it is useful to resort to more complex methods. For cast structures or transverse cross-sections, it is possible to calculate the free space around each austenitic region by a Euclidean distance transform. The procedure is outlined in Fig. 4. In (a), a section of a micrograph is shown after binarization. To each austenite component is allotted a domain, taken as the mid line between adjoining austenite regions (b). For a correct distance estimate, it is necessary to remove domains touching borders (c). The remaining grains (d) are then used for plotting equidistant curves, as shown in Fig. 4e.
using a thermographic scale. A red coloration indicates a shorter distance to the next neighbor, yellow-white coloration a longer distance.

This procedure gives a distance estimate between austenite regions without directional preference. From the distance map in Fig. 7e, it is possible to extract parameters such as max, min and average distances between austenite components. It is also possible to calculate mean distances between components for any given direction in the image.

3.4 Complex Parameters: Grain Size

Another parameter which necessitates a significant amount of processing power is the grain size. As it is a parameter with a strong influence on mechanical properties, it is frequently measured as a part of delivery acceptance testing. Hence, it is of interest to automate the procedure to avoid operator dependence, and to increase speed. Today, a large part of the commercially available software work with a watershed transform to distinguish between different grains after polishing and etching. Descriptions on how to perform grain size measurements is standardized, for example as described in ASTM E112.

For duplex stainless steels, the issue is complicated by their dual phase structure, which makes it difficult to find an etch method that gives satisfactory contrast in both austenite and ferrite simultaneously. In addition, it is also interesting to study material after non-optimal heat treatments, for example welding, which tend to invoke the presence of ternary phase. These difficulties can be illustrated by the structure in Fig. 5, where the austenite regions appear as bright contrast and ferrite as dark. It is possible to see grain boundaries in the ferrite, but they are also intertwined with nitride clusters. It should be stated that this structure is not typical to as-delivered material. The nitrogen is normally dissolved into the austenitic region during the final heat treatment, which also sets the mechanical properties. The objective with this exercise was to attempt to find a stable algorithm, which also works for complex structures. In practical work, the images are much larger, giving less relative influence of boundary effects.
Fig. 5. Original image (a) with corresponding histogram (b). After a blurring operation on the complement image, the austenite regions appear as dark contrast (c) and the histogram (d) with an improved separation.

Fig. 5a shows the original micrograph with corresponding histogram (5b). To obtain a better separation in the histogram, the image was closed by a 25-pixel disc shaped structure element. This results in the blurred complement image that can be seen in Fig. 5c, together with its corresponding histogram having a distinct phase separation, Fig. 5d. The complement of the blurred image, Fig. 5c, is then later used for classifying of individual as either austenitic or ferritic.

To suppress the nitride clouds, a sequence of filter operations was undertaken. The first was a fast Fourier transform (FFT) with a band pass filter, with the intention to suppress smaller particles having a high spatial frequency. The resulting image with enhanced grain boundary contrast is shown in Fig. 6. Following FFT filtering, the edges were identified using a Canny-type detector. This resulted in two types of features: elongated and thin corresponding to grain boundary segments, as well as shorter and round elements, corresponding to nitrides. These components were separated by defining a curvature index and using a second order image moment. The dimensionless curvature index was defined as

\[ \chi = \frac{l_p^2}{A_{box}} \]  

(1)

where \( l_p \) is the length of the skeletonized line segment, and \( A_{box} \) is its bounding box. The curvature index should be low for elongated and somewhat straight components such as grain
boundaries. The discrimination power of a second order image moment was also investigated. The definition, taken from [5], is:

\[
\mu_{22} = \sum_{x=0}^{m-1} \sum_{y=0}^{n-1} (x - \bar{x})^2 (y - \bar{y})^2 f(x, y)
\]

(2)

where \( \bar{\text{bar}} \) indicates the center point and \( f \) is the value in pixel position \((x, y)\). For a binary image, \( f \) takes the value 0 or 1. Grain boundary segments would be expected to have larger second order moments compared to nitrides.

Fig. 6. Image after suppressing nitrides and carbides using a band pass fast Fourier transform filter.

Fig. 7. Scatter plot of the connected components after Fourier filtering and Canny edge detection. The coloration was made by area (pixels)
The scatter plot for these parameters can be seen in Fig. 7, where the size and color of each point corresponds to the area of the selected component. As nitrides are smaller and more curved than grain boundaries, the grain boundary segments were identified by retaining those components with an angular momentum >10 and a curvature index < 40.

After nitride removal, the edge detection algorithm was found to give double lines, see Fig. 8. These are then removed by a closing operation followed by a skeletonization. To complete some of the boundaries, an edge completion procedure was used to connect existing boundaries. The resulting image was skeletonized once more.

Following the parameter selection procedure, grain centers were detected using a distance transform, where peak values indicate the points farthest away from any boundary. These peak values were then set as sinks in the subsequent watershed transform. This procedure gives a grain count that is close to what is estimated by visual inspection. The grain boundaries are overlapping if detected and approximated in regions where nitride clouds were too dense for an efficient separation. Once the individual grain regions have been defined, they were classified as austenitic or ferritic by averaging the intensities from the corresponding regions in Fig. 5c. The resulting austenite and ferrite grain regions with no connection to image edges are displayed in Fig. 9. The image in this example is a $\frac{1}{4}$-section of the full image, so for a full calculation,

![a) Edge filtered and feature removal](image1.png) ![b) After boundary completion](image2.png)

Fig. 8. The edge detection algorithm applied on the Fourier image (Fig. 6) detects double lines (a), which can be removed by a closing operation followed by a skeletonization and edge completion up to 25 pixels. The result is given in (b).

![a) Austenite grains](image3.png) ![b) Ferrite grains](image4.png)

Fig. 9. Grains divided into austenite and ferrite after removing those touching borders.
there is less influence of grains touching boundaries. Once the grain size distribution is obtained, it is straightforward to extract parameters such as average ASTM number, standard deviation, skew and kurtosis.

4. Correlation Example: Impact Toughness

After the parameter extraction process, it is possible to make correlations to material properties. In one run, more than 30 parameters were extracted from each image, and more than 2,000 images, recorded from different positions in the material, were processed. One of the first parameters tested for correlation was impact toughness. A positive correlation factor indicates that the parameter increases with increasing impact toughness. Among the factors correlating strongly with impact toughness, one finds the serrated boundary index and the length/width relation of the austenite regions, see Fig. 10a. All these parameters are related to the austenite/ferrite interface. Among the factors with a strong negative correlation, one finds parameters related to austenite spacing, see Fig. 10b, both using the conventional austenite spacing tool, as well as the method developed for extracting inter-austenite spacings from a random structure. It is also worth noting that structure parameters showed a stronger correlation to impact toughness in comparison with any other parameter related to composition.

5. Acknowledgements

The sample preparation was made by Mats Kihlander. Fruitful discussions and constructive remarks were made by Fredrik Sandberg, Henrik Häll, all at Sandvik Materials Technology.
6. References

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EARLY STAGES OF DELETERIOUS PHASES IN SUPER- AND HYPER DUPLEX STAINLESS STEEL AND THEIR EFFECT ON TOUGHNESS

Abstract

Duplex stainless steels combine excellent mechanical properties with good corrosion resistance. Consequently, they are in frequent use in various highly demanding applications, like Oil&Gas, chemical processing, pulp & paper and desalination plants. Due to their high alloying contents super and hyper duplex are susceptible to the formation of detrimental secondary phases such as chromium nitrides, chi and sigma phase.

The presented investigation deals with the precipitation of those phases in super and hyper duplex by employing rapid isothermal heat treatments on a Gleeble 3800 thermo-mechanical simulator. Charpy-V impact toughness was measured as a function of sensitization time and temperature in order to characterise their effect on low temperature toughness. Both alloys suffer from severe embrittlement at the early stages of sensitization. In super duplex at 850°C for 20 seconds, chromium nitrides are precipitated, chi phase is formed after 200 seconds and small amounts of sigma after 500 seconds. In hyper duplex, the precipitation sequence is the same, but significantly faster. In this alloy sigma phase is encountered after merely 50 seconds and ferrite is completely consumed after 500 seconds.

Keywords

Super Duplex Stainless Steel, Hyper Duplex Stainless Steel, Isothermal Heat Treatment, Sigma-Phase, Chi-Phase, Chromium Nitride, Precipitation, Embrittlement, Impact Toughness

1. Introduction

Duplex stainless steels consist of balanced amounts of ferrite and austenite, resulting in high corrosion resistance and excellent mechanical properties [1]. By increasing the alloying content super and hyper duplex were developed [2]. Both duplex steels are stronger than equally resistant austenitic stainless steels and considerably cheaper than nickel base alloys. Hence, they represent a cost effective alternative when mechanical strength and corrosion resistance are required at the same time. However, the high alloying content in super and hyper duplex may result in the precipitation of unwanted detrimental phases. The most prominent in that regard are chromium nitrides, chi and sigma-phase. They typically form between 700 - 1000°C, due to inadequate cooling or excessive reheating during fabrication, processing or welding. These secondary phases result in severe embrittlement and reduce the corrosion resistance due to segregating alloying elements.

Proper information about the precipitation kinetics of intermetallic phases in super duplex is available in literature [3–6], but it is limited for hyper duplex [7,8]. However, most of the reported investigations consisted of quenching from the solution annealing temperature with subsequently reheating to a designated sensitization temperature. In many cases, this was
done with a slow heat transfer from air to steel. Hence, short tempering durations include a substantial uncertainty in respect to the actual material temperature, this blurs transformation temperatures and kinetics substantially.

Since the formation of deleterious phases in super and hyper duplex occurs rapidly, a precise time-temperature control is necessary. To ensure that in the presented investigation, a Gleeble 3800 thermo-mechanical simulator with conductive heating was used to apply a proper heat treatment.

2. Experimental

Both investigated Super- (SDSS) and Hyperduplex (HDSS) were melted in an electric arc furnace, subsequently treated by argon oxygen decarburization and casted in blocks. The castings were forged on a rotary forging machine to diameters of 205 and 168 mm for SDSS and HDSS, respectively. The concluding solution heat treatment consisted of soaking and water quenching. SDSS was annealed at 1100°C for 1 hour and HDSS at 1120°C for 1 hour. The chemical compositions and PREN(W)-values for both investigated alloys are shown in Table 1.

Table 1: Chemical composition and PREN(W) of SDSS and HDSS, in wt. %

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Cu</th>
<th>N</th>
<th>PREN(W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDSS</td>
<td>0.25</td>
<td>0.50</td>
<td>25.35</td>
<td>3.58</td>
<td>0.53</td>
<td>0.57</td>
<td>0.23</td>
<td>41.7</td>
</tr>
<tr>
<td>HDSS</td>
<td>0.19</td>
<td>2.93</td>
<td>26.30</td>
<td>4.61</td>
<td>0.45</td>
<td>0.20</td>
<td>0.37</td>
<td>48.2</td>
</tr>
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</table>

Samples with 10.2 x 10.2 x 100 mm were machined from the forgings in longitudinal direction. The sensitization treatments were carried out on a Gleeble 3800 by conductive heating, the sample arrangement can be seen in Fig. 1. Copper jaws were used as sample holders and heat sinks, with a free span of 40 mm. The thermo-couple was centered between the jaws. According to [9], the chosen arrangement results in a near constant temperature field, expanding roughly 10 mm from the center. The heating rate from ambient to the soaking temperature was 200K/min. The soaking temperatures for SDSS and HDSS were 1100 and 1120°C, respectively, for 300 seconds each. Soaking was followed by rapidly quenching to the sensitization temperature (750 to 1000°C), which was maintain for 20 to 500 seconds. After sensitizing, the heat treatment was concluded by rapidly quenching to room temperature, in order to minimize further uncontrolled phase transformations. An exemplary presentation of an applied heat treatment can be seen in Fig. 1. Rapid quenching always refers to the maximum amount of free cooling, without further external heat input.
After applying the heat treatment a notch was machined at the connecting sites of the thermo-couple, to ensure a constant temperature in the tested volume.

The impact toughness was determined according to [10], at a temperature of -46°C. Electrochemical etching with 4% NaOH was applied to reveal the microstructure in the tested area after impact testing. A SEM Zeiss Ultra 55 was used for further microstructural characterisation; all samples were grinded and subsequently polished with OPS.

3. Results

According to Fig. 2, a sensitization treatment at 1000°C for 20 seconds in HDSS yields an impact toughness of 30 J. Maintaining this temperature up to 500 seconds does not result in a reduced toughness. By decreasing the temperature to 950°C, no initial decline in toughness is visible after 20 seconds. However, an extended sensitization result in a deteriorating impact toughness, which drops to 5 Joules after 500 seconds. A further reduction in temperature to 900 or 850°C results in 30 J after 20 seconds and longer treatments cause a more pronounced drop then at 950°C. Maintaining 850 and 900°C for 200 seconds or longer reduces the toughness to 5 Joules. After 20 seconds at 800°C, the measured toughness is 45 J. However, toughness declines when sensitizing is maintained and ultimately reaches 6 Joules after 500 seconds. At 750°C, the impact toughness remains at approximately 30 J for durations up to 200 seconds. Longer sensitization results in a decrease to 20 Joule after 500 seconds. The observed decline in impact toughness between 800 to 900°C correlates to the logarithm of the sensitization duration, indicated by reasonably high $R^2$-values.
**Fig. 2:** Charpy-V impact toughness of HDSS at sensitization temperatures between 750 to 1000°C for 20 to 500 seconds

As illustrated by Fig. 3, sensitizing SDSS at 950°C for 200 seconds results in an impact toughness of 300 Joules, after 500 seconds it declines to 240 J. A reduced sensitization temperature of 900°C results in 220 J after 20 seconds, which gradually declines to 10 Joules by extending the heat treatment up to 500 seconds. Further lowering the sensitization temperature reduces toughness after 20 seconds; at 850°C an impact toughness of 115 J is obtained, at 800 and 750°C it declines to 90 J. At 850 and 800°C, impact toughness is immediately reduces by temperature exposure longer than 20 seconds, thereby following a logarithmic trend. Whereas at 750°C, no initial decline is obtain during the first 50 seconds, but further temperature exposure gradually reduces impact toughness.
**Fig. 3:** Charpy-V impact toughness of SDSS at sensitization temperatures between 750 to 950°C for 20 to 500 seconds

Fig. 4 depicts the impact toughness of sensitized SDSS and HDSS as a function of sensitization temperature. Isochronal lines correspond to individual tempering durations. Both alloys show a declining impact toughness with lower temperatures and longer sensitization. SDSS exhibits a more pronounced drop, mostly due to higher initial values. However, the impact toughness in HDSS is much smaller for any combination of time and temperature. Furthermore, between 800 and 950°C, hyper duplex shows a distinct temperature range with very lower toughness. The fastest decline of occurs between 850 to 900°C, which corresponds to the nose temperature of hyper duplex.

**Fig. 4:** Impact toughness in SDSS and HDSS as a function of sensitization temperature with isochronal lines for 20, 50, 100 (only HDSS), 200 and 500 seconds of sensitization
During the early stages of sensitization, SDSS exhibits a low toughness below 850°C. The lowest impact values after an extended temperature exposure is obtained at 850°C, which corresponds to the maximum rate of embrittlement (the nose temperature).

Figs. 5 (a)-(e) depict the microstructure in HDSS at the nose temperature of 900°C, from 20 to 500 seconds of sensitization. As shown in Figs. 5 (a), after 20 seconds, the microstructure is free of chi or sigma and mainly consists of ferrite and austenite. However, at some ferrite/ferrite interfaces, white fringes are detectable. Maintaining this temperature for 50 seconds, as seen in Figs. 5 (b), leads to small amounts of sigma phase near the ferrite/ferrite and ferrite/austenite interfaces. This is accompanied by a near continuous grain boundary precipitation along the ferrite/ferrite interfaces. These precipitates correspond to chi-phase, which seems irregular and edgy, and appears to act as nucleation site for sigma phase. Prolonged tempering for (c) 100, (d) 200 and (e) 500 seconds leads to a steadily increasing phase fraction of sigma phase, which completely consumes ferrite after 500 seconds of sensitization. No indication for any transformation of austenite was found.

Figs. 5 (a)-(e): Microstructure in hyper duplex after sensitizing at 900°C for (a) 20, (b) 50, (c) 100, (d) 200 and (e) 500 seconds. Austenite is etched white or lightly brown, ferrite appears in a bold brown or blue.
Figs. 6 (a)-(d) show the microstructure in SDSS at a nose temperature of 850°C, from 20 to 500 seconds of sensitization. Similar to hyper duplex, super duplex is free of chi and sigma phase after 20 seconds, as can be seen in Figs. 6 (a). Occasionally, some ferrite/ferrite interfaces exhibit white fringes with black features (chromium nitrides) in their center. An extended tempering duration of 50 seconds, illustrated in Figs. 6 (b), results in a more noticeable precipitation of nitrides along the grain boundaries. However, neither chi nor sigma are detectable at this stage. After 200 seconds, as shown in Figs. 6 (c), white irregular precipitates, corresponding to chi-phase manifested along the ferrite/ferrite interfaces, though no sigma phase precipitated. After 500 seconds at 850°C, demonstrated by Figs. 6 (d), small quantities of sigma phase eventually formed at the decorated grain boundaries, which appear to act as nucleation sites for sigma.

Figs. 6 (a)-(d): Microstructure of super duplex after sensitizing at 850°C for (a) 20, (b) 50, (c) 200 and (d) 500 seconds. Austenite etches white; ferrite appears in a bold brown.

Fig. 7 shows a ferrite/ferrite and ferrite/austenite interface in super duplex at 850°C after 200 seconds of sensitization, this corresponds to Figs. 6 (c). Precipitates are clearly visible at both interfaces, with an overall higher amount at the ferrite/ferrite grain boundary. At this site, the precipitates appear serrated, with an alternating arrangement of two precipitate species. Both were identified by EDX, as chromium nitride and chi-phase, appearing in black and white, respectively. The ferrite/austenite interface reveals a less dense occupation with precipitates, especially in regards to nitrides. Furthermore, chi-phase appears in a smooth and rounded rather than serrated shape, compared their appearance at the ferrite/ferrite interface.
Fig. 7: Grain boundary precipitates at a ferrite/ferrite and ferrite/austenite grain boundary in super duplex at 850°C after 200 seconds of sensitization

Figs. 8 (a) and (b) illustrate the microstructure in super duplex for an identical sensitization duration of 50 seconds, but at different temperatures. At 750°C, as seen in Figs. 8 (a), fringes with chromium nitrides manifested at the ferrite/ferrite interfaces. They already cover large parts of the interface. At 900°C, as illustrated by Figs. 8 (b), the microstructure is free of grain boundary precipitates and solely consists of austenite and ferrite.

Figs. 8 (a)-(b): Microstructure of super duplex after 50 seconds of sensitization at (a) 750°C and (b) 900°C

4.Discussion

Regardless of the actual alloying composition, small amounts of precipitates cause severe embrittlement in super and hyper duplex stainless steel. At -46°C even precipitate free hyper duplex hardly reaches 30 Joules of impact toughness and consequently falls behind super duplex, which maintains 300 J in a precipitate free condition. This difference may be caused by dissimilar ductile-to-brittle transition temperatures, however due to limited information regarding the transition temperature in hyper duplex this is up for debate.
Regardless, hyper duplex exhibits a lower toughness in every tested combination of time and temperature. Both alloys initially form chromium nitrides during the early stages of sensitization at their respective nose temperature. Nitrides are most frequently present at ferrite/ferrite grain boundaries. Further sensitization leads to the precipitation of chi-phase, mainly decorating ferrite/ferrite grain boundaries and in smaller quantities ferrite/austenite interfaces. Longer temperature exposure results in the formation of sigma-phase at both interfaces. This precipitation sequence is particularly well documented for super duplex, as can be seen in Figs. 6 (a) to (d). In this case, sigma phase is preceded by chi and chromium nitrides, and is eventually formed after 500 seconds of sensitization. In hyper duplex the precipitation at nose temperature is considerably faster and noticeable amounts sigma phase are already present after 50 seconds.

Nevertheless, in both alloys sigma phase is not solely responsible for a low impact toughness, especially during the early stages of sensitization. This becomes particularly obvious by comparing high and low sensitization temperatures in super duplex. At 900°C and after 50 seconds, the microstructure is free of nitrides and toughness remains at 200 Joules. However, after sensitizing at 750°C for 50 seconds, nitrides form and toughness drops to roughly 100 Joules. The subsequent formation of chi further reduces toughness substantially, even before sigma precipitates. This detrimental effect of nitrides and chi is known in literature, though sigma is mostly seen as root cause for low impact values, which is clearly not the case in the presented investigation.

These unforeseen results most likely arise from diverging heat treatment parameters between this investigation and those in literature. Firstly, most of available literature data concerns quenched and tempered material. By quenching to ambient temperature and subsequently reheating, diffusion processes may influence the precipitation sequence. Secondly, nitrides and chi-phase form rapidly, especially at the nose temperature. Uncontrolled reheating conditions can distort early precipitation states and hide the formation of chromium nitrides and chi-phase.

Therefore, inaccurate sensitization conditions are of particular concern for hyper duplex, with its rapid precipitation kinetics. Sigma formation occurs in under one minute of tempering and insufficient reheating conditions would hide the detected precursor phases.

5. Conclusion

Early stages of intermetallic phases and their effect on toughness in super and hyper duplex stainless steel were investigated:

- Hyper duplex forms detrimental phases multiple times faster than super duplex, which leads to rapid embrittlement, especially at low service temperatures.
- Minute quantities of detrimental phases result in a substantial reduction of impact toughness. No discrimination between the contributions of the individual phases was possible.
- The following precipitation sequence was observed in both alloys: chromium nitride over to chi-phase over to sigma-phase. This was shown for the peak transformation temperatures of 850 and 900°C in super and hyper duplex, respectively.
- Chromium nitrides form especially fast at temperatures below the nose temperature and mainly cover the ferrite/ferrite interfaces.
References

INFLUENCE OF THE ALLOY COMPOSITION OF FILLER METALS ON THE MICROSTRUCTURE OF WIRE AND ARC ADDITIVE MANUFACTURED COMPONENTS MADE OF DUPLEX STAINLESS STEEL

Abstract

Current recommendations for welding duplex stainless steels focus on achieving a precipitation-free weld metal microstructure with balanced proportions of ferrite and austenite during joint welding and cladding. However, the application of these recommendations regarding energy per unit length and filler metals results in a predominantly austenitic microstructure in WAAM duplex stainless steel components. The modification of the filler metals is an option to increase the ferrite content in the duplex weld metal. This article describes the increase of the ferrite content as a result of adjusting the alloy composition. For producing the specimens, both a filler metal with reduced nickel content and a filler metal with increased silicon content were used. The nickel content was specifically graded by mixing different alloys during welding by means of GMAW cold wire technology. The reduction of the nickel content particularly proved to be an effective way to reduce the austenite content in the weld metal. The increase of the silicon content also resulted in an increase of the ferritic microstructure. Thus, test specimens with ferrite contents between 32-50 % were produced.

Keywords

Wire and Arc Additive Manufacturing, Duplex Stainless Steel, Filler Metals, Alloy Composition, G 22 9 3 N L, GZ 22 5 3 L

1. Introduction

Duplex stainless steels (DSS) are characterized by a balanced ferritic-austenitic microstructure after manufacturing. This is achieved by the chemical composition and a special heat treatment consisting of solution annealing and water quenching. When welding DSS, the weld pool initially solidifies primary ferritic. During further cooling, the ferrite partly transforms diffusion controlled into austenite. The resulting ferrite content depends both on the alloy composition and on the cooling rate [1]. The microstructure ensures the characteristic properties of DSS. This includes high resistance to corrosive media (aqueous media containing \( \text{H}_2\text{S} \), chlorides and solutions with low pH values), high resistance to pitting and stress corrosion cracking as well as high strength. These properties qualify DSS for applications in petrochemical, paper, food and construction industries [2].

Over the past decades, several welding recommendations have been developed for successful welding of high-alloyed corrosion-resistant DSS. These aim at the formation of a two-phase microstructure with a ferrite content of about 30-70 % as well as the absence of intermetallic phases and precipitations to guarantee the required material-specific properties of the welds. The welding recommendations include, for example, the adherence to specific energy...
input per unit length and interpass temperatures as well as the use of similar filler metals with an increased nickel content compared to the base metal.

When welding 22%Cr DSS, the energy per unit length should be between 0.5-2.5 kJ/mm and the interpass temperature should not exceed 250 °C. Preheating and post heat treatment are not generally required [2, 3]. Multi-component shielding gases with helium are particularly suggested in order to reduce the viscosity of the weld pool, to improve wetting, to cool more slowly and thus to precipitate more austenite or, if necessary, to increase the welding speed. Nitrogen admixtures are also used to increase the proportion of austenite in the weld metal. For improving the penetration behaviour, CO₂ additions of max. 2-3 % are recommended as well. [3, 4, 5, 6].

2. State of knowledge on WAAM of duplex stainless steel components

The layer-by-layer production of components by arc welding offers numerous advantages. These include new design freedom, a high degree of material utilization and the possibility of a more flexible, decentralized manufacturing [7, 8, 9]. Some 3D metal printing systems are already commercially available. A challenge in wire and arc additive manufacturing (WAAM) is the very low cooling rate compared to joint welding. The low heat dissipation and the resulting low cooling rate can cause both high residual stresses and distortion as well as changes in the microstructure and cracking [10, 11].

When processing DSS, the cooling rate is of decisive importance for the ferrite-austenite ratio, since the austenite content of the weld metal significantly depends on the t₁₂/₈ cooling time [1]. Thus, similar filler metals with increased nickel content compared to the base metal are used for joint welding and cladding. These ensure a sufficient proportion of austenite in the weld metal despite short cooling times. First investigations on the production of turbine blades by WAAM with the standard filler metal 22 9 3 N L show an excessively austenitic microstructure with ferrite contents of less than 30 % [12]. The reason for the excessive precipitation of austenite is the increasing cooling time with increasing layer height as well as the repeated dwell time in the temperature range between 1200-800 °C during welding of the subsequent layers [13, 14]. It is generally recommended to use a lower energy per unit length for WAAM than it is suggested in the common processing guidelines. Low energy per unit length results in higher cooling rates due to smaller weld pools and thus in a slight increase in the ferrite content. However, the technical measures, such as reducing the energy per unit length or lowering the interpass temperature, are not sufficient to ensure an adequate ferrite content in WAAM components made of DSS [14].

3. Methodical approach

The process-related reduced cooling rate requires an adaptation of the filler metals to achieve a balanced microstructure with ferrite contents of 30-70 % when wire and arc additive manufacturing of DSS components. This can be achieved by increasing the ferrite stabilizing alloying elements and lowering the austenite stabilizing alloying elements. In order to maintain the typical properties and to avoid adverse precipitations, a reduction of the nickel content is most promising.

In this article, the influence of a reduced nickel content as well as the influence of an increased silicon content on the resulting weld metal microstructure were investigated. Furthermore, decreasing nickel contents in the standard duplex weld metal were generated by
mixing two filler metals with different nickel contents. The filler metals were mixed using a GMAW cold wire technology.

The weld specimens were then analytically characterized. Optical emission spectroscopy (OES) and carrier gas melt extraction (CGME) were used to determine the chemical composition of the specimens. The ferrite content was determined over all layers both by magnetic induction using Fischer Feritscope on macrosections and by image analysis on microsections. In addition, the microsections were examined for intermetallic phases and precipitations. Moreover, radiographic tests were performed to identify inner imperfections.

4. Experimental

4.1 Filler metals and shielding gas

A standard filler metal with a nickel content of around 9 wt.% and a specially designed filler metal with a nickel content of around 5 wt.% were used for the welding tests. In addition, a standard filler metal containing a slightly higher percentage of silicon was used. Table 1 shows the chemical compositions of the different electrodes.

<table>
<thead>
<tr>
<th>Type</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N*</th>
<th>Cu</th>
<th>Nb</th>
<th>C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>G 22 9 3 N L</td>
<td>22.48</td>
<td>8.77</td>
<td>3.09</td>
<td>1.54</td>
<td>0.48</td>
<td>0.1402</td>
<td>0.09</td>
<td>0.02</td>
<td>0.175</td>
</tr>
<tr>
<td>G 22 9 3 L Si</td>
<td>22.98</td>
<td>8.71</td>
<td>3.13</td>
<td>1.49</td>
<td>0.76</td>
<td>0.1603</td>
<td>0.09</td>
<td>0.03</td>
<td>0.0151</td>
</tr>
<tr>
<td>GZ 22 5 3 L</td>
<td>22.15</td>
<td>5.51</td>
<td>3.23</td>
<td>0.75</td>
<td>0.45</td>
<td>0.1404</td>
<td>0.18</td>
<td>0.02</td>
<td>0.0185</td>
</tr>
</tbody>
</table>

The calculation of the corresponding chromium (formula 1) and nickel equivalents (formula 2) according to the WRC-1992 diagram predicts a slight increase in the ferrite content when using the electrode type G 22 9 3 Si and a significant increase in the ferrite content when using the electrode type GZ 22 5 3 compared to the standard electrode G 22 9 3, see Table 2.

\[
\text{Cr}_{\text{Eq}} = \text{Cr} + \text{Mo} + 0.7\text{Nb} \\
\text{Ni}_{\text{Eq}} = \text{Ni} + 35\text{C} + 20\text{N} + 0.25\text{Cu}
\]

Tab. 2: Chromium and nickel equivalents as well as ferrite numbers (FN) of the filler metals according to the WRC-1992 diagram

<table>
<thead>
<tr>
<th>Type</th>
<th>Cr_{Eq}</th>
<th>Ni_{Eq}</th>
<th>FN (WRC-1992)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G 22 9 3 N L</td>
<td>25.6</td>
<td>12.2</td>
<td>46</td>
</tr>
<tr>
<td>G 22 9 3 L Si</td>
<td>26.1</td>
<td>12.5</td>
<td>50</td>
</tr>
<tr>
<td>GZ 22 5 3 L</td>
<td>25.4</td>
<td>9.0</td>
<td>&gt; 100</td>
</tr>
</tbody>
</table>

The diameter of the filler metals was 1.2 mm each. All welds were produced with an inert shielding gas consisting of 70 % argon and 30 % helium.
4.2 Production of specimens

The layer-by-layer technique was used to produce wall structures with a length of 200 mm and 20 layers using the GMAW-CMT process, see Figure 1. The deposition welds were performed with a neutral torch position, a contact tube distance of 12 mm and a shielding gas flow rate of 18 l/min. The single layers were welded in PA (1G) position with alternating welding direction.

Fig. 1 Specimen geometry

To generate different nickel contents from 5.51-8.77 wt.%, the electrodes G 22 9 3 and GZ 22 5 3 were mixed by cold wire feed during GMAW welding. The cold wire was fed at an angle of 35° in relation to the sheet plane and at a distance of 2 mm from the base of the electrode.

The welding parameters were kept constant over all layers. To ensure comparability between the specimens, all specimens were produced with the same parameter setting. At a wire feed speed of 5.0 m/min and a welding speed of 0.5 m/min, the average energy per unit length was 0.44 kJ/mm. A maximum interpass temperature of 50 °C was always maintained.

5. Results and discussion

5.1 Layer structure and dimensions of the specimens

The specimens show an even layer structure. The build-up welding of 20 layers without cold wire feed results in an average specimen height of 40 mm and an average specimen width of 6.8 mm in the as welded condition using the standard electrode 22 9 3. The use of the electrodes 22 9 3 Si and 22 5 3 leads to similar values. Only the width of the specimen produced with the filler metal 22 5 3 is slightly smaller. A difference in the specimen geometry appears for specimens produced with additional cold wire feed. For example, when CMT welding with 23.1 % cold wire (percentage relative to the total weld metal) results in an increase in the specimen height of 28 % with approximately the same specimen width, see Figure 2. A comparison of the macrostructure illustrates that not only the specimen height increases when welding with cold wire, but also the waviness of the specimen surface.
Fig. 2 Geometric dimensions as well as macrosections of representative specimens consisting of 20 layers each, (a) height and width of the specimens in as welded condition, (b) macrosection of specimen welded without cold wire, (c) macrosection of specimen welded with 23.1 % cold wire feed

5.2 Chemical analysis

Table 3 shows the chemical compositions of the specimens determined by OES and CGME as well as the Cr and Ni equivalents with corresponding ferrite numbers (FN) calculated according to the WRC-1992 diagram. Based on chemical analyses of the weld metals, ferrite numbers between 42-90 FN are to be expected, which indicates an approximate ferrite content of 29-63 %.

Tab. 3: Chemical composition of WAAM walls in wt.% determined by OES and CGME* as well as Ferrite number determined by WRC-1992

<table>
<thead>
<tr>
<th>weld metal of</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N*</th>
<th>Cu</th>
<th>Nb</th>
<th>C*</th>
<th>CrEq</th>
<th>NiEq</th>
<th>FN_WRC</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% 22 9 3</td>
<td>22.50</td>
<td>8.77</td>
<td>3.08</td>
<td>0.1477</td>
<td>0.10</td>
<td>0.02</td>
<td>0.0228</td>
<td>25.6</td>
<td>12.5</td>
<td>42</td>
</tr>
<tr>
<td>100% 22 9 3 Si</td>
<td>23.04</td>
<td>8.72</td>
<td>3.15</td>
<td>0.1605</td>
<td>0.09</td>
<td>0.03</td>
<td>0.0228</td>
<td>26.2</td>
<td>12.8</td>
<td>47</td>
</tr>
<tr>
<td>100% 22 5 3</td>
<td>22.26</td>
<td>5.46</td>
<td>3.19</td>
<td>0.1791</td>
<td>0.18</td>
<td>0.02</td>
<td>0.0165</td>
<td>25.5</td>
<td>9.7</td>
<td>90</td>
</tr>
<tr>
<td>90.9% 22 9 3 +</td>
<td>22.29</td>
<td>8.61</td>
<td>3.11</td>
<td>0.1441</td>
<td>0.10</td>
<td>0.02</td>
<td>0.0188</td>
<td>25.4</td>
<td>12.2</td>
<td>45</td>
</tr>
<tr>
<td>9.1% 22 5 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>83.3% 22 9 3 +</td>
<td>22.29</td>
<td>8.30</td>
<td>3.14</td>
<td>0.1493</td>
<td>0.11</td>
<td>0.02</td>
<td>0.0187</td>
<td>25.4</td>
<td>12.0</td>
<td>48</td>
</tr>
<tr>
<td>16.7% 22 5 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>76.9% 22 9 3 +</td>
<td>22.21</td>
<td>8.13</td>
<td>3.15</td>
<td>0.1512</td>
<td>0.11</td>
<td>0.02</td>
<td>0.0193</td>
<td>25.4</td>
<td>11.9</td>
<td>50</td>
</tr>
<tr>
<td>23.1% 22 5 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>76.9% 22 5 3 +</td>
<td>22.11</td>
<td>6.29</td>
<td>3.23</td>
<td>0.1757</td>
<td>0.16</td>
<td>0.02</td>
<td>0.0185</td>
<td>25.4</td>
<td>10.5</td>
<td>73</td>
</tr>
</tbody>
</table>

Due to the use of an inert shielding gas there is almost no burning loss or pickup of alloying elements as expected. Nevertheless, oxygen and, above all, nitrogen pickup have been
observed. A significant increase in nitrogen with an increasing percentage of the filler metal 2253 can be noted, while the oxygen pickup is approximately constant, see Fig. 3. The nickel content in the weld metal decreases with increasing percentage of the filler metal 2253. The lower the nickel content, the higher is the nitrogen solubility in molten iron [15]. The combination of increasing nitrogen solubility and the process-related slow cooling rate is to be considered as reason for the increased nitrogen pickup despite inert shielding gas.

![Nitrogen and oxygen pickup of WAAM walls depending on the mixing ratio of filler metals](image)

**Fig. 3** Nitrogen and oxygen pickup of WAAM walls depending on the mixing ratio of filler metals

5.3 **Ferrite content**

Figure 4 shows the ferrite numbers of the specimens determined by magnetic induction compared to the ferrite percentages determined by image analysis. The optical determination of the ferrite content leads to wide scattering of the results. Investigations by Putz et al. [16] show that even an increase in the number of evaluated micrographs does not significantly minimize the scattering. The determination of the ferrite number by magnetic induction was performed both in cross section of the specimens and on unmachined specimen surfaces. Due to the even surfaces of the structures produced without cold wire, ferrite measurements using the Feritscope are also possible non-destructively directly at the welded structure.

Independent of the method, both diagrams show similar tendencies. The application of the silicon-alloyed filler metal leads to a moderate increase in the ferrite content. However, a significant increase in the ferrite content can be achieved by reducing the nickel content.
The increase in the ferrite content using modified filler metals can also be seen in the microphotographs, see Figure 5.

Figure 6 illustrates the adjustment of different ferrite contents in the specimens as a result of mixing the filler metals 22.93 and 22.53 by cold wire feed. The ferrite numbers actually measured on the weld metal are very similar to those expected according to WRC-1992. Only the weld containing about 5.5% nickel (100% 22.53) resulted in a significantly lower ferrite content than predicted.

Since the chromium equivalent of all specimens is approximately the same, the increase in the ferrite content can be attributed to the reduction in the nickel equivalent. Although the increase of the nitrogen pickup with decreasing nickel content counteracts the reduction of the nickel equivalent, the reduction of the nickel content in the filler metal is decisive.
Fig. 6 Ferrite number of specimens depending on the mixing ratio of filler metals, Cr\textsubscript{Eq} \& Ni\textsubscript{Eq} calculated according to WRC-1992 based on the chemical composition of the weld metals

5.4 Hardness

The variation in the ferrite content is also represented in the hardness values of the specimens. The increase in the ferrite content leads to an increase in hardness, see Figure 7. The weld metal with an average of 43 FN shows a hardness of 272 HV10, whereas the weld metal with an average of 79 FN shows a hardness of 296 HV10.

Fig. 7 Hardness of WAAM specimens depending on the ferrite number determined by Feritscope on macrosections
5.5 Inner imperfections

The radiographic testing of the flat milled specimens shows an isolated formation of small pores. Figure 8 illustrates an exemplary radiograph. The application of cold wire technology for producing specimens with different nickel contents did not cause any further inner imperfections.

![Radiograph of a WAAM structure showing two small pores](image)

**Fig. 8** Radiograph of a WAAM structure showing two small pores

6. Summary and outlook

The present investigations show that a balanced ferrite-austenite ratio in WAAM structures made of DSS can be achieved by modifying the alloy composition of filler metals. The mixing of different alloys using the GMAW cold wire technology is a suitable method to find an appropriate alloy composition.

In subsequent investigations, it is mandatory to verify the characteristic material properties (strength, toughness and pitting corrosion resistance) of the specimens produced with a modified alloy composition to prove the suitability for practical use.

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References


THE DUPLEX-STAINLESS-STEEL 1.4462 FOR FLOW LINES

Abstract

Today the duplex-steel 1.4462 is often used for flow-lines and a lot of money is spent worldwide into finding the right joining process for the circumferential welds of these pipes. A central collection of welding variables and their efficient processing will result in a prediction of the mechanical properties and fracture mechanical values out of the data of the preceding joining process and save trial and error procedures and costs. This paper deals with the prediction of the mechanical properties, such as yield strength, tensile strength, impact energy, and hardness, and the fracture mechanical values, such as CTOD- (Crack Tip Opening Displacement-) values, from welding parameters, for example heat-input, of the joining process. The problems met in determining and predicting the yield strength, the tensile strength, the impact energy, the hardness, and the crack tip opening displacement are discussed in detail and the results are compared. Finally the different resulting values are compared with each other and with numerous values from literature. The tested materials have been the base material, the weld metal, and the heat affected zone of welds, using different welding processes, as for example Manual Metal Arc Welding, Gas Metal Arc Welding, Gas Tungsten Arc Welding, or Submerged Arc Welding, of the duplex-steels 1.4462.

Keywords

Duplex-steel, 1.4462, base material, weld metal, heat affected zone, different welding processes, Manual Metal Arc Welding, Gas Metal Arc Welding, Gas Tungsten Arc Welding, Submerged Arc Welding, mechanical properties, impact energy, hardness, yield strength, tensile strength, fracture mechanical values, CTOD (Crack Tip Opening Displacement).

1. Introduction

In former times construction steels with low yield strength and then normalized and micro alloyed C-Mn-steels were used for natural gas pipelines [1]. The next important step started 1970 with the use of the thermomechanical treatment [2] for the steel production for pipes. According to this procedure since about 1973 the steel X60 and since 1977 the steel X70 were produced as the dominant pipeline-steel types. The development for onshore natural gas pipelines in practice led to higher tensile and yield strength, so to the steel X80, X100 or possibly X120 [3].

In case of a higher corrosion resistance demanded, as in the case of flow-lines, the duplex-steel type 1.4462, X 2 CrNiMoN 22 5 3 is used. According to [4] the development of this steel type has started after world war two with a real breakthrough in the 1970s. Today there are about twenty companies worldwide producing about 100 different types of duplex-steels [5].

It should be mentioned, that the welding tests have been performed in the field, joints welded on the building site, as well as in the laboratory, and therefore, bigger scatter bands in the results may occur. The basis of most of the diagrams and figures are a few hundred values.
This paper gives an overview of the chemical compositions, the mechanical properties, tensile, hardness as well as impact energy values, and the fracture mechanical, CTOD - (Crack Tip Opening Displacement-) values according to BS 7448 [6] using three point bend specimens of the duplex-steel 1.4462 according to different standards, by using different welding processes, as manual metal arc welding, gas tungsten arc welding, gas metal arc welding, flux cored arc welding or submerged arc welding, especially also the numerous welding process variables, including preheating temperature, interpass temperature, weld configuration, consumable type, positioning, operating voltage and amperage, travel speeds etc., for various consumables are described.

2. Materials for Pipelines

Development of Duplex-Stainless-Steels:

The first clue as how to produce austenitic-ferritic stainless steel grades were supplied by Bain and Griffiths in the year 1927 after research on the ternary system Fe-Cr-Ni, and they discovered the advantages in regards to strength and corrosion, especially in regards to the resistance against intercrystalline corrosion. In 1930 the company Avesta in Sweden fabricated some structures and component parts considered as spectacular. Also in France corrosion resistant austenitic-ferritic alloys were patented since 1935 and sold. Because of issues related to the toughness and corrosion behavior occurring over and over again, they were not spread effectively. Finally, the economic pressure caused by the nickel shortage in 1969 showed a breakthrough by using better production and manufacturing conditions. Since the 1970th, duplex-steels were continuously developed by optimizing the chemical composition and improving the manufacturing process to gain suitable property profiles in regards to strength, corrosion resistance, and wear resistance.

The steel 1.4462 is according to DIN 17 440 [7], DIN 17 441 [8], SEW 400 [9], OENORM EN 10 088, part 1 to 3 [10] to [12], and TÜV-Austria [13] (1.4462 according to OENORM EN 10 027 – 2 [14], X 2 CrNiMoN 22 5 3 according to OENORM EN 10 027 – 1 [15] or S31803 according to ASTM UNS).

Figure 1 shows the chemical composition according to different standards for the duplex-steel 1.4462 used for flow lines. The bounding values in the standards, if specified, do not always correspond. Therefore, it is important to define in the planning period of the pipeline according to which standard the steel is chosen.

Figure 2 shows the bounding values of the strength and impact energy values according to different standards for the steel 1.4462.
Fig. 1. Comparison of the chemical composition of the steel 1.4462 according to OENORM EN 10 088 – 1 (EN) [10], TÜV Austria (TÜV) [13], SEW 400 (SEW) [9], and ASTM according to IIW [16] with the tested steels 1.4462 (r ... rolled, pl ... plate, p ... pipe)

Fig. 2. Comparison of the mechanical properties of the steel 1.4462 according to OENORM EN 10 088 – 1 (EN) [10], TÜV Austria (TÜV) [13], SEW 400 (SEW) [9], and ASTM according to IIW [16] with the tested steels 1.4462 (r ... rolled, pl ... plate, p ... pipe)

For this steel the minimum value for the yield strength and the tensile strength according to OENORM EN 10 008 - 1 and ASTM are lower than the one according to TÜV and SEW 400, and the minimum values of the impact energy according to OENORM EN 10 008 - 1 are also lower than those according to TÜV and SEW 400, whereas they are not defined in ASTM.

Typical microscopic structures of the tested steels are shown in Figure 3. For further information see [3].
3. Weldability and Heat Treatments

For longitudinal or spiral welds of pipelines for natural gas mainly
- Submerged Arc Welding (12, SAW)
is used, whereas for circumferential welds the following welding processes are used:
- Manual Metal Arc Welding (111, MMAW),
- Gas Metal Arc Welding (GMAW) in the variations of
  MIG (131) and
  MAG (135),
- Flux Cored Arc Welding (136, FCAW),
- Gas Tungsten Arc Welding (141, GTAW),
- Submerged Arc Welding (12, SAW) (in case of double or triple joints).

Figure 4 shows the chemical composition and Figure 5 the mechanical properties of
different welding metals for the duplex-steel 1.4462 according to different welding processes.
More details about welding gases are given in [3].

![Fig. 3. Structure of the tested duplex-steels 1.4462 (r ... rolled, pl ... plate, p ... pipe) [3]](image)

![Fig. 4. Chemical composition of the weld metal of the duplex-steel 1.4462 [3]](image)
(111 … manual metal arc welding, 141 … tungsten inert gas welding, 135 … gas metal arc welding with active gas and solid wires, 136 … flux core arc welding, 12 … submerged arc welding)

In regards to the welding parameters, the preheating and interpass temperatures, and for further information about comparisons of welding processes see [3], [17] to [19].

Figure 6 shows the great differences in the impact energy values over the temperature for different welds on the duplex-steel 1.4462.

![Graph showing mechanical properties of the weld metal of the duplex-steel 1.4462](image)

**Fig. 5.** Mechanical properties of the weld metal of the duplex-steel 1.4462 [3] (111 … manual metal arc welding, 141 … tungsten inert gas welding, 135 … gas metal arc welding with active gas and solid wires, 136 … flux core arc welding, 12 … submerged arc welding)

![Graph showing impact energy over the temperature for different welds on the steel 1.4462](image)

**Fig. 6.** Impact energy over the temperature for different welds on the steel 1.4462 [3] (111 … manual metal arc welding, 141 … tungsten inert gas welding, 135 … gas metal
4. Welding and Mechanical Technological Tests

The extreme upper and lower limits for the amperage, the welding velocity, and the heat-input according to data of different producers for the welded joints out of the duplex-steels are shown in [3]. The heat-input \( S \) [kJ/cm] is calculated of the values of the amperage \( I \) [A], the welding velocity \( v \) [cm/min], and the voltage \( U \) [V] according to Formula (1):

\[
\text{heat - input} \text{ (per layer)} = S = \frac{U \cdot I \cdot 60}{v \cdot 1000} \tag{1}
\]

According to this formula, by using the values \( v \) and \( U \) of the welding procedure specification the heat-input of the single welded layers is determined and for welded joints with more layers according to formula (2) the average heat-input of all layers is calculated. In all cases according to [20] the efficiency of the welding machines is not taken under consideration. Therefore, the calculated values seem high, but as they are just compared with each other, this can be neglected.

\[
\text{heat - input} \text{ (average)} = \frac{\sum_{i=1}^{n} S_i \cdot A_i}{\sum_{i=1}^{n} A_i} = \frac{\sum_{i=1}^{n} U_i \cdot I_i \cdot 60}{\sum_{i=1}^{n} v_i \cdot 1000} \text{[kJ/cm]} \tag{2}
\]

\( i \) ... layer
\( n \) ... amount of layers in a welded joint
\( U \) ... voltage [V]
\( I \) ... amperage [A]
\( v \) ... welding velocity [cm/min]

In the formula (2) the values of the heat-input for every single layer out of formula (1) are averaged over the area of the cross-sections of the weld. The cross-sections of the weld of the single layers are estimated to be the areas of ellipses and determined according to (3), whereas \( a_i \) and \( b_i \) are half of the length of the main axis of the ellipse, see also Figure 7.

\[
A_i = a_i \cdot b_i \cdot \pi \tag{3}
\]
Afterwards the resulting mechanical properties of the welds, such as hardness values and impact energy, are represented as a function of the heat-input values for different welding processes, see figure 8 and 9.

**Fig. 7.** Cross-sections of the weld A_i for the calculation of the heat-input of the entire joint

**Fig. 8.** Comparison of the resulting hardness values over the average heat-input for different duplex-steels and the used welding processes (111 … manual metal arc welding, 141 … tungsten inert gas welding, 135 … gas metal arc welding with active gas and solid wires, 12 … submerged arc welding)
Fig. 9. Comparison of the resulting impact energy values over the average heat-input for different duplex-steels and the used welding processes (111 … manual metal arc welding, 141 … tungsten inert gas welding, 135 … gas metal arc welding with active gas and solid wires, 12 … submerged arc welding)

5. Fracture Mechanical Tests and Material Physical Examinations

CTOD (Crack Tip Opening Displacement) specimens according to BS 7448 [6] have been taken out of the base material, different welds, and their heat affected zone. For further information about the dimensions and the manufacturing of the specimens, and the description of the tests see [3], [21] and [22].

In Figures 10 and 11, photographs of some typical fracture surfaces of the tested specimens are reproduced. The bright zones show the fracture surfaces resulting of the final brittle breaking of the specimens at a temperature of about −196 °C.

Fig. 10. CTOD-values over the temperature for the base material and the weld metal of 1.4462 with corresponding fracture surfaces (r ... rolled) [3]
Fig. 11. CTOD-values over the temperature for different weld metals of 1.4462 with corresponding fracture surfaces (r ... rolled, pl ... plate, p ... pipe) [3]

The CTOD-tests on the rolled base material of the duplex-steel 1.4462, see Figure 10, have been performed in a temperature range of -180 to -20 °C. The resulting CTOD-values are between 0.23 and 0.36 mm. The weld metal tests performed between -100 and -20 °C result into CTOD-values between 0.07 and 0.3 mm [3]. The comparison of the shielded metal arc weld (SMAW, 111, DUPSP2) in Figure 11 to the submerged arc weld (SAW, 12, DUPSP3) give CTOD-values between 0.36 and 0.43 mm for SMAW with basic electrodes and CTOD-values between 0.22 and 0.33 mm for SAW, all at -20 °C. The tests carried out on a cast pipe (DUPSP4) between -80 and -20 °C result into CTOD-values between 0.18 and 0.53 mm.

Figure 12 shows the CTOD-values over the temperature for different weld metals.
Fig. 12. CTOD-values over the temperature for different weld metals on duplex-steels [3], (111 … manual metal arc welding, 141 … tungsten inert gas welding, 131 or 135 … gas metal arc welding with inert or active gas and solid wires, 136 … flux core arc welding, 12 … submerged arc welding, BM … base material, WM … weld metal, HAZ … heat affected zone)

Additionally
- metallographic examinations with the light microscope, micro-hardness tests, quantitative micro-structure analysis, and electron probe microanalysis, and
- fractographic examinations with the scanning electron microscope have been performed with various results as e.g. Figure 3 [23] to [25].

6. Discussion of the Results

A worldwide central collection of welding variables and efficient processing will result in a prediction of mechanical properties and fracture mechanical values out of the data of the preceding joining process and save trial and error procedures and costs.

References

Abstract

The duplex stainless steel family is widely used in many structural applications due to its high mechanical resistance with a yield stress of about two times the austenitic’s and its outstanding corrosion resistance. An example of this is the grade EN 1.4462, with a yield stress value usually higher than 450 N/mm$^2$ and the tensile strength value between 650 and 880 N/mm$^2$. Another important mechanical property is its toughness, which must be higher than 100 J at room temperature and above 40 J at -40 ºC. The mechanical properties are sensitive to the microstructure, especially the toughness. So the annealing treatment, following the hot rolling stage, must be designed to get the right microstructure and the desired mechanical properties. The present paper describes the investigation carried out to evaluate the influence of the annealing conditions on the microstructure and toughness at low temperature of duplex EN-1.4462. Several commercial hot rolled samples of this steel grade have been treated at lab scale. After that, the toughness has been tested at -40 ºC and the microstructure of the treated samples has been analysed by light and field emission gun scanning electron microscopy (FEG-SEM). The main result of the investigation is the influence of the microstructure on the impact test results, not only the phase balance and the presence of intermetallic phases but also the grain size and recrystallization level of the main phases.

Keywords

Duplex, toughness, grain size, recrystallization level, FEG-SEM.

1. Introduction

Duplex stainless steels are a family of grades combining good corrosion resistance and high strength. All the duplex stainless steels have chloride stress corrosion cracking resistance significantly greater than that of the 300-series austenitic stainless steels. They all provide significantly greater strength than the austenitic grades while exhibiting good ductility and toughness. Their room temperature yield strength in the solution-annealed condition is more
than double that of standard austenitic stainless steels not alloyed with nitrogen. This may allow the design engineer to decrease the wall thickness in some applications. Compared with carbon steel or ferritic stainless steels, the ductile-to-brittle transition is more gradual. Duplex stainless steels retain good toughness even to low ambient temperature, for example [1].

The mechanical properties of the stainless steels are quite sensitive to the microstructure, in relation to the recrystallization, the grain size and the presence of intermetallic phases. However, in the case of duplex stainless steels normally these are related with the phase balance and the precipitation of embrittlement phases [2, 3, 4, 5]. This paper wants to show how other metallurgic parameters like grain size and recrystallization level of each phase are very important to get good mechanical properties on duplex stainless steels, especially for the toughness at low temperature.

2. Materials

The study has been carried out on hot rolled 22 mm Ø bars of duplex 1.4462 from two heats, which have been supplied by Roldán. The chemical compositions have been analysed by X-ray fluorescence spectrometry and Leco analyzers and are shown in Table 1.

<table>
<thead>
<tr>
<th>Chemical compositions</th>
<th>Heat A</th>
<th>Heat B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>Mn</td>
<td>1.65</td>
<td>1.85</td>
</tr>
<tr>
<td>Ni</td>
<td>4.73</td>
<td>4.77</td>
</tr>
<tr>
<td>Cu</td>
<td>0.19</td>
<td>0.13</td>
</tr>
<tr>
<td>Cr</td>
<td>22.25</td>
<td>22.32</td>
</tr>
<tr>
<td>Mo</td>
<td>3.14</td>
<td>3.14</td>
</tr>
<tr>
<td>Ti</td>
<td>0.011</td>
<td>0.016</td>
</tr>
<tr>
<td>C</td>
<td>0.019</td>
<td>0.023</td>
</tr>
<tr>
<td>S</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>N</td>
<td>0.162</td>
<td>0.157</td>
</tr>
</tbody>
</table>

3. Experimental

3.1 Annealing treatments

In order to produce different microstructures and get several levels of toughness at low temperature, thermal treatments have been applied on hot rolled 22 mm Ø bar samples in an electric resistance furnace at lab scale in Roldán’s facilities following the next conditions:

Temperature: 1020 and 1070 ºC
Holding time: 15, 45 and 90 minutes

3.2 Characterization of the material under study

The material has been characterized in relation to its microstructure and toughness with and without the annealing treatment.

The microstructural characterization has been carried out by: light microscopy, for the identification of the majority (ferrite and austenite) and brittle phases, with Olympus GX71, and quantification of the phase balance with image analysis software Analysis Inclusion.
Inspector, and through electron microscopy, for the identification and quantification of each main phases, analysis of the recrystallization level of each one of them and grain size of the ferrite and austenite by a field emission gun – scanning electron microscope (FEG-SEM), Zeiss Ultra 55, with EBSD detector [6, 7].

The mechanical behaviour of the hot rolled samples and the lab thermal treated specimens has been analysed through impact test at -40 ºC on a Charpy pendulum, Amsler PSW 750-A.

4. Results

4.1 Thermodynamic calculation

The phase diagrams of the selected chemical compositions and the phase balance at 1020 ºC and 1070 ºC have been analysed by ThermoCalc software (TCW5, database TCFE5). The Table 2 shows the ferrite content at the selected temperatures for both heats.

<table>
<thead>
<tr>
<th>Ferrite content (%)</th>
<th>Heat A</th>
<th>Heat B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020 ºC</td>
<td>46.6</td>
<td>46.7</td>
</tr>
<tr>
<td>1070 ºC</td>
<td>51.8</td>
<td>52.7</td>
</tr>
</tbody>
</table>

Both duplex heats have similar phase diagrams at equilibrium conditions. The Figure 1 shows the phase diagram for the chemical composition of heat A of duplex 1.4462, it is characterized by a dual phase ferrite:austenite structure from 1310 ºC until 920 ºC, temperature at which the precipitation of sigma phase starts. The formation of this embrittlement phase reaches its maximum at 850 ºC and the precipitation of chromium nitride and carbide type M23C6 begins at 950 ºC and 850 ºC respectively.

![ThermoCalc phase diagram of the heat A of duplex 1.4462.](image)

**Fig. 1.** ThermoCalc phase diagram of the heat A of duplex 1.4462.
4.2 Microstructural characterization

4.2.1 Light microscopy

All samples show the typical duplex microstructure formed by ferrite (dark phase) and austenite (light phase) without any presence of intermetallic sigma phase. The interphases ferrite:austenite are more serrated in the commercial samples without annealing treatment than in the thermal treated specimen at lab scale. As example of this, the micrographs of the hot rolled sample and annealed specimen at 1070 °C with a holding time of 90 minutes for the heat A are shown in the Figure 2.

![Fig. 2. LM images of the hot rolled sample (left) and annealed specimen at 1070 °C during 90 minutes (right), both of them from the heat A of duplex 1.4462.](image)

The ferrite content of the several samples has been measured by image analysis, the Table 3 collects these results.

*Table 3. Ferrite content of all samples by image analysis.*

<table>
<thead>
<tr>
<th>Ferrite content (%)</th>
<th>Hot rolled</th>
<th>1020 °C</th>
<th>1070 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15’</td>
<td>45’</td>
</tr>
<tr>
<td>Heat A</td>
<td>64.6</td>
<td>60.1</td>
<td>60.7</td>
</tr>
<tr>
<td>Heat B</td>
<td>60.5</td>
<td>58.9</td>
<td>62.0</td>
</tr>
</tbody>
</table>

The results of the measurement of the ferrite content reveal that the studied microstructures are more ferritic than austenitic (~60:40), the higher annealing temperature the higher ferrite content, mainly for the heat A. In relation to the holding time, except for the heat B at 1020 °C, the phase balance is not affected by this parameter.

4.2.1 Electron microscopy

The electron microscopy study for identification of phases is carried out through the analysis of phases in ¼ of the thickness by EBSD; the BCC structure is marked in red and the
FCC one in blue in the phase maps, an example of this can be observed in the Figure 3. The ferrite content measured by EBSD is collected in the Table 4.

![Phase maps](image)

**Fig. 3.** Phase maps of the hot rolled sample (left) and annealed specimen at 1070 °C during 90 minutes (right), both of them from the heat A of duplex 1.4462.

**Table 4. Ferrite content of all analysed samples by EBSD.**

<table>
<thead>
<tr>
<th>Ferrite content (%)</th>
<th>Hot rolled</th>
<th>1020 °C</th>
<th>1070 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15’</td>
<td>45’</td>
</tr>
<tr>
<td>Heat A</td>
<td>58.8</td>
<td>58.1</td>
<td>57.8</td>
</tr>
<tr>
<td>Heat B</td>
<td>58.3</td>
<td>56.9</td>
<td>58.0</td>
</tr>
</tbody>
</table>

These results confirm the obtained ones from light microscopy in relation to the microstructures are more ferritic than austenitic. Despite of that the variability of the phase balances measured by EBSD is smaller than of the image analysis ones, the same effect of the temperature and holding time is observed.

The analysis of the recrystallization level has been made with EBSD. The recrystallization maps are formed by recrystallized grains marked in blue, partial recrystallization grains in yellow and/or strained grains in red, as the Figure 4 shows. The recrystallization quantity has been measured for each sample, these results are summarized in the Table 5.
**Fig. 4.** Recrystallization maps of the hot rolled sample (left) and annealed specimen at 1070 °C during 90 minutes (right), both of them from the heat A of duplex 1.4462.

<table>
<thead>
<tr>
<th>Table 5. Recrystallization level of all samples by EBSD.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recrystallization (%)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Heat A</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Heat B</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

According to these results, the hot rolled samples for both heats have less recrystallization level than the annealed ones, the higher temperature and holding time the higher recrystallized phase quantity.

The grain size has been measured by EBSD through grain boundary maps where the grain frontier is denoted in black, the twins of the austenite phase are marked in red and the accumulation of boundary subgrain is represented in white, an example of these maps is the Figure 5. The results of grain size of each phase are collected in the Table 6.
Fig. 5. Grain boundary maps of the hot rolled sample (left) and annealed specimen at 1070 °C during 90 minutes (right), both of them from the heat A of duplex 1.4462.

Table 6. Grain size by EBSD.

<table>
<thead>
<tr>
<th>Grain size (μm)</th>
<th>Hot rolled</th>
<th>1020 °C</th>
<th>1070 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15'</td>
<td>45'</td>
</tr>
<tr>
<td>Heat A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCC</td>
<td>7.3</td>
<td>8.5</td>
<td>9.9</td>
</tr>
<tr>
<td>FCC</td>
<td>5.3</td>
<td>6.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Heat B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCC</td>
<td>9.9</td>
<td>9.9</td>
<td>11.1</td>
</tr>
<tr>
<td>FCC</td>
<td>6.6</td>
<td>6.9</td>
<td>7.4</td>
</tr>
</tbody>
</table>

The values of grain size points out that the higher temperature and holding time the higher grain size of each phase.

4.3 Mechanical characterization

The mechanical behaviour of the hot rolled samples and annealed specimens has been checked through impact test at low temperature (-40 °C) with Charpy pendulum, according to the standard UNE-EN ISO 148-1. The toughness results are summarized in the Table 7.

Table 7. Toughness -40 °C results.

<table>
<thead>
<tr>
<th>Toughness -40 °C (J)</th>
<th>Hot rolled</th>
<th>1020 °C</th>
<th>1070 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15'</td>
<td>45'</td>
</tr>
<tr>
<td>Heat A</td>
<td>133</td>
<td>288</td>
<td>203</td>
</tr>
<tr>
<td>Heat B</td>
<td>43</td>
<td>108</td>
<td>96</td>
</tr>
</tbody>
</table>

The results of the impact tests show the influence of the microstructure on the toughness of the material, which is consequence of the chemical composition and process conditions (hot rolling and annealing treatment).
5. Discussion

From the microstructural analysis of the several samples of duplex 1.4462 with and without annealing treatment and its correlation with the impact test results, a clear relationship between the phase balance, recrystallization level and grain size of each phase and the toughness at -40 ºC must be established.

In relation to the phase balance, the values from light and electron microscopy analysis are quite similar. When the annealing temperature increases, the phase balance is more ferritic and the toughness value is reduced, as it is shown in the Figure 6. However, this effect is not so clear with the holding time, in the case of the heat A the phase balance is not modified with the time for a given temperature, however the heat B changes its ferrite content with the holding time, mainly for 1020 ºC, while the toughness varies with the time for both heats. So, the phase fraction ferrite:austenite is not the only parameter that affects on this mechanical property.

In the case of the recrystallization level, this parameter has a very important effect on the toughness results. In all cases, when the sample is thermal treated the recrystallization level of the phases increases with the temperature and holding time, this is observed in the Figure 7 for the case of the ferrite. Although the higher recrystallization level the higher toughness is expected, mechanical behaviour is improved after the treatment at 1020 ºC but it falls at 1070 ºC. Hence, the toughness of the material must be affected by another microstructural parameter.
Concerning to the grain size, this variable also has an important role on the mechanical response of the material. In all samples, after the annealing treatment the grain size of the ferrite and austenite grows up, as it can be checked in the Figure 8 for the case of the ferrite.

As it is well known, the coarsening grain reduces the mechanical properties, so that is the reason why the toughness drops when the temperature and holding time increase. According to the results of this study for this duplex 1.4462, approximately from the 97% of recrystallization of the phases the coarsening grain could happen reducing the mechanical behaviour of the material. A grain size bigger than 10.0 μm for the BCC phase and 7.0 μm for the FCC phase reduces considerably the toughness at low temperature of the material.

All results of the microstructure and mechanical characterization of the analysed samples have been mathematically treated to know the weight of each microstructural variable on the toughness value. The following $IT_{-40 \degree C}$ factor, defined by the equation 1, has deduced from this work.

$$IT_{-40 \degree C} = \frac{[Recr_\alpha + Recr_\gamma]^3 \cdot X_\gamma \cdot \left[\frac{GS_\gamma}{GS_\alpha}\right]^4}{\left[GS_\alpha + GS_\gamma\right]^4 \cdot X_\alpha}$$  (1)
Where:

\[ \text{Recr}_\alpha = \text{recrystallization level of the ferrite phase} \]
\[ \text{Recr}_\gamma = \text{recrystallization level of the austenite phase} \]
\[ X_\alpha = \text{ferrite mass fraction} \]
\[ X_\gamma = \text{austenite mass fraction} \]
\[ \text{GS}_\alpha = \text{grain size of the ferrite phase} \]
\[ \text{GS}_\gamma = \text{grain size of the austenite phase} \]

The calculated \( IT_{-40} \) factor, from the microstructural characterization, and the toughness of each tested sample have been plotted in the Figure 9 showing a lineal adjustment with a correlation coefficient \( R^2 \) of 0.809. So, it is expected that the higher \( IT_{-40} \) factor the higher toughness.

![Figure 9](image-url)

**Fig. 9.** Graphic representation of the toughness and \( IT_{-40} \) factor for all samples

### 6. Conclusions

In duplex stainless steel family, the thermal input applied during an annealing treatment is used to reach the phase balance of equilibrium conditions for a given temperature, at the same time the recrystallization of each phase happens and also the grain of each phase grows up. When the phase balance reaches its equilibrium and the recrystallization is almost completed, the remaining thermal input is used to continue the growing grain until produce the phenomenon of embrittlement by coarsening grain, reducing the mechanical properties of the material.

So, the annealing treatment after the hot rolling step for duplex 1.4462 is quite important to get the desirable mechanical properties. The conditions of temperature and time of the thermal cycle must be designed to get the proper microstructure; good phase balance, absence of intermetallic phases, correct recrystallization level and fine grain size.
Finally, not only the microstructure influences on the toughness of the material, as it is shown by the correlation coefficient of the IT\textsubscript{40 °C} factor with a value of 0.809, the chemical composition is another variable that affects the mechanical behaviour [8, 9]. However, this parameter has not been taken into account because the selected heats are quite similar in relation to the chemical composition, so there is not enough variability of the allowing elements to be considered in the IT\textsubscript{40 °C} factor.

7. References

DESIGN AGAINST BRITTLE FRACTURE IN DUPLEX STAINLESS STEEL CONSTRUCTIONS BY USING THE EN 1993-1-10 MODEL AND THE INFLUENCE OF PLATE THICKNESS ON THE IMPACT TOUGHNESS

Abstract

In the design of steel structure, the avoidance of brittle fracture is of great importance as e.g. steel bridges are fatigue loaded and can be exposed to low temperatures. In the supplementary rules for the design of stainless steel structures in the European standard EN 1993-1-4 as part of the Eurocode 3 family, toughness requirements for stainless steels are given. However, the toughness requirements for duplex stainless steels are insufficient for practical use. Due to this fact, investigations have been carried out on various duplex stainless steel base materials and welded specimens based on the fracture mechanic-based concept of EN 1993-1-10. The results show that the investigated duplex stainless steels show a very good toughness behaviour and that the EN 1993-1-10 model can be transformed for application of duplex stainless steels. Discussion was also made on the correlation between the austenite spacing and the impact toughness in the ductile-to-brittle transition temperature region. Observation indicates that the austenite spacing is strongly influenced by the degree of reduction from the hot-rolling which may set constraint on the full utilization of the derived maximum permissible values of structural element thickness according to EN 1993-1-10.

Keywords

Duplex stainless steel, steel construction, fracture toughness, impact toughness, choice of steel material, Eurocode 3

1. Introduction

Duplex stainless steel has an austenitic-ferritic microstructure with a phase balance of approximately 50% austenite and 50% ferrite. The structural use of duplex stainless steels in steel construction has increased significantly in the last twenty years thanks to their high mechanical properties and good corrosion resistance. Duplex stainless steel in steel constructions has often been specified primarily based on a combination of highly aesthetic considerations and a need for long life of appearance. However, in the last few years, several projects have also been completed using duplex stainless steel as the main structural material where aesthetics were less important, but long life, low maintenance and low life cycle costs as well as low environmental impact were the main drivers, e.g. floodgates, road and railways bridges [1]. Road and railway bridges can be exposed to low temperatures in combination with fatigue loads due to traffic. Herewith, the question arises whether duplex stainless steels show sufficient toughness to avoid brittle fracture, especially when they are welded.
The choice of stainless steel material to avoid brittle fracture is covered in EN 1993-1-4 [2] as EN 1993-1-10 [3] is strictly restricted to ferritic carbon structural steel material S235 to S690. The toughness requirements for duplex stainless steels specified in EN 1993-1-4 for EN 1.4062, EN 1.4162, EN 1.4362, EN 1.4462, EN 1.4482 and EN 1.4662 are expressed rather simple: they can be used down to -40 °C service temperature. But: as duplex stainless steels exhibit a temperature transition behaviour comparable to ferritic structural steels with a rather high toughness at ambient temperatures, low toughness at very low temperatures and a temperature transition range in between, such a simplified regulation is insufficient.

EN 1993-1-4 refers to the product standards for stainless steels which are EN 10088-4 [4] and EN 10088-5 [5]. Besides others, they specify the required minimum ISO V Charpy toughness. Exemplary, for EN 1.4362 and EN 1.4462 plate and strip material, the minimum Charpy toughness are 100 J in longitudinal and 60 J in transverse direction, both at room temperature. The objective of the presented investigations was to check whether the fracture mechanics calculation model including the Wallin Master Curve concept originally developed and approved for ferritic structural steel behind EN 1993-1-10 [6],[7] can as well be applied for duplex stainless steel at low service temperatures not only for base material, but also for welded material. Charpy and fracture mechanics tests have been evaluated for EN 1.4462, EN 1.4362 and EN 1.4162 duplex stainless steels of 30 mm and 50 mm thick base materials and weldments [8] to verify the Master Curve concept. The results have been used to apply the basic approach of EN 1993-1-10 considering the structural detail of a welded bridge girder with transverse stiffener and welded longitudinal attachment with a semi elliptical surface crack at the weld toe [6],[7],[8] for the calculation of maximum allowable thicknesses, see Fig. 1.

Fig. 1 Basic structural detail of EN 1993-1-10: welded bridge girder with transverse stiffener and welded longitudinal attachment with a semi elliptical surface crack at the weld toe [6],[7].

2. The evaluated Charpy V and fracture mechanics tests

In principle, the fracture mechanics concept of EN 1993-1-10 relies on a transition temperature correlation combined with a Master Curve approach for temperature dependent
fracture toughness [6],[7]. The applicability of the concept to duplex stainless steels has been checked using existing results of Charpy and fracture mechanics tests for selected duplex stainless steels [9],[10]. As for this kind of analysis both Charpy toughness and fracture mechanics toughness must be obtained for the same material batch (chemical composition, heat treatment etc.), only a limited number of evaluable tests were available. The investigations have been carried out for 30 mm and 50 mm thick base material (BM) and weldments (WM) of duplex stainless steels EN 1.4462 (Forta DX 2205), EN 1.4362 (Forta DX 2304) and EN 1.4162 (Forta LDX 2101). For EN 1.4462, submerged arc welding (SAW) was used on K-prepared joints [9]. For EN 1.4162 and EN 1.4362, the weldments were produced in double-V joints by using shielded metal arc welding (SMAW) for the root bead and flux core arc welding (FCAW) for subsequent passes [10]. The chemical composition can be found in Table 1. The filler metals have higher nickel contents for improved austenite formation and to increase the toughness [10].

Table 1 The chemical composition for the investigated duplex stainless steels in wt.%

<table>
<thead>
<tr>
<th>Grade/filler metal</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Cu</th>
<th>N</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN 1.4162, 30 mm</td>
<td>21.5</td>
<td>1.60</td>
<td>0.29</td>
<td>4.92</td>
<td>0.28</td>
<td>0.23</td>
<td>0.032</td>
</tr>
<tr>
<td>EN 1.4362, 30 mm</td>
<td>22.7</td>
<td>4.69</td>
<td>0.31</td>
<td>1.44</td>
<td>0.25</td>
<td>0.10</td>
<td>0.020</td>
</tr>
<tr>
<td>EN 1.4462, 30 mm</td>
<td>21.5</td>
<td>5.50</td>
<td>2.98</td>
<td>1.46</td>
<td>0.17</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>EN 1.4462, 50 mm</td>
<td>21.7</td>
<td>5.58</td>
<td>3.01</td>
<td>1.49</td>
<td>0.16</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>LDX 2101, SMAW</td>
<td>24.9</td>
<td>8.97</td>
<td>0.13</td>
<td>0.83</td>
<td>0.08</td>
<td>0.13</td>
<td>0.020</td>
</tr>
<tr>
<td>LDX 2101, FCAW</td>
<td>24.1</td>
<td>7.35</td>
<td>0.21</td>
<td>0.69</td>
<td>0.22</td>
<td>0.13</td>
<td>0.045</td>
</tr>
<tr>
<td>2304, SMAW</td>
<td>24.6</td>
<td>9.13</td>
<td>0.13</td>
<td>0.78</td>
<td>0.10</td>
<td>0.14</td>
<td>0.025</td>
</tr>
<tr>
<td>2304, FCAW</td>
<td>24.8</td>
<td>8.95</td>
<td>0.12</td>
<td>0.80</td>
<td>0.07</td>
<td>0.12</td>
<td>0.021</td>
</tr>
<tr>
<td>2205, SAW</td>
<td>22.5</td>
<td>7.31</td>
<td>3.08</td>
<td>1.36</td>
<td>0.16</td>
<td>0.15</td>
<td>0.014</td>
</tr>
</tbody>
</table>

The Charpy tests have been evaluated using a hyperbolic tangent function proposed by Wallin [11]. Exemplary, the results for the 50 mm EN 1.4462 base material and weldment are shown in Fig. 2.

Fig. 2 Impact energy-temperature diagrams for 50 mm thick EN 1.4462 [8].
3. Transition temperature correlation between impact toughness and Master Curve

The Master Curve derivation was originally developed for ferritic steels, see e.g. [11]. Starting with the ECOPRESS project [9], Outokumpu continued further investigations into different grades and weldments to validate the applicability of the Master Curve concept to duplex stainless steels. Within the presented investigations, these results [9],[10] have been re-evaluated according to ASTM E 1921 [12] and thereby verified with respect to the Master Curve concept. The aim of this analysis was to show the scatter of the individual $K_{Jc}$-values and to verify whether all results can be described by the Master Curve. Fig. 3a shows the individual $K_{Jc,i}$ values plotted against the temperature difference $T_i - T_{100,i=1}^{exp}$ (with $n$ is the number of tests per set), where $T_i$ is the individual test temperature. $T_{100}$ is the temperature where the median fracture toughness is 100 MPa$\sqrt{m}$. For each data set, the test temperature of any test point was unified with the $T_{100,i=1}^{exp}$-temperature. Additionally, the Master Curves for 5%, 50% and 95% failure probability are presented. In total, 59 tests have been evaluated. It can be seen that all fracture mechanics results fall between the upper and lower bound and can be described by the Master Curve.

The temperature correlation of the so-called modified Sanz-Correlation [6],[13],[14], $T_{100} = T_{27J} - 18^\circ C \pm 2\sigma$, has been used to calculate $T_{100}$ based on the Charpy transition temperature $T_{27J}$ and a standard deviation of $\sigma = 0^\circ C$ to achieve mean values. Fig. 3b shows the relationship between both transition temperatures $T_{27J,exp}$ and $T_{100,exp}$ for all evaluated test series in comparison with the calculated $T_{100}$. It becomes obvious that the experimental results vary in the range limited by the lower and upper bounds considering a two-fold standard deviation ($\sigma$). Generally, the results obtained for the welded materials fit well with the mean curve, whereas those obtained for the base material are close to the lower bound, which gives some additional safety. For the one pink point located on the upper bound (2304, BM, t = 30 mm), $T_{27J,exp}$ is statistically uncertain as only a small number of test results were available for the evaluation of the Charpy energy-temperature curve. Herewith, this result can only be taken informative. Nevertheless, based on the given results, it can be concluded that the transition temperature correlation according to the modified Sanz-Correlation is applicable to the investigated duplex stainless steels.

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**Fig. 3** a) Verification of fracture mechanics results with respect to the Master Curve concept, b) transition temperature correlation for duplex stainless steels. Grades EN 1.4462 (Forta DX 2205), EN 1.4362 (Forta DX 2304) and EN 1.4162 (Forta LDX 2101) [8].
3. Application of the fracture mechanics approach of EN 1993-1-10 to duplex stainless steels

The approach of EN 1993-1-10 provides a simplified selection of carbon structural steel material by tabulated maximum allowable plate thicknesses dependent on three stress levels \((0.75 f_y, 0.5 f_y \text{ and } 0.25 f_y \text{ with } f_y: \text{nominal yield strength})\) based on the reference temperature \(T_{Ed}\) at the potential fracture location given by equation 1:

\[
T_{Ed} = T_{md} + \Delta T_e + \Delta T_{\sigma} + \Delta T_{R} + \Delta T_{\varepsilon} + \Delta T_{\varepsilon_{cr}} \geq T_{Rd} = T_{0.06} + \Delta T_{27J}
\]  

\((1)\)

\(T_{md}\) is the lowest air temperature with a specified return period, \(\Delta T_e\) is an adjustment for radiation loss, \(\Delta T_R\) is a safety allowance reflecting different reliability levels for different applications, \(\Delta T_{\varepsilon}\) is the adjustment for a strain rate other than the reference strain rate \(\dot{\varepsilon}_0\), \(\Delta T_{\varepsilon_{cr}}\) is the adjustment for the degree of cold forming \(\varepsilon_{cf}\) and \(\Delta T_{27J}\) is an adjustment for a possible inhomogeneity of the toughness over the thickness [6],[7]. \(\Delta T_{\sigma}\) is the adjustment for stress and yield strength of material, crack imperfection and member shape and dimensions considering the Master Curve approach, see equation 2:

\[
\Delta T_{\sigma} = -52 \cdot n \left\{ \frac{(K_{\text{mat}} - 20) \left( \frac{b_{\text{eff}}}{25} \right)^{0.25}}{70} - 10 \right\}
\]  

\((2)\)

with the effective thickness \(b_{\text{eff}} = 5 \, a_d\), where \(a_d\) describes the design crack depth at which brittle fracture occurs. \(K_{\text{mat}}\) is the stress intensity factor for the structural detail considering effects due to secondary stresses, local plasticity and residual stresses using the Failure Assessment Diagram (FAD), and the CEGB-R6 procedure [6],[7],[8].

As stainless steel exhibits material nonlinearity already below the 0.2 % proof strength and does not show a pronounced yield strength as most carbon structural steels, in a first step, the effect of the continuous yield strength on the allowable plate thickness has been investigated [8]. The calculation was performed for a nominal yield strength and 0.2 % proof strength of 460 MPa (pronounced and continuous), a \(T_{27J}\)-temperature of -50 °C (approximately \(T_{40J}\) at -40 °C) and a modulus of elasticity of 200.000 MPa for duplex stainless steel according to EN 1993-1-4. The obtained results were compared with those of EN 1993-1-10 for carbon structural steel S460ML/NL, see Table 2. It could be shown that for the material with the pronounced yield strength, a good agreement between the calculated values and those existing in EN 1993-1-10 can be found. The analysis performed for the material with a continuous yield strength showed about 10 % lower allowable plate thicknesses at the highest stress level of 0.75 \(f_y\). The decrease is very small at the level of 0.5 \(f_y\) and not existent for the lowest stress level of 0.25 \(f_y\). The decrease for the highest stress level can be explained by the different limit curves in the FAD for steels with pronounced and continuous yield strength [8]. The limit curve for continuous yielding drops down faster as the one for a pronounced yield strength above the level of \(L_r = 0.5\). A lower \(K_{\varepsilon}\)-value results for a smaller allowable thickness [8]. It should also be pointed out that a design stress of 0.75 \(f_y\) will probably not be used for most constructions, meaning in
practice a very small difference in allowed element thickness between duplex and the carbon structural steel S460ML/NL.

These values still have to be verified with large scale experimental tests in order to check whether the implicitly considered safety element of +7 K is valid for duplex stainless steel as it was originally derived for carbon steel by large scale tests [6],[7]. Furthermore, the maximum permissible plate thicknesses have to be extended to higher proof strengths (for e.g. EN 1.4410 and EN 1.4477) and it has to be checked whether a distinction has to be made for the various kinds of duplex stainless steel. To answer these and other questions, a German research project has just been started in 2019.

Table 2 Possible maximum permissible values of element thickness $t$ in mm for duplex stainless steel, max. $R_{p0.2}$ = 460 MPa in comparison to S460ML/NL acc. to EN 1993-1-10.

<table>
<thead>
<tr>
<th>Charpy Energy</th>
<th>Reference Temperature $T_{ld}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>at $T$ [°C]</td>
<td>CVN [J]</td>
</tr>
<tr>
<td>-40</td>
<td>10 0 -10 -20 -30 -40 -50</td>
</tr>
</tbody>
</table>

$1) f_y(t) = R_{p0.2,nom}$ (or $f_y,nom$ for S460ML/NL) – 0.25 ($t/l_0$) with $l_0 = 1$ mm. $^2)$ restricted to 200 mm.

4. Discussion about the relation between austenite spacing and expected toughness of thick plates

The ductile-to-brittle transition temperature region for the duplex stainless steels (e.g. in Fig. 2) is due to the ferrite becomes susceptible to cleavage fracture. Because of the duplex microstructure the fracture process becomes complex in the ductile-to-brittle transition temperature region as the austenite normally fractures in a ductile manner whereas the ferrite can either have a ductile fracture process or a brittle fracture process. For final fracture to occur, the cleavage cracks of the ferrite must be linked up by widening and final shearing and necking down of the austenite bridges between the ferrite cracks, a fracture process that increases the toughness of the material [15]. In Charpy V impact toughness testing and fracture mechanical testing, extensive secondary fracture (known as splits or delaminations) is usually observed for the duplex base materials in the ductile-to-brittle transition temperature region [16]. This further complicates the fracture process.

As for steel in general, the impact toughness is significantly influenced by some parameter describing the size of the microstructure (e.g. the grain size). For duplex stainless steel it is the austenite spacing (i.e. the width of the ferrite lamellas) that has been found to give good correlation with the toughness in the ductile-to-brittle transition temperature region. An example of the correlation between the austenite spacing and the impact toughness is given in Fig. 4. In this case, it was slabs of EN 1.4162 that had been hot-rolled to different plate thicknesses. The austenite spacing was measured perpendicular to the rolling direction according to DNV RP-F112 [17].
In the following section, the discussion will be about the influence of the solution annealing and hot-rolling on the austenite spacing, regarding the plate thickness and its ability to pass the requirement of 40 J Charpy V impact toughness at -40 °C (recall Table 2).

The solution annealing of duplex stainless steels is carried out between 950 °C to 1120 °C (depending on the duplex grade) \([4,5]\). In this temperature range the thermodynamic equilibrium phases are austenite and ferrite. With time the microstructure will coarsen which result in larger austenite spacing. An example of this is given in Fig. 5 for a 214 mm diameter bar of EN 1.4410 which was solution annealed for different times and temperatures within this temperature range. Thus, excessive solution annealing may decrease the sub-zero temperature impact toughness of the duplex stainless steels due to increased austenite spacing (i.e. coarsening of the microstructure).

For the duplex grades susceptible to intermetallic precipitation when exposed to the 700 °C to 1000 °C temperature range (e.g. EN 1.4410) the situation becomes more complex as solution annealing is also needed to dissolve possible intermetallic content. Thus, from an Charpy V impact toughness point of view there exists a balance between decreasing the intermetallic content and avoiding excessive coarsening of the microstructure for these duplex grades. Another aspect is also the cooling from solution annealing temperature which for high alloyed duplex has to be fast enough to avoid precipitation of detrimental amounts of intermetallic phases and generally for all duplex stainless has to be slow enough for avoiding detrimental amounts of nitride precipitation. It is important to realize though that the sensitivity for intermetallic content decreases with a decrease of the alloying content, meaning that e.g. EN 1.4162 is less sensitive than EN 1.4410.
To examine how the austenite spacing differs between different plate thicknesses, 200 mm thick continuously cast slabs of EN 1.4162 was hot-rolled to plates with different thicknesses (12, 30, 50 and 70 mm). The result indicates that the austenite spacing is directly related to the degree of reduction from the hot-rolling, see Fig. 6a. The relation between the austenite spacing and the degree of reduction could be fitted with a linear equation. By using this equation, the austenite spacing as function of the plate thickness from different slab thicknesses were estimated (in this discussion we assume that the cast structure is similar between different slab thickness and that the previously discussed solution annealing is similar). As seen in Fig. 6b, thicker slabs result in smaller austenite spacing (i.e. finer microstructure) and thus one can expect higher impact toughness at sub-zero temperatures when using thicker slabs compared to thinner.

![Graph a)

Fig. 6  a) the austenite spacing as function of the degree of reduction of a 200 mm slab, b) estimated austenite spacing as function of plate thickness for different slab thicknesses.

With the previous discussion in mind, the maximum plate thickness in the European material standard for steel constructions, EN 10088-4:2009 [4], is 75 mm for the duplex stainless steels. When compared to the results in Table 2 it is evident that the fracture mechanical model allows for far greater element thickness than the material standards allows for plate thickness for most combinations of the reference temperature and the design stress. The EN 10088-4 allows for thicker plates when the mechanical properties may be agreed between the customer and the producer. A comparison on the publicly offered plate dimensions of some major duplex steel producers indicates a maximum thickness between 80 to 120 mm. One can therefore expect that delivering plates for the full utilization of Table 2 can be challenging due to the limited degree of reduction for very thick plates (which are constrained by the available slab thickness and available force during hot-rolling). This is likely more of an issue for the lean duplex grades where high sub-zero temperature impact toughness is more dependent on having fine microstructure due to the lower nickel content compared to the standard grades [15],[18].

6. Summary

An evaluation of fracture mechanics data has been performed for duplex stainless steels EN 1.4462, EN 1.4362 and EN 1.4162 and their welded joints to examine the applicability of the transition temperature correlation and the Master Curve approach of EN 1993-1-10. It could be shown that the Master Curve approach and the transition temperature correlation are applicable for the analysed duplex stainless steels base material and weldments. Furthermore, possible maximum allowable plate thicknesses have been determined for duplex stainless steels with an 0.2 % proof strength of 460 MPa which are comparable to those of carbon structural steel except for the highest stress level of 0.75 f_y(t) at which about 10 % smaller values are achieved due to the continuous proof strength.
Discussion was also made on the correlation between the austenite spacing and the impact toughness in the ductile-to-brittle transition temperature region. Observations indicate that the austenite spacing is strongly influenced by the degree of reduction from the hot-rolling which may set constraint on the full utilization of the derived maximum permissible values of structural element thickness according to EN 1993-1-10.

7. References


Electrically enhanced plastic deformation of duplex stainless steel
UNS S32750

Abstract

It is well known that increasing the temperature softens the materials and increases formability. This could be done in many ways, one of which is by joule heating. In the late fifties it has been observed an enhancement of formability for certain alloys when heated by electrical current, compared to traditional heating method. This led the researcher to investigate the effect of electrical current on the plastic flow of metallic materials discovering a new effect called Electroplastic Effect (EPE). EPE is used in the so called Electrically Assisted Manufacturing processes (EAM). The stacking fault energy (SFE) describes the dislocation dynamics of metallic materials and it has been hypothesized an a-thermal effect which is caused by direct interaction between dislocations and electrical current. High SFE materials show an increase of formability while low SFE materials reach the fracture prematurely. In this work, duplex stainless steel (DSS) UNS S32750 has undergone uniaxially tested with the aid of continuous and pulsed electrical current in order to study the EPE of a metallic material that presents two different phases, high SFE (ferrite) and low SFE (austenite). Different current densities (continuous and pulsed) were tested while to separate the EPE from the effect of temperature some thermal tensile counterpart tests has been conducted. The DSS was then characterized through optical microscopy, scanning electron microscopy and x-ray diffraction. The DSS tested shows an increase in the elongation at rupture, either for the continuous current set-up and much more evident in the case of the pulsed current compared to the thermal tests, while the ultimate tensile strength and the yield strength were barely affected.

Keywords

Electroplasticity, Pulsed current, Tensile test, SFE, Duplex, Stagnation theory

1. Introduction

An increase in elongation at rupture and a decrease of the UTS when deformed under an applied voltage were observed for the first time by Machlin in 1959 on a sodium chloride crystal [1]. Troitski and his research group [2–5] were one of the first to study this phenomenon on metallic materials such as zinc, tin, lead, indium together with an American research group headed by Conrad [6–8]. They concluded that the increase in formability and the decrease of the stress wasn’t just due to the joule heating effect but because of a new phenomenon which they have called Electroplastic Effect (EPE). Electrically Assisted Manufacturing (EAM) are all the processes that exploit the EPE in order to enhance the
formability of the materials such as rolling [9–11], extrusion [12,13], cutting [14,15], forging [16,17], sintering [18–20], bending [21,22] and in some peculiar heat treatment [23–25].

A lot of theories have been formulated in order to explain the EPE: Kravchenko [26] believes that the increase in formability is due to the force the electrons exert on the moving dislocation (Electron Wind Force) thanks to the transfer of momentum from the high energy electrons of the electrical current. Other researchers say the effect observed are because of the increased rate of depinning of dislocation from weak obstacles due to the induced magnetic field [27,28].

Magargee observed a peculiar material sensitivity to the EPE related to a current density threshold material-dependent [29] while other researchers proposed a more simple localized microscopic joule heating effect as the explanation for the EPE [30].

A recent work done by this research group [31] proposed a correlation between the Stacking Fault Energy (SFE) of the material and the EPE. It has been observed that higher SFE materials [32] show an increase in uniform elongation during tensile test under continuous electrical current, while in low SFE materials [33] the uniform elongation decreased.

In this frame of reference, it has been decided to investigate the effect of continuous and pulsed electrical current on Duplex Stainless Steel (DSS) UNS S32750 which have a biphasic microstructure consisting of a high SFE phase (δ-ferrite) and a low SFE phase (γ-austenite).

Thanks to its biphasic microstructure DSSs have high mechanical properties (double in comparison with the austenitic stainless steels) and very good corrosion resistance (high Pitting Equivalent Resistance Number PREn). To obtain the best mechanical and corrosion properties a very well balanced microstructure (50/50 austenite and ferrite) is mandatory. It requires a proper solubilizing heat treatment depending on the DSS grade [34,35]. DSSs cannot work for more than few minutes in the temperature range between 600 °C and 1000 °C because they suffer from secondary phase precipitation that are deleterious for the mechanical and corrosion properties [36–38].

In this work superduplex stainless steel UNS S32750 has been investigated under continuous and pulsed current during tensile test to study the EPE on material with two very different SFE phase.

2. Materials and Methods

The material was kindly supplied by the Italian division of Outokumpu S.p.A. in form of 2 mm thick warm rolled sheet. The composition of the investigated steel is reported in **Tab. 1**

<table>
<thead>
<tr>
<th>UNS S32750</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>W</th>
<th>P</th>
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<th>N</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.018</td>
<td>0.26</td>
<td>0.84</td>
<td>25.08</td>
<td>6.88</td>
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<td>0.17</td>
<td>-</td>
<td>0.019</td>
<td>0.0010</td>
<td>0.294</td>
</tr>
</tbody>
</table>

Specimens for the tensile tests were obtained along the rolling direction according to the ASTM E8 standard with length gage reduced to 45 mm due to the small dimension of the sheet provided. Secondary phases and phase balance were conducted through X-ray diffraction with a Siemens D500 X-ray diffractometer equipped with copper X-ray tube and monochromator in front of the detector.
Tensile tests were conducted on an MTS 322 capable of 50 kN of force modified to conduct electroplasticity tests. To isolate the machine from the current flow, special self-made isolated copper jaws were used.

The gage length of the specimen was painted with opaque heat resistive lack to get a uniform emissivity of 0.8 for the temperature reading through a FLIR A40 thermocamera.

Tensile tests under continuous current were conducted at 5 A/mm², 10 A/mm² and 15 A/mm² to limit the maximum temperature reached due to joule heating under 450 °C with the aid of a cooling device with air at a pressure of 8 bar. Direct and pulsed continuous electrical currents were provided by a Powerel generator capable of delivering 6000 A at 10 V. Temperature was recorded to perform the thermal test at the same temperature reached by the electrical current tests, to separate the contribution of joule heating from the current ones. Pulsed tensile tests were conducted with a pulse duration of 2 ms and a frequency of 2 Hz at 50 A/mm², 100 A/mm², 150 A/mm², 200 A/mm² and 250 A/mm². For each condition three test have been done to verify the repeatability. The deformation rate was 10⁻¹ s⁻¹ for the test conducted in continuous current and the thermal counterpart and 10⁻² s⁻¹ for the pulsed current.

Standard polishing procedure has been conducted with decreasing grit sandpaper from 500 to 1200 and final polish on rotating clothes with polycrystalline diamond suspension of 6 µm, 1 µm and finally with silica colloidal suspension of 200 nm.

Microstructure observation has been conducted on a LEICA DMRE optical microscope and a Leica Cambridge Stereoscan 440 scanning electron microscope operating at 29 kV in backscattered electron mode and at 15 kV in secondary electron mode.

3. Results

The as received material shows a very well-balanced microstructure secondary phase free according to x-ray diffraction pattern with just the peaks of δ-ferrite and γ-austenite and to SEM-BSE micrographs.

Phase balance was evaluated through Rietvield analysis on the x-ray diffraction pattern which resulted in almost equal volume fraction of austenite and ferrite (0.48±0.04 and 0.52±0.05 respectively).

The as received material shows a microstructure consisting of fragmented austenite islands (bright region) dispersed in a ferritic matrix (dark regions) as can be seen in Fig. 1. Rolling direction is highlighted by the black arrow. Austenite morphology is quite fragmented due to the warm rolling process the material was subjected.
Fig. 1 Microstructure of as received UNS S32750: light phase austenite, dark phase ferrite, black arrow is rolling direction, etching solution modified Beraha

Fig. 2 shows the flow stress curves under electrical flow and the corresponding thermal counterpart for the UNS S32750. It can be seen a constant decrease in elongation at rupture as the temperature and the current density increases. The baseline refers to the test conducted at room temperature. Serration on the flow stress curves at higher temperature and higher current density can be referred to a phenomenon known as Dynamic Strain Aging (DSA).

Fig. 2 Electrical flow stress curves on the right and thermal counterpart on the left for the UNS S32750

To study the influence of electrical current on the tensile test it must be considered the decrease in cross section with increase in strain. The electrical generator delivers a constant electrical current, so as the cross section decreases because of plastic deformation, the nominal current density gradually increases. When the material reaches plastic instability, the decrease in cross section is localized in a very narrow area, hence, as the electrical current is constant the nominal current density increases abruptly along with joule heating effect in that specific region. Therefore, elongation at rupture cannot be compared between the two sets of tests, a
better parameter to consider is the elongation in correspondence of ultimate tensile stress (i.e. uniform elongation).

![Graph showing relative uniform elongation]

**Fig. 3** Relative uniform elongation. Red circle refers to the thermal test while blue square to the electrical tensile test.

Relative uniform elongation was normalized with respect to the uniform elongation of the baseline.

As can be seen in Fig. 3, all the tests conducted with the electrical current show an increase in the relative uniform elongation up to approximately 17.5% for the current density of 10 A/mm² in comparison with the relative thermal counterpart, denoting a positive influence of the electrical current on the behaviour of the material. The relative uniform elongation at the highest current density and its related thermal test are much close together compared to the other test, because of the difficulty in extrapolating the data due to the onset of DSA, as can be seen by the error bars. Overall, electrical current tests show an increase in uniform elongation compared to the thermal tests. On the other hand, yield stress and ultimate tensile stress were not affected by the electrical current.

![Graph showing flow stress curves and temperature]

**Fig. 4** Flow stress curves of UNS S37250 under different pulsed current densities on the left, temperature reached by the steel subjected to different pulsed current densities on the right.
On the right side of Fig. 4 the temperature reached by the steel subjected to different pulsed current densities of duration of 2 ms and frequency of 2 Hz are shown. It can be seen an approximately linear increase in the global temperature of the material reaching a maximum of 370 °C for the highest current density. The pulse duration and the frequency were chosen to get the maximum possible current density the generator could deliver, limiting the highest temperature up to 450 °C. On the left side of Fig. 4 the flow stress curves of the steel subjected to the current densities previously mentioned are reported. The first difference compared to the continuous current is the small segmentation of the flow stress curves due to the different nature of the electrical current compared to that of Fig. 2. Another difference between the continuous current tests and the pulsed ones is that there is no clear trend between elongation at rupture and current density, moreover it is not observed the decrease in elongation at rupture with the increase in the thermal regime compared to the continuous current case. The test performed at 200 A/mm² shows the onset of DSA as in the continuous current case. Even though it seems that there could be an influence on the elastic behaviour of the material between the baseline and the pulsed tests, no extensometer has, so no consideration can be done on the elastic modulus of the material. All the tests show an elongation at rupture comparable, with no trend with respect to the current density.

**Fig. 5** Relative uniform elongation. Red circle refers to the thermal tests while blue square to the pulsed current tests.

Pulsed electrical tensile tests (Fig. 5) compared to the thermal ones show an increase in uniform elongation much more evident compared to the continuous current case. All relative elongations are comparable except for the test conducted at higher current density because of the higher temperature. The increase in uniform elongation with respect to the baseline is more than 30%, moreover it remains constant for all the current densities. It seems like the increase in current density compensates for the decrease in uniform elongation due to the joule heating, as can be seen for the thermal test. In this case, some considerations can be done on the elongation at rupture since localize plastic instability accounts for a very small duration of the test, and joule heating due to pulsed current is lower than that due to continuous current. Therefore, elongation at rupture is constant and comparable with that of the baseline, despite the increase in the test temperature, as opposed to the continuous current tests.
Overall, the effect of pulsed current is much more evident in comparison to the continuous current even though the electrical energy is much lower in the first case.

4. Discussion

The peculiarity of this material is the copresence of two phases with very different SFE: ferrite with high SFE and austenite with low SFE. In previous work it has been found that electroplasticity seems to be SFE-dependant [31], more precisely low SFE materials show a reduction in elongation at rupture when deformed under applied continuous current, conversely high SFE material such as ferritic stainless steels or aluminium show an increase in elongation at rupture.

Duplex stainless steels start to solidify from a fully ferritic microstructure from which, as the temperature decreases, austenite starts to precipitate. This means that the ferrite phase acting as the matrix is percolating throughout the entire microstructure while isolated islands of austenite are dispersed in it.

The two phases have a different composition and because of the different SFE they work harden in a very different way, which leads to different resistivity of each phase. It has been hypothesized that the electrical current does not flow uniformly throughout each phase, but it follows preferential paths, probably inside the ferritic matrix, that is why an overall positive effect of the current can be observed. Moreover, very extensive phase boundary due to the fragmented austenite because of cold rolling is present and acts as an additional barrier for the flow of electrons to overcome to transit into the austenite. Other researchers [39] tried to explain the electroplastic effect through heterogeneous joule heating and they developed a theory called Electron Stagnation Theory. They suppose that in correspondence of inclusions, defects, dislocation bundles, precipitates etc, there could be a stagnation of electrons that can change the electron to atom ratio leading to a weakening of the bonding energy of the atoms therefore, easing dislocations motion. This could be happening in this case in proximity of phase boundary and at ferrite/ferrite grain boundaries much more compared to austenite/austenite grain boundary causing an increase in temperature easing dislocation motion and facilitating annihilation of dislocations as well.

5. Conclusions

In this work the influence of different continuous and pulsed current densities during uniaxial tensile test on UNS S32750 has been studied. Thermal tests have been done to compare the electrically assisted tensile test to study the contribution of the electrical current to the plastic flow of the duplex stainless steel.

The tensile tests conducted under continuous electrical current (approximately 15% more) result in increasing the uniform elongation, compared to the thermal counterpart and to the baseline, but no significant reduction in yield stress or UTS was observed. Elongation at rupture was also increased with respect to the thermal test but, as stated before, it is not a valid parameter to consider due to localized plastic instability which leads to an abrupt increase in joule heating.

The tensile tests conducted with pulsed current result in a uniform elongation, significantly higher compared to that obtained with continuous current (approximately 30% more compared to the baseline) but UTS and yield stress were not affected. Elongation at
rupture for the pulsed tensile test was constant, despite the increase in temperature of the material and comparable to that of the baseline, as opposed to the continuous current case.

The occurrence of electroplastic effect in duplex can be explained by the uneven distribution of current due to the presence of the ferrite matrix in a biphasic alloy. The ferrite has a lower resistivity than austenite, so the current flows preferentially in ferrite and austenite acts as obstacles to current flow.

Further tests at different current densities, pulses duration and frequencies must be conducted as well as modelling in order to verify this possible explanation for this steel grades.

6. References


Breda, M.; Pezzato, L.; Pizzo, M.; Calliari, I. Effect of cold rolling on pitting resistance in duplex stainless steels. La Metallurgia Italiana (2014, Volume 6), pp.15–19.

VAHID HOSSEINI¹, STEN WESSMAN¹, KJELL HURTIG¹, AND LEIF KARLSSON¹

PREDICTING FERRITE FRACTIONS IN SINGLE PASS SUPER DUPLEX STAINLESS STEEL WELDS – THERMAL CYCLE ANALYSIS AND PHASE TRANSFORMATION MODELING

Abstract

The relationship between welding process parameters, welding thermal cycle, and the final microstructure is of great importance for reliable fabrication of welded super duplex stainless steels (SDSS) structures. The present study was primarily aimed at investigating the relationship for root/single pass welding of type 2507 SDSS. Fourteen welds were produced using GMAW, GTAW, SAW, and SMAW with different joints geometries, plate thicknesses, and welding parameters. Thermal cycles were recorded using several thermocouples attached to the plates and thermocouples were also harpooned into the weld pool. Weld pool geometries and base metal dilution in the weld metal were determined for all welds. The general trend was that the ferrite fraction of the weld zone increased with increasing cooling rate and base metal dilution in the weld metal. The ferrite fraction was in the range 49-64% for all welds. Kinetics of austenite formation was modeled using computational thermodynamics (Thermo-Calc & DICTRA) to predict the ferrite fractions in the weld zone and calculated fractions were in good agreement with experimental results. Some conflicting results showed that in addition to dilution and cooling rate, the possible nitrogen loss must be taken into account when evaluating and predicting ferrite fraction. It was concluded that the above approach can be used for prediction of the ferrite fraction of super duplex stainless steel single pass welds.

Keywords: Ferrite fraction; arc welding; super duplex stainless steels; simulation; Dictra;

1. Introduction

Duplex stainless steels (DSS) provide an excellent combination of high corrosion resistance and superior mechanical properties [1]. Super duplex stainless steels (SDSS), containing a higher content of alloying elements (such as Ni, Cr, Mo, and N) compared to lean and standard duplex stainless steels, may be used in applications with a higher demand for strength and corrosion resistance [2,3]. Welding of SDSS, however, is more challenging than for lean and standard duplex stainless steels as achieving the desired balanced ferrite/austenite fraction is sometimes conflicting with the more rapid formation of deleterious phases in SDSS [4].

The combination of thermal history and weld metal chemical composition plays a crucial role for the SDSS microstructure [5]. Flat and tubular products normally have about 50/50 ferrite/austenite ratio, which has been claimed to create the optimum properties [6]. Achieving the balanced ferrite/austenite ratio is challenging in welding, as the chemical composition and thermal cycle are

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more difficult to control compared to in the primary production routes such as hot working and solution annealing. A single-pass SDSS weld consists of weld zones, high temperature heat affected zone (HTHAZ), and low temperature heat affected zone (LTHAZ). The weld zone forms from the solidification of a filler metal and base metal mixture. Heat affected zones (HAZ), on the other hand, are parts of the base metal experiencing high peak temperatures in the solid state.

Filler metal, gas-melt and slag-melt reactions, shielding and backing gases, and dilution of the base metal in the weld zone are factors influencing the weld zone chemical composition [4]. As austenite formation is restricted during rapid cooling, austenite stabilizing alloying elements play an important role to achieve the desired phase balance in the weld zone. The common practice is to use filler metals over alloyed with Ni for all arc welding processes. In addition, for Gas Tungsten Arc Welding (GTAW), nitrogen containing shielding gases are employed to promote austenite formation [4]. Dilution of the base metal in the weld zone is dependant on the welding parameters and joint geometry. In addition to the weld zone chemical composition, melting and solidification followed by solid state phase transformation create a complex metallurgical condition to achieve the required phase balance. Rapid cooling after solidification restricts austenite formation and results in precipitation of nitrides [7,8]. Slow cooling, on the other hand, can cause the formation of sigma and chi phase [3,9]. These unwanted phases cause the degradation of corrosion resistance and/or mechanical properties [10-12].

Different standards have introduced the allowable ferrite fraction in base metal, heat affected zone and weld metal for DSS welds. For instance, API technical report 938-C [13] requires the ferrite fractions of 30-65% for base metal, 40-65% for HAZ and 25-60% for weld zone. NACE MR0175 [14] states that the ferrite fraction shall be between 35-65% for wrought and cast structures and 30-70% for weld zone root and un-reheated weld cap.

Much research is ongoing to measure and predict ferrite fractions in DSS welds [15-22]. This study is part of a research project where a combination of instrumented welding, thermodynamic and kinetics modeling, thermal cycle modeling, and verification welding has been employed to develop a database for a software predicting ferrite fractions in duplex stainless steels. In the first step of the project, a methodology was developed to measure the ferrite fraction [23], which is background knowledge for this work. The present paper focuses on single pass SDSS welds, where the influence of thermal history and dilution on final ferrite fraction is investigated. Based on the experiments, Dictra simulations were also performed for different cases to develop a model to be used for database development.
2. Experiments and modeling

2.1. Material

Type 2507 SDSS plates with different thicknesses were used for welding experiment. The chemical compositions of plates and welding consumable used for the experiment are detailed in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
<th>Cu</th>
<th>W</th>
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<tr>
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<tr>
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<td>0.7</td>
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<td>24.1</td>
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<td>3.8</td>
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<td>0.03</td>
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<td>25.0</td>
<td>6.9</td>
<td>3.8</td>
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<td>-</td>
</tr>
<tr>
<td>10 mm</td>
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<td>0.4</td>
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<td>0.8</td>
<td>0.021</td>
<td>0.001</td>
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<tr>
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<td>24.7</td>
<td>6.8</td>
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<td>0.24</td>
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<td><strong>Welding wire and electrode</strong></td>
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<td>TIG/MIG</td>
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<td>0.014</td>
<td>0.001</td>
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<td>4.1</td>
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<td>SMAW*</td>
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<td>0.9</td>
<td>0.017</td>
<td>0.003</td>
<td>25.3</td>
<td>9.3</td>
<td>4.3</td>
<td>0.21</td>
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<td>0.6</td>
<td>0.015</td>
<td>0.001</td>
<td>24.9</td>
<td>9.2</td>
<td>3.9</td>
<td>0.26</td>
<td>0.09</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*All-weld metal composition

2.2. Welding

Designations of the thermocouples used for recording the thermal cycles are shown in Fig. 1 and Figure 2. The locations of thermocouples were selected to cover thermal cycles in different locations of the joint producing enough data for calibration of the future temperature field modeling.
Fig. 1: Designations of thermocouples attached to record welding thermal cycles.

Fig. 2: Experimental set-up showing locations of the two sets of thermocouples on the front side and the thermocouple harpooned into the weld pool.
Gas-Metal Arc Welding (GMAW): A TransPlus Synergic 5000 CMT R power source was used and an ABB welding robot was employed to perform the GMAW experiments. The plates were placed in a fixture and the start and stop points of welding were located for the guidance of the robot. The shielding gas was Mison 2He (2% CO₂, 30% He, 275 ppm NO and bal. Ar) and backing gas was pure N₂.

Gas-Tungsten Arc Welding (GTAW): Welding was done in the same way as for GMAW but the shielding gas was Mison N₂ and no backing gas was used.

Shielded Metal Arc Welding (SMAW): A Miller XMT 350 MPa power source was employed to perform the experiment and manual welding was implemented.

Submerged arc welding (SAW): A Miller Summit Arc 1250 power source was used and mechanized welding was employed to perform the experiment.

Table 2: Welding parameters used to produce welds.

<table>
<thead>
<tr>
<th>No.</th>
<th>Thickness (mm)</th>
<th>Configuration</th>
<th>Process</th>
<th>Voltage (V)</th>
<th>Current (A)</th>
<th>Speed (mm/s)</th>
<th>Arc energy (kJ/mm)</th>
<th>Heat input* (kJ/mm)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>13</td>
<td>T</td>
<td>GMAW</td>
<td>25</td>
<td>220</td>
<td>5.0</td>
<td>1.1</td>
<td>0.9</td>
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<tr>
<td>2</td>
<td>13</td>
<td>T</td>
<td>GMAW</td>
<td>26</td>
<td>220</td>
<td>3.0</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>L</td>
<td>GMAW</td>
<td>25</td>
<td>220</td>
<td>5.0</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>L</td>
<td>GMAW</td>
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<td>220</td>
<td>3.0</td>
<td>1.9</td>
<td>1.5</td>
</tr>
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<td>5</td>
<td>13</td>
<td>L</td>
<td>SAW</td>
<td>29</td>
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<td>GMAW</td>
<td>24</td>
<td>213</td>
<td>4.5</td>
<td>1.2</td>
<td>0.9</td>
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<td>7</td>
<td>13</td>
<td>V-grooved plate</td>
<td>GTAW</td>
<td>14</td>
<td>213</td>
<td>2.0</td>
<td>1.5</td>
<td>0.9</td>
</tr>
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<td>9</td>
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<td>V-grooved plate</td>
<td>SAW</td>
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<td>450</td>
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<td>1.2</td>
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<td>10</td>
<td>3</td>
<td>Root, V joint</td>
<td>GTAW</td>
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<td>140</td>
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<td>11</td>
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<td>GTAW</td>
<td>12</td>
<td>170</td>
<td>1.2</td>
<td>1.7</td>
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<tr>
<td>12</td>
<td>21</td>
<td>Root, V joint</td>
<td>GTAW</td>
<td>11</td>
<td>170</td>
<td>1.2</td>
<td>1.6</td>
<td>0.9</td>
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<tr>
<td>13</td>
<td>21</td>
<td>Root, joint</td>
<td>GMAW</td>
<td>28</td>
<td>239</td>
<td>4.5</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>14</td>
<td>25</td>
<td>Root, joint</td>
<td>GTAW</td>
<td>11</td>
<td>172</td>
<td>1.2</td>
<td>1.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*To calculate the heat input, arc efficiencies of 1 for SAW, 0.8 for GMAW, and 0.6 for GTAW and SMAW were considered.

2.3. Characterization of microstructure

Cross sections of the welds were ground and polished using an automatic polishing machine. Then, they were etched using modified Beraha’s reagent for 20-30 s. Ferrite percentages were measured using image analysis of 20 images in each location at a magnification of 200X. Ferrite numbers were measured using a Ferritoscope on the cross section of the weld using 10 measurements in each location. More details about ferrite measurement may be found in Ref [23].
2.3.1. Calculation of dilution

A typical cross section of a weld and the method for calculation of base metal dilution in the weld zone is shown in Fig. 3. The weld zone (Fig. 3 a) is divided into two regions, melted BM and added filler metal (Fig. 3), based on the original sketch of each welds shown in Fig. 1. Then, the BM dilution is calculated using the following formula:

\[
\text{BM dilution in weld metal (\%) } = \frac{\text{Melted BM area}}{\text{Weld zone area}} \times 100
\]

Fig. 3: Cross section of a SAW weld to show how the BM dilution was calculated a) weld zone b) weld zone divided into portions coming from the BM and added filler.

2.4. Modeling

The thermodynamic calculations were done using Thermo-Calc and the TCFE8 database and the kinetic simulations using DICTRA with the TCFE8 and the MOBFE3 databases. The simulations were done using a 10 μm cell and linear compositions (See section 3.4). The starting temperature was 1600 °C and the finish temperature of 1000 °C using linear cooling. The start was 100 % ferrite and the driving force to precipitate austenite was 1E-5 xRxD J/mol.

Modde Pro software employs the principle of design of experiment (DOE) to give useful information based on the raw data. In the present study, DOE was not performed using Modde Pro, but raw data measured from different welds was entered into the software using the “paste data” mode. Therefore, the software was only employed to fit ferrite fraction, weld zone size and cooling time, based on experimental data points. It should be noted that as DOE was not done based on the software, the fitting only gave general ideas about the trends of change.
3. Results

3.1. Thermal cycle analysis

A typical thermal cycle in the weld zone during solidification is shown in Fig. 4. Although several thermocouples were attached to the joint, the thermal cycle recorded by the harpooned thermocouples were used in this evaluation, as the aim of the paper was to study the ferrite fraction in the weld metal. Cooling times between 1200-800°C (Δt_{1200-800}) and 800-500°C (Δt_{800-500}) were calculated from the data recorded by the thermocouples.

![Time-temperature curve for the weld zone of SMAW.](image)

**Fig. 4:** Time-temperature curve for the weld zone of SMAW.

The Δt_{1200-800} and Δt_{800-500} cooling times are detailed in
Table 3. The observations are summarized as follows:

1. In GMAW, T and L joint, the cooling time increased with increasing heat input.
2. In GTAW, with increasing the plate thickness, the cooling time decreased for similar heat inputs.
3. No obvious relationship was found when comparing GTAW and GMAW for the same thickness.
4. Comparison of sample 6 with samples 1 and 3 shows that V-joints cooled down slower compared to L and T joints without any groove, although welding parameters were almost similar.
Table 3: Cooling time in the fusion zone of welds.

<table>
<thead>
<tr>
<th>No.</th>
<th>Thickness (mm)</th>
<th>Configuration</th>
<th>Process</th>
<th>Heat input (kJ/mm)</th>
<th>Δt_{1200-800} (s)</th>
<th>Δt_{800-500} (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>T</td>
<td>GMAW</td>
<td>0.9</td>
<td>4.0</td>
<td>7.7</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>T</td>
<td>GMAW</td>
<td>1.5</td>
<td>8.5</td>
<td>22.5</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>L</td>
<td>GMAW</td>
<td>0.9</td>
<td>3.1</td>
<td>7.6</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>L</td>
<td>GMAW</td>
<td>1.5</td>
<td>5.8</td>
<td>25.4</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>L</td>
<td>SAW</td>
<td>1.6</td>
<td>5.2</td>
<td>17.2</td>
</tr>
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<td>GMAW</td>
<td>0.9</td>
<td>6.6</td>
<td>23.3</td>
</tr>
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<td>7</td>
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<td>GTAW</td>
<td>0.9</td>
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</table>

3.2. Macrostructure and dilution

The cross sections of the 14 welds produced in the present study are shown in Fig. 5. The details about the calculated dilutions and weld zone sizes are presented in Table 4. The dilution range was from 25-76% and the weld zone size was in the range of 16-82 mm².

The first row in Fig. 5 shows the weld zone of L and T joints produced using GMAW and SAW. The geometry of the weld pool is similar for L and T GMAW samples produced with the same heat input. The SAW L joint, however, showed a different weld pool geometry. Although the size of the weld zone was almost similar in GMAW and SAW samples, the BM dilution in the weld metal was 18% higher for the SAW sample.

Fig. 5: Cross sections of the 14 studied welds. The first row shows T and L joints, the second row shows the influence of welding process on the same geometry, and the third row shows...
root pass welding of different thicknesses.

In the second row of Fig. 5, the weld zone geometries produced by different welding process on V-grooved 13-mm thick plates are shown. With the same heat input for welds number 6 and 7, GMAW produced a larger weld zone and deeper penetration, but lower dilution compared to GTAW. The largest dilution and weld pool size were produced by SAW for this joint geometry.

In the third row of Fig. 5, the weld zone geometries for the root pass of joints with GTAW and GMAW welds are shown for different plate thicknesses. The weld pool size decreased with increasing the plate thickness from 10 mm to 25 mm in GTAW samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>Thickness (mm)</th>
<th>Configuration</th>
<th>Process</th>
<th>Heat input (kJ/mm)</th>
<th>Weld zone size (mm²)</th>
<th>Remelted BM size (mm²)</th>
<th>Dilution of WM with BM (%)</th>
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<td>GMAW</td>
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<td>58</td>
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<td>SMAW</td>
<td>0.7</td>
<td>16</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>V-grooved plate</td>
<td>SAW</td>
<td>1.2</td>
<td>61</td>
<td>41</td>
<td>66</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>V joint</td>
<td>GTAW</td>
<td>0.5</td>
<td>26</td>
<td>20</td>
<td>76</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>V joint</td>
<td>GTAW</td>
<td>1.0</td>
<td>37</td>
<td>19</td>
<td>49</td>
</tr>
<tr>
<td>12</td>
<td>21</td>
<td>V joint</td>
<td>GTAW</td>
<td>0.9</td>
<td>32</td>
<td>20</td>
<td>62</td>
</tr>
<tr>
<td>13</td>
<td>21</td>
<td>V joint</td>
<td>GMAW</td>
<td>1.2</td>
<td>67</td>
<td>31</td>
<td>46</td>
</tr>
<tr>
<td>14</td>
<td>25</td>
<td>X joint</td>
<td>GTAW</td>
<td>0.9</td>
<td>21</td>
<td>12</td>
<td>56</td>
</tr>
</tbody>
</table>

3.3. Microstructure

The microstructures of as received plates are shown in Fig. 6. The 3-mm thick plates showed the smallest austenite grain size with a single modal size distribution of the grains, without the presence of any intragranular austenite. The austenite grain size was largest for the 25 mm plate with a bimodal distribution of the grain sizes, where intragranular austenite grains were located between the elongated large austenite grains.
Fig. 6: Microstructures of base metal with different thicknesses. The smallest austenite grain size is for 3 mm thick plate and the largest is for 24 mm thick plate.

The microstructures of the welds are shown in Fig. 7. The measured ferrite numbers and fractions are detailed in Table 5. All welds had a typical fused structure with intergranular, Widmanstätten and intragranular austenite grains. The ferrite fraction was within the range of 49-64%. One interesting observation was that with equal ferrite fraction for the V-grooved SAW and 21-mm thick GTAW samples, the SAW sample contains more intragranular austenite grains with a finer microstructure. As the evolution of ferrite fraction is the result of chemical composition and cooling time, more details about the interconnection of the results will be explained in the discussion section.

Fig. 7: Microstructures of the weld zones, the first row shows T and L joints, the second row shows the influence of welding process for the same geometry, the third row shows root pass welding for different thicknesses.
Table 5: Ferrite fractions for welds.

<table>
<thead>
<tr>
<th>No.</th>
<th>Thickness (mm)</th>
<th>Configuration</th>
<th>Process</th>
<th>Heat input (kJ/mm)</th>
<th>Ferrite number (FN)</th>
<th>STDEV (FN)</th>
<th>Ferrite fraction (%)</th>
<th>STDEV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>T</td>
<td>GMAW</td>
<td>0.9</td>
<td>49</td>
<td>3</td>
<td>55</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>T</td>
<td>GMAW</td>
<td>1.5</td>
<td>49</td>
<td>3</td>
<td>52</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>L</td>
<td>GMAW</td>
<td>0.9</td>
<td>66</td>
<td>4</td>
<td>58</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>L</td>
<td>GMAW</td>
<td>1.5</td>
<td>49</td>
<td>3</td>
<td>49</td>
<td>4.4</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>L</td>
<td>SAW</td>
<td>1.6</td>
<td>66</td>
<td>3</td>
<td>56</td>
<td>2.2</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>V-grooved plate</td>
<td>GMAW</td>
<td>0.9</td>
<td>54</td>
<td>5</td>
<td>49</td>
<td>3.5</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>V-grooved plate</td>
<td>GTAW</td>
<td>0.9</td>
<td>66</td>
<td>2</td>
<td>59</td>
<td>3.8</td>
</tr>
<tr>
<td>8</td>
<td>13</td>
<td>V-grooved plate</td>
<td>SMAW</td>
<td>0.7</td>
<td>72</td>
<td>2</td>
<td>63</td>
<td>1.1</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>V-grooved plate</td>
<td>SAW</td>
<td>1.2</td>
<td>68</td>
<td>5</td>
<td>64</td>
<td>4.2</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>V joint</td>
<td>GTAW</td>
<td>0.5</td>
<td>69</td>
<td>5</td>
<td>63</td>
<td>4.7</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>V joint</td>
<td>GTAW</td>
<td>1.0</td>
<td>61</td>
<td>2</td>
<td>56</td>
<td>2.6</td>
</tr>
<tr>
<td>12</td>
<td>21</td>
<td>V joint</td>
<td>GTAW</td>
<td>0.9</td>
<td>63</td>
<td>2</td>
<td>64</td>
<td>3.6</td>
</tr>
<tr>
<td>13</td>
<td>21</td>
<td>V joint</td>
<td>GMAW</td>
<td>1.2</td>
<td>55</td>
<td>3</td>
<td>53</td>
<td>2.6</td>
</tr>
<tr>
<td>14</td>
<td>25</td>
<td>X joint</td>
<td>GTAW</td>
<td>0.9</td>
<td>63</td>
<td>3</td>
<td>64</td>
<td>2</td>
</tr>
</tbody>
</table>

3.4. Thermodynamic modeling

As pointed out earlier, the final ferrite fraction is a function of cooling rate and chemical composition in as deposited (not reheated) weld metal. Based on the information obtained in the previous section, therefore, six cases were defined for Dictra simulation. The simulation matrix includes average dilution with maximum and minimum cooling rates, the average cooling rates with maximum and minimum dilution, and the average cooling rate and dilution. This matrix thereby covers the boundary of the experimental matrix. In addition to these five cases, case 6 was defined to study the possible influence of nitrogen loss. Therefore, it was considered that the nitrogen content decreased from 0.27 wt.% to 0.20 wt.%, compared to in case 5.

Table 6: Ferrite fraction Dictra modeling matrix.

<table>
<thead>
<tr>
<th>Case</th>
<th>Cooling Rate (°C/s)</th>
<th>Dilution (%)</th>
<th>C (wt.%)</th>
<th>Si (wt.%)</th>
<th>Mn (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Ni (wt.%)</th>
<th>Mo (wt.%)</th>
<th>N (wt.%)</th>
<th>Cu (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>50</td>
<td>75</td>
<td>0.01</td>
<td>0.3</td>
<td>0.7</td>
<td>25.3</td>
<td>8.5</td>
<td>4.0</td>
<td>0.27</td>
<td>0.1</td>
</tr>
<tr>
<td>Case 2</td>
<td>50</td>
<td>35</td>
<td>0.01</td>
<td>0.3</td>
<td>0.7</td>
<td>25.4</td>
<td>7.7</td>
<td>3.9</td>
<td>0.27</td>
<td>0.2</td>
</tr>
<tr>
<td>Case 3</td>
<td>133</td>
<td>55</td>
<td>0.01</td>
<td>0.3</td>
<td>0.7</td>
<td>25.4</td>
<td>8.1</td>
<td>3.9</td>
<td>0.27</td>
<td>0.1</td>
</tr>
<tr>
<td>Case 4</td>
<td>27</td>
<td>55</td>
<td>0.01</td>
<td>0.3</td>
<td>0.7</td>
<td>25.4</td>
<td>8.1</td>
<td>3.9</td>
<td>0.27</td>
<td>0.1</td>
</tr>
<tr>
<td>Case 5</td>
<td>50</td>
<td>55</td>
<td>0.01</td>
<td>0.3</td>
<td>0.7</td>
<td>25.4</td>
<td>8.1</td>
<td>3.9</td>
<td>0.27</td>
<td>0.1</td>
</tr>
<tr>
<td>Case 6</td>
<td>50</td>
<td>55</td>
<td>0.01</td>
<td>0.3</td>
<td>0.7</td>
<td>25.4</td>
<td>8.1</td>
<td>3.9</td>
<td>0.20</td>
<td>0.1</td>
</tr>
</tbody>
</table>
The ferrite fractions for the cases detailed in Table 6 are shown in Fig. 8. As may be seen, with an identical cooling time but increasing the dilution as from case 1 to case 2, ferrite fraction increased about 5%. With constant dilution but decreasing the cooling rate as from case 3 to case 4, ferrite fraction decreased about 7%. As expected, case 5 has higher ferrite fraction than case 1 because of a lower Ni content and case 4 because of a higher cooling rate, but lower than the others. Nitrogen has a significant influence on the ferrite fraction as only 0.07% nitrogen loss increased the ferrite fraction about 10%.

**Fig. 8:** Evolution of ferrite fraction simulated by Dictra software for cases defined based on the experiment with different dilution, cooling rate, and nitrogen content (Table 6). The highest ferrite fraction was for case 6 and the lowest was for case 4.

4. Discussion

In the present section, the influence of welding parameters on weld pool size and thermal cycle is briefly discussed. Then the evolution of ferrite fraction with cooling time and dilution is explored. The results are compared with Dictra simulations.

4.1. Welding Parameters

By considering all welds, the influence of thickness and heat input on the weld zone size was found, as shown in Fig. 9 using the fitting of the experimental data in the Modde software. As may be seen, the weld zone size increased with increasing heat input. In contrast, the weld zone size decreased with increasing plate thickness. However, the influence of the plate thickness is not as significant as the heat input.
Fig. 9: Influence of plate thickness and heat input on weld zone size, shown in white squares (mm²). The diagram was calculated using the Modde software with experimental data as input.

The influence of heat input and plate thickness on $\Delta t_{1200-800}$ is shown in Fig. 10 for GTAW samples (fitted using Modde software). It was not rational to take all welds into consideration for the fitting, as a large difference between welding parameters such as current and welding speed can introduce a huge error in the results. Therefore, it was decided to only fit the results for GTAW samples, as they have similar welding parameters. As may be seen, $\Delta t_{1200-800}$ increased with increasing heat input and decreasing plate thickness. The heat sink increases for thicker plates, which results in faster cooling. It should be noted that these values only show general trends. Therefore, further experiments and modeling are needed to study the influence of welding variables.

Fig. 10: Influence of heat input and plate thickness on $\Delta t_{1200-800}$ (s), shown in white squares, in GTAW samples.
The diagram was produced using the Modde software with experimental results as input.

4.2. Evolution of ferrite fraction

The evolution of ferrite fraction with BM dilution in weld metal and $\Delta t_{1200-800}$ is shown in Fig. 11. For better understanding the trend, the results were roughly fitted using Modde software, as shown in Fig. 12. The general trend shows that the ferrite fraction increased with increasing dilution and decreasing cooling time. This trend was expected as a higher BM dilution in weld metal decreases the Ni fraction and results in less austenite formation. In addition, a lower $\Delta t_{1200-800}$ decreases the time for austenite formation.

**Fig. 11:** Influence of BM dilution and cooling time on the ferrite fraction. a) 3D diagram, b) 2D diagram. Arrows show that similar ferrite fractions were obtained with a large difference in cooling time but almost similar dilution. Circle shows that with similar dilution and cooling
time the ferrite fraction can vary about 10%.

**Fig. 12:** The influence of dilution and cooling time on ferrite fraction, shown in white squares (%). Ferrite fractions simulated by Dictra (black points) are plotted on the predicted Modde map.

It should be noted that the fitting is not perfect as the number of welds was not sufficient to cover the number of experimental variables (process, welding parameters, plate thickness, shielding gas, and joint geometry). Therefore, some inaccuracies in the fitted results are expected. For instance if the constant dilution of 55% is considered, the influence of cooling time on ferrite fraction shows a mild slope in Fig. 12, meaning the cooling time is not very critical (about 1% difference for most of the dilutions). However, looking at the experimental results, for instance in sample 1 and sample 4, shows that with quite a similar dilution, a 7% difference in ferrite fraction was seen due to the different Δt1200-800. It raises the question that in addition to dilution and Δt1200-800, another factor must be taken into account for the calculation of ferrite fraction. This factor could be nitrogen content, as dilution does not fully cover the true changes in chemical composition. For example, a comparison of sample 12 and sample 9, showed that the welds with almost similar dilution (66% and 62%), but a huge difference in Δt1200-800 (2.6 s for SAW and 11.6 s for GTAW) have similar ferrite fractions (62%). The most probable reason could be nitrogen loss during GTAW which is well known to occur. The slag protection characteristics of the SAW process can restrict the nitrogen loss. In addition, the welding speed in SAW was much higher than that in GTAW, which resulted in faster solidification and shorter time for the possible nitrogen loss from the weld pool. As may be seen in Fig. 7, more intragranular austenite formed in the SAW sample and its microstructure is finer due to the faster cooling. In contrast, the GTAW sample contained more grain boundary austenite due to the slower cooling. Nitrogen loss has indeed been observed for GTAW welding in different studies, both for samples welded with pure argon [5] and with Ar-2%N₂ [24].
As may be seen in Fig. 12, Dictra simulation fits well with the diagram generated using experimental data. For instance, cases 2 and 4 showed less than 1% difference with Modde fitted results. However, there is still some inaccuracies such as case 3 with around 10% deviation between Dictra and Modde results. It, therefore, shows that Dictra simulation can be beneficial to predict the ferrite fraction but that it is important that correct parameters such as chemical composition, cell size, and cooling rate are employed for the simulation.

Dictra simulation was also used to quantify the possible influence of nitrogen loss, as mentioned above. A comparison of case 5 and case 6 showed that for similar dilutions and cooling times, but a realistic nitrogen loss during welding, ferrite fraction can increase up to 10%. It, therefore, explains the points with similar ferrite fraction and dilution for a big difference in cooling time (such as sample 12 and sample 10). The other samples that clearly shows the possible effect of nitrogen loss are indicated by a circle in Fig. 11. As may be seen, three samples with similar cooling times and dilutions had the ferrite fractions of 56%, 59%, and 64%. It, therefore, can be concluded that nitrogen loss is a likely cause of this difference.

4.3. Future study

The next steps toward the development of a software for prediction of ferrite fractions when welding duplex stainless steels are as follows:

- Instrumented multipass welding of SDSS plates to record the evolution of ferrite content and possible formation/dissolution of secondary phases.
- Modeling of thermal cycle in single pass and multipass welds.
- Developing a Dictra model to study the evolution of ferrite fraction and the formation of secondary phases in multipass welds.
- Calibration of temperature and Dictra models using instrumented multipass welds.
- Performing industrial welds with industrial partners for verification of models.
- Compiling all results in a web-based software.

5. Conclusions

The influence of welding thermal cycles and dilution of base metal in the weld zone on the ferrite fraction of 14 single/root pass SDSS welds was investigated. A Dictra model was developed to predict ferrite fraction in the weld zone. The study is a part of a larger project aiming at developing a software for prediction of ferrite fractions in welding of duplex stainless steels. The conclusions are as follows:

1. The weld zone size increased with increasing the heat input and decreasing plate thickness.
2. For GTAW, the cooling time between 1200-800 °C increased with increasing heat input and decreasing plate thickness.
3. Ferrite fractions were between 49 ± 3% to 64 ± 3%. The general trend was that the ferrite fraction decreased with increasing Δt_{1200-800} and increasing BM dilution.
4. Nitrogen levels in the weld zone must be taken into account to fully understand changes in the ferrite fraction.
5. A Dictra model was developed, assuming an initially fully ferritic microstructure and a cell size of 10 μm. The model predicted ferrite fractions of 58-64 % for different cases defined based on the experiments. Predictions were in good agreement with the measured fractions.
6. The influence of nitrogen loss was also studied using the Dictra model. A 10% increase in ferrite fraction was calculated in the case of a nitrogen drop from 0.27 wt.% to 0.20 wt.%.

Acknowledgments
The great support received from the DuWelTool project partners (Outokumpu AB, Sandvik Materials Technology, ELGA AB, Svetskommissionen, Jernkontoret, Thermo-Calc Software AB, Voestalpine Böhler Welding Nordic AB, and Forsmarks Kraftgrupp AB) is acknowledged. Financial support from Vinnova foundation for the DuWelTool project (project number: 2016-02834) is appreciatively acknowledged.

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ON THE USE OF COMPUTATIONAL THERMODYNAMICS FOR PREDICTING THE PRECIPITATION AND GROWTH OF SECONDARY PHASES IN STAINLESS STEELS

Abstract

Stainless steels are high-alloyed, usually with multiple components and often also dual matrix phases, as for duplex stainless steels. This makes predictions and calculations of alloying effects on equilibria and phase transformations a challenge. Computational thermodynamics has emerged as an indispensable tool for calculations within these complex systems on predictions of equilibria and precipitation & growth. This paper offers examples illustrating how computational methods can be applied both to thermodynamics and kinetics of stainless steels in order to predict microstructure comprising of the desired matrix phases ferrite and/or austenite, as also the less desired secondary phases such as intermetallic phases and nitrides.

1. Introduction

The field of computational thermodynamics emerged as a response to the growing possibilities with computers to rationalise large amounts of experimental information to enable calculations of vital thermodynamic properties. The software uses thermodynamic data stored in databases and each phase is represented by Gibbs energy expressions. The CALPHAD (CALculation of PHAse Diagrams) technique is the international modus operandi to collect and describe the thermodynamics of a system in databases [1]. The foundations of these calculations are descriptions of the Gibbs energy for components and phases. The equilibrium is represented by the minimum Gibbs energy and this is assessed by calculations of the phases involved in the system. With good thermodynamic models and system assessments it is thus possible to perform predictive calculations in multicomponent systems beyond lower level assessments.

In order to describe the growth of phases and rates of reactions it is necessary to be able to describe of how atoms and phase boundaries move in the material. The foundation for such diffusion calculations are Fick’s first and second law and data for diffusion are systematically assessed and described using mobilities in databases for this purpose. The multicomponent diffusion equations in the various regions of a material are solved under the assumption that thermodynamic equilibrium holds locally at all phase interfaces.

Stainless steels are high-alloyed, usually with multiple components and often also dual matrix phases, as for duplex stainless steels. High levels of alloying elements, necessary to achieve high strength and good corrosion resistance, may make the steels sensitive to the precipitation of undesired secondary phases such as, for example, intermetallic phases and/or nitrides. The properties such as strength, toughness and corrosion resistance critically depend on correct balance of matrix phases and avoidance or minimisation of secondary phases during manufacture, processing, fabrication, joining and use.

This paper offers examples illustrating how computational methods can be applied on key aspects of stainless steels in order to predict matrix phase balance and correlation to the

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precipitation to secondary phases. Important aspects in simulation work and consequences and correlation to experimental results are discussed.

2. Modus operandi

The work within this paper was done using the software Thermo-Calc and DICTRA [2] and the moving phase boundary model. The databases used were TCFE8 Steels/Fe-alloys databases for the thermodynamics and the MOBFE2 Steels/Fe-Alloys database for the mobilities. Some calculations were also done with the experimental thermodynamic database FROST [3]. The distribution of alloying elements at start of simulations and cooling rates were approximated as linear. The driving force for precipitation of inactive secondary phases was $10^{-5} \cdot R \cdot T \text{ J/mol}$ in the DICTRA calculations.

In order to allow for reasonable computational times in DICTRA the materials in this study, well known commercial duplex stainless steels, were simplified to comprise nominal levels of the five major components Fe, Cr, Ni, Mo and N. Omitted were C, Si, Mn, P, S, Cu and tramp elements. The manganese is however a major alloying element in LDX 2101 and was therefore included for this material, omitting nominal 0.3 Mo instead.

LDX 2101: Fe-5Mn-21.5Cr-1.5Ni-0.22N
2304: Fe-23Cr-4.8Ni-0.3Mo-0.10N
2205: Fe-22Cr-5.5Ni-3Mo-0.17N
2507: Fe-25Cr-7Ni-4Mo-0.27N

3. Results

The influence of the database, comparing TCFE8 with FROST, is given in Fig. 1 using Thermo-Calc for making a pseudo phase diagram with temperature versus nitrogen content. The phases liquid, ferrite and austenite were included in the calculation and composition was Fe-25Cr-7Ni-4Mo, that of 2507 super duplex. A dotted line for 0.27 % N is given which is the nominal nitrogen content for 2507.

The influence of number of components involved in a DICTRA simulation is shown in Fig. 2 with ferrite content versus temperature for 2205 using TCFE8 & MOBFE2, a 10 µm cell, a cooling rate of 50 °C/s from 1600 °C and ending at 1000 °C. The nominal composition Fe-22Cr-5.5Ni-3Mo-0.17N was the reference, adding 0.02C, 0.5Si, 1.5Mn and 0.2Cu. Calculations in this context with more than 8 components, Fe-0.5Si-1.5Mn-22Cr-5.5Ni-3Mo-0.2Cu-0.17N or Fe-0.02C-0.5Si-1.5Mn-22Cr-5.5Ni-3Mo-0.17N or Fe-0.02C-0.5Si-1.5Mn-22Cr-5.5Ni-3Mo-0.17N or were not successful, at least not by the author. As a benchmark in this context, ferrite content versus temperature for the five component Fe-22Cr-5.5Ni-3Mo-0.17N with a +/- 5 % variation in the nitrogen content is shown in Fig. 2.

The influence of system size on the precipitation of chromium nitrides in duplex stainless steel was studied using a dual precipitation set-up. The set-up was similar as in previous case with austenite precipitating during cooling and the additional feature is the precipitation of nitride (Cr$_2$N) at the other side of the cell. This is intended to feature austenite precipitating at the grain boundary and nitride at the grain centre. At a given cooling rate 10, 50 and 100 °C/s the cell size was increased until the nitrogen level, austenite always precipitates per se, was high enough for nitride precipitation. This was done for LDX 2101, 2304, 2205 and 2507 and the results are given in Fig. 3 as critical cell size for formation of nitride versus cooling rate and ferrite content at 1000 °C versus cooling rate. A further parameter which can be evaluated is the austenite spacing [4], the distance in ferrite between two adjacent austenite units. In the
present it was evaluated as twice the grain size, as the simulation involves half a grain unit, and multiplied with the ferrite fraction and the results are given in Fig. 3.

**Fig. 1.** Temperature [°C] versus nitrogen content [wt.-%] for Fe-25Cr-7Ni-4Mo using the TCFE8 database (l.) and the FROST database (r.).

**Fig. 2.** Ferrite content [vol.-%] versus temperature [°C] for 2205 at 50 °C/s using different level of components in the simulation set-up (l.) and with nominal and +/- 5 % nitrogen content (r.).

The work in the previous section was recycled for a component distribution study and composition versus position in the cell at 1000 °C, the simulation end, was plotted for the cell sizes 10, 20, 30 and 40 µm. The results for the lean duplex LDX 2101 and components Cr, Ni and Mn are shown in Fig. 4 and the results for the super duplex 2507 and components Cr, Ni and Mo for in Fig. 5.

The precipitation and dissolution of sigma phase in a 2507 super duplex stainless steel in the form of a TTT (Time - Temperature - Transformation) diagram was calculated and are given in Fig. 6. The starting point was a 20 µm cell with 10 µm of ferrite and 10 µm of austenite using the composition of respective phase from an equilibrium calculation at 1100 °C as set-up. The time to precipitate 1 % of sigma phase between the ferrite and the austenite was assessed and given as the typical “nose” in the temperature - time diagram. Parallel to this the composition profile from an isothermal simulation 950 °C/60 s was assessed, ferrite/sigma phase/austenite and used in dissolution simulations. The time to dissolve the sigma phase was assessed and the results plotted as temperature versus time.
**Fig. 3.** Cell size for nitride formation [µm] (top l.), ferrite content for nitride formation [vol.-%] (top r.) & austenite spacing for nitride formation [µm]; all versus cooling rate [°C/s] for LDX 2101, 2304, 2205 and 2507.

**Fig. 4.** Cr (top l.), Ni (top r.) and Mn (l.) profiles [wt.-%] for cell sizes 10, 20, 30 & 40 µm at 1000 °C after cooling 10 °C/s versus position [µm] for LDX 2101.
Fig. 5. Cr (top l.), Ni (top r.) and Mo (l.) profiles [wt.-%] for cell sizes 10, 20, 30 & 40 µm at 1000 °C after cooling 10 °C/s versus position [µm] for 2507.

Fig. 6. Temperature [°C] versus time [s] and TTT curve using DICTRA for 1% sigma phase and time-to-dissolve TTD curve for the sigma phase precipitated after 60 s at 950 °C; both 2507 super duplex.
4. Discussion

4.1 Database

The database is the cornerstone of the simulation and the quality and accuracy of the results will depend on that of the database. However, good knowledge of the material is vital for making a good simulation since otherwise interpretation of the simulation results can be difficult and/or erratic. The results in Fig. 1 illustrate how the different databases TCFE8 and FROST treat the fully ferritic region in a 2507 duplex stainless steel. The existence of this region in duplex stainless steel has been questioned, however quite unambiguously concluded by Pettersson et al. [5]. The results presented here indicate that the fully ferritic region is correctly predicted by the FROST database, however not by TCFE8. Consequently, the ferrite – austenite simulation with TCFE8, as shown in Fig. 2 for example must be viewed with some caution. The consequences in this case were discussed in [6] and one outcome, which can be seen in Fig. 2, is that the start of austenite formation is higher than expected in reality. This is due to that, when not considering liquid but only ferrite and austenite, the ferrite line in Fig. 1 will be extrapolated to a temperature of about 1440 °C, when in reality it should be below 1380 °C at least, probably lower due to nucleation and depending on cooling rate. However, as shown in [6], good accuracy of ferrite – austenite balance at ambient temperature can still be achieved.

The conclusion was that, while this inaccuracy in the database likely was adding an error to the calculations, this is manageable and other factors are more important to consider. A different approach was used in [7] with liquid, ferrite and austenite which enabled calculations of mixed mode, ferritic-austenitic, solidification, also with the TCFE8 database and the collateral consequences at solidus with this. The conclusion on the issue of database is thus that it usually is not negotiable and consequently the best option is to be aware of any inconsistencies and to correlate, when possible with experimental results in order to be safe. The good news in the above discussion is that Thermo-Calc Software AB participated in the FROST project where the TCFE8 database was used as reference. The TCFE10 database, to be released in December 2019, will include the work and new system evaluations that was carried out in the FROST project. Consequently, the TCFE10 database will reproduce the fully ferritic region in duplex stainless at high temperatures steel adequately.

4.2 Components

Thermodynamic (Thermo-Calc) calculations such as those in Fig. 1 are fairly simple to perform and rapidly executed, also with a large number of components included. This may however not be the case for kinetic calculations (DICTRA). Such calculations involve both a thermodynamic and a kinetic database and calculation time may be days instead of seconds. The facile solution to this is to reduce the number of components and the consequences of such an approach is shown in Fig. 2 where ferrite content versus temperature, calculated as austenite reformation during, for a 2205 duplex stainless steel has been calculated. The calculations range from five components and Fe-22Cr-5.5Ni-3Mo-0.17N to eight components including also 0.02C, 0.5Si, 1.5Mn and 0.2Cu. Trials were made to make a calculation with all these nine components but they were not successful, at least not by the author. The final results, ferrite content, at end of simulations 1000 °C were:

- Fe-22Cr-5.5Ni-3Mo-0.17N: 69.6 vol.-%
- Fe-0.02C-22Cr-5.5Ni-3Mo-0.17N: 66.3 vol.-%
- Fe-0.5Si-22Cr-5.5Ni-3Mo-0.17N: 71.4 vol.-%
<table>
<thead>
<tr>
<th>Composition</th>
<th>Ferrite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-1.5Mn-22Cr-5.5Ni-3Mo-0.17N</td>
<td>68.3</td>
</tr>
<tr>
<td>Fe-22Cr-5.5Ni-3Mo-0.2Cu-0.17N</td>
<td>68.9</td>
</tr>
<tr>
<td>Fe-0.5Si-1.5Mn-22Cr-5.5Ni-3Mo-0.2Cu-0.17N</td>
<td>69.2</td>
</tr>
<tr>
<td>Fe-0.02C-0.5Si-1.5Mn-22Cr-5.5Ni-3Mo-0.17N</td>
<td>66.6</td>
</tr>
</tbody>
</table>

The results thus range from 66.3 to 71.4, i.e. 5.1 vol.-% and with the five component calculation as base the results were 69.6 \( \pm 1.8 \) to 3.3 vol.-%. Compared to standard methods for ferrite measurements such as point counting, image analysis or magnetic methods this is reasonable. The intricate question is however if an eight component calculation is more accurate than the five component counterpart? The answer to this question is however not available here and a reasoning is presented instead, leaning towards a no. There are other parts of the simulation which play a more significant role such as database, cell size and cooling for example. The role of the database is crucial, as discussed previously, and further it is based on system assessments which can be reviewed in the description. There is thus not perhaps an improvement in adding more components if the respective sub systems have not been evaluated and included in the database. The role of the cell size is complex and will be discussed further later but it can be said here that choice of cell size is critical and best based on metallography and a representative value. Cooling is another parameter which here was set linear while in reality the rate is non-linear. As an illustration of sensitivity a +/- 5% variation in nitrogen content was tried, i.e. 0.1615 and 0.1785 wt.-%. The results at 1000 °C were 68.1 and 71.0, i.e. 2.9 vol.-%. This illustrates that small variations in critical elements, nitrogen loss a well-known issue in welding, can have a large impact on phase fractions. Connecting this to the previous discussion on number of components it can be concluded that this type of predictive calculations is important additional information and provide an important support to the material users.

4.3 System size:

The system size is illustrated via an approach to try to capture the precipitation of chromium nitrides in duplex stainless steels. Nitrides are not desired precipitate since they drain vital chromium and nitrogen from the matrix thereby reducing the corrosion resistance of the same. It should be emphasised that this discussion is limited to nitrides emerging in the ferrite due to rapid cooling and not those from isothermal heat treatments. The precipitation of nitrides in the ferrite is due to that the solubility rapidly decreases with decreasing temperature and they can be seen as “clouds” in the centre of larger ferrite grains. While slower cooling and a sufficient austenite available nearby will inhibit the precipitation, this may not always be the case. It should also be mentioned that the calculations are limited to Cr\(_2\)N nitrides and the precipitation of CrN as a precursor is not considered [8].

The results in Fig. 3 for LDX 2101, 2304, 2205 and 2507 are results disseminated from the same calculation sequences i.e. to capture the cell size at which the nitride precipitates at opposite side as the austenite. This can be interpreted either as a cell size, a ferrite content or an austenite spacing; all in Fig. 3. The results indicate that 2304 can tolerate larger ferrite content than the other alloys without precipitating nitrides, and vice versa for LDX 2101. The measure of austenite spacing gives the sequence 2304, LDX 2101, 2205 and 2507 for increasing sensitivity to precipitate nitrides according to the calculations. This is a corollary for each alloy of the increasing end nitrogen content with increasing spacing and the nitrogen solubility by means of mainly Cr and Mn, yet to be verified versus experiments and experience.

The straight lines for critical ferrite content in Fig. 3 may look confusing but it should be realised that there is a required driving force for precipitation set, by default to \(\times 10^{-5} \text{R} \cdot \text{T} \text{J/mol}\).
There were also results from trials with varying system size on the distribution of alloying elements which were not expected, shown in Fig. 4 and Fig. 5 for LDX 2101 and 2507. The figures show the distribution of Cr, Ni & Mn for LDX 2101 and Cr, Ni & Mo for 2507 versus cell position at sizes 10, 20, 30 & 40 µm at 1000 °C after cooling 10 °C/s. As can be observed for 2507 there is a shift 10/20 µm for Cr and the austenite, to the right in all figures, actually has a higher concentration at the boundary than the opposing ferrite. This is related to Mo and was observed also for 2304 with 0.3Mo and 2205 with 3Mo, but not for LDX 2101 with Mo omitted. The figures for LDX 2101, as also the other figures for 2507, show a monotonic and predictable behaviour. It was also observed with tungsten instead of molybdenum. The consequences are interesting because a ferrite with decreased chromium and increased Mo content is prone to precipitate chi phase rather than sigma phase. This would consequently be another piece of information for the lengthy discussion of chi versus sigma in duplex and Mo versus W [9], and an additional explanation why chi phase sometimes may act as a precursor to the sigma phase.

4.4 TTT diagram:
The possibility to make a TTT diagram via computational thermodynamics was shown in [10] where experimental work from [11] on super duplex weld metal was made use of. In the simulation paper a simplified approached was used, considering only ferrite and sigma phase, omitting the austenite and the secondary austenite forming from the ferrite decomposition. The results did however prove fruitful and the typical “nose” of a TTT diagram could be computed with good accuracy. The TTT results, 1 % sigma phase, for a somewhat more complex approach are shown in Fig. 6 with sigma phase forming in-between ferrite and austenite. The purpose of the simulations were however to study the dissolution of the sigma phase and this was done by making a precipitation simulation of 950 °C/60 s which is marked in the diagram and give about 1.2 % sigma phase. The resulting phase and alloying element distributions were then used in a sequence of simulations 1040-1200 °C and the time for dissolution of the sigma phase assessed and plotted in the TTT diagram, thus compiling what can be called a TTD Time-Temperature-Dissolution diagram. The results indicate a rapid dissolution of the sigma phase, however converging to long times when approaching the stability range of the sigma phase slightly above the TTT nose.

5. Conclusions

In this paper different approaches for applying computational thermodynamics on stainless steel issues are shown. The precipitation of matrix phases and secondary phases were illustrated with examples and supported with experimental results, when available:

- The importance of an adequate database was illustrated with the critical fully ferritic region in duplex stainless steel at elevated temperatures. It should however be acknowledged that the database often is a boundary condition and cannot be altered, but then awareness of any inconsistencies must be considered and accounted for.
- The simulation set-up and number of elements to consider is a known challenge and the conclusion is that five components give an adequate answer. For stainless steels the main elements Fe-Cr-Ni-Mo-N are feasible for a reasonably rapid calculation and possibly also Mn, W, Cu et cetera if they are important in the calculation context.
- The precipitation of secondary phases was illustrated with two cases, precipitation of chromium nitride Cr2N and sigma phase. While the latter readily can be supported with experimental results, the former is quite a challenge and the approach shown must be considered as a concept demonstration rather than providing actual results.
The reason for this is the nature of nitride precipitation with a cluster of very small precipitates, compared to sigma phase which precipitate as discrete particles.
- This paper provides a discussion around the critical geometry parameter which is necessary for kinetic simulations, illustrating the grain size or similar concept. This parameter can be readily chosen from metallography or, more pragmatic, from the outcome of the simulations. Initially it was chosen based on metallography and for duplex stainless steel based on the austenite spacing. The work presented here, with a systematic variation, suggests that the matter is more complicated that previously realized. It is suggested that the alloying elements Cr and Mo interact so that they affect the distribution of Cr and Mo in the matrix phases thus leading to a cell size depending precipitation of secondary phases, sigma or chi phase.

Acknowledgement

The results presented here have emerged within the member program Stainless at Swerim AB and the project Digitalt verktyg för prediktering av egenskaper i svetsar i duplexa material, Vinnova - Sweden's innovation agency project no. 2016-02834 with Outokumpu Stainless AB, Thermo-Calc Software AB, AB Sandvik Materials Technology, voestalpine Böhler Welding Nordic AB, Forsmarks Kraftgrupp AB, Elga AB, The Swedish Welding Commission, University West and Swerim AB.

References

INFLUENCE OF SIGMA PHASE PRECIPITATION IN THE 600 TO 750 °C RANGE ON MECHANICAL PROPERTIES OF SAF 2205

Abstract

SAF 2205 duplex stainless steel has a combination of good corrosion resistance, mechanical strength and weldability at a relatively low price. Nevertheless, it is susceptible to sigma phase precipitation at elevated temperatures. The sigma phase is a hard and brittle intermetallic phase that occurs in the Fe-Cr system. The temperature range from 600 to 950 °C is critical for the sigma phase precipitation. The effects of time and temperature on the intermetallic phase precipitation and phase transformations in SAF 2205 were investigated. The specimens were isothermally annealed at different temperatures from 600 to 750 °C for 1 min, 10 min, 100 min and 1000 min. The influence of annealing temperature and time on mechanical properties were investigated. The specimens were examined by optical microscopy and ferritoscope measurements were also performed. The tensile strength, hardness and impact toughness were analysed.

Keywords

Duplex stainless steel, sigma phase, mechanical properties, isothermal annealing, intermetallic phase precipitation.

1. Introduction

Duplex stainless steels (DSS) have the advantage of good pitting corrosion resistance, stress corrosion cracking resistance, resistance to intergranular corrosion, high mechanical strength, corrosion fatigue resistance, wear resistance, super plastic behaviour and good weldability. [1–8] But they can prove difficult to control during the hot working process. [2,9,10] The difficulties in hot working process arise from different softening mechanisms of ferrite and austenite. Ferrite grains soften through dynamic recovery (DRV), while austenite grains soften through dynamic recrystallization (DRX) [8, 11]. Another challenge during hot working originates from harmful intermetallic phase precipitation, namely the sigma phase. Sigma phase is a Cr and Mo rich intermetallic phase. The precipitation of the intermetallic sigma phase can occur during cooling from high temperatures or after annealing at temperatures from around 650 to 950 °C. The precipitation of the sigma phase increases hardness but it decreases the impact toughness and corrosion resistance due to local depletion of Mo and Cr. [12–16]

Sigma phase precipitation starts at the ferrite/ferrite and ferrite/austenite interface and moves into ferrite grains until the ferrite is almost exhausted. [13–20] The diffusion rate is faster in ferrite than in austenite, so precipitation kinetics are much faster in DSS compared to austenitic steels. [13]

The effect of intermetallic phase precipitation in SAF 2205 on the mechanical properties and ferrite content is described in this work.
2. Experimental

Duplex stainless steel SAF 2205 with chemical composition given in Table 1 was used for the investigation. Isothermal annealing in air atmosphere was performed at four different temperatures (600, 650, 700 and 750 °C) and for four different times (1, 10, 100 and 1000 min). The specimens were investigated by optical microscopy using optical microscope Microphot FXA, Nikon with 3CCD-camera Hitachi HV-C20A. Hardness measurements were performed according to EN ISO 6508-1:2015 on Instron B2000 instrument. Charpy impact toughness was measured using PSW300 equipment according to EN ISO 148-1:2017. Tensile tests were performed according to EN ISO 6982-1:2017 on Instron 8802 universal testing machine. Measurements of the ferrite contents were performed using feritscope MP30 instrument.

Table 1: Chemical composition of investigated steel SAF 2205 in mass%.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>0.021</td>
<td>0.32</td>
<td>1.58</td>
<td>0.026</td>
<td>0.002</td>
<td>22.95</td>
<td>5.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Mo</th>
<th>V</th>
<th>Ti</th>
<th>Nb</th>
<th>Al</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass%</td>
<td>0.26</td>
<td>2.742</td>
<td>0.15</td>
<td>0.005</td>
<td>0.008</td>
<td>0.012</td>
<td>0.141</td>
</tr>
</tbody>
</table>

3. Results and discussion

The results of Rockwell hardness measurements are presented in Fig. 1. We can observe a minor hardness increase after annealing in all samples compared to the as received specimen (from 22 HRC to 23 HRC). At the lowest two annealing temperatures (600 and 650 °C) no significant changes of hardness were observed for all annealing times. More noticeable, an increase of hardness due to sigma phase formation can be observed after annealing at 700 °C for 1000 min (27 HRC). The same hardening can be observed at 750 °C after annealing for 100 min (26 HRC), while after 1000 min the hardness increases to 35 HRC.

![Fig. 1: Influence of annealing time and temperature on the Rockwell hardness measurements.](image-url)
When investigating the Charpy impact toughness of specimens, the changes are much more pronounced compared to the hardness. Impact toughness of as received samples was approximately 300 J, while all the samples that were annealed had impact toughness under 250 J (Fig. 2). The decrease of impact toughness after 1 minute and 10 minutes at 600, 650 and 700 °C was about 16%, while at 750 °C the decrease was over 30%. At longer times (100 and 1000 minutes) the decrease at 600 and 650 °C was about 50 % (150 J) or 80 % (60 J) respectively. At the highest temperature, the decrease was over 85 % (43 J) after 100 minutes, while after 1000 minutes the impact toughness was only 8 J.

![Fig. 2: Influence of annealing time and temperature on the Charpy impact toughness.](image)

The results of tensile tests reveal that when measuring yield strength ($R_{p0.2}$) no significant influence of annealing temperature and time in the investigated range of temperature and time can be observed (Fig. 3). There were deviations of measured yield strength from 485 to 521 MPa in all the samples. When investigating tensile strength (Fig. 4) no increase of tensile strength after 1 and 10 minutes was observed. After longer annealing times (100 min) an increase of $R_m$ from 760 MPa to 785 MPa can be noticed, while after 1000 min at 750 °C the tensile strength increases to 850 MPa, presenting a 16 % increase.

![Fig. 3: Influence of annealing time and temperature on the yield strength.](image)
Fig. 4: Influence of annealing time and temperature on the tensile strength.

In the case of specimen elongations after fracture (Fig. 5) no significant decrease of elongation can be noticed for the shortest two times (1 min and 10 min) compared to the as received specimen, where the elongation was 35 %. After 100 minutes of annealing at 750 °C elongation was 27.7 %, presenting 21 % decrease of elongation. At the longest time elongation drops to 13.7 % (61 % decrease).

Fig. 5: Influence of annealing time and temperature on the elongation.

The samples were etched with Murakami’s etchant at 60 °C for 20 seconds for metallographic analysis. The microstructure of the as received sample (Fig. 6) consist of austenite (lighter) and ferrite (darker) phase. The microstructure of the annealed specimens, 1000 minutes at all four temperatures are shown in Fig. 7. No sigma phase can be found in the microstructure during the annealing at 600 °C. At 650 °C after 1000 minutes some sigma phase precipitates can be found at ferrite grain boundaries. With the increasing temperature the amount of sigma phase precipitates increases and the amount of ferrite decreases. Ferrite, austenite and the sigma phase are presented in more detail in Fig. 8.

The ratio between ferrite and austenite during annealing was determined using the feritscope and the results are presented in Fig. 9. In as received specimen the ratio between
ferrite and austenite was approximately 50:50. After 1 minute of annealing, no changes in the ratio can be observed at all four temperatures. After 10 minutes the decrease of ferrite content is more clearly visible at the highest annealing temperature, where ferrite content drops to 45%. After 100 minutes of annealing ferrite content at 750°C drops to 42%, while at lower temperatures remains around 50%. After the longest annealing time the ferrite content drops to 45% at 600 and 650 °C, while at 700 °C it drops to 40%. While at 750 °C for 1000 minutes ferrite content drops to only 16%.

Fig. 6: Initial microstructure of investigated steel in as received condition

Fig. 7: Microstructure of investigated steel after annealing for 1000 min at four different temperatures.
Fig. 8: Microstructure of investigated steel after annealing for 1000 minutes at 750 °C with marked austenite (A), delta ferrite (F) and sigma phase (σ).

Fig. 9: Influence of annealing time and temperature on the ferrite content in the steel SAF 2205.

The analysis of the Charpy specimens fracture surface is shown in Fig. 10. The lateral expansion of the specimens decreases with increased temperature or prolonged annealing time. There is practically no expansion and the appearance looks completely brittle after annealing at 750 °C for 1000 min (Fig. 10d). The microstructure close to the fracture of the specimens after the longest annealing times at 600 and 650 °C (Fig. 11) show a fragmented austenite phase, this is a consequence of deformation and flow of material due to lateral expansion of specimens. At higher two temperatures transgranular crack propagation is clearly seen and there is no fragmentation of the austenite phase (Fig. 11 c and d).
Fig. 10: Fracture appearance of Charpy ISO-V specimens after 1000 min annealing at different temperatures.

Fig. 11: Crack propagation on Charpy ISO-V specimens after 1000 min annealing at different temperatures.
4. Conclusions

In this work the influence of isothermal annealing of duplex stainless steel SAF 2205 on mechanical properties and microstructure was analysed. The following conclusions can be drawn:
- The influence of annealing is much more pronounced in the case of impact toughness compared to hardness. When the hardness increases for 20 %, the impact toughness decreases for 80 %.
- The yield strength is not strongly affected by annealing, while the tensile strength can increase up to 100 MPa and the elongation decreased for more than 50 % in the case of the annealing at 750 °C for 1000 min.
- The sigma phase formation is sluggish at lower temperatures (up to 650 °C), only a few precipitates can be found at 1000 min of annealing at 650 °C. At higher temperatures the precipitation rate increases and the ferrite decomposes faster, at 750 °C and 1000 minutes of annealing the ferrite content drops from approximately 50 % to only 16 %.

References

Metallurgy
REAL-TIME AND CONTACTLESS MOLD THERMAL MONITORING: IMPROVING METALLURGY, QUALITY AND PRODUCTIVITY OF BILLETS AND BLOOMS

Abstract

Today the mold thermal mapping technology is typically applied to the CCMs for slabs with solutions based on the installation of thermocouples (TC) or optical fibre cables (OFC), inserted into channels machined in the plate molds. The final installation is complex since every single mold must be machined and the quantity of cables is considerable, making any mold change a complex and time-consuming activity. Extending TC or OFC application to billets and blooms would require invasive and expensive CNC machining of the curved mold tubes.

In order to overcome these limits, Ergolines designed a new system based on contactless ultrasound technology, which provides the real-time mold thermal map without the need to machine the copper, offering a new reliable tool also to the CCMs for small sections. By providing real-time data of the thermal distribution of the mold, Ergolines’ system can be fruitfully used by the technical personnel to improve the casting practice, the steel quality and the plant productivity.

Keywords

Initial solidification, stainless steel solidification, mold thermal mapping, breakout prevention, mold powder feeding control, ultrasonic sensor

1. Introduction

Steel solidification is a complex process, involving several variables and a variety of different physical dynamics. It is well-established that the dynamics of fluid flow and steel solidification in the mold has a direct impact on the quality of the cast product [1-4]. A typical example is stainless steel casting, due to its particular solidification characteristics during the initial solidification where a “soft” cooling in the first part of the mold is required.

As a consequence, the first solidification in the mold is the key of the continuous casting process: The casting speed, the quality of the product, the reliability of the process and of the casting machine are strongly related with this aspect.

With the progress of the sensor technology, the interest in monitoring the thermal status of the mold has significantly increased in the recent years. The state of the art is based on the application of thermocouples (TC) or optical fibre cables (OFC) within the copper mold [5]. Both applications require considerable CNC machining of the copper mold and the management of multiple cables in a critical area with reduced free space. Due to these limitations, mold thermal mapping through TC or OFC is mainly used only in the CCMs for slabs, based on plate molds, but it is not common in the CCMs for blooms and billets, equipped with curved copper tubes.

1 ERGOLINES LAB s.r.l.; Italy
Ergolines proposes a completely different approach [6], developing a technology able to provide in real time an accurate thermal mapping without any contact with the copper tube: The installation of the sensor is in fact on the external side of the water jacket. The copper tube is not machined at all, in contrast to the typical installation of thermocouples or optical fibres, providing remarkable cost savings and installation advantages. Being fully contactless and compact, Ergolines’ system (UT-MAP) can be easily installed in small molds such as the ones used for billets, extending the thermal mapping tool, today prerogative only of slabs and big blooms, also to small sections.

The first solidification process can be monitored in real time and the information achieved can be exploited to improve the casting practice by gaining insight into the solidification behaviour, by tracking the 100% of the billets and, finally, by increasing the CCM productivity through breakout prevention.

2. Why mold thermal mapping?

This question is not a purely academic one, but it involves several practical aspects. Being only apparently a steady-state process, steel solidification in fact involves physical conditions which change continuously, leading to complex dynamics which are challenging to model and difficult to predict.

Some of the most relevant quality defects are related with the initial solidification, which takes place in the mold. As a consequence, the mould conditions have a crucial impact on product quality. This holds true particularly for stainless steel grades. The majority of stainless steel grades have a solidification behaviour of “peritectic” conditions, with high solid contractions and susceptibility to cracks [7]. The statistical occurrence of events such as bleeders, depressions and longitudinal and transversal cracks is higher compared to the carbon steels. The availability of a tool for real-time and contactless thermal monitoring of the mold is therefore of high interest for the CCM experts [8].

The whole spectrum of professionals managing the continuous casting process is interested in keeping it repeatable, ensuring constant quality and achieving the maximum productivity compatible with the quality targets. Not only is productivity affected by the liquid steel throughput, i.e. casting speed, but it is also affected by the reliability of the solidification process. Process criticalities such as breakouts in fact lead to significant losses in terms of production and damages to the CCM.

The ability to obtain real-time data on the solidification behavior inside the mold therefore provides key information, which can be exploited to improve both quality and productivity.

Up to now there is no applicable technology able to detect the solidification details of the steel inside the mold. However, the thermal mapping of the copper mold provides indirect information to be further developed. By using proper mathematical techniques, it is in fact possible to “invert” the temperature detected in the copper mold, achieving several information about the solidification behavior. As an example, the heat transfer from the mold walls can be calculated to estimate the steel skin thickness in a precise location. Any substantial deviation of the heat flux can be analysed and identified as a possible solidification problem.
The process automation can fruitfully use this information to implement several interesting features such as:

- breakout prevention system
- real-time detection of meniscus position
- real-time powder thickness measurement, enabling automatic mold powder feeding in closed-loop control mode
- strand quality tracking
- indication of the mold status (wear) for maintenance purposes.

Fig. 1. The users of thermal mapping tools.

By analysing a real-time thermal map of the copper mold, the metallurgist has the possibility to understand deeply the most critical topics about the initial solidification and to propose effective solutions, including fine-tuning of the casting parameters, improvement of the operative casting practice and optimized mold design.

As an example, the heat transfer efficiency can be used either in real time, to understand the actual heat transfer (lubrication, skin growth behavior, etc), or offline, to optimize mold taper design. This information can in turn be correlated with the relevant casting parameters and be used to set up and validate a solidification model, with the possibility to propose improved casting recipes.

The importance of the flux powder quality and feeding procedure is strictly correlated with the heat flux in the mold and with the product quality. As related by many authors, the quality of mold powder and its ability to provide proper lubrication are fundamental to achieve high-quality stainless steel.

By using this tool, the Quality Manager is able to implement quality controls by tracking the 100% of the billets, thus identifying casted sectors showing quality problems. A quality benchmark can be defined every time the heat flux substantially deviates from the “standard” conditions, allowing the identification of the precise sector where the deviation has occurred. An offline analysis can then highlight the influence of the deviation on product quality.

Since the initial solidification is strictly related with breakouts, also the Production Manager has a relevant interest in the installation of this technology because of the potential benefits in terms of improved CCM reliability. As an example, when casting with high-speed range, the availability of a breakout prevention system provides increased confidence and safety margins.

2. The instrumented mold

The state of the art of the so-called “instrumented mold is typically installed on the CCMs for slabs [2].

The reason is quite evident since these CCMs are more complex compared to the CCMs for billets. Furthermore, the molds are based on plates featuring grooves for the cooling-water circuit. It is therefore easier to prepare a copper plate to be equipped with thermocouples or
optical fibres [5]. Nevertheless, in this case not only is it necessary to perform heavy (for TC) or limited (for OFC) CNC mold machining, but it is also necessary to manage several cable outlets in a congested area with limited free space. Additionally, in order to further increase the grid for thermal mapping in terms of density or extension, even more CNC machining and cabling is needed.

These kinds of installations have several disadvantages because every single plate of the mold must be machined, installation and cabling are expensive and time-consuming. Furthermore, the technical personnel in charge of installation must receive specialized training. All these aspects represent a main inconvenience for the maintenance team.

Up to now, the CCMs for blooms (curved mold) and the majority of CCMs for billets have been excluded from this technology, not only because the “importance” of these machines is “smaller” compared to the CCMs for slabs, but also because the mold is a curved copper tube, with much smaller dimensions than plate molds, making the machining significantly more complex.

Other non-negligible limitations are the following: The tube is inside a water jacket, the cables must be located in through-holes with sealing problems and, furthermore, multiple cable outlets must be arranged in a limited space. Proportionally, this installation is much more expensive and complicated than in the slab caster.

Despite these drawbacks, thermal mapping for blooms and billets would certainly provide key information to process specialists

3. Ergolines’ approach: Contactless Thermal Mapping with ultrasounds

Ergolines’ idea is to solve these problems by using a completely different approach:

- To develop a non-intrusive, real-time and fully contactless ultrasonic system, without any necessity of CNC machining or customization of the copper tube.
- To provide a cost-effective system, with a long life and virtually no maintenance.

Ergolines’ UT-MAP (Ultrasonic Temperature MAPping system) has very compact dimensions. As a main key-point, the installation of the UT-MAP ultrasonic sensor is outside the water jacket. This is a huge advantage because the customization is made with minimal machining on the water jacket only (long life component) and not on every single copper tube, as currently done with TC or OFC systems. Today the ultrasound technology is mature to provide consistent answers for all these features and has a significant development potential.

UT-MAP is the result of Ergolines’ R&D efforts shared with key clients: The result is an innovative technology enabling real-time and contactless thermal mapping of the copper mold in the meniscus region. The detection region can be potentially extended to the complete mold geometry.

The Ultrasonic Sensor, as shown in the Figure 2, measures the average copper temperatures at four locations in the meniscus region. Each temperature is averaged over a copper volume of approximately 2 cm$^3$. The Meniscus Thermal Profile is obtained by plotting the four temperature values versus the vertical position of the centre of each volume. The temperatures are labelled T1, T2, T3 and T4, where T4 is the closest to the top of the copper tube and T1 is the lowest one in the mold. In fact, for the reconstruction of the meniscus thermal profile and the determination of the steel level from the profile shape, at least four temperature points are needed.
If a larger mold area needs to be monitored, more UT-MAP modules can be installed on the water jacket, increasing the number and extension of the temperature points at different locations along the mold tube.

The installation is quite simple: The water jacket is machined to create an opening for sensor mounting (Fig. 3). As in any billet CCM, the standard copper tube is then inserted into the water jacket without interfering with the UT-MAP sensor case. Since the UT-MAP is equipped with one single cable outlet, it is very easy and practical to bring it out from the mold cartridge.

It is crucial to underline once more that the sensor is installed on the external side of the water jacket and therefore the copper tube does not require any machining or customization. Another important benefit is that there is only one single cable connecting the sensor body with the electronic unit, leading to much easier installation and cable management with respect to
thermocouples or optical fibres. The mold tube remains unaffected and can be changed very easily and quickly at the end of its life, as in any standard installation. As can be seen on the right side of Fig. 3, the front side of the sensor is aligned with the inner wall of the water jacket, enabling the primary cooling water to flow in front of the sensor.

After crossing the water gap, the ultrasound propagates along the copper wall of the mold, and it is then collected by an array of receivers. The raw ultrasonic signals are processed by a mathematical inversion algorithm. The sensor is able to read the copper temperatures with a high sampling frequency. However, one might wonder how fast the system reacts to a sudden temperature variation inside the mold. Due to the high thermal conductivity of the copper, the heat is moving very fast through the mold wall, reaching the “steady state” temperature in few tenths of second. As a direct consequence, a closed-loop control based on the sequence “temperature detection → event recognition → alarm → casting speed modification” is completed in a time frame of one second, corresponding to less than 100 mm of billet path.

<table>
<thead>
<tr>
<th>Topic</th>
<th>TC</th>
<th>OFC</th>
<th>UT-MAP</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Horizontal detection points number</td>
<td>Low</td>
<td>High</td>
<td>Med</td>
</tr>
<tr>
<td>Vertical detection points number</td>
<td>Low</td>
<td>Low</td>
<td>Med</td>
</tr>
<tr>
<td>Maintenance</td>
<td>High</td>
<td>Med</td>
<td>Low</td>
</tr>
<tr>
<td>Response time</td>
<td>Low</td>
<td>Med</td>
<td>Med</td>
</tr>
<tr>
<td>Measurement accuracy</td>
<td>Med</td>
<td>Med</td>
<td>Med</td>
</tr>
</tbody>
</table>

Table 1. Instrumented mold technology: Ultrasonic Technology versus Thermocouples or Optical Fibre Cables.

4. Results of field-testing

Ergolines’ UT-MAP sensor is currently installed in several European billet casters producing mainly high-quality steel. A single UT-MAP module can measure four or eight copper temperatures located at the top of the mold in the meniscus area. In the eight-point configuration the detection area is more than doubled with respect to the 4-point arrangement. The applications are conceived for a real-time thermal mapping of the near-meniscus area, providing information about the first solidification process and the meniscus behavior.

As a second application, both UT-MAP configurations can also be used to measure the instantaneous mold powder thickness, serving as feedback to drive an automatic mold powder feeder in closed-loop mode [10].

The UT-MAP system is typically installed on CCMs for square billets, casting high-quality steels, where achieving a steady-state process with repeatable casting conditions is a must to get a high-quality product.

Fig. 4 and 5 show some interesting field results of real-time temperature detection of the copper tube with UT-MAP.
The steel level is regulated with the feedback from the radiometric sensor. As a consequence, the radiometric signal is constant (dark blue). Powder is added manually. The UT-MAP temperatures T4 (light blue) and T3 (pink) are close to the meniscus and therefore are sensitive to variations of the meniscus position: The UT-MAP sensor clearly detects the typical meniscus perturbation due to manual feeding, visible at the centre of the graph. The saw-tooth pattern of T3 (pink) and T4 (light blue) is well-known: When the operator adds powder, the steel level drops because of the radiometric feedback; when powder is consumed, the steel level rises again.

**Fig. 4.** Negative effects of manual feeding are detected by UT-MAP (four temperatures are measured in the “near meniscus” area, steel level is controlled by the radiometric, powder is added manually).

In Fig. 5, open-loop gravitational powder feeding was performed, and steel level was controlled by the radiometric sensor (blue). The UT-MAP sensor was used to detect copper temperatures at eight locations along the mold. No feedback was provided to the gravitational feeder (open-loop): The UT-MAP was used for monitoring purposes only, not for driving powder feeding. UT-MAP temperature trends clearly show that steel level oscillates significantly when powder is dropped into the mold, causing defects in the final product.

This is an example of how UT-MAP helps process specialists to detect anomalies in powder feeding and to correct them.

**Fig. 5.** Eight-point UT-MAP installed in the “near meniscus” area.

In Fig. 5, the blue line is the set-point of the radiometric sensor. The triangular-wave variation of the radiometric set-point was used to reduce SEN wearing. The T5, T4, T3 trends follow the steel level variation, which is in turn affected by both the radiometric set-point oscillation and the gravitational powder feeding. In this case, due to a significative steel level variation, also the T3, T2 and T1 temperatures are influenced.
5. Potential developments

Ergolines’ has a consolidated experience in the implementation of closed-loop mold powder feeding with inductive or optical sensors [9,11,12,13,14,15,16]. In the recent years, Ergolines has also implemented closed-loop mold powder thickness control based on the ultrasonic sensor [10]. The present installations of UT-MAP are working mainly to provide thermal information of the initial solidification but in several cases the ultrasonic sensor is used also to measure and control mold powder thickness, providing a feedback signal to the automatic powder feeders [6,10].

The temperature trends were cross-correlated with the results of steel quality analysis on tracked billets: Billets cast under manual powder feeding (left side of Fig. 6) featured several occurrences of bleedings and powder entrapment events caused by the saw-tooth meniscus perturbation. On the other hand, defects occurrence was reduced by 80% when powder was added in automatic mode, providing a more stable steel meniscus (Fig. 6, right side).

![Fig. 6. UT-MAP trends detect difference between manual feeding, leading to defects occurrence on tracked billets, and automatic feeding (open-loop), leading to marked defect reduction.](image)

The UT-MAP system is very flexible and suitable for expansions because it is modular. In fact, the sensor arrays can be installed on the water jacket in several positions according to the extension of the area to be monitored: Multiple UT-MAP sensors can be used to obtain an extended thermal mapping of the mold through a modular approach. As an example, an installation with a comprehensive mold thermal mapping for a square billet mold can be based on 48 detection points. The availability of a large number of detection points provides the basis for a very powerful diagnostic tool for the CCMs for billets or blooms: the breakout prevention system.

6. Example of tool utilization: rules for breakout detection

The breakout is mainly generated by the “sticker” effect and its consequence is the loss of the cast, a production stop for hours and high maintenance costs for repairing the damaged strand. The phenomenon has been largely discussed in the literature and one of the outcomes is...
that there is a strict correlation between the temperature trends observed in the mold and the sticker. A typical trend of the temperatures between two consecutive vertical points where the sticker occurs shows a double peak (upper and lower detection point), with a propagation speed a bit lower than the casting speed [2].

The UT-MAP software is able to recognize a deviation from the normal conditions and can suggest an action. The system can implement a lot of different rules that can be fine-tuned by the metallurgist by analysing the events database. The rules interpret the shape correlations of the temperature information. The thermal map is mathematically analysed, and the output of the system is the generation of the “casting status”. According to the system output, the system can suggest to the strand PLC a possible action classified into normal, warning and alarm. The level of confidence (detection of false alarms) can be determined by the metallurgist. This fine-tuning period is fundamental for system reliability increase.

Fig. 7 shows the temperature trends of two vertically consecutive detection points with a sticker event detection. The time frame is 25 s.

The upper temperature T2 (orange) and the lower temperature T1 (azure) are monitored and mathematically analysed. The safety signal (pink) has a minimum (warning threshold) after 7 s from the T2 slope starting and the corresponding raise up of T1 slope, having an intensity similar to T2. The strand PLC suggests to slow down the casting speed.

![Image](image_url)

**Fig. 7.** UT-MAP and Sticker detection.

The possible breakout is prevented and the billet with the sector suffering the sticker can be further analysed to have the confirmation of the solidification defect.

Similar cases can be detected, such as bleeders, corner distortion, powder entrapment events and surface depressions. Every single solidification defect has a different behavior that can be interpreted with a different set of mathematical rules.

**Conclusions**

The CCMs for billets and blooms are generally not equipped with mold temperature probes such as thermocouples or optical fibre cables. In fact, the installation on every single curved copper tube is difficult to perform and very expensive, due to complex machining and congested cabling.

On the other hand, Ergolines’ contactless ultrasonic technology UT-MAP can be installed on the water jacket without any mechanical machining of the copper tubes. The mechanical concept of the mold assembly and of the copper tube remains unchanged. This feature is definitely attractive for the mold thermal mapping applied to billets and blooms CCMs, setting the stage for new potential developments.

Ergolines’ UT-MAP is able to provide real-time mold thermal mapping without a direct contact with the copper mold. Crucial information on the first solidification is obtained from the data provided by the ultrasonic sensors. The detection points are read by a sensor array and
the signal is then processed by a dedicated software, allowing a deep understanding of the progress of the solidification. The system is extremely easy to install and can be applied to both mold temperature monitoring (with possible implementation of break-out prevention) and closed-loop mold powder feeding.

References


[7] Brimacombe, Kumar, Hlady; The continuous casting of stainless steels; Infacon 6, Johannesburg, 1992


ADVANCED TECHNOLOGIES FOR CONTINUOUS BRIGHT ANNEALING OF STAINLESS STEEL STRIP PRODUCTS IN PURE HYDROGEN ATMOSPHERE

Abstract

Stainless steel strip products have a variety of challenging applications in different market segments. Depending on the application of the final product, different heat treatment concepts are required to achieve the target properties in the most cost-efficient way.

This paper reviews the versatile heat treatment applications of continuous bright annealing lines operating under pure hydrogen process atmosphere.

Typically, such lines are used to process various stainless steel grades or special alloys, whose alloying elements have a high affinity to oxidation and are therefore heat treated in hydrogen atmospheres with extremely low dewpoints. This ensures a brilliant surface finish.

The paper will give a practical overview of the challenges, benefits and typical use cases of such lines in different market segments, such as

- Classical austenitic, ferritic, martensitic grades with a focus on highest production rates
- Precision strips with a focus on ultra-thin gauges
- Ni-base alloys with a focus on highest peak metal temperatures

Keywords

Bright annealing, hydrogen, process atmosphere, precision strips, Ni-base alloys

1. Introduction

EBNER Industrieofenbau GmbH is headquartered in Linz/Austria, with subsidiaries in the USA, China and India and a world-wide service network. The company produces heat treatment facilities for the steel, aluminum and copper base metals industries. EBNER is the world market and technology leader in many sectors, and manufactures a wide variety of industrial heat treatment facilities for a wide range of applications.

Facilities used to produce stainless steel flat products include:

- HICON/H₂® bell annealer facilities to base anneal ferritic and martensitic hot rolled steel strip coils
- HICON/H₂® bell annealer facilities to recrystallize ferritic and martensitic cold rolled steel strip coils
- Continuous HICON/H₂® bright annealing lines to recrystallize all grades of stainless steel in process atmosphere
- Continuous HICON/H₂® hardening and tempering lines to harden and temper martensitic grades

This article examines the case of continuous annealing of high-alloyed steel strip in process atmosphere.
2. Challenges and targets of heat treatment

Recrystallization of the microstructure
Following the cold rolling process, work hardened microstructures must be recrystallized in order to achieve a soft structure suited to further processing. With austenitic (CrNi-alloyed) steels, annealing temperatures in the 1100°C - 1150°C range followed by rapid cooling are necessary to achieve a perfect austenite grain without grain boundary precipitation.

Ferritic (Cr alloyed) steels require annealing temperatures in the 850°C - 950°C range, depending on the alloy.

For martensitic (Cr alloyed) steels, particular attention must be paid to avoiding hardening effects (martensite transformation) during heat treatment. Typical annealing temperatures are therefore around 750°C.

Oxidation-free heat treatment cycle
High alloy steels with a content of approx. 18 % Cr, 2 % Mn, 1 % Si and traces of Ti and Al can only be bright annealed using a high hydrogen concentration and the lowest possible dewpoint. Alloys with higher proportions of Mn or Ti are even more difficult. The diagram in Figure 1 illustrates the problems associated with bright annealing steel when it contains alloying elements that have a high affinity to oxygen. It shows the connection between atmosphere dewpoint and annealing temperature in 100 % hydrogen atmosphere.

While for example iron (Fe) can be kept bright at a temperature of 700°C in pure hydrogen with a dewpoint of +60°C, a dewpoint of -60°C is needed at the same temperature as soon as chromium is introduced as an alloying element. In order to prevent oxidation of the chromium (e.g. in the cooling zone, where the temperature passes through the critical range), a low dewpoint and thus a process atmosphere with a high reduction potential is necessary.

Pure hydrogen has the following advantages compared to nitrogen or nitrogen/hydrogen mixtures containing only 4 % hydrogen:
- 7 times the thermal conductivity
- 60 % higher rate of thermal transfer
- stronger reductive effect to prevent oxidation, particularly in combination with lower dewpoints
- improved lubricant decomposition due to hydrogenizing effect
- 1/14 the density, meaning decreased energy consumption for cooling gas circulation
- no nitriding of strip or furnace components
In modern HICON/H$_2^\circledR$ bright annealing facilities, the use of a pure hydrogen process atmosphere with the lowest possible dewpoint (-60°C) is the state-of-the-art technology. This ensures the best possible quality of the annealed products. With a high H$_2$/H$_2$O ratio, the reaction

\[ Me + H_2O \rightarrow MeO + H_2 \]  \hspace{1cm} \text{Eq. 1}

is suppressed and a high reduction potential created in the atmosphere. The reduction potential with a 100 % hydrogen atmosphere and a dewpoint of -60°C (= about 10 ppm H$_2$O) can be calculated as follows:

\[ \frac{H_2}{H_2O} = \frac{1000000 \text{ ppm } H_2 (\approx 100\%)}{10 \text{ ppm } H_2O (\approx -60^\circ \text{C})} = 100000 \]  \hspace{1cm} \text{Eq. 2}

Such a high atmosphere reduction potential is only possible with a metallically encapsulated workload space and a well-engineered sealing system.

**Excellent strip geometry and a flawless strip surface**

In order to achieve flat, ripple-free strip geometry, strip tension must be kept low and precisely regulated during annealing. This is particularly important with thin strip (e.g. precision strip up to 0.02 mm thickness).

To protect the strip surface from mechanical damage, heat treatment must be contact-free: either in a vertical (vertical strand annealer) or horizontal (catenary furnace) arrangement.

### 3. Configuration of a typical vertical bright annealing line

*Figure 2* shows the typical layout of a continuous HICON/H$_2^\circledR$ vertical bright annealing line. The main facility sections are as follows:

- **Pay-off- / inlet section**, consisting of coil cars, pay-off reels, pinch rolls, flatteners, shears, bridles, steering guide rolls, looper, etc. to unwind and transport the cold rolled strip.

- **Strip joining section**, to join strip head- and tail ends and so form a continuous strip.

- **Strip cleaning section**, to remove lubricant residues and iron fines from the strip before it enters the heat treatment section.

- **Heat treatment section** (furnace section), to heat treat the strip in hydrogen (H$_2$) atmosphere.

- **Outlet- / take-up section**, consisting of looper, bridles, inspection stand, steering guide rolls, shear, take-up reel, pinch rolls, coil car, etc. to transport and coil the annealed strip.

- **Electrical equipment with process control system**, to control, supervise and visualize the entire process sequence, calculate annealing programs with automatic setpoint allocation and exchange data with higher-level systems.

HICON/H$_2^\circledR$ vertical bright annealing lines are ideally matched to the strip dimensions and production capacity specifications. They can cover the following spectrum of dimensions and throughputs:

- strip widths: 400 to 1600 mm
- strip thickness: 0.02 to 4.5 mm
- throughputs: approx. 1 to 28 t/h
4. The unique features of a HICON/H$_2$® vertical bright annealing line

**High-precision strip tension regulation using an integrated dancer**

The strip enters the heat treatment section through an inlet seal with driven rolls, passes over a precisely-balanced dancer roll and through the furnace from bottom to top contact-free. Because the dancer is located after the inlet seal (i.e. it runs in process atmosphere), the tension applied to the hot strip is as low as possible and can be adjusted very precisely. This is because the tension is not influenced by friction at the inlet seal. See Figure 3 and Figure 4. Relatively little tension is caused by the weight of the strip, and none or virtually none is added by the dancer. This means that even in long furnaces the lowest possible tension is maintained and excellent strip geometry is ensured.
Low emissions through state-of-the-art burner technology

The heating zone consists of a fiber insulated furnace with a gas-tight muffle (Figure 5), which is heated from outside by all-metal high-velocity gas burners. The stack gas circulates around the muffle, and then passes through a central recuperator into the open. The energy from the entire volume of the stack gas is used to preheat the combustion air. Thanks to the latest ECOburn® burner technology, lowest emissions are achieved - despite the high annealing temperature and high combustion air preheating temperature.

Clean process atmosphere through muffle design

The interior of the muffle forms the workload space, in which the strip is heated up in an extremely dry hydrogen atmosphere. In modern HICON/H₂® bright annealing facilities, the use of a pure hydrogen process atmosphere with the lowest possible dewpoint (-60°C) is standard technology. This ensures the best possible quality of the annealed products. Such a high atmosphere reduction potential is only possible with a metallically-encapsulated workload space and well-engineered sealing systems.

Maintenance-friendly muffle with long service life

When a muffle is heated it expands, and the resulting elongation needs to be accommodated without risk of leaks occurring. The solution for this is a ring-shaped liquid seal, into which the lower end of the muffle extends. This also has the advantage that the heavy inlet plug and seal are not flanged onto the lower end of the muffle; instead they are mounted on top of the inlet seal box and do not move with the muffle (see Figure 6). As a result, the tension on the muffle is as low as possible and permanent elongation of the muffle - due to grain growth at elevated temperatures - is slowed. This increases the stability of the shape of the muffle and extends its service life.

Another advantage of this concept is that the irreversible elongation of the muffle can be counteracted by simply shortening it with a plasma torch. This work can be carried out without removing the muffle and no welding is required.

Symmetrical cooling

Immediately downstream of the heating zone is the symmetrical, multi-stage HICON/H₂® jet cooler, in which the strip is plunge-cooled in hydrogen process atmosphere (Figure 7). The recirculation fans are connected gas-tight to the frequency controlled fan motors and the cooler shell. The cooling gas is re-cooled by a low-maintenance heat exchanger.

A special jet nozzle system provides a high cooling rate and excellent strip stabilization, without risk of overcooling the strip edges. The amount of atmosphere blown onto the strip can be adjusted over the strip width. The adjustable dampers, together with the special design of the jet nozzles and the low strip tension, ensure best possible strip geometry.
Because the cooling zone is located above the heating zone and can be moved sideways away from the facility center line, it is a straightforward procedure to remove the muffle if needed. This can be done within the building tower without need for additional building height.

Beyond the cooling zone, the strip passes through the top roll box (which is equipped with a centering system) and the outlet seal (also equipped with centering system).

**Defined process atmosphere flow**
The inlet and outlet seals are both located at the same level, a design feature that balances the updraft of the hydrogen. Nitrogen locks are also provided in order to ensure the highest degree of safety. The process atmosphere flows against the direction of strip transport from the HICON/H₂® jet cooling zone towards the inlet seal. This achieves the best cleaning effect.

All hydrogen-containing parts are metallically encapsulated and sealed with machined flanges and O-ring seals. Thanks to the entire system being ppm-tight, a dewpoint of -60°C can be maintained inside the workload space when processing with 100 % hydrogen. This prevents partial oxidation of alloying elements with an affinity to oxygen, and enables the processing of materials that are otherwise difficult to bright anneal. In addition to the standard Cr/-CrNi- alloyed grades, Cr-Al-Fe-alloy and Titanium strip can also be annealed. For the latter, argon is used as a process atmosphere.

**Low operating costs**
The highly-efficient design of the facility minimizes utility consumption and operating costs. Compared to alternative designs, savings of up to 55% in operating costs can be achieved. [1], [2], [4]

A hydrogen recycling system can also be implemented to regenerate contaminated process atmosphere. Such a system can reduce the consumption of fresh atmosphere gas by 50 - 70 %. The waste heat from the furnace is recycled in the facility itself, e.g. it is used to preheat the combustion air and to heat both the strip cleaning section and the strip dryer.

**Digital services**
To achieve annealing results that are consistently and reproducibly excellent, an optimized facility design must be paired with a highly-efficient control system. A new approach to this issue is the concept of a "digital twin", into which mathematical models of processes are integrated. These are used to continuously optimize production. The uninterrupted recording of all machinery and production data makes it possible to carry out advanced analyses and machine learning applications, which in turn contribute to the increase in the overall availability and efficiency of the facility. Automated predictions of potential malfunctions and recommendations for proactive response, supporting both preventative maintenance and spare part acquisition, assist the operators and maintenance personnel in their daily tasks.

5. **Wide range of applications in a variety of market segments**

The facility design described above has a wide range of applications. A number of different materials can be processed. These range from the usual types of austenitic, ferritic and martensitic stainless steels to duplex steels, titanium and titanium alloys, nickel-based alloys, cobalt alloys, etc.

In the following sections, a number of these applications in different segments of the market will be examined.
5.1. Use case 1: Market segment - Classical austenitic, ferritic, and martensitic grades, with a focus on the highest production rates

These materials are widely used in the household products industry (washing machine drums, cooking utensils), construction industry (cladding for elevators and facades, street furniture), automotive industry (exhaust systems, tanker trucks), the food and beverage industry (wine tanks, beer kegs, brewery tanks, silos, industrial kitchens) and the petrochemical industry (heat exchangers, pipework). To survive in the market, these products require a manufacturing process that is technologically advanced, energy-efficient, and provides a high production capacity.

<table>
<thead>
<tr>
<th>materials:</th>
<th>cold rolled stainless steels (AISI 200-, 300-, 400- series)</th>
</tr>
</thead>
<tbody>
<tr>
<td>strip width:</td>
<td>max. 1600 mm</td>
</tr>
<tr>
<td>strip thickness:</td>
<td>0.2 - 3.2 mm</td>
</tr>
<tr>
<td>process speed:</td>
<td>max. 80 m/min</td>
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<td>throughput capacity:</td>
<td>max. 28 t/h</td>
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<tr>
<td>heating system:</td>
<td>natural gas</td>
</tr>
<tr>
<td>operating temperature:</td>
<td>max. 1150°C</td>
</tr>
<tr>
<td>process atmosphere:</td>
<td>100 % H₂</td>
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<tr>
<td>dewpoint:</td>
<td>&lt; -60°C</td>
</tr>
</tbody>
</table>

Table 1: Technical data of a high-performance BA-line, based on the example of BGL 1600 at Outokumpu Nirosta / Krefeld / Germany

The highly dynamic operation of the heat treatment section, paired with the precise tuning of the other facility components, allows throughputs up to 28 t/h to be achieved. The heat treatment result is supervised on-line, meaning that process speeds can be optimized to suit the material grade currently being processed and the desired surface finish.

Heat treatment takes place in 100 % hydrogen atmosphere, at the lowest possible dewpoint (-60°C). This ensures a bright strip surface, even with steels containing alloying elements with a high oxygen affinity. In the example of Outokumpu Nirosta, the passivation section that had previously been installed downstream of the bright annealing line was no longer needed: the extremely pure atmosphere made it superfluous.

Together with E³ (Ebner Energy Efficiency) systems like hydrogen preparation and recycling units, a large recuperator, a waste heat recovery system to heat the strip cleaning section, etc. the energy efficiency of the facility is massively increased and extremely low operating costs are ensured.

Figure 8: Cooling zone of a HICON/H₂® high-capacity bright annealing line
5.2. Use case 2: Market segment - Precision strip, with a focus on ultra-thin gauges

These materials are widely used in the automotive industry (catalytic converters, head gaskets, fuel cells), the electronics industry (etched components, stamped components for smartphones, solar/PV/OLED substrates), the food and beverage industry (cartridge filters), the petrochemical industry (filters, heat exchangers, pipework), the medical supply industry (scalpels, needles, clamps, pacemakers, prosthodontics), the construction industry (window spacers) and the footwear industry (safety shoe inlays).

To compete in the market, these products require a manufacturing process that is technologically advanced, energy-efficient and meets extremely high requirements for surface finish. To keep production efficiency as high as possible, there is a trend towards the production of wider and wider strip.

<table>
<thead>
<tr>
<th>materials:</th>
<th>cold rolled stainless steels (AISI 200-, 300-, 400- series)</th>
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<tbody>
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<td>max. 1575 mm</td>
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<td>strip thickness (typical):</td>
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<td>line speed:</td>
<td>max. 70 m/min</td>
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<tr>
<td>throughput capacity:</td>
<td>abt. 8 t/h</td>
</tr>
<tr>
<td>operating temperature:</td>
<td>max. 1150°C</td>
</tr>
<tr>
<td>process atmosphere:</td>
<td>100 % H₂</td>
</tr>
<tr>
<td>dewpoint:</td>
<td>≤ -60°C</td>
</tr>
</tbody>
</table>

*Table 2: Technical data (typical) of HICON/H$_2$® bright annealing lines for precision steel strip*

One of the most important elements in the successful heat treatment of thinnest gauges is precise regulation of the strip tension in the furnace section. This is carried out by a dancer integrated into the workload space, which can be accurately adjusted to very low tension settings. Once past the integrated dancer, which is located just beyond the inlet seal, the strip moves through the muffle of the heat treatment section and the cooling zone without coming into contact with any components.

Together with the high reduction potential of the process atmosphere, this ensures perfect surface quality.

In the spring of 2019, the world's widest bright annealing line for precision strip successfully started production at Arinox S.p.A. / Sestri Levante / Italy. The facility is capable of processing strip with dimensions of 1575 x 0.07 mm.

*Figure 9: HICON/H$_2$® bright annealing line for wide precision stainless steel strip*
5.3. Use case 3: Market segment - Nickel-based alloys, with a focus on the highest peak metal temperatures

These materials, which are extremely resistant to corrosion and heat, have applications in the electronics and electrical industries (heating conductors and resistance strip, magnetic components, electromagnetic shielding), the chemical and petrochemical industries (welded tubes, heat exchangers, industrial furnaces, vessels and tanks), welding (strip electrodes, build-up welding) and the automotive industry (fuel cells, etc.).

These products require a manufacturing process that is technologically advanced and extremely energy-efficient, even as it provides the highest possible material temperatures.

To meet these requirements without losing the advantages of a vertical muffle design, a new facility design has been developed: a vertical double muffle bright annealing furnace.

<table>
<thead>
<tr>
<th>materials:</th>
<th>cold rolled Ni-based alloys (Alloy 602 CA, Alloy 625, Alloy 601, etc.) cold rolled Fe-based alloys (Aluchrom Y Hf, Aluchrom W, Crofer 22 H, etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>strip width:</td>
<td>max. 830 mm</td>
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<tr>
<td>strip thickness:</td>
<td>0.4 - 4.0 mm</td>
</tr>
<tr>
<td>line speed:</td>
<td>max. 20 m/min</td>
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<tr>
<td>heating system:</td>
<td>natural gas</td>
</tr>
<tr>
<td>operating temperature:</td>
<td>max. 1230 °C</td>
</tr>
<tr>
<td>process atmosphere:</td>
<td>100 % H₂ or Ar</td>
</tr>
<tr>
<td>dewpoint:</td>
<td>≤ -60°C</td>
</tr>
</tbody>
</table>

Table 3: Technical data of a HICON/H₂® double muffle bright annealing line, based on the example of VDM Metals / Werdohl / Germany

Vertical muffle furnaces are the current state of the art in the manufacture of stainless steels. They are operated at temperatures between 1130 and 1150 °C. Increasing the operating temperature by 80 - 100 °C, to 1230 °C, means a quantum leap in the demands placed on the materials used and the furnace design. At a temperature of 1230 °C, even the best muffle materials become extremely soft and have only the lowest creep strengths. The challenge is thus to ensure that this furnace component, the one exposed to the highest thermal stresses, has a long service life at high production rates. This challenge can only be met with highly-refined furnace and muffle designs, as well the careful selection of fabrication materials.

In typical furnace designs, with a horizontal muffle, the length of the muffle is restricted: beyond a certain limit, the muffle deforms too severely and fail. Significantly longer muffles with much more shape stability can be used in vertical designs, providing both longer service lives and higher production rates.

To do so, the heated muffle length is split between two muffles. The lower muffle (no. 1) is operated in a "normal" temperature range (1150 °C - 1170 °C), and can be designed to be any required length. The upper muffle (no. 2) is the "high-temperature muffle", and operates at temperatures up to 1230 °C. This muffle is designed to be shorter, and so can be fabricated to suit the special requirements of its application.

In the spring of 2019, the world's first double muffle bright annealing line successfully started production at VDM Metals / Werdohl / Germany.
6. Summary

As a result of comprehensive experience gained from facilities in operation (64, as of this writing) and intensive collaboration with industrial partners, EBNER is able to perfectly tailor each bright annealing line to each customer's needs - while also developing and manufacturing innovative facility designs. This enables EBNER facilities to operate in a wide variety of market segments.

References


Simulation and modelling
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UNDERSTANDING AND OPTIMIZING AOD PROCESS WITH CFD SIMULATIONS

Abstract

Numerical simulations (CFD) have constantly evolved in the last decades and nowadays play an important role in the design and development of modern steelmaking converters. Although the flow inside the converter is highly complex and comprises many physical phenomena like chemical reactions, heat transfer and the flow of gas bubbles in the liquid melt, it’s possible to capture major effects for the design of new converters with modern simulation tools. It is well known that the decarburization reaction is strongly influenced by the partial pressure of CO. To ensure a low partial pressure of CO a flat bath design with low bath height shows advantages. On the other side the bath height needs to be sufficient to ensure enough time for the reactions of the rising gas plume with liquid melt as well as proper mixing. Primetals Technologies has used extensive numerical simulations to compare various bath geometries for a 120t AOD to improve bath mixing and the interaction between slag and steel phase. As a result an optimized flat bath geometry could be found for both good decarburization and reduction reactions. Within its continues improvement initiative Primetals Technologies has also optimized its bath blowing equipment including the valve station, the process media supply as well as the automation and control concept.

In this paper the most important aspects of numerical modelling the flow and mixing inside an AOD converter are described, followed by a detailed comparison of different vessel geometries and presentation of an optimized version.

Keywords

AOD converter, multiphase flow, Eulerian-Lagrangian model, VOF model, CFD, Bath geometry

1. Introduction

Optimum AOD converter vessel and bath geometry is a key for highest productivity in stainless steelmaking. Several design guidelines and operational experiences exist on how an AOD converter should look like to ensure efficient reaction kinetics, long lining lifetime and short processing times and reduced gas consumptions. Often there is a trade-off between these key performance indicators for different process steps. For first and main process step of decarburization, which is influenced by the partial pressure of CO in the melt, low bath heights show advantages. Whereas for the following reduction step sufficient bath height for good mixing with liquid melt as well as good mass transfer between slag and metal phase is required. For better understanding of the influences of AOD converter design on the metallurgical reactions a new CFD model was developed together with K1-MET GmbH in Linz.

The focus of the present study was the reduction phase with inert gas blowing through submerged side tuyeres. To capture the flow phenomena occurring in the converter additional sub-models were developed. This models are described in detail in Chapter 2. The results of
the CFD simulations were compared with operational data from reference plants. Based on this investigation further insights for optimized AOD bath design could be developed.

2. Numerical modelling

The commercial software package ANSYS Fluent [1] was used for all numerical simulations in this work. Beside the standard models, additional sub-models were implemented in order to capture different converter flow phenomena.

The flow of liquid continuous phases (liquid metal, slag, gas) is calculated in Eulerian reference frame. Thereby, a set of conservation equations for mass (continuity) and momentum (Navier-Stokes equations) is solved for incompressible fluid in every numerical cell in the computational domain. The continuity equation for an incompressible fluid reads as follows:

$$\nabla \cdot \mathbf{u} = 0,$$

where \( \mathbf{u} \) is the fluid velocity. The momentum equation can be expressed as

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} = \mathbf{f}_p - \frac{1}{\rho} \nabla p + \nu \Delta \mathbf{u},$$

\( \rho \) and \( \nu \) are the fluid density and kinematic viscosity, respectively, \( p \) is the static pressure, and \( \mathbf{f}_p \) represents the external body force from the interaction with Lagrangian bubbles, see later. A more detailed elaboration of these equations can be found in textbooks on computational fluid dynamics [2, 3].

For the simulation of multiple interacting continuous phases in an AOD converter the Volume of fluid (VOF) model is used. Thereby, an additional equation for the volume fraction for each phase involved needs to be solved. This equation takes the following form:

$$\frac{\partial}{\partial t} \alpha_i \rho_i + \nabla \cdot (\alpha_i \rho_i \mathbf{u}) = S_{\alpha_i},$$

where \( \alpha_i \) is the volume fraction, \( \rho_i \) is the density and \( S_{\alpha_i} \) is the mass source for the phase \( i \).

For the VOF model the phases share one velocity field \( \mathbf{u} \), which means that the material properties of different phases (density and viscosity) in the momentum equation are averaged by the volume fraction \( \alpha_i \):

$$\psi = \sum \alpha_i \psi_i,$$

whereby the following must apply for every computational cell:

$$\sum \alpha_i = 1.$$

In order to capture the species mass transport from liquid metal to slag and vice versa additional sub-models had to be developed. To model the species transport in these two phases, additional equations need to be solved:
\[ \frac{\partial}{\partial t} \rho_i c_j + \nabla \cdot (\rho_i c_j \mathbf{u}) = -\nabla J_j + S_{c_j}. \]  

(6)

c_j is the mass fraction and \( J_j \) is the diffusion flux of the species \( j \) within the phase \( i \), which arises due to the concentration gradient (the influence of temperature is omitted in this work):

\[ J_j = -\left( \rho_i D_{m_j} + \frac{\mu_t}{Sc_t} \right) \nabla c_j. \]  

(7)

\( D_{m_j} \) is the mass diffusion coefficient of the species \( j \), \( \mu_t \) is the turbulent viscosity and \( Sc_t \) is the turbulent Schmidt number. Using the source term \( S_{c_j} \) the specie’s mass can be transferred between metal and slag. As in the case of volume fractions for phases, the sum of mass fractions of species in a phase must equal 1.

The transferred specie’s mass in metal, \( m_{PM} \), and slag, \( m_{PS} \), is a part of the total mass of the respective phase, and is defined by the mass concentration:

\[ m_{PM} = m_M \cdot c_{PM}, \]  

(8)

\[ m_{PS} = m_S \cdot c_{PS}. \]  

(9)

\( m_M \) and \( m_S \) are the total masses, and \( c_{PM} \) and \( c_{PS} \) are the specie’s mass concentrations in metal and slag, respectively. The specie’s mass concentrations at the interface, \( c_{PM}^i \) and \( c_{PS}^i \), are used to define the specie’s equilibrium ratio,

\[ L_P = \frac{c_{PS}^i}{c_{PM}^i}. \]  

(10)

Finally, the mass transfer equations for a specie in metal and/or slag can be formulated as

\[ \frac{\partial m_{PM}}{\partial t} = -A k' \left( c_{PM} - \frac{c_{PS}}{L_P} \right), \]  

(11)

\[ \frac{\partial m_{PS}}{\partial t} = A k' \left( c_{PM} - \frac{c_{PS}}{L_P} \right), \]  

(12)

with the overall mass transfer coefficient \( k' \), valid both in slag and metal:

\[ k' = \frac{1}{\frac{1}{k'_M} + \frac{1}{k'_S L_P}}. \]  

(13)

\( k'_M \) and \( k'_S \) are the mass transfer coefficients in the respective phase, with the unit of kg/m²s. \( A \) is the area through which the flux is calculated. Bottom-injected argon bubbles are represented by point-particle approach in a Lagrangian reference frame.

The acting force \( f_p \) on a single bubble in a given time step consists of several components: virtual mass force, pressure gradient and buoyancy force, and the bubble drag force modelled by Ishii and Zuber [4]. This drag force model accounts for surface tension effects and the departure from spherical shape for viscous particles at large particle Reynolds numbers. Detailed description of the Lagrangian discrete phase model can be found in [5].
3. The simulation procedure

Three different vessel geometries without so called knapsack were considered for the simulations: LX, LY and LZ, Fig. 1. The vessel heights are 7.702 m, 7.289 m and 6.972 m, respectively. The diameters, where argon injection nozzles are situated, are 2 m, 2.23 m and 3.1 m, respectively. The resulting reaction volume is 0.51 m³/t, 0.55 m³/t and 0.55 m³/t. The bath diameter depth ratio is about 1.38, 1.76 and 2.09.

![Fig. 1. Simulated AOD-vessel geometries](image)

To model the decarburisation phase at the current technical point of view is not possible, because we are not able to model the creation of CO bubbles, resulting from the carbon oxidation reaction, in sufficient accuracy. But these Bubbles have a strong influence on the flow inside the converter. The present CFD study therefore was focused on the reduction phase with inert gas bottom blowing only. In this case Argon is injected through six tuyeres situated at a side wall near bottom. The tuyeres are equally distributed over an angle of 100deg. For all geometries grids consisting of approx. 600 000 hexahedral cells are generated.

Overall masses of metal and slag are $m_M = 120 000$ kg and $m_S = 14 400$ kg, with the densities $\rho_M = 6900$ kg/m³ and $\rho_S = 2600$ kg/m³ and the dynamic viscosities $\mu_M = 6.5 \cdot 10^{-3}$ Pa s and $\mu_S = 0.223$ Pa s, respectively.

The initial concentrations of tracer species in metal and slag are $c_{PM0} = 0.001$ and $c_{P50} = 0.025$, with the mass diffusivities $D_{PM} = 1.45 \cdot 10^{-8}$ m²/s and $D_{PS} = 2 \cdot 10^{-10}$ m²/s. [6].

The mass transfer coefficients are $k'_M = 3.95$ kg/m²s and $k'_S = 1.25$ kg/m²s, and the tracer specie’s equilibrium ratio is assumed constant and set to $L_p = 288$.

The mass flow of argon bubbles is $\dot{m}_p = 2.6$ kg/s, with the constant argon density $\rho_p = 0.8$ kg/m³ and the bubble diameter $d_p = 0.005$ m.

Adaptive mesh refinement is applied in regions where slag is present.
4. CFD Simulation Results

Argon bubbles gain momentum as they rise and spread through the liquid metal. In the region where they rise through the slag the plume eye is formed, and the mixing of slag with liquid metal is enhanced, Fig. 2. At sufficiently high argon flow rates the slag is entirely ripped and mixed with metal and also with the gas from the upper side of the vessel. Argon bubbles are released at the bottom and near the left wall, Fig. 1, and as the liquid metal heights are different for the three geometries, their velocity at the slag-metal interface is also different. The highest bubble velocity develops in the LX-case, so for this case the plume eye is narrower, and the slag retains the most compact form.

In Fig. 3 the multiplied volume concentrations, $\alpha_{\text{slag}} \cdot \alpha_{\text{metal}}$, are shown. The lowest value of this parameter is 0, which means that either $\alpha_{\text{slag}}$ or $\alpha_{\text{metal}}$ (or both) is 0. Maximum value is 0.25, and in these cells both phases are equally present, $\alpha_{\text{slag}} = \alpha_{\text{metal}} = 0.5$. Due to higher bubble velocities and thus higher momentum induced in the liquid metal, the best mixing of metal and slag is reached for the LX-case. The result of this mixing is the enhanced interfacial area between metal and slag and increased tracer specie’s mass transfer rate. This also means that separation of slag from liquid metal at the end of the process will be more tedious for the LX-case.
The influence of vessel geometry, precisely the height of liquid metal in the vessel, on the momentum which is brought into this phase is clearly depicted in Fig. 4, where velocity vectors in a vertical mid-plane for the three cases are shown. The highest velocities appear in the LX-case, the lowest in the LZ-case.

This can also be seen in Fig. 5, where liquid metal mean velocities are monitored over time. As the bubbles are injected asymmetrically, on the left side of a vessel, one huge circular flow pattern is initially formed. This flow pattern is then disturbed by the fluctuations of slag-metal interface and the geometry itself. The weakest flow pattern is formed in the LZ-vessel, because of the lowest height and the largest bottom area of this vessel.
The development of the tracer specie’s concentration in liquid metal is shown in Figs. 6 and 7. As the equilibrium ratio in Eq. 10 is high, the direction of mass transfer is from metal to slag, i.e. the tracer specie leaves the metal and enters the slag. Due to enhanced interfacial area this transfer is highest in the LX-case, whereas for LZ-case only very slow transfer is observed. The tracer concentration in metal decreases with time, so the concentration in slag must increase.

**Fig. 5.** Mean velocities in liquid metal phase
Fig. 6. Tracer specie’s concentration (kg/m³) in liquid metal during the process
Fig. 7. Tracer specie’s concentration in metal and slag

Besides the fast transfer of the specie across the metal-slag interface, its homogenisation in the liquid phase is also of importance. In the case of fast mass transfer (LX), the areas of high concentration deviation from the mean value will always remain for a longer time period. In the LZ-case, the mass transfer is so low that the regions of high deviation develop near the metal-slag interface, and the mixing is too weak to equalize this inhomogeneity over the liquid metal. Thus, the best mixing efficiency and most homogeneously distribution of tracer in the liquid phase shows the LY-case.

5. Comparison with operational data and reference installations

For the CFD simulation only the reduction phase was taken into account, as it is not possible to model the decarburisation phase at the current technical point of view. The CFD simulation pointed out that for the reduction phase a converter with flat bath design shows disadvantages, as we observe lower velocities, worse mixing and a worse mass transfer for a flat bath design. This findings can be transferred also to decarburisation phase to a certain extend. On the other hand it is well known that the decarburization reaction is strongly influenced by the partial pressure of CO. By reducing the partial pressure of CO the equilibrium in the liquid melt is moved. The influence of the partial pressure can be seen on figure 9. As it can be seen from figure 9 for a partial pressure of 1bar a masscontent of 0.1 % for oxygen and carbon can only be achieved only under considerable oxidation of chrome, while by reducing the partial pressure for CO to 0.02 bar an O-content of 0.02, and an C-content of 0.03 can be achieved with an amount of 17% of Cr in liquid melt, without any oxidation of chrome. [7]
Fig. 9. Equilibrium between carbon and oxygen in iron-chrom-heat at 1800°C and an partial pressure of CO of 1bar and at 1600°C and partial pressure of CO of 0.02bar [7]

To ensure a low partial pressure of CO a flat bath design with low bath height shows advantages. This findings fit well to the experience of Primetals technologies that there is an optimum bath geometry that both ensures both high decarburization efficiency and good mixing and high mass transfer rates.

Primetals Technologies as one of the leading suppliers for stainless steelmaking has installed over 25 new AOD converter in the last two decades. In Figure 10 key performance indicators are shown for optimized vessel and bath geometry based on the installed AOD converter. To ensure high blowing rates without risk of slopping a specific reaction volume of around 0.6m³/t showed good results. An optimum bath geometry for both high decarburization efficiency and good mixing could be found with a diameter to depth ratio of around 2. Besides the bath geometry also the tuyere amount and arrangement is very important for high AOD process efficiency and long lifetime of the lining. For the simulation the six tuyeres are equally distributed over an angle of 100degree. From operational experience sufficient distance between the tuyeres is important minimum refractory wear. Therefore an angle of 100 to 120deg is recommended for the tuyere arrangement. Depending on the heat size, the tuyere diameter and number can vary in this range. In a next step the variation of tuyere number and position will be investigated by CFD study and their influence on mixing and mass transfer will be examined.
6. Conclusion

A mass transfer process in an AOD converter is investigated by means of numerical simulation. Thereby, special attention was laid on the influence of different geometries on the development of the metal-slag interface and the associated transfer rate.

This work represents a first step towards a complex converter model, which will incorporate many effects which are important for secondary steelmaking. Although at this state some important phenomena, such as top lance blowing or the decarburisation process, are not yet considered, many observations and comparisons can still be made. The CFD model helps us to better understand the process ongoing inside the converter and how changes in the bath design influence our process.

The CFD simulation pointed out that for the reduction phase a converter with deep bath design (LX-case) shows advantages, as we observe higher velocities and a better mass transfer for a deep bath design. On the other hand it is well known that the decarburization reaction is strongly influenced by the partial pressure of CO. To ensure a low partial pressure of CO a flat bath design (LZ-case) with low bath height is preferred. Thus, the best mixing efficiency and most homogeneously distribution of tracer in the liquid phase shows the LY-case. This findings fit well to the experience of Primetals Technologies that there is an optimum bath geometry that both ensures both high decarburization efficiency and good mixing and high mass transfer rates.

Based on this experience and the feedback from numerous plants a bath geometry with a bath diameter ratio of around two (Design LY) turned out as the best compromise. This support Primetals Technologies latest AOD design and will help to further optimized the bath geometry for increased productivity.

The actual CFD simulation model will be further developed with the goal of more detailed investigation of Argon injection and the influence of the tuyeres amount and arrangement.
References

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THERMOKINETIC SIMULATION OF $\sigma$ PHASE IN DUPLEX STEELS

Abstract
The present paper presents a new thermodynamic modelling of $\sigma$ phase for calculation of thermodynamic equilibria in multicomponent systems. These results are then used for thermokinetic precipitation simulation in austenitic stainless steels and duplex stainless steels. The presented kinetic results are preliminary but the trends are promising in terms of further understanding of the role of $\sigma$ phase on materials degradation and an optimization of the chemical composition of the steel for improved properties.

Keywords
Sigma phase, Sublattice model, Thermodynamic modeling, Heterogeneous precipitation, Kinetics

1. Introduction

The formation of $\sigma$ phase in various technological steel grades is crucial for materials properties due to embrittlement caused by the precipitation of $\sigma$ phase at the grain boundaries. Thus, understanding and prediction of its temperature and composition dependent stability is required, which can be obtained by thermokinetic modeling.

In the present work, we propose a revised thermodynamic modeling based on crystallographic site occupancies of dissolved elements Fe, Cr, Ni, Mo, Si which obey the crystallographic understanding of the $\sigma$ phase. These results are improved thermodynamics of the phase, associated with more physics-based simulative predictions on phase stabilities. The model chosen here for the sigma-phase description in the system Fe-Cr-Ni-Mo-Si has been first developed in the Fe-Cr system [1].

Based on the revised model, we have carried out thermokinetic simulation of the precipitation of $\sigma$ phase in austenitic stainless steels and duplex steels, which allows us to understand the nucleation and growth behaviour of $\sigma$ phase formation as function of steel composition, temperature and time, targeting at optimised alloy and process design for improved materials properties.

2. Thermodynamic model – development and validation

The thermodynamic model is developed with the Calphad (Calculation of Phase Diagram) method based on the compound energy formalism (CEF). We have developed a three sublattice model as described by Jacob et al. [1] which, in Fe-Cr, is written $(\text{Fe, Cr})_{10}(\text{Fe, Cr})_{4}(\text{Fe, Cr})_{16}$. This model allows to describe the full homogeneity range of the $\sigma$ phase in this system and provides consistent site occupancies with experimental crystal-structural data as shown Fig. 8 of [1]. Our extension of the model to multi-components reads $(\text{Fe, Cr, Ni, Mo, Si})_{10}(\text{Fe, Cr, Ni, Mo, Si})_{4}(\text{Fe, Cr, Ni, Mo, Si})_{16}$.

The calculated phase equilibria for duplex steels (chemical composition given in Table 1) are given in Fig. 1 and the obtained chemical composition of the $\sigma$ phase is compared to experimental data [2].

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2 TU Wien/Institute of Materials Science and Technology
Table 1 – Chemical composition (wt. %) of duplex steels according to Villanueva et al [2].

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duplex</td>
<td>0.025</td>
<td>22.04</td>
<td>5.49</td>
<td>2.91</td>
<td>1.72</td>
<td>0.47</td>
<td>0.14</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

![Fig. 1](image)  
**Fig. 1.** Phase stability of Duplex steel according to the present thermodynamic modeling.

![Fig. 2](image)  
**Fig. 2.** Calculated chemical composition of σ phase as compared to experiments [2].
In principle, the calculated chemical σ phase composition as shown Figure 2 from the present work provides good consistency with experimental data. Improvements will focus on the ternary interactions among Fe, Cr and Mo, aiming on stabilising more Fe on cost of Mo and Cr in the phase.

3. Thermokinetic precipitation

Kinetic precipitation simulation was carried out using the Matcalc software package [3]. The particles nucleation and growth is modelled with classical nucleation theory, and the evolution of chemical composition and mean radius of precipitation are evaluated by mean field approach.

In first approach, the new thermodynamic model was tested on austenite stainless steel 316 where there exist experimental data on isothermal aging at 800 °C. Weiss et al. [4] have shown the sequence of precipitation in austenite stainless steels, containing the intermetallic phases χ and σ and Laves phase, and carbide M_{23}C_6. According to Weiss et al. [4], M_{23}C_6 precipitates first, then χ and σ and finally Laves phase. For this simulation, the austenite is used as precipitation domain, the M_{23}C_6 and σ phases are set to precipitate at grain boundaries (gb) and the χ and Laves phase in dislocation.

In Figure 3, time evolution of precipitate phase amount is shown as preliminary results. These results reproduce well the sequence of precipitation, i.e. M_{23}C_6 → χ → σ. Only the Laves phase is not precipitating. Further work must be done, refinement of its thermodynamic...
description and consideration of potential kinetic controls, for the precipitation of this phase to have a conclusive predictive simulation.

Predictive time-temperature-precipitation (TTP) simulation of σ phase precipitation in austenite matrix in stainless and Duplex stainless steel grades using the same kinetic parameter setup as for the presented isothermal case of austenitic stainless steel has been performed. The chemical compositions of the studied materials are given in Table 2.

Table 2 – Chemical compositions of the studied steels (wt. %) in the TTP simulation.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless</td>
<td>0.06</td>
<td>19</td>
<td>12.5</td>
<td>2.7</td>
<td>1.4</td>
<td>0.4</td>
<td>0.1</td>
<td>Bal.</td>
</tr>
<tr>
<td>Duplex</td>
<td>0.03</td>
<td>22.05</td>
<td>5.70</td>
<td>2.26</td>
<td>1.77</td>
<td>0.36</td>
<td>0.14</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Fig. 4. Time Temperature Precipitation (TTP) of σ phase in austenite for stainless and duplex steels.

The TTP diagram (Figure 4) shows an enormous shift of the nose of precipitation of σ phase depending of the kind of steel. In duplex steels, the σ phase precipitates much faster and starts to form at higher temperature. This is due to a higher Cr content, promoting the formation of σ phase. This huge difference is particularly mentionable since the difference of Cr-alloying between the two studied steel grades is only 3 wt.% . Further, this indicates the relevance of precise matching between experimental and predicted dissolutions of elements in the σ phase for quantitative predictions. Our simulation results are thus preliminary, since we
currently work on refined simulative Cr-dissolution in sigma phase and calibration of kinetic parameters, particularly the role of grain boundary energies for heterogeneous precipitates.

**Conclusion and outlook**

In the present work, we have shown preliminary results for precipitation of σ phase in austenitic and duplex stainless steels with a more appropriate thermodynamic modelling of σ phase than previously available.

Based on successful thermokinetic simulation of precipitation trends in setups with individual single alloy matrix phases, we aim on physics-based predictive modeling and simulation of the role of real austenite-ferrite duplex environments. By this, the temperature- and composition dependencies of σ phase formation and evolution, and its competition with other precipitation phases will be better understood.

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COMPUTATION OF COMPETITIVE PRECIPITATION OF ETA CARBONITRIDE PHASE, Z-PHASE NITRIDE, AND INTERMETALLIC G-PHASE AT VARYING NITROGEN CONTENTS IN Nb- AND Si-ALLOYED AUSTENITIC STAINLESS STEEL

Employing computational thermodynamic calculations of equilibrium phase fractions in austenitic stainless steels, the applicability of conventional M6X-model with 4 distinct crystallographic sites for eta-carbonitride phase is discussed. It is shown that this model leads to artificial phase stability and composition at high nominal Si-contents. An improved model with 5 different crystallographic sites can solve this problem and reproduces the experimental tendencies of h-phase stability. Using available compound energy models for intermetallic G-phase, and Z-phase nitride in the thermodynamic MatCalc database ME-Fe, relative precipitate stabilities as function of varied steel composition and heat treatments of stainless steels, as predicted by thermokinetic simulation, are discussed.

Keywords
Cr3Ni2SiX, Eta-carbonitride, M6C, austenitic, stainless, thermokinetic.

1. Introduction

M6C-structured diamond face-centered cubic eta-carbonitride phase (in the following η-phase) precipitates in some Si-containing 20-25 austenitic stainless steel grades [1,2] and irradiated type 316 [3,4]. This phase forms typically after long-term aging of at least several hundred hours. Once nucleated, the phase shows faster growth than other precipitates such as Zet-phase [5]. Eta-carbonitride Cr3Ni2SiX will thus significantly affect microstructure and consequently influence creep strength of the material. Due to structural and morphologic similarities, η-phase is often hard to distinguish experimentally from M23C6 and G-phase. A better knowledge of the theoretic stability of η-phase, by evaluating its Gibbs energy computationally, is a valuable contribution for the prediction of phase relations and related microstructural development of stainless steels. A better knowledge of the theoretic stability of η-phase, by evaluating its Gibbs energy computationally, is a valuable contribution for the prediction of phase relations and related microstructural development of stainless steels.

Here we show that the conventionally used model with 4 distinct crystallographic sites for η-phase (i.e. the M6(C,N) phase description in available thermodynamic databases) leads to an artificial phase stability and wrong composition at high nominal Si-contents. An improved model with 5 different crystallographic sites can solve this problem and reproduces the experimental tendencies of η-phase stability.
2. Previous studies

Typically, \(\eta\)-phase in austenitic stainless steels dissolves Cr, Ni and Si, close to the stoichiometry \(\text{Cr}_3\text{Ni}_2\text{Si(C,N)}\). With 4 distinct crystallographic sites in the conventional 4-sublattice (SL) description \((A2B2D2)\text{(C,N)}, A=\text{Cr}, B=\text{Ni}, D=\text{Cr,Si}\) for Si-containing M6X [6] \((X=\text{C,N})\) one inevitably obtains an artificial, high stabilization of \(\eta\)-phase at nominal Si-alloying above 1.5 wt.% in steel (Fig. 1). Furthermore, under this condition the calculated equilibrium phase dissolves Si far beyond the formula content above, whereas its Cr-content is only half of the typical experimental values.

![Fig. 1a](image1a)
![Fig. 1b](image1b)
![Fig. 1c](image1c)

Fig. 1. (a) Calculated equilibrium phase fractions in austenitic stainless steel as function of temperature with \(\eta\)-phase with \((A2B2D2)\text{(C,N)}\) description included at 1.2 wt.% Si-alloying, (b) calculated equilibrium fraction of \(\eta\)-phase, revealing artificial phase stability to very high temperatures, and (c) Si-content in \(\eta\)-phase in at.% in austenitic stainless steel at varying nominal Si-alloying in wt.% (isolines), modeled with 4-SL description \((A2B2D2)\text{(C,N)}\).

Sourmail & Bhadeshia [1] found \(\eta\)-phase in austenitic stainless steel N709, alloyed with 0.41 wt.% Si. Optimizing of the Gibbs energy of \(\eta\)-phase to reproduce this observation leads to appearance of the phase in equilibrium calculations of Si-containing 9 to 12% Cr-steel grades. This contradicts the experimental observation. Moreover, the widely used 2-2-2-1 description of M6X / M6C in available thermodynamic databases does not obey the reported Wyckoff-positions of the phase. It is clear that the inadequate prediction of thermodynamically stable \(\eta\)-phase in 9 to 12% Cr-steel is related to the model of \(\eta\)-phase, since multi-component databases used (mc_fe [7]), properly consider Si-dissolution in other phases such as Laves-phase and alloy phases. On the other hand, the remaining free Si-content
that can be incorporated in η-phase should thus be depicted correctly, when a physically sound model is chosen for η-phase.

The role of dissolved C for the stability of η-phase has been discussed controversially: Jargelius-Pettersson [2] proposed a composition close to pure nitride, which has been confirmed later by Their et al. [11] and by Sourmail & Bhadeshia [1]. In contrast, older studies suggest significant C-solubility [3,4]. On the other hand, reduced N-alloying will stabilize Ni-Si-rich, N-free G-phase Ni16Nb6Si7 instead of Cr3Ni2SiX in Nb-containing steel grades, such as NF709 [1].

Si has been reported to be particularly prone to segregation and enhanced diffusion during irradiation, and Si, Ni and Cr revealed increased diffusivities, several times higher than their bulk diffusivities. This behavior is clearly relevant for the question of competing Si-stabilized Cr3Ni2SiX and G-phases, and indirectly also the evolution of CrNbN Z-phase.

3. Thermodynamic modeling

In order to reduce the amount of dissolved Si in η-phase modeled by conventional (A)2(B)2(D)2(C,N) M6C-description, we first tried to exchange Si by Ni, Cr or vacancies in the (D)2-sublattice. This, however, led to even stronger stabilization of η-phase. In the conventional M6X model, Si tends to completely fill up the (D)2-site already at 2wt.% Si-alloying. A proper way to prevent this artefact is to allow less, or less preferred structural sites for Si-dissolution in η-phase. We propose the alternative 5-SL M6X model (A)2(B)2[(D)(D')]2(C,N) with split (D)2-site [8]. Theoretically, (A)2 and (B)2 sites have same mean bond lengths to surrounding atoms between 0.23nm and 0.27nm, whereas (D)2 crystallographic site contains two different bond lengths (0.23 to 0.27nm for shorter bonds, and 0.282nm for longer bonds) to surrounding metallic atoms [9]. Si has a significantly smaller atomic radius \( r_a(Si) = 0.11\text{nm} \), than \( r_a(Ni) = 0.15\text{nm} \) and \( r_a(Cr) = 0.17\text{nm} \). Due to this large size difference of more than 25%, Si will be “rejected” from (D)2 sites filled up by larger Cr and Ni and will likely order to “subsite” D’ of (D)2, with associated energetically optimized bonding. Further, interstitial N \( (r_a = 0.056\text{nm}) \) in η-phase can result in some deviations from the ideal crystallographic structure of M6C \( (r_a(C) = 0.067\text{nm}) \). In the modified M6X structural formula, D or D’ will be preferentially filled up by Si. When Si sits, e.g., mostly on D, Cr needs to be the predominant element on D’ in order to keep the typical stoichiometry of η-phase. High Si-alloying will not change this constraint. Our 5-sublattice description results in the formula Cr\(_{3-x}\)Ni\(_{2-y}\)Si\(_{1+x+y}\)N. For stoichiometric η-phase with respect to metallic atoms, Cr\(_3\)Ni\(_2\)Si(C,N), the associated sublattice description reads (Ni)2(Cr)2[(CrNi0Si0)(Si)]2(C,N), and 8.96 wt.% Si are dissolved in the phase. Non-stoichiometric η-phase was reported by Sourmail & Bhadeshia [1] in austenitic stainless steel N709. These authors measured 11 to 16 wt.% Si in η-phase, together with reduced Cr- and Ni-contents relative to stoichiometric Cr\(_3\)Ni\(_2\)Si(C,N). Concerning these reduced solubilities, it should be mentioned that Sourmail & Bhadeshia’s η-phase comprised considerable amounts of Mo and Fe, which complicates exchange mechanisms among atoms dissolved in the M6X structure. Nevertheless, Si-overstoichiometry suggests more than 1 moles of potential crystal sites per formula unit, in accordance with the 5-SL description (Ni)2(Cr)2[(Cr,Ni,Si)(Si)]2(C,N). With this model, Si-overstoichiometry is naturally coupled with Cr- and Ni-understoichiometries, and the η-phase formula becomes Cr\(_{3-x}\)Ni\(_2\)\(_{y}\)Si\(_{1+x+y}\)(C,N). In contrast to the conventional M6X model, solubilities can be well controlled in the model parameterisation of the 5-SL model. Higher local Si-contents will promote η-
phase formation, as indicated by the thermodynamic calculation results shown in Fig. 2. Note that with the 4-SL description (Fig. 1) higher Si-concentrations in steel are required to stabilize η-phase.

Fig. 2. (a) Calculated equilibrium phase fractions in austenitic stainless steel as function of temperature with η-phase with stoichiometric (Ni)2(Cr)2[(CrNi0Si0)(Si)]2(C,N) description included at 0.5 wt.% Si-alloying, (b) calculated thermodynamic stability of η-phase with stoichiometric (Ni)2(Cr)2[(CrNi0Si0)(Si)]2(C,N) description in austenitic stainless steel at varying nominal Si-alloying in wt.% (isolines).

4. Thermodynamic computations and precipitation simulation of Si- and Nb-alloyed, N-containing stainless steel grades

G-phase and η-phase discrimination by electron microscope techniques is difficult, since they both form with an fcc-structure, and even lattice parameters do not differ strongly. Thus, thermodynamic modeling and kinetic precipitation simulation can help to interpret microstructural trends from short- to long-term aging and phase evolution of metastable and stable phases. This will further allow for a clearer picture of the role of phase stabilities for creep resistance. Moreover, irradiation effects on phase stabilities, based on known segregation and diffusion enhancements, can be tackled by thermokinetic simulation. Here, we present comparisons of simulation results using the MatCalc Engineering database ME-Fe, which contains the new η-phase model in addition to proper G-phase and Z-phase models, which makes this database a suitable tool for thermodynamic equilibrium and thermokinetic precipitation computations in complex high Cr-Ni alloyed stainless steels with additions of Si, Nb and N.

Sourmail & Bhadeshia [1] found Z-phase, sigma and Cr3Ni2SiX in NF709 stainless steel with the composition Fe bal. – 20Cr25Ni1Mn1.5Mo0.41Si0.26Nb0.17N0.06C after 10000 h at 800°C, which should represent a close-to-equilibrium state. Fig. 3 shows the thermodynamic equilibrium phase fractions as function of temperature in NF709.
Eta-carbonitride (denoted M6C#01 due to its modeling by a M6X-miscibility gap between (Cr,Mo)6C and (Cr,Ni)6N types, equilibrium dissolution temperature 825°C) is expected to form an equilibrium phase at 800°C, together with Cr2N (hcp_A3#01 with MatCalc, representing the Cr-Nitride hexagonally close-packed structure of the hcp-alloy / Mo-carbide / Cr-nitride miscibility space, i.e. thermodynamically one description with miscibility gaps between alloy phase, carbide and nitride phase), M23C6, CrNbN Z-phase and intermetallic sigma-phase.

Testing isothermal kinetics of competing precipitate evolutions in this steel grade at 800°C (Fig. 4 a), after 10000h η-phase has almost reached its “end of life” after its nucleation, growth and coarsening. This is particularly caused by the increased relevance of Cr2N as function of aging time, i.e. more and more Cr preferably included in Cr2N than in Cr3Ni2SiN phase.

The simulative reproduction test of the isothermal aging treatment of NF709 revealed less stability of Cr3Ni2SiX phase after long time. This changes considerably with only slight increase of Si above the nominal composition of 0.41 wt.%. The simulation for an only
slightly increased Si-content of 0.45 wt.% nominal Si is shown in Fig. 4 (b). Now, Cr3Ni2SiX phase is more than twice the simulation result with 0.41 wt.% Si and remains stable after 10000h of isothermal aging. This result would agree with the experimental observation. Our simulation strongly indicates that prior-to-precipitation Si segregation at earlier heat treatment stages may have cleared the way for favoured Cr3Ni2SiX stabilization as heterogeneous precipitates. This is actually not surprising, since Si-segregation to interfaces is a common phenomenon in stainless steels [3,4], as, e.g., also observed recently by xxx using 3D-APT analysis. For the stabilization of G-phase competing with Cr3Ni2SiX, heavy Si-segregation of more than 1 wt.% Si, and lower temperatures of 500°C long-term isothermal aging would be necessary. Interestingly, in this case Si alone can lead to G-phase stabilization, since our result has been obtained at unchanged nominal N-content of the steel.

Irradiation in nuclear applications of stainless steels can increase the effects of segregation, but also diffusion enhancement has been proposed, for instance for Cr, Ni and Si. For these elements, diffusivities in Fe-matrix, C-doped and N-doped Fe-matrix of 10 times the default diffusivity by using the MatCalc Engineering diffusion mobility database ME-Fe was tested in the simulation. In general, the influences on precipitate fractions were not significant. In the framework of irradiation, and particularly irradiation-induced segregation of Si at various defects, austenitic stainless 316-based materials have been repeatedly researched. For competing nitride and G-phase precipitation, Nb-alloyed variants are interesting. Here, we look at a modified SS316-type with Nb-alloying of 10x the nominal C-content. The increased Nb-alloying compared to NF709 indeed stabilizes G-phase considerably, and even at 0.1 wt.% of Nitrogen G-phase appears as competing equilibrium phase (see Fig. 5) to η-phase and Z-phase below 550°C. Further, M23C6 carbide is found, as well as intermetallic phases sigma and Laves-phase.

![Graph showing phase fractions](image-url)

Fig. 5. Computed thermodynamic equilibrium phase fractions in modified SS316 with Nb-alloying with ME-Fe.

The isothermal kinetic precipitation simulation at 500°C however does not yield G-phase but eta-carbonitride instead (Fig. 6 a), even though the equilibrium phase fraction of G-phase is higher (See Fig. 5). In the following, the diffusive control for this kinetic behaviour is discussed.
The situation changes (as expected) at lower nominal N of 0.01 wt.%, but also and importantly, when an irradiation scenario is mimicked by diffusion enhancement of Cr, Ni and Si by a factor of 5 as compared to the diffusivities of these elements, as included in ME-Fe.ddb. Now, as shown in Fig. 7, G-phase forms and even “overtakes” the η-phase after long-term aging. Kinetic phase fractions in aged SS316 at the relatively low temperature of 500°C are an order of magnitude below the precipitate fractions at 800°C in NF709. At this temperature, neither G-phase nor η-phase can be stabilized in SS316-type, but MX Nb-carbonitride / Z-phase will form instead.

5. Discussion

The relative role of N and C for the η-phase stabilization:

Little is known about the relative roles of N- and C-dissolution in eta.-carbonitride. Here, we discuss this question on our thermodynamic modeling base. Fig. 7 shows the changing equilibrium phase fractions of η-phase with the new modeling, when nominal N- or C-compositions of stainless steel are changed. Other (competing) phase fractions are not shown in the Figures.
Fig. 7. Calculated thermodynamic stability of $\eta$-phase with stoichiometric $(\text{Ni})_2(\text{Cr})_2[(\text{CrNi0Si0})(\text{Si})_2(\text{C,N})]$ description in austenitic stainless steel (a) at varying nominal N-alloying in wt.% (isolines) at constant Si-alloying of 1 wt.% and 0.1 wt.% C, and (b) at varying nominal C-alloying in wt.% (isolines) at constant Si-alloying of 1 wt.% and 0.1 wt.% N.

The calculated phase fraction of $\eta$-phase increases with increasing N-alloying (Fig. 3a), up to a maximum, which is defined by balanced $\eta$-phase and Cr2N fractions (not shown in Figures). At even higher nominal N-contents, Cr2N starts to dominate over $\eta$-phase. The stability of $\eta$-phase decreases with increasing C-alloying (Fig. 3b). This is due to increasing predominance of M23C6. Assessed multi-component thermodynamics propose only slight maximum C-solubility: For typical C-contents of 0.1 wt.% in stainless steel the C-content in $\eta$-phase remains below 0.2 wt.%. Trying to increase this value by the Gibbs energy optimization, one would again obtain inadequate thermodynamically stable $\eta$-phase in 9 to 12% Cr-steel. These findings support the predominant role of N relative to C for the stability of $\eta$-phase.

Competitive precipitation:

With increasing Si-content compared to the nominal NF709 steel composition, and as suggested due to prior-to-precipitation segregation, the $\eta$-phase is more stabilized. The present kinetic simulation suggests that slightly heterogeneous Si-distribution / Si-segregation in this steel grade would be required to prefer $\eta$-phase remaining stabilised after the very long aging time of 10000h. Otherwise, Cr2N is suggested to replace $\eta$-phase as a function of prolonged aging. Only at very high Si-enrichments of more than 1 wt.%, intermetallic G-phase becomes relevant in NF709. In Nb-alloyed SS316 steel, G-phase becomes more important than $\eta$-phase towards long isothermal aging times even at relatively high N-content, when increased Cr-, Ni-, and Si-diffusivities in the alloy matrix are considered. This simulative finding indicates the important role of irradiation-affected diffusion for the stabilization of G-phase relative to Cr3Ni2SiX in Nb-enriched steel grades. Testing Si-increase beyond the nominal composition of 316-type, the same trend of stabilised G-phase relative to $\eta$-phase is found by simulation.
6. Conclusions

The application of conventional 4-SL M6X-description \((A)2(B)2(D)2(C,N)\) in Si-containing austenitic stainless steels revealed problems: \(\eta\)-phase became too stable at high Si-alloying, and its calculated composition deviated strongly from the experimentally determined stoichiometry. The new 5-SL model \((A)2(B)2[(D)(D')]2(C,N)\) solves the problem and is thus an improvement of the thermodynamic M6X-description. Among the interstitial elements, \(\eta\)-phase prefers to dissolve N, whereas thermodynamics suggest only small C-content. Computer-based thermodynamic calculations confirm the influence of local Si-enrichment in steel on the precipitation of \(\eta\)-phase.

In simulations of stainless steel NF709, Cr3Ni2SiX precipitates are stabilized during isothermal aging at 800°C, but tend to be replaced by Cr2N after very long times of 10000h. With increasing Si-content, as suggested due to prior-to-precipitation segregation, the eta-carbonitride \(\eta\)-phase is more stabilized. Only at very high Si-enrichments of more than 1 wt.\%, intermetallic G-phase becomes relevant in NF709.

In stainless steel alloys with higher nominal Nb-contents, combined with relatively high Si, i.e. modified SS316 grade, G-phase is a relevant competitor to \(\eta\)-phase in the precipitation sequence at isothermal aging. In the investigated steel grades, Z-phase nitride CrNbN, and MX-Nb(C,N) are further relevant. Their precipitation is not significantly affected by G-phase.

Our simulations indicate that Si and particularly Si-enrichments by thermally or irradiation induced segregations play a decisive role for the formation of eta-carbide and the potential competition with G-phase. Whereas enhanced diffusivities of Si, but also Cr and Ni do not affect the phase formation of Cr3Ni2SiX significantly, they promote G-phase precipitation.

First principles calculations are planned for atomistic validation of the physical correctness of the new model. Multi-component validation of the new M6X model will have important implications in various steel grades with known M6C formation.

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References

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SIMULATION OF ELECTROMAGNETIC STIRRING IN CONTINUOUS CASTING OF STAINLESS STEEL

Abstract

Electromagnetic stirring in the bending zone of a continuous casting machine is known to increase the amount of equiaxed crystals. A simulation model for the liquid steel flow and temperature under the influence of an electromagnetic stirrer has been developed in order to optimise the design of such a stirrer. The turbulent flow of the liquid steel inside the strand as well as the magnetic field and its forces acting on the liquid steel are calculated in transient simulations. The stirring intensity and the stirrer position are varied in the simulations. The influence of the stirring on the flow, especially on the mould surface flow, and on the superheat are compared for the different parameters. The results show that above a certain stirring intensity, the mould flow is significantly influenced by the stirring and thus the stirring intensity should be chosen below this critical intensity. The superheat temperature is lowered by the stirrer in a region that is distinctly larger than the region where the magnetic forces of the stirrer are relevant. The results show how these regions vary with the stirrer position. Nevertheless, the difference between stirring and no stirring is significantly higher than varying the position of the stirrer.

Keywords

Continuous casting, Electromagnetic stirring (SEMS), constitutional undercooling, Columnar equiaxed transition (CET), numerical flow simulation (CFD)

1. Introduction

Two types of solidification are observed: while columnar crystals grow from the solidification front into the melt, equiaxed crystals originate around impurities (serving as nuclei) in undercooled regions of the free melt. Electromagnetic stirring in the bending zone (SEMS) of a continuous casting machine is known to increase the amount of equiaxed crystals in the solidified product (Fig. 1).

Fig. 1. pictures of columnar and equiaxed strand cross sections of an AISI 430 steel grade with 35 K superheat and different stirring intensities: no stirring (left), mild
stirring (middle, 37% current) and maximum stirring (right, 100 % current); right border of pictures: narrow face of slab

For an optimal design and operating strategy of an SEMS device, the impact of the stirrer on the liquid steel flow and temperature as well as on the solidification process must be known.

The numerical simulation of the liquid steel flow under influence of an SEMS is based on the magnetohydrodynamic equations (combination of the Navier-Stokes equations for the flow with the Maxwell equations for the electromagnetic field). The challenge is to find an accurate but fast method to solve these equations numerically. Dubke [16] derived an analytical solution for the electromagnetic stirring forces in a resting liquid, extended with an empirical relation for the influence of the moving liquid.

Constitutional undercooling arises from the effect that the solidification temperature varies with the alloy concentrations, and that the alloy concentration changes within the concentration boundary layer of the melt along the solidification front (Fig. 2a) [1-4]. Therefore, a region in the melt near the solidification front can establish where the actual melt temperature $T_a$ is lower than the solidification temperature $T_L$ (grey area in Fig. 2a). This effect is intensified by the fact that the concentration boundary layer in liquid metals is significantly thinner than the thermal boundary layer. The relation of the boundary layer thicknesses can be roughly estimated by the relation of the Prandtl- and the Schmidt number of liquid steel:

$$Pr/Sc = \frac{a}{D} \approx 760$$

with the thermal conductivity of liquid steel $a$ and the alloy diffusion constant $D$ (here for the diffusion of carbon as described below). To give an example for realistic temperature curves, Fig. 2b shows both concentration and thermal boundary layers for a turbulent liquid steel flow in a pipe calculated with a 2D steady turbulent flow simulation with resolved boundary layers as described below. The pipe bulk flow velocity is 0.5 m/s, the pipe diameter is 100 mm and the profiles are evaluated 500 mm after the inlet. The pipe walls represent a solidification front and have a constant temperature lower than the liquid entering the tube and a constant alloy concentration also lower than the liquid. In Fig. 2b, the relative temperature differences are plotted, e.g. (actual liquid temperature – wall temperature) / (initial liquidus temperature – wall temperature). While the concentration boundary layer extends to approximately 0.3 mm, the thermal boundary layer extends to the pipe axis 50 mm away from the solidification front.

![Fig. 2. Constitutional undercooling: a) principle after [1-4], b) pipe flow example: melt temperatures for different superheat temperatures (solid lines, $T_a$ in Fig. 2a) and melt liquidus temperature $T_L$ (dotted line) due to the concentration change near the solidification front, calculated with a 2D turbulent flow simulation](image-url)
One could argue that the extent of the undercooled region is directly related to the amount of equiaxed crystals. Stirring intensifies the heat transfer of the melt to the solidification front and therefore decreases the melt temperature, which increases the extent of the undercooled region. According to this approach, it would be sufficient to calculate the extent of the undercooled region in order to predict the amount of equiaxed crystals. A more sophisticated approach was proposed by Hunt [5] based on solidification measurements: he observed the influence of temperature gradients on the solidification velocity and proposed an equation for the growth rate of equiaxed crystals as a function of the undercooling temperature (difference between liquidus temperature and melt temperature). Under the assumption of a resting melt and a constant temperature gradient in the direction normal to the solidification front, he derived a condition for 100 % equiaxed solidification in the melt near the solidification front mainly based on the temperature gradient, the nucleus density and the subcooling temperature of the dendrite tips. Shibata et al. [6] simplified and transformed this condition so that the condition depends only on the temperature gradient and the velocity of the solidification front. They use a simple one-dimensional transient heat transfer model to calculate both temperature gradient and solidification front velocity under the assumption of a resting melt and an empirically increased heat conduction in regions of the SEMS. In this contribution, we analyse the influence of a box-type SEMS on a stainless steel slab casting machine. The SEMS is located on the outer bow of the strand and contains several coils situated on a common iron core (Fig. 3). The magnetic scatter field of the coils penetrates the melt in the strand. The coils are supplied with alternating current and different phase shifts, generating an apparently travelling magnetic field along the wide side of the strand. This travelling field creates a magnetic force on the melt that intends to drag the melt with the field. The stirring intensity as well as the stirrer position and the stirring direction (unidirectional and periodically alternating) are varied. Fig. 3a shows the different investigated positions of the stirrer.

![Fig. 3. a) Strand geometry and positions (1,2,3) of the Box-Type SEMS; b) SEMS principle: 1 strand with rolls, 2 SEMS iron core, 3 SEMS coils, 4 magnetic field travelling direction, 5 magnetic field lines, 6 force acting on the melt in the strand](image)

2. Mathematical Modelling

The turbulent flow and the temperature field of the liquid steel inside of the solidified strand shell are calculated in numerical 3D simulations using the realizable $k - \epsilon$ turbulence model. The solidification front is modelled as a wall, whose shape is calculated a priori with a shell thickness increasing proportional to the square root of the distance to the meniscus. Sink terms at the wall adjacent computational grid cells consider the material loss due to
solidification [14]. The computational grid has boundary layers with 0.3 mm initial thickness. In combination with an enhanced wall treatment [13], it is intended to resolve the thermal boundary layer sufficiently.

Harmonic simulations of the electromagnetic stirrer field and the resulting electromagnetic stirring forces are calculated with a FE solver for a resting melt. For the calculation of the electromagnetic forces in the flow simulation, Dubke’s equations for the electromagnetic stirring forces [15,16] are used. The required magnetic field density amplitude is taken from the maximum in the centre of the stirrer at the outer solidification front of the electromagnetic field calculations. The height of the melt region where Dubke’s forces act on the liquid is chosen such that the overall electromagnetic force on a resting melt is the same as calculated with electromagnetic solver.

For the temperature, a constant temperature $T_W$ at the walls representing the solidification fronts is chosen ($T_W = T_S(c_0)$ in Fig. 2a). The temperature of the melt entering the domain through the submerged entry nozzle is $T_M > T_L(c_0)$ and has an alloy concentration $c_0$, in the following called “initial temperature” and “initial concentration”, respectively. The difference temperature $\Delta T_M = T_M - T_L(c_0)$ is usually called “superheat temperature”. At the mould level, the heat flux through the slag layer is neglected. Since the energy equation is supposed to be linear in the considered temperature range, a dimensionless superheat temperature

$$\vartheta = \frac{T - T_W}{T_M - T_W} = \frac{T - T_S(c_0)}{T_M - T_S(c_0)} \quad (1)$$

can be introduced. For any arbitrary combination of wall temperature and initial temperature (or superheat temperature), the dimensionless temperature field is the same. Thus, it is not necessary to repeat the numerical temperature calculations for different superheat and/or liquidus and solidus temperatures once a dimensionless superheat temperature is calculated from a temperature field resulting from arbitrary temperature boundary conditions. The melt is undercooled in regions where $T < T_L(c)$ where $c$ is the local alloy concentration. For the calculation of the local undercooling temperature, we suppose that the thickness of the concentration boundary layer is negligibly small in comparison to the thermal boundary layer, as e.g. shown in Fig. 2b, resulting in $T < T_L(c_0)$ or $T < T_S(c_0) + \Delta T_L$ with $\Delta T_L = T_L(c_0) - T_S(c_0)$. From the phase diagram, the liquidus and solidus temperatures $T_L(c)$ and $T_S(c)$ for a certain alloy concentration $c$ in the melt can be calculated as sketched in Fig. 2a if the solidus and liquidus curves are approximated linearly by

$$T_S(c) = T_{S,L,c=0} - \mu_S c \quad \text{and} \quad T_L(c) = T_{S,L,c=0} - \mu_L c. \quad (2)$$

Then, the temperature difference between solidus and liquidus temperature $\Delta T_0$ in Fig. 2a for the initial melt alloy concentration $c_0$ is

$$\Delta T_0 = T_L(c_0) - T_S(c_0) = (\mu_S - \mu_L)c_0. \quad (3)$$

In terms of the dimensionless temperature, the melt is undercooled in regions where $\vartheta < \vartheta_L$ with

$$\vartheta_L = \frac{T_L(c_0) - T_S(c_0)}{T_M - T_S(c_0)} = \frac{\Delta T_0}{\Delta T_0 + \Delta T_M} = \frac{1}{1 + (\frac{\Delta T_M}{\Delta T_0 + \Delta T_M}) \frac{c_0}{c_0} \quad (4)}$$

which depends on the initial melt superheat $\Delta T_M$, the initial alloy concentration $c_0$ and the coefficients $\mu_S$ and $\mu_L$ derived from the melt’s phase diagram.
After Hunt [5], the growth rate of equiaxed grains is

\[
\frac{dr}{dt} = A \frac{\Delta T^2}{c_0} = \frac{D}{8c_0(k-1)m\Gamma} \Delta T^2 = \frac{D \Delta T_0}{8\Gamma} \left(1 - \frac{\vartheta}{\vartheta_L}\right)^2
\]

(5)

where \( r \) is the grain radius, \( \Delta T_U = T_L(c) - T \) is the local undercooling temperature, \( D \) is the diffusion coefficient of the solute element, \( k = \mu_S/\mu_L \), \( m = \mu_L \), and \( \Gamma \) is the Gibbs–Thomson parameter [5,6]. The equation is only valid in regions where \( \Delta T_U > \Delta T_N \), where \( \Delta T_N \) is the undercooling at the heterogeneous nucleation temperature [5], otherwise the growth-rate is zero. After [6] \( \Delta T_N \ll \Delta T_U \), resulting in \( \Delta T_U > 0 \) and \( \vartheta < \vartheta_L \), respectively. A fully equiaxed grain structure is reached if \( r > r^* \) with

\[
r^* = 0.54 N_0^{-1/3}
\]

(6)

where \( N_0 \) is the number of heterogeneous substrate particles available per unit volume [5]. While Hunt integrates equation (5) under the assumption of a linear melt temperature profile perpendicular to the solidification front (i.e. a constant temperature gradient), we solve a scalar equation for the local grain size \( r \) in the flow simulation based on the calculated melt temperature field. A substantial derivative \( Dr/Dt \) including convective terms [17] instead of \( dr/dt \) in equation (5) considers that the crystals move with the melt. Like for all other considered conservation equations, sink terms at the wall adjacent computational grid cells consider the material loss due to solidification. Since the grain density is higher than the liquid density, the crystals have a sedimentation velocity depending on their size and temperature-dependent density. Table 1 shows the sedimentation velocity for a ferritic stainless steel grade for grain diameters and undercooling temperatures. On the one hand, the sedimentation velocity is non-negligible and leads to an asymmetric grain size distribution in the solidified strand cross section with larger crystals concentrated near the outer bow (Fig. 1). On the other hand, if a high crystal concentration is reached, the sedimentation is blocked because the crystals touch each other and the solidification front. Both effects are complex to model and will only be considered in future research. For the current results, the crystals are supposed to move with the same velocity as the melt.

In order to be able to compare the flow simulation results with the model of Shibata et al. [6], an explicit one-dimensional transient solver for the heat transfer equation in thickness direction of the strand cross section is implemented. At the beginning of the simulation, the cross section starts at the mould level with the initial temperature as described above. As a boundary condition, a symmetry condition is imposed at the strand centre and a constant temperature is imposed at the solidification front, which moves towards the strand centre with increasing distance from the mould level in the same manner as described above for the flow simulation. The heat conduction in the melt is calculated as if the melt was solid (no convective heat transfer), except for the impact of the SEMS which is modelled as an increase of the thermal conductivity in the region of the SEMS.
For the calculation of the electromagnetic forces acting from the SEMS on the melt, the electrical conductivity of the melt is required. Stainless steels are known to have a significantly lower electrical and thermal conductivity at room temperature, both of them related by the Wiedemann-Franz law [7]. No data for melt temperatures of stainless steels could be found, but the available data [8] shows that the differences of thermal and (as far as available) electrical conductivity between normal and stainless steel decrease with rising temperatures, become very small above 800 °C (Fig. 4) and finally disappear above the liquidus temperature. Therefore, the electrical conductivity $\sigma = 7.14 \cdot 10^5 \, \text{S}$ of a non-stainless steel is used [19]. The heat conductivity of the melt is $\alpha = 6.1 \cdot 10^{-6} \, \text{m}^2/\text{s}$. For the diffusion of carbon in liquid iron, $D = 8 \cdot 10^{-9} \, \text{m}^2/\text{s}$ is assumed as implemented in the Primetals software Dynaphase [10].

### Table 1: nucleus density and maximum equiaxed grain size diameter after equation (6), grain sedimentation velocity for the maximum equiaxed grain size diameter and for different undercooling temperatures due to temperature-dependent density differences for ferritic stainless steel and spherical grain shape [20]

<table>
<thead>
<tr>
<th>nucleus density in 1/m³</th>
<th>1E+05</th>
<th>1E+06</th>
<th>1E+07</th>
<th>1E+08</th>
<th>1E+09</th>
<th>1E+10</th>
<th>1E+11</th>
</tr>
</thead>
<tbody>
<tr>
<td>grain diameter in mm</td>
<td>23.4</td>
<td>10.8</td>
<td>5.0</td>
<td>2.3</td>
<td>1.1</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>grain sedimentation</td>
<td>1.9</td>
<td>64.5</td>
<td>38.6</td>
<td>19.5</td>
<td>8.7</td>
<td>3.3</td>
<td>0.9</td>
</tr>
<tr>
<td>velocity in mm/s for</td>
<td>4.4</td>
<td>99.1</td>
<td>61.8</td>
<td>33.0</td>
<td>15.6</td>
<td>6.4</td>
<td>1.9</td>
</tr>
<tr>
<td>undercooling</td>
<td>7.7</td>
<td>125.0</td>
<td>79.9</td>
<td>43.7</td>
<td>21.1</td>
<td>8.9</td>
<td>2.8</td>
</tr>
<tr>
<td>temperature in K</td>
<td>12.3</td>
<td>146.5</td>
<td>93.0</td>
<td>52.9</td>
<td>25.9</td>
<td>11.1</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>20.6</td>
<td>165.4</td>
<td>105.4</td>
<td>61.1</td>
<td>30.2</td>
<td>13.2</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>65.6</td>
<td>185.4</td>
<td>116.7</td>
<td>68.5</td>
<td>34.0</td>
<td>15.2</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Fig. 5. a) Fe-C phase diagram [12] and b) derived solidus-liquidus temperature difference $\Delta T_0$ for ferritic solidification ($\delta$-Phase) after Fig. 2a and equation (3), without linearization of the solidus/liquidus lines.

<table>
<thead>
<tr>
<th>C mass fraction in %</th>
<th>liquidus-solidus temperature difference in K</th>
<th>dimensionless liquidus temperature for different superheat temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.4</td>
<td>0.074 0.038 0.020 0.013 0.010 0.007 0.006</td>
</tr>
<tr>
<td>0.002</td>
<td>0.7</td>
<td>0.123 0.065 0.034 0.023 0.017 0.013 0.010</td>
</tr>
<tr>
<td>0.005</td>
<td>1.8</td>
<td>0.265 0.153 0.083 0.057 0.043 0.032 0.025</td>
</tr>
<tr>
<td>0.01</td>
<td>3.5</td>
<td>0.412 0.259 0.149 0.104 0.080 0.060 0.048</td>
</tr>
<tr>
<td>0.02</td>
<td>7.1</td>
<td>0.587 0.415 0.262 0.191 0.151 0.114 0.092</td>
</tr>
<tr>
<td>0.05</td>
<td>17.7</td>
<td>0.786 0.639 0.469 0.371 0.307 0.243 0.202</td>
</tr>
<tr>
<td>0.1</td>
<td>35.4</td>
<td>0.876 0.780 0.639 0.541 0.469 0.392 0.336</td>
</tr>
<tr>
<td>0.2</td>
<td>35.9</td>
<td>0.878 0.782 0.642 0.545 0.473 0.395 0.339</td>
</tr>
<tr>
<td>0.5</td>
<td>59.2</td>
<td>0.922 0.855 0.747 0.664 0.597 0.518 0.458</td>
</tr>
<tr>
<td>1</td>
<td>122</td>
<td>0.961 0.924 0.859 0.802 0.753 0.689 0.635</td>
</tr>
<tr>
<td>2</td>
<td>236</td>
<td>0.979 0.959 0.922 0.887 0.855 0.811 0.771</td>
</tr>
</tbody>
</table>

Table 2: liquidus-solidus difference temperature $\Delta T_0$ for different carbon (C) mass fractions and corresponding dimensionless liquidus temperature $\vartheta_L$ for different superheat temperatures $\Delta T_M$ calculated from the Fe-C phase diagram (Fig. 5a, without linearization of the solidus/liquidus lines) and equations (3) and (4). Typical values for stainless steels (0.05 % C and 30 K superheat are highlighted.

For the Gibbs-Thomson Parameter values for AISI 300 ferritic stainless steel $\Gamma = 2.8 \cdot 10^{-7}$ K m [9] and for a low carbon steel (0.05 %) $\Gamma = 1.9 \cdot 10^{-7}$ K m [12] were found. Measured values for the nucleus density are $N_0 = 1.5 \cdot 3 \cdot 10^8$ m$^{-3}$ [6]. Table 1 shows the relation between nucleus density and maximum equiaxed grain size diameter according to equation (6). From the C-Fe phase diagram in Fig. 5a, the temperature difference between solidus and liquidus temperature $\Delta T_0$ as a function of the initial carbon concentration $c_0$ is determined after Fig. 2a and equation (3) as shown in Fig. 5b. Table 2 shows the same result as numerical values and additionally corresponding dimensionless liquidus temperatures $\vartheta_L$ for different superheat temperatures $\Delta T_M$. According to these results, both carbon concentration and superheat temperature have a huge influence on the constitutional undercooling and on the equiaxed crystal growth-rate.
3. Results

Flow simulations are performed for a continuous strand caster as sketched in Fig. 3a with a strand format of 1550 mm x 215 mm and a casting speed 1.1 m/min. Steady and transient calculations without and with SEMS at three different positions (Fig. 3a) and varying stirring intensities and stirring direction modes (constant and periodically alternating) are used to analyse the influence on the SEMS on flow, temperature and solidification structure.

In first simulations the impact of different SEMS stirring intensities on the flow field under steady conditions (unidirectional stirring) is analysed. Fig. 6a shows the typical double vortex flow structure induced by the stirrer with flow velocities increasing with the field intensity. Fig. 6b shows closeups of the mould region: Even for a mild stirring with 60 % magnetic field density, the mould flow pattern seems already to be influenced by the stirrer, and for 80 % and 120 %, the flow pattern becomes very asymmetric due to the strong influence of the stirrer on the mould flow. In these cases the stirring effect near the stirrer may be satisfying, but the asymmetric mould flow will probably be unacceptable and lead to quality problems like e.g. mould slag entrainment. Therefore, the common praxis of periodically alternating the stirring direction is investigated next.

![Fig. 6](image)

**Fig. 6.** velocity field in the centre plane visualised by path lines coloured with the velocity magnitude (colour scale % of entry nozzle flow velocity) for different SEMS stirring intensities; results from steady flow simulations with unidirectional stirring; a) overview, red arrows denote stirrer position and force direction; from left to right: magnetic field amplitude 0 %, 60 %, 85 %, 120 %; b) closeups of the mould region (first row: field amplitude 0 %, 60 %, second row: 85 %, 120 %)
Fig. 7. mean velocity magnitude (a) and mean velocity deviations (mean of the fluctuation velocity magnitude; b) in the centre plane of the strand from transient simulations with periodically alternating stirring direction and varying stirrer positions and intensities (in %); arrows denote the stirrer positions, colour scale in % of entry nozzle flow velocity equal for both pictures.

Fig. 7 shows flow field results time-averaged over a period of 600 s whereas the travelling direction of the magnetic field is flipped every 15 s without and with SEMS at three different positions (ref. Fig. 3a) and intensities. At the two lower positions, the stirring intensity is increased, as the distance from the mould level is higher. Now in all cases with SEMS the velocity field in the mould region seems uninfluenced by the stirrer. In the region of the stirrer, the time averaged flow velocity in Fig. 7a is comparably low to the unidirectional results in Fig. 6a since the flow velocities are in large part extinguished by the stirring direction changes in combination with the time-averaging. In contrast, the fluctuation velocities in Fig. 7b are significantly higher in the region of the stirrer (approx. within ± 2 m above and below the stirrer) than without stirring.

Fig. 8. dimensionless melt temperatures from transient flow simulations (solid lines, maximum over strand cross section averaged over simulation time) without and with SEMS at different positions and stirring intensities in % and from the numerical 1D heat
transfer model (dashed lines, temperature at centre line) with different effective heat conductivities \( \lambda_{\text{eff}} \); grey bars denote the governing SEMS position.

Fig. 8 shows the time averaged maximum dimensionless temperature (defined by equation (1)) over cross sections of the liquid strand core calculated from the transient flow simulations without and with electromagnetic stirring with alternating direction at various intensities and stirrer positions analogous to Fig. 7. Additionally to the simulation results with the realizable \( k - \epsilon \) turbulence model (RKE), a result with the SAS turbulence model is shown for the case without stirring. In contrast to the RKE model, turbulent structures are resolved more detailedly with the SAS model and therefore, the results are more precise. Nevertheless the observable differences are relatively small. The dimensionless temperature of the melt entering the mould through the submerged entry nozzle is 1. In the first considered cross section 0.5 m below the mould level, the maximum dimensionless temperature is only about 0.5, which means that half of the superheat is already lost in the mould region due to the intensive heat transfer induced by the submerged entry nozzle jets. In all considered SEMS cases, the stirring significantly decreases the melt temperature in comparison to the simulation without SEMS, starting about 2 m above the SEMS position, and reaching a maximum temperature decrease at the position of the stirrer. Additionally to the results from the numerical flow simulations, the results from a heat transfer model as used by Shibata et al. [6] and described above are shown in Fig. 8. These results differ significantly in comparison to the flow simulation results since they treat the melt like a solid and do not consider the convective heat transfer induced by the submerged entry nozzle jets. As a consequence, the heat transfer in the upper part of the strand is rather low and the maximum dimensionless melt temperature decreases only to about 0.85 before the influence of the SEMS becomes noticeable at around 1.8 m distance from the mould level. In contrast, the flow simulation predict a maximum dimensionless melt temperature of only 0.2 to 0.25.

Fig. 9. a) iso-lines in the strand centre plane of constant dimensionless time-averaged melt temperatures, logarithmic scale with 10 iso-lines per decade; b) time-averaged melt undercooling temperature in K for a liquidus-solidus difference temperature \( \Delta T_0 = 15 \) K and for a melt superheat temperature \( \Delta T_M = 35 \) K (same cases as in Fig. 7). Arrows indicate stirrer positions.
In Fig. 9a, iso-lines of the time-averaged dimensionless melt temperatures are shown in the centre plane of the strand for the same cases as in Fig. 7 and 8, giving a more spatial impression of the temperature distribution than Fig. 8. Using the dimensionless temperature allows to interpret the plots for arbitrary liquidus temperatures and liquidus-solidus difference temperatures by calculating the dimensionless liquidus temperature according to equation (4): the corresponding iso-line represents the limit between superheated and undercooled steel. In Fig. 9b, the time-averaged melt undercooling temperature for a liquidus-solidus difference temperature $\Delta T_0 = 15$ K and for a melt superheat temperature $\Delta T_M = 35$ K is shown as an example to get an impression of the spatial undercooling temperature distribution: In the case of SEMS (especially for the two upper stirring positions), the undercooling starts earlier as without SEMS and the maximum undercooling is reached faster with SEMS. Both Fig. 9a and 9b show clearly that only in the upper part of the strand, the undercooled region is restricted to a small boundary layer near the solidification front (like assumed by 00), but for a great part of the strand, the melt is undercooled over the whole liquid cross section due to the intensive heat transfer of the turbulent flow.

Based on the calculated time averaged melt temperature fields, the equiaxed grain radius is calculated by solving the scalar transport equation (5). In Fig. 10, the radius values at the solidification fronts of the simulation domain are projected on the strand cross section [14], showing the equiaxed grain size distribution in the solidified strand as if there was no constraint for the grain growth (refer equation (6)). According to Table 1 and Fig. 1, the grain size may be limited to a few millimetres. While the grain radius is similar high in the core region of the cross section for both unstirred in stirred cases, the radius increases in the outer regions due to the stirring. Since the sedimentation velocity of the equiaxed crystals (table 1) is neglected in the simulations, the grain size distribution is in vertical direction should by more asymmetric. Nevertheless the difference may be smaller than expected from experiences based on experiments (Fig. 1).

![Fig. 10. Equiaxed grain size radius in the solidified strand cross section calculated based on the time averaged melt temperature fields of the simulations without (upper picture) and with SEMS (Position 2, 100 % magnetic field intensity, lower picture) by solving the scalar transport equation (5) for a liquidus-solidus difference temperature $\Delta T_0 = 15$ K and for a melt superheat temperature $\Delta T_M = 35$ K: as contour plots of the grain radius (first]
two rows, colour scale in mm), as circles with the local grain diameter drawn on random positions.

4. Conclusions

The flow simulations of a stainless steel continuous casting process without and with electromagnetic stirring at different vertical positions, magnetic field intensities and operating modes (unidirectional stirring, periodically alternating stirring direction) show that an alternating stirring direction is essential to avoid a probably unfavourable impact of the stirring on the mould flow. The temperature field of time-averaged results of transient simulations with alternate stirring direction is analysed to figure out the increase of the extent of undercooled melt regions due to the stirring. In contrast to 1D thermal models used for the prediction of equiaxed crystal amount [6], the performed flow simulations show that the consideration of convective heat transfer leads to a significant stronger decrease of the superheat temperature in the upper part of the strand. Hunt’s model for equiaxed crystal growth rate [5] is applied to the temperature field to calculate the equiaxed grain size distribution in the solidified strand cross section under the assumption of an unconstraint growth and zero grain sedimentation velocity. Although the so calculated grain size distribution should be more accurate than previously published results, the model still needs refinements (consideration of neglected, but non negligible effects like e.g. grain sedimentation and growth limitation) and validation.

Acknowledgments

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References

Abstract

In duplex stainless steels (DSS) the desired microstructure after solution heat treatment is a ferritic matrix with austenite islands, maintaining approximately equal amounts of both phases. However, during several manufacturing processes, such as welding, the formation of deleterious phases could happen, and the one of greater influence is the sigma phase, resulting in loss of corrosion resistance and toughness. The present study worked on developing DICTRA® simulation models that could assess the volume fraction of sigma as a function of the aging time of DSS, obtained in previous experimental works of these research team. Simulation models analysed have planar or spherical symmetry with different dimensions for ferrite and austenite. In the models, it was assumed ferrite and austenite volume fractions and compositions as the same obtained in Thermo-Calc® equilibrium calculations of the solution treatment temperature. Sigma phase composition was obtained in equilibrium simulation at the aging temperatures. It was concluded that the simulation model which best assess the formation of sigma phase is a spherical configuration with austenite in the centre, surrounded by ferrite, placing sigma as active phase between the two former phases with negligible thickness.

Keywords


1. Introduction

The combination of high toughness, mechanical strength and corrosion resistance allowed duplex stainless steels (DSS) to be used in oil and gas, chemical, and petrochemical industries. DSS are composed approximately by equal amounts of ferrite (α) and austenite (γ), and high amounts of Cr, Ni, Mo and N. [1, 2]

However, DSS are susceptible to deleterious phase’s formation, such as chromium nitrides (Cr₂N), chi (χ) and sigma (σ) [3]. Those phases are usually formed between 823 K (550 °C) and 1273 K (1000 °C) [4-7]. Sigma is the most deleterious phase in DSS, and is mainly formed by Fe, Cr and Mo. Sigma formation is responsible for loss of corrosion resistance due to Cr and Mo depletion of the surrounding matrix [8-10], and occurs preferentially in heterogeneous nucleation sites of the matrix such as α/γ interfaces [11,12,13,14].

Kinetics of sigma phase formation, in a simplified approach, can be described by the Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation [15,16]. Computational modelling of sigma phase is performed by the research group of the authors of this paper [17,18] showing that sigma phase formation kinetics can be also assessed by DICTRA® simulations. Previous paper from one of the authors of this contribution [16] described the kinetics of sigma phase formation during isothermal aging of a UNS S310803 DSS, at temperatures between 700°C and 900°C, presenting experimental data points of sigma phase volume fraction as a function

1 FEI University
of aging time at a specific temperature, and obtaining an adjusted KJMA equation for this phase transformation.

This paper evaluated the possibility of assess the volume fraction of sigma phase formed during isothermal aging through DICTRA® simulations, comparing them to the experimental data found in the previous paper mentioned before [16].

2. Computational modelling

Using Thermo-Calc® version 2018b with TCFE8 database, equilibrium volume fraction of phases and composition of phases were determined for the UNS S310803. It was used the composition of the alloy studied elsewhere [16], Fe-22.2%Cr-5.7%Ni-2.98%Mo-0.16%N, and composition of ferrite and austenite was determined at the temperature were volume fractions of ferrite and austenite were 0.409 and 0.591, the same reported in the reference paper [6]. Equilibrium composition of sigma phase were also determined for the ageing temperatures (700 °C, 750 °C, 800 °C, 850 °C or 900 °C) for use in DICTRA simulations, described in the sequence.

DICTRA® software using TCFE8 database for calculation of local equilibrium at interfaces, and MOBFE3 mobility database to assess diffusion coefficients were used for simulation of the kinetics of sigma phase formation at isothermal ageing temperatures. Two different geometrical models were implemented. The planar model (Fig. 1a) consider uniaxial diffusion perpendicular to the interface between ferrite (α) and austenite (γ), and the length of the phases was set as half of ferrite or austenite mean size of those phase thickness, in accordance to the reference work [16] that indicates phases sizes considering the elongated microstructure of austenite islands in a ferritic matrix. Spherical Model (Fig. 1b) considered a spherical region of austenite with radius equal to the radius of austenite in the reference work [16], surrounded by a volume of ferrite with thickness that generated the volume ratio between ferrite and austenite 0.409:0.591. Sigma was placed in the models as an active phase of negligible size (0.01μm thickness) at α/γ interface. Composition of phases in DICTRA® simulations did not consider N content due to its negligible influence on sigma phase formation, as previously used in literature [18,19]. This procedure avoids N supersaturation problems, and the need in thermodynamic calculations of MN type (Face Centered Cubic, FCC) or M₂N (Hexagonal Close Packed, HCP) nitrides, allowing DICTRA® here proposed.

![Fig. 1. (a) Planar and (b) spherical models used in DICTRA® simulations.](image-url)
Results of sigma volume fraction from DICTRA® were compared to the experimental results previously published in the reference work [16] already mentioned, in order to validate the models, and by comparison determining which is the best for assessment of the kinetics of sigma phase formation through computational simulation.

3. Results and discussion

Equilibrium volume fractions of phases as a function of temperature are obtained through Thermo-Calc® simulations, and are presented in Fig. 1. The temperature of 993 °C were chosen as the one that allowed volume fractions of ferrite and austenite of 0.409 and 0.591, the same reported in the reference work [16]. Compositions of ferrite and austenite at 993 °C, and compositions of sigma at studied ageing temperatures (700 °C, 750 °C, 800 °C, 850 °C or 900 °C) were determined in Thermo-Calc® and were used in DICTRA® simulations of kinetics of sigma phase formation.

![Fig. 2. Equilibrium diagram for the studied steel obtained in Thermo-Calc® simulation with TCFE8 database.](image)

Results of sigma phase volume fraction as a function of isothermal aging times at 700 °C, 750 °C, 800 °C, 850 °C or 900 °C were previously reported by one of the authors [16], and those results were compared to the DICTRA® simulations here proposed, as presented in Fig. 2 to Fig. 6.

As expected, the spherical model simulation results show sigma phase volume fraction growth at higher rates than the planar model, due to the greater number of diffusion flux directions provided by the spherical model, when compared to the planar, where the flow of diffusion is perpendicular to the interface between the phases of the planar model.

The results of the simulations with the spherical model (Fig. 2 to 6) are the ones that better assess the experimental results presented in [16]. However, it should be noted that the proximity of the spherical model simulations to the experimental data is higher at temperatures of 700 and 750 °C (Fig. 2 and 3). This can be an indication that different aging temperatures could lead to changes in sigma formation mechanisms, and the higher the tested temperature, the worst is the assessment of sigma volume fraction by DICTRA® using the
proposed spherical model, which only represents in a simplified manner the complex morphology of sigma phase in aged DSS, as extensively presented in literature [2,13,14,16-19].

4. Conclusions

It was concluded that the simulation model which best assess the formation of sigma phase during isothermal ageing of a UNS S31803 DSS is a spherical configuration with austenite in the centre, surrounded by ferrite, placing sigma as active phase between the two former phases with negligible thickness. However, different aging temperatures could lead to changes in sigma formation mechanisms, and the higher the tested temperature, the worst is the assessment of sigma volume fraction by DICTRA® using the proposed spherical model.

![Graph showing volume fraction of sigma as a function of aging time at 700 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].](image_url)
Fig. 4. Volume fraction of sigma as a function of aging time at 750 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].

Fig. 5. Volume fraction of sigma as a function of aging time at 800 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].
Fig. 6. Volume fraction of sigma as a function of aging time at 850 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].

Fig. 7. Volume fraction of sigma as a function of aging time at 800 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].
References

MARIA CAROLINA PAYARES-ASPRINO¹, PATRICIA MUÑOZ-ESCALONA²

PREDICTION OF PERCENTAGE OF FERRITE AS A FUNCTION OF HEAT INPUT IN ROBOTIC GAS METAL ARC WELDING OF DUPLEX STAINLESS STEEL SAF 2205 WELDS

Abstract

Dual phase duplex stainless steels with ferrite and austenite as part of their microstructure have shown an outstanding strength and corrosion resistance despite of the aggressive and hostile environments they can be subjected to. In the last years a worldwide rapid growth demand and consumption of duplex stainless steel, particularly in petrochemical, marine, power plant, food industry and other engineering applications have taken place especially where welding processes were required. Joining of duplex alloys is a challenging task, due to the formation of embrittling precipitates and metallurgical changes they go through during the welding process. Generally, the quality of a weld joint is strongly influenced by the welding conditions and imbalance phase ratio between the austenite and ferrite, these factors lead to solidification cracking, corrosion susceptibility, and lower ductility. To achieve high quality welds mathematical models have been developed in order to predict the ideal bead geometry to achieve optimal mechanical properties. This paper focuses on determining the percentage of ferrite in GMAW welds of duplex stainless steel SAF 2205. An experimental model for the prediction of weld bead geometry was developed and applied. The values of weld penetration and reinforcement areas were calculated using a statistical approach and the amount of ferrite in the duplex stainless steel welds were determined applying the rule of mixture and the Schaeffler diagram. These predicted values of ferrite were later on compared with experimental values obtained through chemical. The results indicate 0.7% of error between experimental and predicted values of ferrite when using heat inputs higher than 0.9kJ/mm²

Keyboards

Robotic GMAW welding, Weld penetration, Weld reinforcement, Duplex stainless steels, Rule of Mixture, Ferrite Content.

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1. Introduction

Duplex stainless steels (DSS) are widely used in many engineering applications such as those found in the petrochemical, pulp and paper, and oil and gas industries, since they exhibit good mechanical properties and high corrosion resistance. Properties such as high tensile strength, high fatigue strength, good toughness even at low temperature, adequate formability and weldability and excellent corrosion resistance (e.g. stress corrosion cracking and pitting) result from the almost equal amount of ferrite ($\alpha$) phase and austenite ($\gamma$) phase present in this steel. The presences of these two phases combine the attractive properties of austenitic and ferritic steels [1-4]. There is an increase used of DSS in the pipe industry compared to austenitic stainless steels, particularly where chloride or sulphide stress corrosion cracking is of primary concern [5]. However, the solidification of duplex stainless steel welds does not always produce near equal amounts of ferritic ($\alpha$) and austenitic ($\gamma$) phases, as occurs in the parent metal; thus deteriorating the mechanical properties and corrosion resistance of the weld joint. The microstructures developed in the weld’s fusion zone and the heat-affected zone (HAZ) also have a significant influence on the mechanical properties and corrosion resistance of duplex stainless steels [3-6]. To guarantee the excellent combination of properties in DSS, it is essential to maintain a ferrite-austenite ratio close to 50:50. This phase balance however changes during the welding process due to the rapid cooling process involved in most thermal cycles, resulting in weld ferrite contents with an excess of 50%. In order to restore the phase balance, weld filler materials usually alloyed with 2-4% more of Ni compared to the base metal are used [7,8]. Hsieh et al. [9] reported that the austenite contents lower than 25% are unacceptable for most industrial application, since excessive ferrite in the heat-affected zone (HAZ) and weld metal (WM) causes a loss of toughness and a decrease in corrosion resistance. Norsok standard recommended that a minimum in austenite content of 30% is required to accept the welded pipes [10].

Various researchers reported that controlled heat input is the most important factor in order to maintain the phase balance after the welding process of DSS. Other researchers [11-13] reported that the cooling rate is the parameter that controls the phase balance in weldments, and also dictates the heat input range to be used. Giridharan et al. [14] reported that heat input has a significant impact on the bead geometry, metallurgical, mechanical and corrosion resistance properties of the welds. Similarly, Karunakaran [15] reported that the rate of heat input during welding followed by the nature of cooling has a strong influence on the grain’s size and phase formation. Recommendations in relation to super-duplex stainless steels have also been made, where a moderate heat input should be used (depending on material’s thickness and joint’s geometry) in order to obtain beneficial outcomes such as corrosion resistance [16]. From the open literature it is well inferred that a low heat input and a fast cooling rate produces the formation of Cr$_2$N precipitation and higher heat inputs lead to the formation of X or $\sigma$ phases which have been reported as deleterious phases affecting the mechanical properties of weldments [17, 18]. Hence, the importance of using an optimal heat input to control the formation these phases. With regards the arc current Ozlati et.al reported that the strength resistance of welds conducted on duplex stainless steel rod decrease with when increasing arc current [19]. Other researchers formulated empirical models that are able to predict the approximate weld bead contour of duplex stainless steel welds from established ranges of welding parameters [20,21].

This present work focuses on the influence of heat input on the percentage of ferrite in duplex stainless steel welds. The cross-sectional area of weld reinforcement and weld
penetration were calculated using a developed mathematical model and these values were used to predict the percentage of ferrite using the Rule of Mixture and Schaeffler Diagram [22].

2. Experimental Procedure

2.1 Workpiece Characteristics

Duplex Stainless Steel SAF 2205 was selected as parent material as it is widely used in the petrochemical industry. Table 1 shows the chemical composition of SAF 2205 DSS and filler metal ER-2209 (electrode) of 1 mm diameter as recommended by ASTM A815 and A789 procedures GMA welding process.

Table 1. Chemical composition of the DSS SAF 2205 plate and ER 2209 filler metal

<table>
<thead>
<tr>
<th>Material</th>
<th>%C</th>
<th>%Si</th>
<th>%Mn</th>
<th>%P</th>
<th>%S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
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<td>5.31</td>
<td>3.34</td>
<td>0.08</td>
</tr>
<tr>
<td>ER 2209</td>
<td>0.015</td>
<td>0.54</td>
<td>1.87</td>
<td>0.023</td>
<td>0.006</td>
<td>23.31</td>
<td>9.81</td>
<td>3.77</td>
<td>0.14</td>
</tr>
</tbody>
</table>

2.2 Welding Parameters.

Single bead-on-plate welds were developed using GMA welding (FANUC 100iB®) on DSS under different welding conditions. Equation 1 was used for heat input calculations, where recommended values for heat input ranged between 0.5 and 2.5 kJ/mm for stainless steel duplex SAF 2205 [2]. The bead-on-plate (BOP) welds were manufactured using the conditions shown in Table 2. Figure 1 shows a Schematic drawing of the Bead on Plate (BOP) welds and dimensions of the plate.

\[
HI (\text{Heat input}) = \frac{\text{Arc current} \times \text{Arc voltage} \times 60}{\text{Welding speed} \times 1000} \quad (1)
\]

Where

HI (kJ/mm), Arc Voltage (V), Arc Current (A), Welding speed (mm/min).

As it is known, robots (automatic welding) only allow to set the arc voltage, the wire feed transfer (WFT) and the welding speed during the welding process. In order to obtain values of arc current, a graph of arc current vs WFT was developed based on data collected from the robot. The developed graph and a mathematical expression of arc current as a function of WFT is shown in Figure 2.
To study the weld bead cross sectional area geometry, a small sample was cut from the weld track 150 mm away from the weld’s starting point (middle of the weld track) where welding parameters are stabilized (see Fig 1). Table 2 shows the combination of welding variables used and resulted heat input. All samples, 13 in total were metallographic prepared following ASTM E3-01 standard and then etched with Kalling # 2 (5g de CuCl₂, 100ml Ethanol, 100ml HCl and 100 ml H₂O).

Table 2. Selected welding parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Arc Voltage (V)</th>
<th>WFT (in/min)</th>
<th>Arc Current (A)</th>
<th>Welding speed (mm/min)</th>
<th>Heat Input (kJ/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.00</td>
<td>450.00</td>
<td>212.00</td>
<td>480.00</td>
<td>0.740</td>
</tr>
<tr>
<td>2</td>
<td>28.00</td>
<td>525.00</td>
<td>224.50</td>
<td>480.00</td>
<td>0.790</td>
</tr>
<tr>
<td>3</td>
<td>28.00</td>
<td>450.00</td>
<td>210.50</td>
<td>300.00</td>
<td>1.180</td>
</tr>
<tr>
<td>4</td>
<td>28.00</td>
<td>525.00</td>
<td>230.30</td>
<td>300.00</td>
<td>1.290</td>
</tr>
<tr>
<td>5</td>
<td>28.00</td>
<td>525.00</td>
<td>230.30</td>
<td>300.00</td>
<td>1.900</td>
</tr>
<tr>
<td>6</td>
<td>30.00</td>
<td>350.00</td>
<td>202.00</td>
<td>480.00</td>
<td>0.760</td>
</tr>
<tr>
<td>7</td>
<td>30.00</td>
<td>450.00</td>
<td>230.13</td>
<td>480.00</td>
<td>0.860</td>
</tr>
<tr>
<td>8</td>
<td>30.00</td>
<td>350.00</td>
<td>205.00</td>
<td>300.00</td>
<td>1.230</td>
</tr>
<tr>
<td>9</td>
<td>30.00</td>
<td>450.00</td>
<td>235.00</td>
<td>300.00</td>
<td>1.410</td>
</tr>
<tr>
<td>10</td>
<td>30.00</td>
<td>375.00</td>
<td>207.50</td>
<td>300.00</td>
<td>1.250</td>
</tr>
<tr>
<td>11</td>
<td>30.00</td>
<td>450.00</td>
<td>226.25</td>
<td>300.00</td>
<td>1.360</td>
</tr>
<tr>
<td>12</td>
<td>30.00</td>
<td>350.00</td>
<td>202.00</td>
<td>360.00</td>
<td>1.010</td>
</tr>
<tr>
<td>13</td>
<td>30.00</td>
<td>400.00</td>
<td>218.00</td>
<td>300.00</td>
<td>1.310</td>
</tr>
</tbody>
</table>

The chemical composition of each sample was obtained conducting a spectrographic chemical analysis SPECTROLAB 5L and following ASTM A1016 standards. Since chemical composition were similar for similar values of heat input, these were re-arranged in 3 groups for simplicity purposes These values are reported in Table 3.
Table 3. Results of the spectrographic chemical analysis for different heat inputs.

<table>
<thead>
<tr>
<th>HI (kJ/mm)</th>
<th>%C</th>
<th>%Si</th>
<th>%Mn</th>
<th>%Cr</th>
<th>%Mo</th>
<th>%Ni</th>
<th>%Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>0.0490</td>
<td>0.399</td>
<td>1.7110</td>
<td>21.7900</td>
<td>3.4970</td>
<td>7.0400</td>
<td>0.0059</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0398</td>
<td>0.4411</td>
<td>1.6870</td>
<td>21.8800</td>
<td>3.5630</td>
<td>7.5300</td>
<td>0.0077</td>
</tr>
<tr>
<td>1.4</td>
<td>0.0433</td>
<td>0.4177</td>
<td>1.7250</td>
<td>21.9300</td>
<td>3.4270</td>
<td>7.3000</td>
<td>0.0153</td>
</tr>
</tbody>
</table>

3. TECHNICAL APPROACH

3.1. Estimation of %Ferrite through rule of mixture

3.1.1. Rule of Mixture (Predicted values)

The percentage of ferrite content in the weld’s fusion zone generated through a GMAW process was obtained using the rule of mixture shown in Equation 2 [24].

\[
\% X_{\text{weld}} = \frac{B}{B+D} \left[ \% X_{\text{BM}} \right] + \frac{D}{B+D} \left[ \% X_{\text{FW}} \right]
\]  

(2)

where:

- \( \% X_{\text{weld}} \) is element percentage content in the fusion zone.
- \( \% X_{\text{BM}} \) is element percentage content in the base metal.
- \( \% X_{\text{FW}} \) is element percentage content in the filler metal.
- \( B \) is the area of penetration of the weld.
- \( D \) is the reinforcement area.

i) Dilution for GMAW Welds

Weld dilution was determined using metallographic methods by measuring the individual cross-sectional areas of the deposited filler metal and melted substrate. The ratio of the melted substrate (\( B \)) to the total melted cross-sectional area from the filler metal and substrate (\( B+D \)) describes the level of dilution:

\[
\text{Dilution} = \frac{B}{B+D}
\]  

(3)

Note that the area of the melted substrate (on a transverse cross-section) \( B \) represents the penetration area of the weld, and \( D \) represents the reinforcement area of the weld.

ii) Calculation of experimental weld bead’s cross sectional area geometry contour

In order to predict the %Ferrite using the rule of mixture equation, calculations of the experimental weld’s cross sectional area geometry contour is required. For this purpose photographs of the samples cut from the welded track were obtained using an optical microscope Olympus BX53M. Each image was uploaded in Mathematica 7 ® software for processing.
More than one hundred (100) points were used to develop the contour of the cross sectional area geometry of the weld bead. This allowed to produce a representation in Cartesian coordinates (X-Y) for each combination of welding parameters (13 samples-Table 2). Once the cross sectional area geometry contour was completed, the Mathematica 7 ® Software allowed for the calculation of the centroid of the generated shape based on the geometry developed through the combination of the welding parameters [23].

3.2. Estimation of % Ferrite through Shaeffler’s Diagram (experimental values)

To estimate the % ferrite thought the Schaeffler’s diagram, it is necessary to calculate the nickel and chromium equivalent using Equations 4 and 5 respectively [22]. These values of Ni$_{eq}$ and Cr$_{eq}$ were obtained by substituting the values of chemical analysis obtained through the spectrographic chemical analysis and reported in Table 3. The results were later plotted on the Schaeffler diagram to predict % ferrite as indicated in Figure 3.

\[
\text{Ni}_{eq} = \% \text{Ni} + 30\% \text{C} + 0.5\% \text{Mn} \quad (4)
\]
\[
\text{Cr}_{eq} = \% \text{Cr} + \% \text{Mo} + 1.5\% \text{Si} + 0.5\% \text{Nb} \quad (5)
\]

Fig 3. Shaeffler Diagram [22]

4. Results and Discussion

4.1 Prediction of reinforcement area and penetration area of weld bead using the Experimental Model for GMAW welds.

Figure 4a show an example of photographs of the cross sectional geometry of the weld bead on DSS weld and Figure 4b its digital contour representation of the cross sectional area’s geometry. The centroid of the developed contour was obtained through electron microscope using a JEOL JSM -5800.
Fig. 4. Cross sectional area of weld bead when using 224.5A, 28V and 480 mm/min taken 150 mm away from weld’s starting point. a) Image of cross sectional area and b) Digital representation obtained through Mathematica 7. The centroid of the developed contour is indicated with red dot.

Once the digital contour for each condition was developed, the image was rotated and translated to Cartesian axes as shown in Figure 5.

Fig. 5. Rotation and translation the developed contour in Cartesian axes for a weld developed using 230.13A, 30V and 480 mm/min

It must be highlighted that X and Y axis represent number of pixels which were later transformed in a program that was set-up to run on windows, where welding parameters were used as input values and the outputs are the cross sectional area’s geometry and contour as observed in Figure 6, where values of height of the reinforced area and value of depth of penetration as well as the width of the weld are calculated based on numbers of pixels obtained in the geometry’s contour.
Fig. 6. Example of the contour of the weld bead geometry

4.2 Comparison of % predicted and experimental values of %Ferrite Content of DSS Welds

Experimental and predicted values of %Ferrite obtained through Schaeffler diagram and rule of mixture respectively are shown in Figure 7 for different values of heat inputs.

Fig. 7. Comparison of predicted and experimental values of %Ferrite vs Heat input

When analysing Figure 7, it is observed how %Ferrite decreases when increasing the heat input. The results are very encouraging especially for HI >0.9 kJ/mm where the predicted and experimental values are very similar, with an error of 0.7%. For HI < 0.9 kJ/mm a maximum error of 10% between predicted and experimental values was obtained when using HI values near 0.5 kJ/mm. This result is in agreement with Mohammed et.al who reported that low heat input results in high volume of fractions of ferrite [25].

5. Conclusions:

- The developed model is capable of predicting geometry of the weld’s reinforcement and penetration of DSS welds
The developed model showed to provide reliable results when using it for the estimation of %Ferrite content through the rule of mixture.

The ferrite content in the fusion zone decreased with increasing heat input for DSS ROBOTIC GMAW welds for all the methods studied.

Welds manufactured using similar heat inputs resulted in similar chemical composition content

6. References:

THERMO-CALC® AND DICTRA® SIMULATIONS OF THE SOLUTION
HEAT TREATMENT OF SUPERDUPLEX STAINLESS STEELS

Abstract

The aim of the present work was to perform computational simulations of the equilibrium and phase transformation kinetics of a superduplex stainless steel UNS S32750 in two different heat treatment cycles: “i” during heating to 1250°C from its initial duplex condition, or “ii” during heating at temperatures to obtain duplex structure from the equilibrium microstructure obtained at 1250°C solution treatment. Thermo-Calc® and DICTRA® simulations were executed, as well as the experimental validation in the laboratory of some of the simulations’ results. The experimental validation showed, by quantitative stereology, that equilibrium phase fractions stabilize after 30 min of heat treatment in both thermal cycles, reaching 71% of ferrite in cycle “i” and 51% of austenite in cycle “ii”, validating the kinetic simulations concerning phase fractions. However, simulations showed that during heat treatment cycle “i”, although ferrite fraction stabilizes in 16 min, chemical elements took 36 min to come into equilibrium in ferrite, and 10h in austenite, indicating that equilibrium is only fully attained long after the phases’ fractions stabilize, a fact which the experiments are not able to detect. The geometric model that simulates planar grains and considers the ‘reduced composition’ is the one that best describes the experimental results.

Keywords


1. Introduction

Superduplex stainless steels (SDSS) are produced for noble applications, including petrochemical, aeronautical and oil and gas sectors, as they combine mechanical strength, toughness and high corrosion resistance, especially the pitting corrosion resistance [1-3]. For SDSS, pitting resistance equivalent number (PREN), defined by Eq. 1, is greater than 40, indicating their potential high pitting corrosion resistance [1,3-5].

\[
\text{PREN} = \text{wt } \% \text{Cr} + 3.3 \times \text{wt } \% \text{Mo} + 16 \times \text{wt } \% \text{N}
\]  

Typical microstructure of SDSS is composed by equal volumes of austenite (γ) and ferrite (α) obtained by solution heat treatment between 1000°C and 1300°C, as described in literature [2-3,6], followed by water cooling to keep the duplex structure at room temperature [6].

In this study, simulation of the common thermal condition imposed during forging of a UNS S32750 (SAF 2507) SDSS was conducted, performing heating at 1250°C and evaluating changes in volume fraction of phases in different times. Equivalent analysis was employed simulating the solution-treatment of an alloy that was prior subjected to heating for 3 h at 1250 °C, studying the changes in ferrite-to-austenite volume fraction at a temperature where

1 FEI UNIVERSITY
the duplex structure can be formed. Thermo-Calc® simulations were used to determine equilibrium conditions in different temperatures for the alloy, and DICTRA® simulations were used to evaluate the kinetics of austenite-to-ferrite or ferrite-to-austenite transformations [7-8]. Verification of the validity of the computer simulations was carried out with laboratory experiments.

2. Computational Modelling

Computational modelling was done for two different heat cycles. Cycle “i” simulated the thermal condition imposed during forging, which basically is the heating to 1250°C of a typical duplex microstructure, and cycle “ii”, which simulated the necessary solution-treatment to develop the duplex structure after the previous forging cycle “i”.

To determine the solution-treatment temperature which allow the formation of 50% of ferrite and 50% of austenite, thermodynamic phases’ equilibrium was obtained throughout Thermo-Calc® version 2018b, using TCFE8 database, for two different chemical compositions of the UNS S32750 steel: one is the complete composition, as shown in Table 1, and the other is called “reduced composition”, that is, only with the main elements of interest, Cr, Ni, Mo, N and Fe.

| Table 1 – UNS S32750 complete chemical composition (wt %) |
|-----------------|---|---|---|---|---|---|---|---|
| Cr   | Ni  | Mo | N  | Mn | W  | C  | Fe  |
| 25.17 | 6.88 | 3.61 | 0.25 | 0.60 | 0.69 | 0.01 | balance |

Considering the results of both simulations, it was noticed that the differences between simulations using the complete or the reduced chemical compositions are minimal. For this reason, only the reduced chemical composition was used in computer simulations, saving simulation time in the kinetics simulations using DICTRA®. It was found that 1088 °C is the solution-treatment temperature to develop the duplex structure. For simulating forging conditions, 1250 °C was chosen as the temperature during a typical hot working.

DICTRA® simulations, using TCFE8 and MOBFE3 databases, were performed to simulate planar or spherical geometric models of the microstructure, to define which one better describes the experimental results conducted for validation. Geometric models are shown in Fig. 1. In planar model (Fig. 1a), the phases’ lengths were estimated considering the average grain size of the phases measured by optical metallography and respecting the volumetric fraction of phases determined in Thermo-Calc® simulation for the initial condition of the simulation model. Spherical model consider as phases’ lengths the austenite medium grain radius with a spherical ferrite shell since ferrite is usually described as the matrix phase in SDSS. The grain sizes were calculated by the method of the linear intercepts in optical micrographs obtained after metallographic preparation and electrolytic etching in 10% oxalic acid solution under 6 Vcc for 30 s.

Fig. 1. Geometric models: a) planar; b) spherical.
Before cycle “i”, the material in the supplied condition was in thermodynamic equilibrium, since it was treated at 1120 °C for 1 h and 30 min and immediately water cooled, were the system reached the balance of ferrite and austenite fractions of 49:51, respectively. The real phase fractions were used as parameters for the simulations, which phase with a determined chemical composition in Thermo-Calc®.

Before cycle “ii”, considering that the material was heat-treated at 1250 °C for 3 h and the system reached a balance of ferrite and austenite fractions of 70:30, respectively, the simulations also considered as chemical composition of such phases the ones determined in Thermo-Calc® simulations for equilibrium at 1250 °C.

For each model, the simulations took approximately 10h to complete, using a computer with Intel® Core™ i7-4770 CPU @ 3.40 GHz and 8 cores.

The parameters used for the forging and solution-treatment to duplex structure simulations can be seen in Table 2 and Table 3, respectively.

### Table 2 – Parameters used in heat cycle “i” simulation.

<table>
<thead>
<tr>
<th>Simulation time</th>
<th>Temperature</th>
<th>Geometric model</th>
<th>α length</th>
<th>γ length</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 h</td>
<td>1250 °C</td>
<td>Planar</td>
<td>10 µm</td>
<td>10 µm</td>
</tr>
<tr>
<td>16 h</td>
<td>1250 °C</td>
<td>Spherical</td>
<td>1.3 µm</td>
<td>5 µm</td>
</tr>
</tbody>
</table>

### Table 3 – Parameters used in heat cycle “ii” simulation.

<table>
<thead>
<tr>
<th>Simulation time</th>
<th>Temperature</th>
<th>Geometric model</th>
<th>α length</th>
<th>γ length</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 h</td>
<td>1088 °C</td>
<td>Planar</td>
<td>67 µm</td>
<td>28 µm</td>
</tr>
<tr>
<td>20 h</td>
<td>1088 °C</td>
<td>Spherical</td>
<td>6.9 µm</td>
<td>14 µm</td>
</tr>
</tbody>
</table>

### 3. Experimental procedures

Isothermal heat treatments were conducted at both thermal cycles for different times, described in the Table 4. Samples treated in cycle “ii” were pre-treated at 1250 °C for 3 h and water quenched.

### Table 4 – Heat treatments realized

<table>
<thead>
<tr>
<th>Thermal cycle</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>1250 °C</td>
<td>1 min, 2 min, 40 min, 3 h</td>
</tr>
<tr>
<td>ii</td>
<td>1088 °C</td>
<td>2 min, 30 min, 3 h, 12 h, 36 h</td>
</tr>
</tbody>
</table>

Metallographic specimens of all heat-treated samples were prepared to be analysed under optical microscopy, using the modified Beraha reagent, which promotes selective etching of phases, and using electrolytic etching with oxalic acid, aiming to reveal grain boundaries, allowing the measurement of its mean size, following the method of linear intercepts.
Stereological quantitative analysis for determination of ferrite and austenite volume fractions was performed using optical microscopy images of the Beraha etched specimens, using Olympus AnalySIS docu software, performing measurements in 20 random fields at 100 times magnification.

4. Results and discussion

Equilibrium simulation using Thermo-Calc® defined the solution-treatment temperature of 1088 °C to reach the SDSS initial duplex condition, achieving 50% of austenite and 50% of ferrite, as shown in Fig. 2. In the chosen temperature for simulation of the forging conditions, 1250 °C, the microstructure is estimated to have 30% of austenite and 70% of ferrite.

![Fig. 2. Equilibrium diagram as a function of temperature for the studied SDSS. TCFE8 database](image)

Microstructures formed in samples after thermal cycles “i” or “ii” at different times are presented in Fig. 3 and Fig. 4. A typical SDSS microstructure can be observed, with a ferritic matrix in dark color, and the austenitic phase in the light color.

Heating at 1250 °C for 1 min (Fig. 3a), lead to only smaller grains and balanced amounts of both phases, whereas between 2 min and 40 min (Fig. 3b and 3c, respectively) the ferrite volume fraction increased. Analysis by stereological quantitative confirms the evolution of the ferritic phase observed in the micrographs, showing that the equilibrium is reached after 30 min (1800 s) of heat treatment, with 71% ± 2.5% of ferrite, as shown by the experimental points in Fig. 5. The sample treated at 1250 °C for 3 h (Fig. 3b) was used as reference of equilibrium at 1250 °C, and the mean size of grains was used as the length of phases in DICTRA® simulations of the cycle “ii”, as shown in Table 3.

Sample heated at 1088 °C during 2 min (Fig. 4a) presented only small amounts of austenite, whereas after 30 min (Fig. 4b) the volume fraction of austenite increased and remain practically constant up to 36 h of heat treatment (Fig. 4c and 4d), indicating that equilibrium was reached in this time frame. It is also observed that at 3 h of heat treatment
(Fig. 4c) there is nucleation of austenite inside the ferrite’s grains, which cannot be implemented in the geometry of the simulation models. For longer times (Fig. 4d), coalescence of austenite is observed. Quantitative volume fraction of phases (experimental dots in Fig. 6) showed that thermodynamic equilibrium of volume fraction of phases at 1088 °C is also reached after 30 min (1800 s) of heat treatment, resulting in 51% ± 2.2% of austenite.

![Fig. 3](image)

**Fig. 3.** Optical microscopy of the samples solubilized at 1250 °C for different times, etched with modified Beraha in a) 1 min, b) 2 min, c) 40 min and electrolytic etched with oxalic acid in d) 3 h.

The volume fractions of phase’s evolution are presented in Fig. 5 and Fig. 6 for the two heat cycles, comparing DICTRA models to the experimental results, with an expected sigmoidal behaviour [9]. It was shown that the planar geometry model does not describe the experimental results obtained in cycle “i” (Fig. 5), except at equilibrium, when it reaches the expected ferrite fraction, 71%. However, the planar model for cycle “ii” (Fig. 6) describes the experimental results, reaching the measured austenite fraction during all treatment time. Moreover, the spherical geometry grains model is only able to describe the experimental results of cycle “ii” (Fig. 6) after 30 min, since the curve overlaps the planar one. Thus, none of the geometric grain models are able to exactly describe heat cycles, however, the planar geometry is the one closest to the experiments results.
Fig. 4. Optical microscopy of the samples solubilized at 1088 °C for different times, etched with modified Beraha in a) 2 min, b) 30 min, c) 3 h and d) 36 h.

Chemical elements profiles at specific ageing times for both cycles and geometries of simulation were obtained as a function of the length model in DICTRA® simulations. Fig. 7 exemplifies the chromium profile at 1250 °C for the planar model.

Initial interface between ferrite and austenite can be seen in the composition profile associated to time zero of simulations at the horizontal distance of 10 μm. With the progress of simulation, during heating at 1250 °C, gradient profiles are developed at ferrite-austenite interface. Those composition profiles also indicate that the elements took longer to come into equilibrium in comparison with the phase’s volume fraction. For the chromium profile in Fig. 7, attenuation of the composition gradient, which indicates full equilibrium, was only achieved after 10 hours at 1250 °C. Thus, if the material is thermally treated in only 30 min, time required for stabilization of the ferrite and austenite, there will still be a gradient of chemical composition and, consequently, heterogeneity of corrosion resistance along the phase extension, different from what is desired in practice, since there is a direct relation with PREN and pitting potential (EP). Regions with smaller PREN, like Cr- and Mo-depleted areas, will present reduced localized corrosion resistance [10-12], and this information can only be obtained with simulation in DICTRA®.
Fig. 5. Comparison between experimental results and simulation models of the ferritic phase volume fraction as a function of treatment time at 1250 °C.

Fig. 6. Comparison between experimental results and simulation models of the austenitic phase volume fraction as a function of treatment time at 1088 °C.
Fig. 7. Chromium profile in different times at 1250 °C obtained at planar model simulation.

5. Conclusions

1. None of the geometric models used in DICTRA® simulations was able to perfectly describe the changes in volume fraction of phases at forging or solution treatment conditions. However, planar model is the one that better assess the behaviour of volume fraction phase’s changes for both heat treatments.

2. It is verified that the fractions of ferrite and austenite stabilize after 30 min of heat treatment, obtaining 71% of ferrite at 1250 °C and 51% of austenite at 1088 °C, and simulations results of volumetric fraction of phases are validated with those results.

3. Although the phases stabilize after 30 min, it is noticed that the equilibrium of chemical composition, marked as the absence of compositional gradients, is established long after the achievement of the equilibrium volume fraction of phases. The information about total attenuation of gradient profiles can only be obtained in DICTRA® simulations.

References

3D ViSE
SIMULATION OF A COMPLETE PROCESSING LINE

Abstract

State of the art metal processing lines need to suit to customer requirements, which are driven by short commissioning periods, fast start-up curves, large material flow rates and high demands in product quality. Minor problems encountered in engineering phase have big impact on to meet these requirements. To solve engineering problems during commissioning takes lots of time and goes along with enormous additional costs for customers and sellers. Highest priority customer needs during start-up phase will be to learn the efficient operation of the new production line in a short time to start immediate production after commissioning. Skilled operators and maintenance personnel already at start-up will increase initial earnings and are the way to sustained success. A tool was developed which helps increasing the software quality in a first approach. The complete production line is integrated in an external 3D environment and acts as virtual Level 0. In an early state of software engineering it is already possible to test the engineered automation program and sequences at the Digital Twin. Logic faults can be identified immediately. A second approach of the tool includes an integration of virtual control elements but real controller hardware to allow operating the whole virtual production line. This gives a big amount of application areas. To train operator personnel in advance on the Digital Twin, and to shorten amount of commissioning days, are just a few use cases. A parallel operation of the Digital Twin beside the real production line offers many advantages for problem identification, troubleshooting and supporting customer’s personnel during production.

Keywords

3D Virtual Simulation Environment; Digital Twin; Virtual Control Panel; Earlier production of prime quality; Faster ramp-up of production capacity; Initial earnings increase; Smooth start-up; Skilled operators right at start-up; Operator Training; Application for verification of software functionality; Controller independent simulation tool.

1. Introduction

Metal processing business is driven by faster engineering phases and shorter commissioning periods. A simultaneously increase of product quality and faster ramp-up of production capacity are the demands of customers. The fields of automation systems for industrial metal applications should develop in such a way to reduce the programming expenditure and to increase the flexibility and reusability of machine parts with consistently high demands in software quality. The standardization of control applications is the first most important step to achieve this goal. Standard software parts can be evaluated by their function and quality. Standardized routines and tools are not available for high quality function tests of complete automation systems and their applications. Often, existing procedures for function tests are custom made inside the Level 1 application, executed directly on the control
hardware. More complex scenarios for whole metal processing lines are not covered. The significance of internal simulation mechanisms does not meet the qualitative requirements in industries. Every software part has its own test- and simulation mechanisms with non-standardized tools as well as different multiple communication interfaces to other simulation tools and function groups which easily falsify the simulation results.

We propose an external simulation tool called 3D Virtual Simulation Environment (3D ViSE) which is not included in the Level 1 control software. 3D ViSE is based on the application VINCENT (Virtual Numeric Control Environment) [1]. It acts as a complete standalone application which replaces the real processing line. Consequently, 3D ViSE gives a defined condition of the plant and sends this information to the automation system over a standardised interface. In the same way the automation control system sends commands to 3D ViSE. Depending on the plant conditions, actions and feedbacks are generated inside of 3D ViSE and reported back to the automation system. Beside the command execution and report of information a more intuitive feedback is generated with our simulation tool. 3D ViSE gives a fully animated 3 dimensional model of the processing line. It is possible to have immediate visual feedback of reactions by triggered actions. The design of the simulation tool allows an assembly of a complete virtual production line out of a library. This library includes single machine parts which can be easily arranged or exchanged. Every single machine part works with standardized signal exchange for every valve, motor and sensor. The communication interface and protocol is defined in 3D ViSE concepts as well as the integration of the switchover in the Level 1 software between operation with the real world Level 0 or the Digital Twin presented by 3D ViSE. Standard communication protocols allow an integration of the 3D ViSE communication layer at control software independent from the automation system brand.

The paper is structured as follows: in the next section the system architecture and integration in the Level 1 and Level 2 System of 3D ViSE is described. Section three and four are concerned with the representation of the production line and the developed control architecture in 3D ViSE. Finally section five concludes this paper and provides an outlook.

2. System Architecture

3D ViSE is designed to fit in any automation configuration which provides an Ethernet based communication interface. This gives the independency of the used automation control hardware. For the Level 1 controller it makes no difference if the feedbacks are generated by real sensors from Level 0 field level or by the Digital Twin. To guarantee the seamless switchover between real Level 0 and the Digital Twin the communication interface is standardized for devices like valves, motors, binary- and analogue sensors. The communication between one or more Level 1 controller and 3D ViSE application is based on TCP or UDP protocol. A so called 3-way operational software switch is implemented to allow the change of the operation mode between:

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Mode</td>
<td>Normal operation mode; signals of metal processing line are exchanged with Level 1 controller and Level 0 peripheries</td>
</tr>
<tr>
<td>Ghost Coiling Mode</td>
<td>Special operation mode of Andritz metal processing lines; Line is in semi-operation with Level 0 peripheries and all sequences on Level 1 controller but with virtual</td>
</tr>
</tbody>
</table>
In a simplified network overview is shown in Fig. 1. One or more Level 1 Controllers communicate to the standard Level 1 HMI application as well as Level 2 (MES) System. Depending on the operation mode, commands and feedbacks are exchanged with Level 0 peripherals or the Digital Twin. Additionally, this system can be extended by virtual control panels. This Andritz designed application allows visualizing any desired control panel of the production line on a touch screen. As a result, in a very early stage of engineering phase the complete virtual operation of a production line. For smaller applications soft controller can be used instead of real Level 1 controllers. This depends on the capability of soft-controllers (referrer to controller manufacturer).

The communication interface is set up in a clean, efficient structured way. As communication protocol TCP or UDP can be used. Communication cycles less than 20ms can be realized. The communication is based on structures which are addressed to instances of motors, cylinders, binary sensors and analogue sensor.

### 3. Application single machines parts

As basic input data, 3D mechanical drawings from STEP files are used (e.g.: designed in Solid Edge). In an application relevant level of details the 3D elements are imported in 3D ViSE for further progress. Depending on the machine part itself the mechanical structure and their kinematics are mapped in 3D ViSE. Machine Bodies are linked to rotation and translation axes and form a functional kinematic loop. All functional relevant information is integrated in the properties of axes.

Fig. 2 shows a basic kinematic loop of a single machine.
The concept of 3D ViSE allows creating for all single machines this kind of basic kinematic structure which defines all simulation relevant functions like: movements of cylinders and motors, feedbacks of binary and analogue sensors. Physical values like the speed of a moving cylinder axis, its linked movements of machine parts or the movements of motor driven motions are depict in 3D ViSE. This allows getting exact feedback of movements and their timings. This kinematic loop can be tested already in offline sequences. Once connected to a control system single functions and basic interlocks can be tested and verified online on the real controller hardware.

Depending on the application, basic kinematic structures can be extended for simulation and testing of more complex functions. This gives possibility to test automation sequences in a more realistic way with all positioning capabilities.

The communication to right Level 1 controller is defined directly in the properties of the axis and sensor elements. In analogy to assignment of field machine I/Os, signals of the Digital Twin are assigned in the same way to a specific controller.
4. Application complete processing line

The organization of single machines as a library allows generating a complete processing line by step by step arrangement of single machines in 3D ViSE. Pre-tested single machines are arranged in a master project file and linked to final communication interfaces and control hardware. Fig. 4 shows the step by step integration of a single machine in a master project file. Depending on the size of the processing line different machine areas can be organized in multiple projects like Entry Section, Process Section or Exit Section. This gives the advantage of monitoring functions and movements in different plant sections at the same time.

![Fig. 4 from application single machine to application complete processing line- machine arrangement](image)

During SW-Development, 3D ViSE gives possibilities to test functions and sequences related to more single machines in one or more plant areas. In the same way training on single machine functions or complete processes and sequence flows in whole plant areas is possible. Operator trainings on different machine parts at the same time can be performed. This gives a more realistic simulation experience.

Beside simulation of machine movements, 3D ViSE gives the possibility to simulate material flows in the meaning of production material which is transformed by threading through the production line. Material instances are simple metal sheets or complete metal coils, with different physical and logical properties; like length, width, diameter and a lifecycle. During virtual production, the material properties are changed as a result of used machineries and their functions. The manipulation of the material instances, as well as their connection point (weldseam) affects the function of automation sequences of the complete production line. 3D ViSE allows the repeatable test of sequences including production material in different desired plant conditions. Fig. 5 and Fig. 6 show realisation and a use case of material instances like, metal sheet, metal coil or weldseam.
The combination of simulated movements with real physical timings and material instances makes it possible to verify important coil change timings for continuous production lines inside 3D ViSE. With the integrated physical behaviours of movements, timings of automatic sequences which include more machine parts will be verified too. Optimizations on the right machine parts in mechanical or automation belongings can be performed to increase production capacity.
The integration of touch controlled virtual control panels allows operating the line either from main control desk or any desired local control box from the field area. In this way customer personnel gets familiar with control elements in an easy way. Operators can be trained with respect to critical situations in production, to be able to set correct actions immediately. Impact of damaged or not reliable equipment or I/O signals can be simulated and the results are visualized immediately. Training sessions before or during start-up of a production line helps customers to get stress-free trainings on the new plant for sustained success. The V.I.P. Control Room (Virtual Interactive Plant Control Room) is a designated control room which allows customer personnel to join efficient training sessions. Normal production cycles or special operating conditions can be simulated. The used control desks are equipped with touch panels to show all needed local control panels, Level 1 HMI (Human Machine Interface) Screens and if desired Level 2 / MES (Manufacturing Execution System) Application.

5. Conclusion

Increasing the initial earnings and guarantee a smooth and faster ramp-up of production capacity with skilled personnel is the key factor for success in metal processing industry. To help customers to achieve these goals 3D ViSE is a well-qualified tool. Knowledge transfer and a common understanding from an already very early state of engineering help our customers to perform a smooth start-up.

With this tool our next steps are the extension of functionality to have a more realistic simulation of the production line with more dependencies in material and machine behaviors. In the same way reduction of complexity of the 3D Model regarding specific functions is necessary to improve the quality of simulation.

We focus on the further development of the V.I.P. Control Room concept to supply the best solution for trainings. Beside the V.I.P. Control Room, 3D ViSE can be installed on real processing lines in a parallel (shadow) mode. This supports the operator / maintenance personnel to address and show in an intuitive way desired machine parts or equipment. The integration of AR technology will be one of the next steps to link the information of 3D ViSE with the real production line.

References

Corrosion and in service problems
CORROSION BEHAVIOUR OF SLM 316L FOR DIFFERENT BUILD DIRECTIONS AND SURFACE CONDITIONS

Abstract

Selective laser melting (SLM) is an additive manufacturing technology that fabricates components from metallic powder. In this study, the pitting corrosion behaviour of austenitic stainless steel 316L produced by SLM is investigated. Electrochemical polarisation tests using a three-electrode set up (reference-working-counter electrode) were performed to evaluate the variance in corrosion and the pitting potential as well as the corrosion rate in 3.5 wt% NaCl solution. Investigations indicate the evident effect of surface roughness on the corrosion behaviour with the as-built surface exhibiting diminished resistance. Additionally, dissimilarity in the pitting corrosion behaviour for different build directions (δ=0/45/90°) was observed. Results indicate a dependent relationship between residual porosity and pitting resistance. Microstructural analyses (SEM-EDS) and roughness investigations were conducted and a link to the observed corrosion behaviour could be found.

Keywords

Selective Laser Melting, 316L, austenitic stainless steel, corrosion resistance, build directions, surface roughness.

1. Introduction

Stainless steels have a wide range of application in numerous industries owing to their high resistance to corrosion which is attributed to the thin (2-3 nm) passive film that forms spontaneously on the surface in an oxidizing environment [1]. Chromium concentration (>10.5 wt%) plays the dominant role in conferring passivity together with other alloying elements such as molybdenum and nickel [2]. The passive layer has a dual structure consisting of iron oxide as the external layer and chromium oxide as the internal layer [3]. The passive and more stable chromium oxide layer is heterogeneous due to the presence of defects on the surface of the material such as inclusions or pores [4,5]. This makes stainless steels more prone to localized corrosion.

Selective laser melting (SLM) is an additive manufacturing (AM) technology, which fabricates complex components from metal powder. For this, a high intensity laser beam melts the powder layer-by-layer within an inert gas atmosphere to produce parts directly from CAD-data. In the past years, SLM has transferred from rapid prototyping to a promising manufacturing technology which allows the production of parts with excellent mechanical and technological properties [6,7]. Furthermore, as the parts are built in layers, SLM allows the creation of highly complex parts and structures by a process in which the typical boundaries of conventional manufacturing can be neglected.
316L is a well-established material for the SLM process, characterized also by good processability [8,9]. Past research has focused on the investigation of process parameters, such as laser power, scanning speed, etc. to understand their influence on the microstructure, porosity and mechanical properties of 316L, processed by SLM [10–12]. The microstructure is a fine dendritic structure with cellular subgrains [13–17]. The size of the cellular subgrains is typically below 1 µm, and the width of the columnar subgrains is similar in size [18,19]. The research literature reports high relative density (> 99%) for 316L achievable with SLM [19–21]. The percentage of residual porosity present in the material after the SLM process is dependent on the laser energy density used and the heating and cooling rates of the melt pools [13,22]. Mechanical properties, such as tensile strength or elongation, can also be compared to values of conventionally manufactured 316L SS, or can even exceed them [10,11,23].

Stainless steels are known to exist in different phases; martensitic, ferritic, austenitic and duplex. The SLM produced 316L alloy shows the formation of pure austenitic phase. Previous work [14,15,24], using XRD analysis indicates high levels of purity for samples without the presence of any martensitic phase. Thus, no effect of the presence of a dual phase on the pitting behaviour can be asserted.

Stainless steels are particularly susceptible to pitting and crevice corrosion in media containing halide ions such as chloride [1]. Pitting takes place when these chloride ions are concentrated in a localized region resulting in the accelerated dissolution of the underlying metal [2]. Pitting behaviour for different materials can be compared using the parameter of pitting potential which is influenced by many factors such as surface condition, alloying composition, microstructural defects, potential, environmental composition, temperature etc. The pitting resistance of the SLM stainless steels has been reported to be notably higher than the wrought specimens produced by conventional manufacturing techniques like cold rolling or casting [15,17,24,25]. The primary reason for the enhanced resistance to pitting for SLM samples is the negligible presence of any sulphide based inclusions. These inclusions (manganese sulphide) have been found to be detrimental to the pitting potentials as they promote the breakdown of the passive layer [5,26].

SLM parts show relatively high roughness values in the as build state [27]. Post-processing (e.g. blasting, machining, polishing etc.) decreases the surface roughness of parts fabricated by SLM, but is time and cost-consuming tasks. Internal structures, such as cooling channels, make the smoothing of surfaces an even more effortful or virtually impossible task. The question thus arises, whether (effortful) surface improvement of SLM parts also affects the corrosion behaviour positively. As corrosion is a surface phenomenon, the exact condition of the surface has a major influence on the pitting behaviour of the material [2]. For example, pitting potential of type 302 stainless steel with 120 grit finish was shown to be, approximately, 150 mV lower than that with 1200 grit finish over a range of Chloride concentrations [28]. Schaller et al. [16], also reported that a higher surface roughness of SLM 304L specimens decreased the corrosion resistance and pitting potentials (up to 300 mV) in sodium chloride solutions. However, in all cases the surface of studied samples was modified by grinding and was not tested in their as built state.

The literature has widely reported the effect of process induced defects during SLM such as porosity on the corrosion behaviour of stainless steels, although the reported results are contradictory. Sander et al. [25] state that the results indicate no significant influence of porosity on the corrosion potential, corrosion current density and pitting potential of 3D printed 316L. Sun et al.[29] reported on the contrary, increased metal dissolution, breakdown of passivity and lower pitting potentials with increasing porosity volume. Moreover, Fedrizzi et al. [30] examined the role of pores on the corrosion resistance of sintered steels in sodium chloride solution. This work postulated that low resistance to corrosion of the sintered compared to wrought steels may be due to the formation of a galvanic coupling between the
free surface and the interior if the pore is acting as the anode. However, no conclusive microscopic investigation was conducted to support the claim. Another process induced defect apart from porosity observed in specimens made from SLM is Balling [13,31]. Its effect on the corrosion behaviour, however, is not yet explicitly understood.

The SLM process can be used to melt the powder at different angles thus, allowing it to form complex geometries and providing a high degree of freedom for manufacturing compared to conventional techniques. Different build angles can lead to variations in the microstructure (consisting of overlapping weld pools) and influence the material properties. Anisotropic effects are thus also expected to be true for corrosion behaviour. There is a paucity of work relating to the effect of different build directions on the corrosion behaviour of AM stainless steel. The objective of this paper is twofold; a) To simulate and compare the corrosion behaviour of the SLM 316L alloy in an as-built and polished state. b) To achieve a better understanding of the effect of different build directions (δ=0/45/90°) during the SLM process on the corrosion characteristics and microstructure. The simulation is performed by means of electrochemical polarization tests and the comparison is made on the basis of parameters like corrosion potential, pitting potential and corrosion rate.

2. Materials and methods

2.1. SLM parameters and specimen production

All specimens for corrosion experiments were fabricated with a SLM 280HL machine from SLM Solutions Group AG. The machine operates with a 400 W single-mode continuous wave (CW) ytterbium fibre laser. The specimens were produced out of 316L SS powder from Oerlikon Metco Europe with a particle size distribution D90 = 46 µm.

Fig. 1 shows the SEM micrograph of the morphology of the 316L stainless steel powder. The powder particles have a spherical shape with a few satellites. The elemental composition of the powder is shown in Table 1. The elemental weights% are within the values specified for the ASTM 316L grade. The powder used in this study is recycled multiple times. Negligible difference in the number of satellites and elemental composition was observed between the unused and recycled powder. The observation is supported by prior investigations made by Whittaker [32].

<table>
<thead>
<tr>
<th>Element (wt %)</th>
<th>C</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Mo</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>O</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
<td>17.66</td>
<td>0.06</td>
<td>0.38</td>
<td>2.34</td>
<td>12.78</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.4</td>
<td>0.04</td>
<td>0.07</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 1. Elemental composition of the 316L powder.

Specimens were built in three directions (0°/45°/90°, see Fig. 2). All specimen had a diameter of 15 mm and a thickness of 2 mm. The specimens were built with a layer thickness of 30 µm with rotating hatching, filling and border contour. Argon was used as shielding gas and the oxygen level in the build chamber was kept below 0.1%. The preheating temperature of the build platform was 100°C. The main scanning parameters are shown in Table 2. The support structure was removed manually. In total, 80 specimens were fabricated. For later investigation of the influence of the surface roughness on the corrosion behaviour, half of the samples were kept in the as-built state and the other half was polished.
Figure 1: SEM images and EDS spectra of particles for (a, c) Recycled (b, d) Unused powder.

Figure 2. Build directions of the 316L SLM specimen. The z-axis marks the build direction of the layers.

<table>
<thead>
<tr>
<th></th>
<th>P&lt;sub&gt;b&lt;/sub&gt;=75 W</th>
<th>v&lt;sub&gt;b&lt;/sub&gt;=400 mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Border</td>
<td>45°</td>
<td>90°</td>
</tr>
<tr>
<td>Filling</td>
<td>P&lt;sub&gt;f&lt;/sub&gt;=113</td>
<td>v&lt;sub&gt;f&lt;/sub&gt;=800 mm/s</td>
</tr>
<tr>
<td>Hatching</td>
<td>P&lt;sub&gt;H&lt;/sub&gt;=150 W</td>
<td>v&lt;sub&gt;H&lt;/sub&gt;=800 mm/s</td>
</tr>
<tr>
<td></td>
<td>h&lt;sub&gt;H&lt;/sub&gt;=120 µm</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. SLM parameters- P laser power; v scan; speed; h hatch distance per layer.

The surface roughness was measured with a Waveline W20 tactile measurement device from Jenoptik. For each specimen configuration, at least five roughness measurements were performed. Due to the limited space on the specimens, four sampling lengths (l<sub>r</sub>) with a cut-off (λ<sub>c</sub>) of 2.5 mm were chosen, following DIN EN ISO 4288:1998 [33].
2.2. Metallographic preparation and SEM-EDS

Specimens for metallographic characterization were embedded in epoxy resin. The mounted specimens were ground in steps from 320-1200 grit size under running water. Further, polishing was carried out to 1 µm surface finish using diamond suspension. The polished specimens were then cleaned ultrasonically in an ethanol bath for 30 minutes, and rinsed with DI water and dried. Scanning electron microscopy (SEM) was conducted using a Tescan Mira 3 SEM equipped with an Energy Dispersive X-Ray Spectrometer (EDXS) detector. A nominal acceleration voltage of 10 kV and a working distance of 15 mm was used for the SEM analysis.

2.3. Porosity measurement

15 images each for different build directions were collected using the SEM at a fixed view field of 1000×1000 µm². The images were taken arbitrarily at different locations on the surface along three different radii of the specimen moving radially outwards from the centre. All images were analysed using ImageJ software to determine the area fraction of the pores. The mean of all the individual area fractions determined gives the porosity percentage for the respective build direction.

2.4. Potentiodynamic test

SLM specimens of different build directions were tested in their as-built and polished state. Tests were performed using the VersaSTAT 4 potentiostat from Princeton Applied Research. The conventional three electrode cell configuration was used with Ag/AgCl (3M KCl) reference electrode and Pt plate as counter electrode. The specimens with a surface area of 1 cm² were used as the working electrode. A 3.5 wt% NaCl solution was used as the electrolyte in a 1 litre cell. All tests were conducted at room temperature (22°C) and at a pH of 6.7 ±0.2. The tests were performed at a scan rate of 0.167 mV/s from -0.3 mV to +0.9 mV vs. OCP. Before starting the potentiodynamic test the specimens were immersed in the electrolyte for a duration of 120 minutes for the stabilization of the open circuit potential.

2.5. Linear polarization resistance

This method was used to calculate the corrosion rate for the different specimens tested. Tafel fit was performed using the Verasstudio software. The applied potential to find the anodic and cathodic Tafel slopes (ba, bc) was ±50 mV vs OCP. The Stern Geary equation is used to calculate the corrosion current density (i_corr) and the Corrosion rate (CR) in mpy. The calculation is made according to ASTM G59 [34] (Equivalent weight 25.5 g with valences Fe/2, Cr/3, Mo/3; Density 7.98 g/cm³) shown in Table 3.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion current density</td>
<td>( i_{corr} = \frac{B}{R_p} )</td>
</tr>
<tr>
<td>Stern-Geary coefficient</td>
<td>( B = \frac{ba \cdot bc}{2.303(ba + bc)} )</td>
</tr>
<tr>
<td>Polarization resistance</td>
<td>( R_p = \frac{\partial E}{\partial i} \quad i = 0 ) ( \frac{dE}{dt} \to 0 )</td>
</tr>
<tr>
<td>Corrosion rate</td>
<td>( CR = \frac{K \cdot i_{corr} \cdot EW}{Den} )</td>
</tr>
</tbody>
</table>

Table 3. Formulae used for linear polarization resistance.

3. Results and discussion

3.1. Microstructural characterization

SEM images were used to investigate the surface morphology of the samples in the as-built and the polished state. Fig. 4 shows the surface of the three build directions in the as-built state.

![Figure 4: SEM micrograph in SE mode showing the as-built surface of (a) 0° (b) 45° and (c) 90°.](image)

The surface shows the presence of spattered droplets adhered to the surface. This phenomenon is known as balling, which is an inherent process induced defect primarily resulting in a poor surface finish. It is clearly evident from Fig. 4 that balling increases as the building direction angle increases from 0° to 90°. Balling is governed by the wetting and surface tension characteristics of both molten powder, solid powder and solid surface and is strongly influenced by the temperature of both the molten powder and the solid surface [35].

Fig. 5 shows a magnified view of the surface of a polished SLM specimen. The overview in (a) exhibits a network of overlapping solidified melt pools on the surface, observed in case of all building directions. The direction of flow of the molten metal in the melt pools is governed by the laser scanning pattern in the plane parallel to the building direction [17]. The detailed Fig. 5(b) reveals a fine dendritic microstructure with cellular and columnar sub-grains. The dendritic structure is formed due to rapid cooling of the fused molten metal and the direction of grain growth depends on the flow of heat during the solidification process. At the interface between two melt pools, a finer sub-grain structure appears which may be indicative...
of a higher temperature gradient (high cooling rate) present at the interface.

![Fig. 5a](image)
![Fig. 5b](image)

Figure 5: The SEM image of the polished surface for a 90° SLM specimen illustrating a) an overview of solidified melt pools and b) a detailed image showing a fine dendrite structure within the melt pool.

An EDS linescan was performed over a length of 65 µm which is shown in Fig. 6. The result shows a highly homogeneous matrix with negligible macro-segregation of the alloying elements on the surface, although the observed dendritic structure is associated with micro-segregation of Cr and Mo at the walls [17,36,37]. Schaller et al. [16] used TEM-EDS to show the segregation and observed elevated concentrations of Cr at the cell walls compared to the centre of the cell. This kind of preferential segregation at the walls can have an adverse effect on the corrosion behaviour due to the formation of a Cr depleted zone. However, studies have been conducted to minimise this segregation and Qiu et al. [14] showed negligible segregation of elements using a pulsed laser mode for the SLM process and also showed that if the solidification rate can be increased during the process it would cause solute trapping, thus minimising segregation at the walls.

![EDS Linescan](image)

Figure 6: EDS Linescan of the 90° polished specimen plotting the variation in elemental composition over the surface.
As already mentioned, SLM allows the creation of parts with complex structures and geometries. But even for SLM, specific design rules, must be taken into consideration, as for any other manufacturing technology. In this context, one of the main characteristics is the downskin angle $\delta$ (see Fig 7). It is defined as the angle between the build platform and the downskin surface. The downskin angle is a measure for the necessity of support structures for the SLM process. Support structures are required to keep the part in position and to transfer the heat during the melting process. Opposite to the downskin, the upskin surface can be found. For complex parts, the direction of upskin and downskin surface varies constantly. Thus, a difference in the build direction would cause variation in the cooling rates resulting in different levels of micro-segregation in specimens. Further investigations need to be conducted to validate the effect of building direction in SLM on the elemental micro-segregation.

![Figure 7: Downskin surface (D) with downskin angle $\delta$.](image)

Fig. 8 illustrates the surface morphology for different build directions and plots the corresponding porosity volume%. The porosity is observed to be the highest for the 45° (1.01%) and lowest for 90° (0.15%). Previous investigations [10–13,25,29] determining porosity for specimens made using SLM, reported that the major factors affecting porosity is the laser energy density and the scanning pattern. In addition, it was proved that the porosity volume% is also affected by the build direction, keeping other process parameters fixed. Fig. 9 shows the magnified images of the pores, in which two different morphologies appeared: (a) representing the larger size irregular shaped pores with a high aspect ratio and, (b) representing the smaller size spherical shaped pores. The former are due to lack of fusion, predominantly present at the interface between the hatching lines [38]. The latter are gas pores formed due to entrapped gas bubbles in the solidified metal formed [38]. Due to the large size of lack of fusion pores their contribution to the volume% of porosity is more significant than that of gas pores.
Figure 8: SEM images in the BSE mode of the polished surface for build directions a) 0° b) 45° c) 90°. The dark contrast represents residual porosity, values plotted in (d).

Figure 9: SEM image illustrating different morphology of pores with a) lack of fusion pore b) gas pore.

The SEM analysis for all three build directions illustrates the surface that is present with nano-scale circular inclusions, which are distributed randomly throughout the matrix. EDS spot analysis was performed to investigate the chemical composition of these inclusions shown in Fig. 10. It is observed that these spots are enriched in Si, Mn and O as compared to the bulk.
and thus are most probably the rhodonite inclusion type reported in previous studies [39,40].
They could be formed due to the high affinity of Si to form oxides with the residual oxygen present in the SLM chamber at high temperature. Yan [40] identified these inclusions as Zener-pinning particles inhibiting the grain growth and increasing the mechanical strength of as-built SLM 316L. However, additional investigations are required to correlate the effect of different build directions will present on the volume percentage of these inclusions.

Figure 10: EDS spot analysis spectra for the inclusions present on the 90° specimen.

3.2. Roughness measurement

<table>
<thead>
<tr>
<th>Specimen Configuration</th>
<th>Ra (µm)</th>
<th>Rz (µm)</th>
<th>Rmax (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Std-Dev.</td>
<td>Mean</td>
</tr>
<tr>
<td>As-built, 0°</td>
<td>14.88</td>
<td>0.81</td>
<td>92.84</td>
</tr>
<tr>
<td>As-built, 45°</td>
<td>11.09</td>
<td>1.87</td>
<td>74.91</td>
</tr>
<tr>
<td>As-built, 90°</td>
<td>8.29</td>
<td>1.19</td>
<td>53.89</td>
</tr>
<tr>
<td>Polished, 0°</td>
<td>0.21</td>
<td>0.14</td>
<td>3.46</td>
</tr>
<tr>
<td>Polished, 45°</td>
<td>0.15</td>
<td>0.03</td>
<td>2.44</td>
</tr>
<tr>
<td>Polished, 90°</td>
<td>0.12</td>
<td>0.05</td>
<td>1.35</td>
</tr>
<tr>
<td>316L sheet material, polished</td>
<td>0.02</td>
<td>0.01</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 4: Results of roughness measurements on SLM and 316L sheet material – mean values and standard deviation.
The surface roughness was investigated for SLM specimens of the three build directions in as built and polished state, as well as for sheet metal to provide a reference. The values are presented in terms of the roughness average (Ra), the mean roughness depth (Rz) and the maximum roughness depth (Rmax) in Table 4, conventionally used in industries. As expected, the roughness of the polished specimens is substantially lower than that of the as-built specimen due to the absence of any balling on the surface. Even after polishing, the roughness of the SLM specimens, regardless of the build direction, is much higher than that of sheet metal. The lower roughness magnitude for the sheet metal is to be zero due to the assumed porosity. Within the different build directions, the 0° specimen has the highest and 90° the lowest roughness in both surface conditions. In the as-built state the high roughness of the 0° specimen is due to the cover layer which is not remelted. Furthermore, in the polished state the deviations are probably a result of the difference in porosity.

3.3. Electrochemical investigation

Table 5 exhibits the determined electrochemical parameters derived from the measured potentiodynamic curves for SLM specimens (0°, 45° and 90°) in Fig. 11. The evaluation of open circuit potential (E_{corr}), pitting potential (E_{pit}) and current density (i_{corr}), generally results in a lower corrosion resistance for the as-built surface condition compared to the polished surface, irrespective of the building directions.

<table>
<thead>
<tr>
<th>Build Direction (deg)</th>
<th>E_{corr} (mV)</th>
<th>E_{pit} (mV)</th>
<th>i_{corr} A/cm²</th>
<th>CR (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLISHED</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>-161.33</td>
<td>900.79</td>
<td>1047n</td>
<td>0.430</td>
</tr>
<tr>
<td>45</td>
<td>-161.02</td>
<td>622.31</td>
<td>49.89n</td>
<td>0.021</td>
</tr>
<tr>
<td>0</td>
<td>-134.64</td>
<td>754.80</td>
<td>30.85n</td>
<td>0.013</td>
</tr>
<tr>
<td>AS-BUILT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>-168.38</td>
<td>668.93</td>
<td>1380n</td>
<td>0.567</td>
</tr>
<tr>
<td>45</td>
<td>-181.26</td>
<td>416.20</td>
<td>139.39n</td>
<td>0.057</td>
</tr>
<tr>
<td>0</td>
<td>-165.32</td>
<td>465.58</td>
<td>29.03n</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 5: Results of the potentiodynamic test conducted in 3.5 wt% NaCl solution for as-built and polished specimens. Open circuit potential (E_{corr}), pitting potential E_{pit}, current density at the open circuit (i_{corr}) and corrosion rate (CR).
Figure 11: Potentiodynamic polarization graphs for SLM 316L for different build directions and surface conditions, left: polished and right: as-built condition.

$E_{\text{corr}}$ is a measure of the materials passivation state at open circuit. The higher the $E_{\text{corr}}$ the more passive is the material [29]. The as-built specimens have a slightly lower $E_{\text{corr}}$ than the polished specimens, and are thus similar in susceptibility to corrosion.

$E_{\text{pit}}$ defines the susceptibility against pitting corrosion. The as-built specimens have a decreased $E_{\text{pit}}$, lower by ~200 mV compared to the polished specimens. This observation supports the results published in the literature [16,28,41] which concur that rougher surfaces show a reduced Epit as they provide more occluded sites wherein the concentration of the chloride ions may increase, causing accelerated breakdown of the passive film and thus leading to pit initiation.

The $i_{\text{corr}}$ is used to determine the metal dissolution rate during the corrosion process at the $E_{\text{corr}}$. The as built surfaces in both the 90° and 45° building directions show the expected higher values of $i_{\text{corr}}$ in comparison to the polished ones. Interestingly, there is no significant difference in $i_{\text{corr}}$ and corrosion rate for the 0° specimen with different surface conditions. Ni et al. [42] reports a similar behaviour in the case of 0° build direction.

The potentiodynamic polarization curves shown in Fig. 11 highlight the difference in the corrosion behaviour for the specimens with different build directions. In the as built and the polished state, $E_{\text{corr}}$ is higher for 0° compared to 45° and 90°, however the difference in potentials is minimal. The pitting resistance evaluated through $E_{\text{pit}}$ values indicates the highest resistance for the 90° and lowest for the 45° build direction. The observed difference is appreciably high and is greater than 250 mV. The larger passivation region for the 90° specimen is indicative of a more stable passive film at high anodic potentials. This is believed to be due to the low porosity% in the 90° specimens compared to the 0° and 45° build directions. The passive layer around the pores is more prone to breakdown due to the increased concentration of Cl⁻ ions, and decreases the pH locally causing growth of the pit due to the autocatalytic nature at the pore. $E_{\text{pit}}$ is also dependent on the size and composition of the inclusions present on the surface. Preferential pit initiation has been reported in the literature at the position of oxide particles. Rhondonite ((Mn,Si)O₂ inclusions) has been observed on the surface as discussed in the previous section.

The 90° specimen shows the highest $i_{\text{corr}}$ and also passive current density, despite having the highest $E_{\text{pit}}$. The passive current density is a measure of the quality and electrical conductivity of the passive layer formed. The increased current density may be attributed to an increased area fraction of oxide inclusions present on the surface. This may have a
detrimental effect on the formation of a compact layer and increase the current density by the formation of nano-galvanic couples due to the higher nobility of Si. Nonetheless, the size of these inclusion is very small and too small to deleteriously effect the $E_{pit}$. Schaller et al. [16] also hypothesizes that these nano-scale oxide inclusions may enhance the pitting resistance compared to the large size inclusions seen in the wrought material. Moreover, the $E_{pit}$ may be shifted to more positive values in the 90° specimen because of the protective action of the corrosion product formed on the surface given the higher passive range current density.

A comparison to the sheet metal is also provided in the Fig. 11. The result clearly proves enhanced pitting resistance seen for the SLM produced specimens irrespective of the build direction or surface condition. This behaviour has been studied previously and higher pitting potentials for the SLM specimens has been ascribed to the absence of MnS inclusions and a finer microstructure compared to the sheet 316L. The sulphur based inclusions, observed on the surface of the sheet specimen in the previous section, act as sites of pit nucleation and promote stable pit growth [4,5].

Fig. 12 shows SEM micrographs of the surface of the SLM 0° and 90° specimens at pore sites after 2 different immersion times in a pH=1 HCl solution. The analysis shows negligible pitting attack after 21 days of immersion. Similar immersion tests were conducted on sheet 316L in acidic and alkaline environments which demonstrated stable pitting growth through the surface in significantly lower immersion times [43].

![Figure 12: SEM micrographs in BSE mode for polished specimens immersed in HCl, (a)0° 0 days, (b) 0° 21 days, (c) 90° 0 days and (d) 90° 21 days.](image)

4. Conclusion

In the present study the corrosion resistance of SLM 316L for different surface conditions and build directions was evaluated. The corrosion behaviour was correlated with the investigated surface defects present in the SLM specimens. The following are the conclusions drawn:

1. The microstructure of the SLM specimens in all the build directions reveals a network of overlapping melt pools directed by the laser scanning in the plane parallel to the scanning. Within the melt pools a dendritic structure is observed with a preferential grain growth direction depending on the flow of heat during solidification.

2. SLM specimens exhibit a range of surface defects such as; balling, process induced porosity, presence of inclusions and increased surface roughness. The proportion of these defects is greatly influenced by the build direction.

3. Balling on the surface increases with increasing inclination of the build angle in the ascending order from 0° to 90°. The porosity percentage is also different for a build angle of 90° exhibiting the minimum compared to 0° and 45°. EDS analysis also
indicates the presence of nano-scale (<50 nm) inclusions enriched in Si, Mn and O.

4. Due to the presence of a number of the defects mentioned, the surface roughness of the SLM specimens is significantly higher than the conventionally produced sheet material. The surface roughness for the 0° displays the highest and 90° the lowest Ra, Rz and Rmax values. This is attributed to the remelting of the cover layer for the 90° specimens.

5. Electrochemical results show substantially improved corrosion resistance (based on $E_{corr}$, $i_{corr}$ and $E_{pit}$) of the polished specimens in comparison to the as-built specimens irrespective of the build direction. Thus, post-processing polishing techniques such as grinding or polishing should be adopted by industries to improve the corrosion behaviour of SLM 316L.

6. The 90° building direction shows the highest and 45° the lowest magnitude of pitting potentials (difference of 250 mV). The process induced porosity is believed to affect the pitting resistance for the different build directions.

7. All the SLM specimens (different surface conditions and build directions) show significantly enhanced pitting resistance compared to conventionally produced sheet material, which is mainly due to the absence of any sulphur based inclusions and a more stable passive film. This result is proved by both the potentiodynamic and the immersion tests.

Acknowledgements

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References


MICHAEL DAVIES

THE USE OF NICKEL-CONTAINING ALLOYS IN THE CHEMICAL INDUSTRY

Abstract

Nickel-containing alloys and stainless steels are effective in preventing corrosion in severe applications within the chemical process and related industries. Examples of their use in handling some of the most common chemicals are given. Conditions for the successful use of these alloys are provided. The role of nickel in these environments will be explained and will summarize their resistance to general and localized corrosion attack.

Keywords

Stainless steels, nickel, acids, alkalis, corrosion, cases

1. Introduction

Nickel has some important electrochemical properties. It is close to hydrogen on the redox potential scale and is able to polarize readily so does not tend to liberate hydrogen during corrosion. In reducing acid systems nickel often assumes an open circuit potential equal to that of platinum. It readily forms a passive film which protects against corrosion in oxidizing environments. Nickel is metallurgically compatible with many other metals such as iron, chromium and molybdenum and has considerable solid solubility for them. It can thus form a wide range of corrosion-resistant alloys, that normally have face centred cubic austenitic structures. With lower concentrations of nickel in stainless steels, a duplex (austenitic-ferritic) structure is formed.

In stainless steels, nickel stabilizes the austenitic structure which enhances the mechanical properties and fabrication characteristics. It is effective in promoting repassivation, especially in reducing environments. In more highly alloyed stainless steels with increased concentrations of chromium, molybdenum or silicon, for example, the level of nickel must also be increased to maintain the austenitic structure. Higher nickel levels increase the stability of the oxide formed at elevated temperatures and decreases spalling.

The chromium-rich layer is responsible for the corrosion resistance of stainless steels but is liable to damage, particularly in the presence of chlorides, which can lead to localized attack, such as pitting and crevice corrosion. Nickel does not directly influence the onset of such local attack but is beneficial in reducing the rate of propagation. The 300 series stainless steels, with a nickel content of around 8% shows a minimum resistance to chloride stress corrosion cracking (CSCC); a concentration lower or higher than this greatly improves resistance to CSCC.

Stainless steels and other nickel-containing alloys are widely and successfully used in the chemical process and related industries. They are specified, for example, in the production of many common industrial chemicals as well as in processes that use these chemicals. The stainless steels in this paper are referred to by their common name and all alloys by their UNS number. [1]
2. Hydrogen chloride and hydrochloric acid

Dry hydrogen chloride gas is not corrosive and carbon steel is satisfactory up to about 250°C. In operations above the dew point, the presence of moisture does not appreciably increase corrosion rates. At lower temperatures where moisture condenses, hydrochloric acid is formed by reaction with water and is highly corrosive to most metals. Types 304 (UNS S30400) and 316 (S31600) stainless steels and their low carbon variants 304L (S30403) and 316L (S31603) are subject to CSCC below the dew point and during shutdown, even at ambient temperature. This can only be prevented by taking precautions to ensure a bone-dry feed to the unit, maintaining shutdown and start up precautions of gas-blanketing and keeping the equipment dry.

Alloy 200 (N02200) is consistently resistant in dry as well as wet HCl gas. In cyclic operating conditions, particularly in the presence of air or oxygen, Alloy 600 (N06600) and Alloy 825 (N08825) offer good all-around resistance.

Hydrochloric acid is a reducing acid, the cathodic reaction is hydrogen evolution upon contact with metals below hydrogen in the electromotive series. Dissolved oxygen or stronger oxidants promote corrosion of many nonferrous metals above hydrogen. All grades of stainless steel become active and are attacked by hydrochloric acid and in very low concentrations the acid can cause pitting, crevice corrosion or CSCC. With duplex grades, the tendency is to attack the ferrite phase preferentially.

Alloy 825 (N08825) and Alloy 20Cb-3 (N08020) have useful corrosion resistance at all concentrations at temperatures <40°C. The super-austenitic molybdenum-containing alloys with nitrogen, such as alloys 254 SMO® (S31254), AL-6XN® (N08367), AL-6XN PLUS® (N08367) and Alloy 926 (N08926) can be used in some applications in hydrochloric acid concentrations < 3 wt%. Alloy 654 SMO® (S32654) with nominal 7.3% Mo can be used up to about 8% acid at room temperature. Alloy 200 and Alloy 400 (N04400) and its’ variants are attacked by hydrochloric acid, only in the presence of dissolved oxygen or stronger oxidants. Alloy 600 (N06600) is basically non-resistant, suffering severe pitting as well as general corrosion.

The 30% Mo materials, i.e., Alloy B-2 (N10665), Alloy B-3 (N10675) and Alloy B-4 (N10629), were developed specifically for this service and resist all concentrations of HCl to the atmospheric boiling point. Dissolved oxygen is a mild accelerant, however, and oxidizing contaminants (usually ferric ions, often derived from handling and storage) can cause very severe corrosion. Alloy C-276 (N10276) has excellent resistance to all concentrations at room temperature, and good resistance (<0.5 mm/y) in all concentrations up to 50°C. Alloy G-30 (N06030) and Alloy G-35 (N06035) have reasonable resistance at ambient temperatures and are especially resistant to hydrochloric acid contaminated with oxidizing salts.

Emission-control equipment is used for the removal of HCl from various industrial gases. Corrosion in parts of this type of equipment can be very severe, and the rate of attack is not always predictable. Alloys such as C-276 and high-chromium, low-iron variants such as C-2000 (N06200) find increasing applications. In some cases, such alloys are applied as thin sheet ‘wallpaper’ to a structural steel structure, giving effective resistance at reduced cost.

3. Sulphuric acid

The corrosion resistance of metals in sulphuric acid is strongly dependent on acid concentration. Under aerated conditions Type 304 will resist 15% acid at ambient temperatures. Type 316 will resist 10% acid under de-aerated conditions, and 30% acid under aerated conditions at room temperature. Corrosion in most industrial acid streams is strongly
influenced by the presence of contaminants; oxidizing ions such as cupric, ferric or nitrate ions, enhance passivation and decrease corrosion rate, or reducing species such as chlorides or fluorides which increase corrosion rate. Conventional austenitic grades, Types 304L and 316L are routinely employed in strong H$_2$SO$_4$, e.g., for nozzle liners, piping, etc, where flow conditions render carbon steel unsuitable. Corrosion resistance of these grades is good up to about 6 m/s in the absence of abrasive particles (although normal design would be limited to about 2-3 m/s). The resistance of these grades can be enhanced by anodic protection, e.g., for Type 316L acid coolers. Unprotected Type 316 is somewhat less resistant than Type 304 in hot acid above about 93% because of the ease of oxidation of the molybdenum component.

Duplex grades, such as Alloy 7Mo PLUS® (S32950) resist 5% acid to the boiling point and up to 40% at ambient temperatures. The ferrite phase in duplex alloys, in general, is potentially subject to selective attack in these weak concentrations. Alloy 7-Mo PLUS® and Ferralium 255® (S32550) have good resistance to concentrated sulphuric acid, e.g. in 98% acid up to about 150°C. Duplex castings such as CD-4MCu (J93370) are also resistant to turbulent concentrated acid.

Super-austenitic grades 6% Mo e.g., Alloy 6XN®, 254 SMO® and the “20-type” copper-bearing Alloy 20Cb-3 offer gradually increasing resistance to intermediate concentrations. Alloy 20Cb-3 is used primarily to resist velocity or turbulence. The cast form, CN-7M (J95150), is used for throttling valves and pumps. Titanium-stabilized Alloy 825 has substantially the same resistance as Alloy 20Cb-3 in concentrated acid. Other variants of Alloy 20, such as Alloy 904L (N08904) resist concentrated sulphuric acid to about 50°C.

In the presence of severe chloride contamination, even more highly alloyed grades such as high chromium 6% molybdenum alloys, e.g. Alloy 31 (N08031) or alloys with 7-8% molybdenum, e.g., Alloy 654 SMO® offer better resistance. The two high molybdenum alloys 25-6MO (alloy 926; N08926) and 27-7MO (S31277) are better than Alloy 825 until the acid strength exceeds about 80% and about 88% respectively, Figure 1. [2] In the more concentrated acid the low molybdenum Alloy 825 is more resistant. Type 316 stainless steel is also included in this Figure for comparison.

![Fig. 1. Iso-corrosion Curve at 5 mpy (0.13 mm/y) for High Molybdenum Stainless Steels in Sulphuric Acid.](image)

High silicon austenitic stainless steels with nominally 5.5% Si, such as SX® (S32615) alloy and the SARAMET® alloys (e.g. S30601) and a 6% silicon alloy, ZeCor® (S38815) are used in hot, concentrated acid and compete with anodically protected 300 stainless steels for use in towers, coolers and piping. There is also a 7% silicon stainless Cronifer 2509Si7® (S70003) which has the highest silicon content in iron-base wrought alloys. Cast Ni-Si alloys typically containing 8 to 10% silicon, were developed for handling hot or boiling sulphuric acid
of most concentrations. They have also been used to resist strong nitric acid (>50%) and nitric-sulphuric acid mixtures.

Nickel-copper alloys, such as Alloy 400 can resist boiling 5% sulphuric acid (which rapidly loses any dissolved oxygen) but very high rates of attack are encountered below the boiling point. At and above 25%, where the acid becomes increasingly oxidizing in nature, both Alloy 400 and Alloy 200 show increasing corrosion. The Ni-Mo alloys e.g., Alloy B-2 and derivatives show good resistance in weak acid, even in the presence of dissolved oxygen, to about 50°C and at the boiling point where the oxygen is removed by ebullition. In concentrated acid these are the best of the nickel-based alloys. They are resistant to 70% acid up to the atmospheric boiling point and to 99+% H₂SO₄ to about 120°C, in the absence of oxidizing contaminants.[3] Traces of oxidizers, e.g. ferric ions or nitric acid will cause attack of these chromium-free grades.[4] The Ni-Cr-Mo grades, based on the original Alloy C and typified by Type C-276 are resistant to about 90°C in the 93-98% range (with <40 ppm chloride) and lesser concentrations above 70% to about 50°C.

4. Nitric acid

Stainless steels are the primary materials used in nitric acid service. All Cr-Ni stainless steels are in the passive state close to transpassivity in 50%, 60% and 67% nitric acid at ambient temperatures. Stainless steels are potentially susceptible to intergranular attack even if fully annealed. Type 304L retains its resistance to corrosion by nitric acid in the HAZ after fusion welding or after any short-term heating above 455°C followed by slow cooling. Type 304L will, however, eventually sensitise if held in the adverse temperature range for prolonged periods, as in thermal stress-relief of very heavy-walled vessels. The 304L grade is generally more resistant than the molybdenum-bearing Type 316L. The equivalent cast version of Types 304 and 304L are CF8 (J92600) and CF3 (J92700), respectively, and they exhibit approximately the same corrosion response as the wrought alloys. Stainless steels especially formulated for nitric acid resistance are now produced under the same UNS number. Type 304NAG or 304 Special (S30403NAG) is essentially S30403 with lower carbon, silicon and phosphorus contents and some special mill processing. [5] Alloy 33® (R20033) is not a stainless steel but is an austenitic alloy based on very high chromium content which has excellent resistance to strong nitric acid and can be used at concentration up to 85% at temperatures up to at least 75°C.

Stainless steels are susceptible to vapour phase corrosion in high concentrations (95%+) of nitric acid under storage conditions at ambient temperature. Stainless steels tanks used to store even 92% nitric acid can be subject to rapid corrosion in the vapour space over the acid where 98% acid can condense on the walls.

At elevated temperature corrosion of stainless steels increases significantly and more highly alloyed stainless steels, nickel-based alloys, titanium, zirconium or tantalum are needed. The major alloying element of benefit in resisting corrosion by nitric acid is chromium. Among the group of high chromium stainless steels suitable for nitric acid service is Type 310L (S31050), Type 310S (S31008) which are both derivatives of the heat-resisting, high-carbon Type 310 (S31000). The modified Type 310 alloys offer significant advantages in corrosion resistance in nitric acid especially at high temperatures and they are often used for condensers in the concentration of the acid.

Another high chromium austenitic stainless steels that resists corrosion in high temperature, strong nitric acid is Alloy 28 (N08028) which has excellent resistance, especially to hot acid, in spite of its molybdenum content. Its corrosion resistance is comparable to type 310L and somewhat better than Alloy 20Cb-3 at high acid concentrations and temperatures.
Silicon is another alloying element that improves corrosion resistance in oxidizing environments. A wrought austenitic stainless steel containing 4% silicon is A610® (S30600) and this has excellent resistance to highly concentrated nitric acid. It is, however, less corrosion-resistant than types 304L, 310 or 446 (S44600) at lower concentrations. The alloy with 5.3% silicon, A611® (S30601) has even better resistance to corrosion by nitric acid. At least three other high-silicon alloys exist. Cast low carbon, high silicon stainless steels have been developed for nitric acid service based on 20% Cr, 13% Ni with varying amounts of silicon up to 6.5%. These cast alloys are being used for pumps and valves in concentrated nitric acid service. A cast version of S30600, Durcomet 5® (J93900) is an austenitic alloy that is solution heat treated and quenched after casting. It has similar resistance to the wrought equivalent and superior resistance to other cast alloys that are used in nitric acid. Only alloy cast iron, Durichlor 51® containing 14.5% Si has better resistance in the hot, strong acid.

The proprietary duplex Alloy 7-Mo® (S32900) has excellent resistance to nitric acid. A modified version of this alloy, 7-Mo PLUS® has less carbon, silicon, phosphorus, sulphur and added nitrogen which gives it improved resistance to reboiling conditions in condenser coolers. The cast duplex alloy CD4MCu (J93370, e.g. Durichlor 100®) with 26% Cr, 5% Ni and 2% Mo is similar to the wrought Alloy 7-Mo®, has good resistance to corrosion by nitric acid and is used primarily for pumps and valves. Alloy 2304 (S32304) is being used successfully in nitric acid applications.

Nickel alloys offer good resistance to pure nitric acid and are particularly effective in mixed acid media (e.g. nitric with sulphuric or phosphoric acids). Ni-Cr-Mo alloys have good resistance to nitric acid even if small amounts of chlorides or fluorides are present. Alloy 800 (N08800) has excellent resistance and is also significantly more resistant to CSCC than the austenitic stainless steels. Alloy 825 has excellent resistance to nitric acid solutions at all concentrations and temperatures up to and including boiling 65% and is stabilized against sensitization by the addition of titanium. It is being successfully used in boiling 65% in nuclear fuel processing applications. Alloy 625 (N06625) also has good resistance to nitric acid, but it is less resistant than Alloy 690 (N06690) in mixed nitric/hydrofluoric acid media. Alloy 20Cbr-3 is widely used in nitric acid, especially where the acid may be contaminated with chlorides or fluorides or involves high velocity flow as in pumps or valves. The cast version of Alloy 20Cbr-3, CN7M (J95150), is compositionally different from the wrought alloy in that it contains less nickel (about 28%) and no niobium stabilization. This cast alloy’s resistance to nitric acid approximates that of the wrought alloy and it is often used in pumps and valves at elevated temperatures. Another nickel-based alloy with high chromium content is Allcorr® (N06610) but with 10% molybdenum its resistance is reduced and in boiling 40% nitric a corrosion rate of 0.025 mm/y was found. [6] Alloy 33® has excellent resistance to strong nitric acid and can be used at concentration up to 85% at temperatures up to at least 75°C.

5. Phosphoric acid

Conventional 300 series stainless steels are the workhorse materials for phosphoric acid service. Phosphoric acid, produced by dissolving phosphate rock is known as wet-process acid and typically contains impurities that have a significant effect on corrosion. Type 304L shows good general corrosion resistance up to 80% pure acid below 74°C but is subject to CSCC in the presence of chlorides. It is also very susceptible to pitting and crevice corrosion from contamination by either chlorides or fluorides. In the active state, it can be rapidly corroded by phosphoric acid with the release of hydrogen gas possibly producing flammable explosive hydrogen/air mixtures. Type 304L has been rarely used for phosphoric acid handling, storage, or manufacturing. Type 316L steel is extensively used and is the preferred minimum alloy in...
the phosphoric acid industry. Type 316L has a corrosion rate of <0.25 mm/y, from <1% to 60% phosphoric acid up to the boiling point. From 60% to about 90% acid, it has good resistance up to about 115°C. In superphosphoric acid; (typically 105% H₃PO₄ with an excess of P₂O₅) Type 316L has excellent resistance at even higher temperatures, i.e. 120–185°C. Maximum corrosion of Type 316 occurs between 79% and 91% acid concentration.

Type 317L (S31703) behaves similarly to Type 316L and can be used interchangeably up to about 60% acid. At this point, 316L apparently exhibits better corrosion resistance than Type 317L in pure acid, although not in wet-process acid. Above 105% H₃PO₄, the two stainless steels show similar corrosion resistance. In 85% acid, oxidizing ions reduce the corrosion rate of Type 316 significantly. Compared with essentially uncontaminated acid (1 ppm cation), about an 80% inhibition (from 0.25 to 0.05 mm/y) is affected with about 10 ppm cupric or 100 ppm ferric ion, whereas arsenic is only about 50% effective.

Duplex stainless steels, e.g. Alloy 255 exhibits corrosion resistance similar to Type 317L but inferior to Type 316L. This relationship would probably change in contaminated phosphoric acid where chlorides and fluorides result in accelerated corrosion of Type 316 and may attack the ferrite phase in duplex grades. Duplex alloy 2205 (S31803 or S32205) has been used for marine cargo applications where seawater is used to wash out cargo tanks after acid transportation.

The Alloys 20Cb3, 20Mo4 (N08024), and 20Mo6 (N08026) stainless steels show no better corrosion resistance than Type 316L stainless steel up to about 60% pure phosphoric acid at boiling temperatures. Between 70% and 90% acid, Alloy 27-7MO (S31277) shows improved corrosion resistance over Type 316L, 317L and Alloy 825 below the boiling point. At higher concentrations and temperature, these alloys would have very high corrosion rates. The 6–7% Mo-containing super-austenitic stainless steels, Alloys AL-6XN®, 254SMO®, 654 SMO®, 1925hMo (N08926), 20Mo6®, and 27-7 MO, may also be useful in contaminated phosphoric acid because of their higher molybdenum content.

Alloy 28 and Alloy 31 (N08031), are similar in alloy composition and have the highest phosphoric acid corrosion resistance of the super-austenitic stainless steel grades because of their increased chromium and molybdenum content. These alloys can be used in pure phosphoric acid up to 80% acid to the boiling point. Their corrosion resistance falls as acid concentration increases between 80% and 90% but resistance is quite good up to 260°C at 110% acid concentration.

The chromium-bearing nickel-rich alloys were developed specifically for wet-process phosphoric acid service where chloride and fluoride contamination is present. The modern G-type alloys comprising Alloys G-3 (N06985), G-30 (N06030), G-35 (N06035), and G-50 (N06950) show excellent corrosion resistance in wet-process phosphoric acid. [7] They are not, however, normally cost-effective in pure phosphoric acid contrasted to the less expensive Types 316L and 317L.

6. Hydrofluoric acid

Conventional austenitic stainless steels tolerate higher temperatures than carbon steel, about 100°C in liquid anhydrous hydrogen fluoride (AHF). They are often utilized for valves, pumps, instrumentation and bolting. Fluorides do not cause stress-corrosion cracking (SCC) directly but do aggravate susceptibility of sensitized grades to intergranular SCC.

The chromium-free Alloy 400 is usually the material of choice, based on both cost and corrosion resistance. It is widely used for valves, valve trim, pumps and piping to at least 100°C. It can, however, fail by SCC in the event of ingress of air and moisture, due to the formation of cupric fluoride (CuF₂) which is the specific responsible agent. Alloy 200 has about the same
general corrosion resistance and is immune to SCC. The most reliable and cost-effective alloy is Alloy 600, which is used especially for vaporizers (which are easily contaminated by air). Alloy 600 has been successfully used at temperatures of 370 - 590°C in the hydro-fluorination of metal oxides. Higher nickel-molybdenum and nickel-chromium-molybdenum alloys offer no advantage in AHF, although Alloy C-276 is probably the most readily available alloy for bellows and instrument parts.

In hydrofluoric acid, none of the conventional stainless steels find applications due to lack of resistance to general corrosion and problems of hydrogen-assisted cracking and velocity effects. Type 316L has good resistance to general corrosion below about 10% acid up to about 25°C but is subject to pitting. The 300 series are less resistant than carbon steel in 70% acid. Alloy 20Cb-3 and Alloy 825 offer only limited improvement and niobium and titanium constituents in weldments suffer preferential attack. Alloy 20 castings may be used for pumps and valves in 70% acid at ambient temperature. Alloys such as 904L, 31, 254 SMO® and 654 SMO® have reasonable resistance to weak acid (<10%) and are especially useful if chlorides are present.

Alloy 200, is resistant, as long as air is absent, below 80°C but less so than Alloy 400. Alloy 400 is preferred for up to 120°C for all concentrations. Rates are usually <0.05 mm/y up to at least 80°C. Weldments must not contain niobium, which is preferentially attacked. Corrosion of Alloys 400 and 500 (N05500) increases dramatically with ingress of air or oxygen. SCC can occur in the vapour space from the formation of CuF₂. Corrosion in the liquid phase is autocatalytic, due to the accretion of cupric ions, although SCC is not then a problem. The nickel-molybdenum alloys, e.g., Alloy B-2, are no more and sometimes less resistant than Alloy 400. Alloy 600 is not susceptible to cracking by CuF₂ but the welding rods typically contain too much niobium to be reliable at elevated temperatures. The Ni-Cr-Mo alloys, e.g., Alloy C-276 and derivatives, are generally less resistant than Alloys 400 and 600. They are, however, superior for reprocessing nuclear wastes, which involve hot 16% acid. The preferred material for pumps and valves for 70% HF at ambient temperature is the CN-7M casting alloy.

7. Chlorine

Conventional 300 series austenitic stainless steels are more resistant to dry chlorine than carbon steels. They can be used up to 350°C but are not often employed because ingress of moisture during shutdown can lead to CSCC or pitting corrosion. Corrosion of the 300 series stainless steels in wet chlorine decreases with increasing temperature, until about 370°C at which point the corrosion rate is 4.6 mm/y and the detrimental effect of moisture disappears. With 20 and 400 ppm water, little difference is seen in corrosion rate below about 100°C for Types 304, 321(S32100) and Alloy 20. At higher amounts at these elevated temperatures, the corrosion rate is significantly reduced compared to that in dry chlorine (20 ppm H₂O max).

Duplex stainless steels, such as Alloy 2205, resist dry chlorine but the ferrite phase is preferentially attacked by HCl formed if moisture is present. Alloy 20 or the cast version CN7M valves are used in refrigerated, liquid chlorine equipment to resist corrosion in the moist chlorine gas that can form under ice on the metal surface. [8] The bolting used on valves for liquid chlorine is usually Alloy C-276. Alloys 200, 201 (N02201), 400 and B-2 resist dry chlorine but are severely attacked if ingress of moisture occurs. An upper temperature limit of 500°C is appropriate for nickel in dry chlorine. The presence of moisture affects the corrosion rate up to this maximum use temperature. 1.5% water vapour can double the corrosion rate of Ni in chlorine, 30% water increases it from 2 to 20 times.

Alloy 400 is commonly used as valve trim but problems can ensue in refrigerated systems. Any water present below the dew point is corrosive to Alloy 400 and other nickel alloys. [9]
Alloy C-276 has a corrosion rate of 0.05 mm/y in water-saturated gas at room temperature. This alloy is the standard valve stem material in carbon steel lines carrying dry chlorine since the stems can be in contact with humid air. Its more highly alloyed variants are not required but are equally resistant. Alloy 200 and Alloy 600 are the alloys most commonly used for reactors, coils, agitators and piping in the 250-500°C range. Alloy 600 is susceptible to chloride pitting below the dew point at intermediate temperatures but should replace nickel to avoid intergranular attack when sulphur compounds are present.

8. Sodium hydroxide (Caustic Soda)

The 300 series stainless steels have a usefully low corrosion rate in caustic soda (NaOH) at all concentrations up to about 65°C. Types 304 and 316 have low corrosion rates in boiling caustic soda at concentrations up to nearly 20%. Type 316 has a better resistance to pitting than Type 304 in caustic solutions, and the low carbon grades are preferred because of the risk of sensitization. Type 316L is a good choice for caustic solutions as long as operating conditions are such that caustic SCC is not a problem. The 300 series stainless steels are susceptible to SCC in hot caustic, e.g., 15% NaOH at about 150°C. In practice, this is most often encountered in caustic-contaminated steam.

Corrosion testing in a range of caustic solutions at the boiling point showed that duplex alloys with and without molybdenum can be used in boiling solutions up to at least 30% with negligible corrosion. These tests also showed that these duplex alloys were not susceptible to SCC in boiling caustic solutions from 20% to 70%. The duplex Alloy 7-Mo® and the ferritic E-Brite® 26-1 (S44627) stainless steels both showed good resistance to SCC and corrosion in 50% caustic at 135°C.

Alloy 200 and Alloy 201, both have excellent resistance to caustic soda, even to the hot anhydrous form. Except for silver, nickel is the most resistant metal for high caustic concentrations at the elevated temperatures which generally prevail. At concentrations up to 73% caustic, the corrosion rate is generally less than 0.025 mm/y. Alloys 200 and 201, Alloy 400, Alloy 600, and Alloy 690 are all susceptible to SCC over a wide range of caustic concentrations at temperatures above 290°C. Nickel, Alloy 400 and variants, and nickel-molybdenum alloys, e.g., Alloy B-2 while generally resistant to caustic itself, are attacked stoichiometrically by chloride or hypochlorite contaminants.

Alloy 400 has corrosion resistance similar to Alloy 200 for concentrations up to 73%, although it is susceptible to caustic cracking at elevated temperatures (e.g., in caustic-contaminated steam at 422 - 448°C). At higher concentrations, the corrosion rate is somewhat greater than Alloy 200. The solution-hardening variants of Alloy 400, e.g., Monel® 404 (N04404) and 405 (N04405) and the age-hardening variants, e.g., Alloy K500® (N05500) have substantially the same corrosion characteristics.

Alloy 600 exhibits resistance similar to Alloy 200 up to and including the anhydrous product. It is favoured for heating coils, because of higher strength at temperature than the pure nickel alloys. It may cause a small amount of contamination from Cr VI ions, compared to the use of Alloy 200. It is subject to caustic cracking under severe conditions in prolonged exposure, and should be used in the stress-relieved condition. Alloy 600 offers an advantage, compared to Alloy 201 when a sulphur-bearing contaminant may be present, in being less susceptible to nickel sulphide eutectic formation which causes intergranular penetration analogous to Liquid Metal Embrittlement (LME). Alloy 600 can offer an advantage over Alloy 200 in caustic from the diaphragm-cell process, in which chlorates and hypochlorites are present. Being oxidizing in nature, these accelerate corrosion of Alloy 200, whereas the resistance of the chromium-bearing alloy is not greatly affected. Alloy 601 (N06601) was
developed primarily for high temperature applications but shows excellent corrosion resistance in up to 98% caustic. The other chromium-containing nickel-based alloy that is sometimes used in caustic soda is Alloy 690. The corrosion rate of Alloy 690 in 70% NaOH at 170°C was 0.03 mm/y. In the same tests, Alloy 400 and Alloy 33 had the same corrosion rate (i.e. 0.03 mm/y), while Alloy 59 (N06059) corroded at 0.48 mm/y and Alloy C-22 at 0.51 mm/y. [14]

Alloy 625 has become the material of choice for corrugated metal expansion joints in high pressure steam, where environmental cracking of austenitic stainless steels occurs due to caustic carry-over while chloride carry-over may cause pitting of Alloy 600, for example. This alloy is practically unaffected by hot caustic up to at least 320°C.

9. Ammonia

In ammonia stainless steels are not normally needed from the corrosion point of view but they do find many applications since all grades are resistant to ammonium hydroxide solutions up to the atmospheric boiling point. Austenitic stainless steels are used in low temperature service since they exhibit excellent notch toughness at temperatures far below the atmospheric boiling temperature of ammonia. In elevated temperature services in ammonia synthesis, they are used because of their resistance to hydrogen attack and nitriding.

The nickel alloys are seldom used in ammonia service except at elevated temperatures. They are resistant to anhydrous ammonia and exhibit good resistance to nitriding but can be attacked when more than about 1% water is present. Nickel-chromium alloys with 50% to 80% nickel resist pure NH₃ to about 500°C. Nickel is attacked by wet ammonia in the presence of air. Alloy 200 will resist ammonium hydroxide only up to about 1% concentration although dissolved oxygen may maintain passivation up to about 10% concentration. Higher concentrations are highly corrosive to nickel even in the presence of air. Alloy 400 is more resistant than Alloy 200 and in solutions of >3% ammonium hydroxide, corrosion rate is increased considerably by aeration and agitation. The corrosion rate of Alloy 800 in 5% and 10% ammonium hydroxide at 80°C <0.003 mm/y in 7-day laboratory tests. [15]

10. Acetic acid

The 300 series stainless steels are the predominant materials for handling acetic acid of almost all concentrations and at normal temperatures. Types 304L, 321 and 347 (S34700) may be used to the atmospheric boiling point in acid less than 10%. In practice the molybdenum-bearing grades are preferred for both corrosion resistance and product purity. Except in mixtures or in the presence of contaminants there is little or no advantage to higher alloyed stainless steels, such as Type 317L. Duplex Alloy 2507 (S32750) is resistant to the boiling point from 0 to 100% acid but seems to offer no advantage over Type 316L except where chloride contamination might cause an excessive corrosion rate and SCC.

Alloy 20Cb-3 has a rate of <0.025 mm/y up to at least 50% boiling acetic acid and <0.13 mm/y in 99% acid. Alloy 825 appears to be substantially equivalent to alloy 20Cb-3, showing <0.025 mm/y in boiling acetic acid solutions in laboratory tests. Alloys which approach a nickel-based composition, such as alloys G, G-3 and G-30, also resist uncontaminated boiling acetic acid up to 100% concentration. Traces of anhydride or chlorides are, however, detrimental to nickel-rich alloys in a manner similar to Type 316L, and the higher Ni-Cr-Mo alloys are a better choice.

The best alloys for hot acetic acid, being little affected by contaminants, are the Ni-Cr-Mo alloys such as Alloy C-276 and its several variants. These are the materials of choice for
reboilers, stills, etc. if there is any question concerning complete control of the oxidizing/reducing conditions.

**General References**

Publications from the Nickel Institute, [https://www.nickelinstitute.org/library/](https://www.nickelinstitute.org/library/)

Abstract

Microbiological methanation is investigated in an underground natural gas reservoir. Since H₂ is involved in the process, hydrogen embrittlement of steel must inevitably be considered. Therefore, a routine for testing has been developed and a unique autoclave test bench was designed to simulate field conditions. The 2205 duplex stainless steel (UNS S31803) was investigated. Constant load tests (CLTs) and immersion tests with subsequent hydrogen analyses were performed. The specimens were exposed to different partial pressures of H₂ under both dry and wet conditions (with brine). Additionally, the influence of CO₂ under wet conditions was covered. Tests were performed at two different temperatures (25 °C and 80 °C) and lasted for 30 days. In general, the duplex stainless steel shows a good resistance to hydrogen embrittlement, but significant differences to other steels in hydrogen uptake were measured.

Keywords

Hydrogen Embrittlement; Hydrogen Uptake; 2205 Duplex Stainless Steel, Methanation

1. Introduction

To achieve the climate goals, so-called green energy is becoming increasingly important. Changing weather conditions lead to fluctuating power outputs, which leads to the fact that the excess electricity needs to be stored. Transformation of electricity to hydrogen via electrolysis is an option, but the lack of adequate infrastructure for the storage and transport of the gas is a problem. This issue can be addressed by methanation of hydrogen and carbon dioxide to obtain natural gas:

\[ 4 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \]  

(1)

A new approach is to use methanogenic archaea that perform the methanation process [1]. Such microorganisms can produce natural gas in an underground natural gas reservoir. With H₂ involved in the process, hydrogen embrittlement must inevitably be considered. This phenomenon, although known since 1874 [2], is not yet fully understood. In presence of H₂ and CO₂, as well as a chloride-containing, humid environment under anaerobic conditions, there are two main potential sources of absorbed hydrogen. The first one is the dissociation of gaseous H₂:

\[ \text{H}_2 \leftrightarrow 2 \text{H}_{ad} \]  

(2)
The hydrogen molecule $\text{H}_2$ dissociates into two adsorbed hydrogen atoms $\text{H}_{\text{ad}}$. According to Sieverts and Krumbhaar [3], the hydrogen solubility of metals increases with increasing temperatures. This is depicted in Sieverts’s law:

$$ S = S_0 \cdot \sqrt{p} \cdot e^{-\Delta H/RT} $$

where $S_0$ is the solubility constant, $p$ the partial pressure, $\Delta H$ the heat of solution, $R$ the universal gas constant and $T$ the absolute temperature [4]. When $\text{CO}_2$ dissolves in water, carbonic acid $\text{H}_2\text{CO}_3$ is formed [5]:

$$ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 $$

The carbonic acid dissociates. The increasing concentration of $\text{H}^+$ results in a lower pH and the cathodic reaction

$$ 2 \text{H}^+ + 2 e^- \leftrightarrow \text{H}_2 $$

is promoted [6]. Simultaneously anodic dissolution of iron takes place:

$$ \text{Fe} \leftrightarrow \text{Fe}^{2+} + 2 e^- $$

Not all of the reduced $\text{H}^+$ ions recombine to $\text{H}_2$ as shown in equation (5), some of the adsorbed hydrogen ($\text{H}_{\text{ad}}$) and can get absorbed ($\text{H}_{\text{ab}}$):

$$ \text{H}^+ + e^- \leftrightarrow \text{H}_{\text{ad}} \leftrightarrow \text{H}_{\text{ab}} $$

Thus, the second potential source of absorbed hydrogen is the corrosion reactions. In general, this source can be neglected when using corrosion resistant alloys (CRAs).

Whiteman and Troiano [7] stated, that the amount of absorbed hydrogen necessary to produce hydrogen embrittlement is one or two orders of magnitude greater for austenitic stainless steels compared to steels with a bcc lattice. Thus, a duplex stainless steel, which is a mixture of both microstructures, is of interest for being tested for an application limit in terms of hydrogen embrittlement.

Since it can be challenging to make suggestions for field service based on standard laboratory tests [8], simulating field conditions is very reasonable. To answer the question of whether steel grades are suitable for underground methanation, a routine for testing has been developed. A unique autoclave test bench was designed to simulate field conditions. In this work, tests were conducted on the 2205 duplex stainless steel (UNS S31803).

### 2. Experimental Procedure

The tested steel grade presented in this work was the duplex stainless steel UNS S31803, commonly known as 2205. Samples were taken from commercially available casing tube sections. The chemical composition of the investigated material is shown in Table 1.
Table 1: Chemical composition of the investigated material

<table>
<thead>
<tr>
<th>C [wt%]</th>
<th>Si [wt%]</th>
<th>Mn [wt%]</th>
<th>P [wt%]</th>
<th>S [wt%]</th>
<th>Cr [wt%]</th>
<th>Mo [wt%]</th>
<th>Ni [wt%]</th>
<th>N [wt%]</th>
<th>Fe [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03</td>
<td>0.55</td>
<td>1.68</td>
<td>0.024</td>
<td>0.001</td>
<td>22.30</td>
<td>3.12</td>
<td>4.98</td>
<td>0.18</td>
<td>bal.</td>
</tr>
</tbody>
</table>

The steel had a pitting resistance equivalent number (PREN) of 35. This value was calculated according to the following equation [9]:

\[
PREN = Cr + 3.3 Mo + 16 N [\text{wt%}]
\] (8)

The mechanical properties of the investigated steel grade are listed in Table 2. Tensile tests were performed on small, non-standard tensile specimens with an initial gauge length of 25 mm and a diameter of 3 mm. The specimens were drawn at room temperature with a crosshead speed of 0.1 mm/min.

Table 2: Specified Minimum Yield Strength (SMYS), Yield Strength (YS), Ultimate Tensile Stress (UTS) and fracture elongation (A) of the investigated material

<table>
<thead>
<tr>
<th>SMYS</th>
<th>YS</th>
<th>UTS</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MPa]</td>
<td>[ksi]</td>
<td>[MPa]</td>
<td>[ksi]</td>
</tr>
<tr>
<td>758</td>
<td>110</td>
<td>822</td>
<td>119</td>
</tr>
</tbody>
</table>

The corrosion tests were conducted within autoclaves made of UNS N06625 (Alloy 625). Fig. 1 shows one of the used autoclaves.

Fig. 1: Autoclave made of Alloy 625.

Each autoclave contained three different specimens: an immersion specimen (Fig. 2 a) i ) for measuring the hydrogen uptake, a coupon (Fig. 2 a) ii ) for determining the presence of pitting or other corrosion phenomena and a small tensile specimen (Fig. 2 a) iii ) for a constant load test (CLT). The load was applied to the CLT specimen with a spring made of a cobalt-base alloy and ceramic nuts (Fig. 2 b) ), the latter ensuring electronic decoupling of the specimen from the more noble spring. The specimens were connected with PTFE parts.
Fig. 2: Specimen assembly to be mounted in the autoclave. a) Three specimens connected with PTFE parts: Immersion specimen (i), coupon (ii) and constant load specimen (iii). b) Small tensile specimen with spring and ceramic nuts for constant load test.

The specimen assemblies were mounted in the autoclaves. The vessels were evacuated and purged with argon several times to get very low partial pressures of oxygen and other atmospheric gases. Further the autoclaves were filled with an aqueous test solution and test gases (Fig. 3 a) and b)). The last step was mounting the autoclaves on rotating shafts within a heated chamber (Fig. 3 c).

Fig. 3: Filling and mounting of the autoclaves: a) Filling of autoclaves with aqueous test solution. b) Pressing the test gas into the autoclave. c) Several autoclaves mounted on rotating shafts within a heated chamber.

Tests were performed with two different partial pressures of H$_2$ gas: 20 bar and 100 bar. Also, the influence of 5 bar of CO$_2$ gas was investigated. In more than half of the tests an aqueous NaCl solution (brine) with a chloride concentration of 15 000 mg/l was used. The tests were conducted at 25 °C as well as at 80 °C (field-near conditions) and lasted for 30 days. Thus, the material was tested under 10 different conditions. An overview for the tested conditions is given in Fig. 4.
The load for the CLTs was 90% of the specified minimum yield strength (SMYS). Load was applied by compressing a spring with a defined load and connecting it with the respective specimen and two ceramic nuts. To simulate the periodically changing conditions in the gas well, the autoclaves were rotated with a speed of 1 RPM. Consequently, the specimens were periodically wetted with the aqueous electrolyte.

Directly after the test, the immersion specimens were removed from the autoclaves and immediately cooled in liquid nitrogen. The cooled specimens were ground with silicon carbide paper (grit 120), rinsed with acetone and blow-dried quickly prior to hydrogen analysis. The hydrogen content was measured with a thermal conductivity cell after hot extraction at 950°C. At the end of the tests, the constant load specimens were examined for possible fractures that occurred. Unbroken specimens were examined with a stereo microscope to see if any cracks or pits were visible. The coupons were examined for pits or other visible corrosion phenomena.

3. Results

None of the specimens constantly loaded at 90% of the SMYS broke under the tested conditions. None of the unbroken specimens showed visible cracks or pits under the stereo microscope. Fig. 5 gives an overview for the results of the constant load tests.
Also, on the corrosion coupons, no pits or other visible corrosion phenomena were detected. The results of the hydrogen analyses of the 2205 tested in autoclave wheel tests at 25 °C are illustrated in Fig. 6. Where two or more tests under same conditions were performed, mean value and standard deviation are shown in the diagrams. For individual tests, a deviation of +/- 15% is shown.

**Fig. 6:** Hydrogen content for 2205 duplex stainless steel (UNS S31803) tested different media in autoclave wheel tests for 30 days at 25 °C. The chloride concentration of the brine was 15 000 mg/l.

In comparison to the uncharged condition, which is shown in each diagram as the leftmost bar, a hydrogen uptake by dry H₂ gas at 20 or 100 bar and 25 °C was not clearly detectable. A similar result was found for 5 bar of CO₂ gas under wet conditions (with brine). In the presence of brine, 20 bar of H₂ led to a slightly elevated hydrogen content. At 100 bar the content was found to be 4.01 ppm, which corresponds to an uptake of 1.76 ppm. Hydrogen contents for tests in the same media, but at 80 °C are shown in Fig. 7.

**Fig. 7:** Hydrogen content for 2205 duplex stainless steel (UNS S31803) tested different media in autoclave wheel tests for 30 days at 80 °C. The chloride concentration of the brine was 15 000 mg/l.

At 80 °C there was no detectable hydrogen uptake in 20 bar dry H₂ gas or in the wet, CO₂ containing atmosphere, while 100 bar dry H₂ led to a measurable hydrogen uptake. In the
presence of brine, H₂ gas led to a hydrogen content of 6.46 ppm (4.21 ppm uptake) at 20 bar and 14.39 ppm (12.14 ppm uptake) at 100 bar.

Both at 25 °C and 80 °C the presence of NaCl brine with a chloride concentration of 15 000 mg/l was found to promote the hydrogen uptake due to H₂ gas. The higher temperature (80 °C compared to 25 °C) led to significantly higher hydrogen contents in the specimens exposed to 20 or 100 bar H₂ gas and brine. Dry H₂ gas only led to hydrogen uptake at 100 bar and 80 °C, although the measured amount was not significant.

Since there were no visible signs of any kind of corrosion found on the coupons exposed to CO₂ gas combined with brine, the only possible major source for hydrogen was not existent. Thus, this environment had no effect on the hydrogen content.

Although hydrogen contents up to 14.39 ppm were measured, no substantial embrittlement at 90 % of the SMYS was observed in the constant load tests. In previous tests on carbon steels it was found that the API 5CT [10] P110, which has the same SMYS as the duplex, had a hydrogen content of 0.38 ppm after being tested under same conditions without a failure. The significant difference in hydrogen content can be explained with the different microstructure (tempered martensite vs. ferrite-austenite). Austenitic structures provide more hydrogen traps, where the small atoms can get stuck. Since the amount of absorbed hydrogen required to produce hydrogen embrittlement of these structures is one or two orders of magnitude greater than that of steels with bcc lattice alone, the mixture of both – present in the investigated material – survives the CLT despite a hydrogen content of 14.39 ppm.

4. Conclusions

- No cracks occurred under constant load of 90 % SMYS within 30 days of testing in rotated autoclaves containing up to 100 bar hydrogen gas with or without brine (15 000 mg/l chloride).
- The 2205 duplex stainless steel (UNS S31803) did not show pitting or other corrosion phenomena after immersion in brine with CO₂ at 25 °C and 80 °C.
- The presence of brine was found to promote the hydrogen uptake due to H₂ gas.
- A temperature of 80 °C led to significantly higher hydrogen contents in the specimens exposed to 20 or 100 bar H₂ gas and brine compared to 25 °C.
- A maximum hydrogen content of 14.39 ppm (uptake of 12.14 ppm) was found in the test with 100 bar H₂ and brine at 80 °C after 30 days.
- The 2205 duplex stainless steel (UNS S31803) seems to be suitable for application in an underground microbiological methanation facility.

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References


Surface properties
MAGNETIC EFFECTS ON AUSTENITIC STAINLESS STEELS AFTER A LOW TEMPERATURE CARBURIZATION

Abstract

Magnetic effects on austenitic stainless steels, formed during a low temperature carburizing depending on the alloy composition are discussed in this paper. Samples of different austenitic stainless steel alloys have been subjected to a multiple low-temperature carburization. Layer characterization with light microscope and hardness profiles show a growth of the layer thickness. The formation of an expanded austenite layer (lattice expansion) could be detected by X-ray diffraction (XRD). Feritscope® was used to determine the magnetizability, whereby not all austenitic alloys form a magnetizability after treatment. Furthermore, test procedures were developed to visualize the magnetizability. For this purpose, magnetic force microscope measurements and investigations with ferrofluid were carried out and a fir tree ferromagnetic layer structure could be proven.

Keywords

Low temperature surface hardening; Ferrofluid; Carburization; Expanded austenite; Magnetic force microscope

1 Introduction

Austenitic stainless steels today have a wide range of applications from the automotive industry to the chemical industry and plant engineering. At room temperature these steels have a face centered cubic lattice (fcc), which is why magnetization at room temperature is not possible. These steels are also used for special applications e.g. watch cases or magnetic actuators. Due to their lattice structure, austenitic steels cannot be hardened conventionally. Surface hardening (low temperature carburization) can be carried out on parts subjected to tribological stress. With such a treatment it is possible to reach up to 5 times of the basic hardness. Due to a diffusion process controlled by temperature, concentration (carbon) and pressure, the carbon atoms are deposited interstitial and do not tend to form precipitates due to the low treatment temperature. This preserves the corrosion resistance after the treatment. The carbon dissolved on interstitials leads to lattice expansion, also known as expanded austenite, which generates high residual compressive stresses in the layer (e.g. up to 7.2 GPa for nitrogen interstitials [1]). The expanded lattice can dissolve carbon in the range of up to approx. 20 at%. Due to the lattice expansion, some alloys of austenitic stainless steels may become magnetizable after treatment. The present research project is focused on basic investigations concerning the magnetizability. For this purpose, the formed layers with their magnetizability are analyzed more precisely in order to gain a better understanding of their metallurgical background. The paper does not include the results of all investigated alloys and presents the subject of four exemplary alloys only.
2 Experimental

2.1 Sample preparation

Nine austenitic stainless steels were selected for the investigation in order to describe the topic of different magnetizability. The chemical composition (determined by spectral analysis) of the four chosen alloys discussed in this paper are shown in Table 1. The sheet plate samples were all ground with 1200 silicon carbide abrasive paper before treatment.

<table>
<thead>
<tr>
<th>Sample-no.</th>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>1.4439/AISI 317LMN</td>
<td>0.027</td>
<td>0.72</td>
<td>1.15</td>
<td>16.96</td>
<td>13.02</td>
<td>4.01</td>
</tr>
<tr>
<td>4</td>
<td>1.4539/AISI 904L</td>
<td>0.018</td>
<td>0.22</td>
<td>1.62</td>
<td>20.75</td>
<td>24.26</td>
<td>4.72</td>
</tr>
<tr>
<td>5</td>
<td>1.4529/AISI 926</td>
<td>0.019</td>
<td>0.40</td>
<td>0.98</td>
<td>21.00</td>
<td>24.25</td>
<td>5.94</td>
</tr>
<tr>
<td>8</td>
<td>1.4465/AISI 310MoLn</td>
<td>0.018</td>
<td>0.42</td>
<td>1.44</td>
<td>24.68</td>
<td>24.34</td>
<td>2.18</td>
</tr>
</tbody>
</table>

*Table 1: Investigated alloys and their chemical composition*

An untreated reference sample was prepared of all the materials examined. The other samples are subjected one to three or one to six times to a low temperature carburization in order to cause a possible supersaturation. The heat treatment was carried out by the company Bodycote with their low temperature carburization process (named Kolsterising®) for company reasons no process parameters are known (treatment duration, temperature, pressure, etc.). The figure after the sample number indicates the number of treatment cycles, e.g. the sample 5-3 was treated three times. Before any tests were performed on the samples, they were cleaned in an ultrasonic bath with ethanol and dried with air. Cross section polishes were made from the sheet samples for layer characterization and further investigations.

2.2 Metallographic examinations and hardness profiles

By color etching (Beraha II) the hardened layer could be developed and then examined with a light microscope (Olympus BX51M). In addition to the measurement of the layer thickness, the layer was examined for possible precipitations in the unetched and etched state.

In order to obtain a statement on the achievable hardness penetration depth after the individual treatment cycles, hardness curves (HV0.025) were measured on the cross-section polishes with a low load hardness tester (LEICA VMHT MOT).

2.3 X-ray diffraction (XRD)

The XRD measurements to determine the lattice expansion were carried out by an external institute. The diffractometer was equipped with a Mo-Kα radiator. The positions of the lattice plane reflections allow the determination of the lattice parameter $a$ from which the absorbed carbon content can be calculated.
2.4 Investigation of the magnetic properties

The formation of magnetizability was determined with a Feritscope®. This magnetoinductive method is tactile and allows a fast measurement of the magnetizability of a stimulated measuring volume. In the excited measuring volume, the magnetizable part is recorded without differentiation, what causes the magnetizability e.g. ferrite or precipitation.

In order to be able to visualize the ferromagnetic areas of the layer using a light microscope, experiments with ferrofluid were carried out. Ferrofluid contains magnetic particles with a size of 0.2 µm to 4 µm, which are finely dispersed in an oily carrier liquid. The investigation aims at the deposition of the magnetic particles in magnetizable areas of the layer in order to make them visible by means of a conventional light microscope. The ferrofluid is applied to a previously magnetized and Beraha II etched cross section polish. The cross section polish is then rinsed with ethanol and dried. The coarser magnetite particles are washed off and only the very fine particles are deposited in the ferromagnetic area of the layer.

Magnetic Force Measurements (MFM) were performed to visualize the structure of the ferromagnetic areas. In the first step of an MFM measurement, a very small measuring tip is rastered over a sample surface with constant force and tactile in order to capture the topography (AFM-mode). In the second step (MFM-mode), the same measuring distance is traversed again with an offset (15-100 nm), while the magnetic measuring tip (tip vaporized with cobalt-alloy) interacts with the magnetic areas of the sample surface and deflects the measuring tip differently [2].

3 Results
3.1 Metallographic examination and hardness profiles

In the unetched as well as in the etched state no precipitations could be detected with a light microscope at maximum magnification (Eyepieces:10x Objective: UMPLANFL 100x/0.90 BD). The layer was well developed by Beraha II etching (Figure 1).

![Fig. 1. Beraha II etching for layer thickness adjustment (white layer), left: 4-ref; middle: 4-1; right: 4-3](image)

The multiple treatment leads the layer thickness to be increased with each new treatment cycle (Figure 2).
The same correlation can also be observed with the hardness profiles (HV0.025), which were carried out to a layer depth of 100 µm. The maximum layer hardness could not be increased by the multiple treatment. Only an increased diffusion depth could be shown. The samples of alloy number 3 and 8 have a slightly lower hardness than those of alloy 4 and 5 regarding the achievable maximum hardness. The multiple treatment had no influence on the core hardness.

3.2 X-ray diffraction and magnetic properties

The X-ray examination revealed a lattice expansion in all treated samples. While it is possible to clearly assign the reflection of the individual lattice planes to the reference samples, it is much more difficult for the multiple treated samples (Figure 3). The peaks of the treated samples shift towards smaller scattering angles with a come along in peak broadening and decrease of intensity. On the one hand, this is due to the large detection depth of the Mo-Kα radiator used, which can achieve a measurement depth of up to 16 µm. At such a detection depth, the lattice expansion varies from the outermost edge layer to the maximum possible measurement depth (16 µm) and can only be regarded as an average value. In order to be able to make a reliable statement about the lattice expansion, new measurements with another radiation source (Cr-Kα), in combination with selected angles of incidence, must be carried out here.
Due to the already mentioned problems with the XRD measurements, only the lattice parameters for the once treated samples are listed in Table 2.

Table 2: Calculated lattice parameters

<table>
<thead>
<tr>
<th>sample-no.</th>
<th>Ref</th>
<th>1x</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.3606±8</td>
<td>0.3760±28</td>
</tr>
<tr>
<td>4</td>
<td>0.3611±7</td>
<td>0.3816±42</td>
</tr>
<tr>
<td>5</td>
<td>0.3614±2</td>
<td>0.3818±30</td>
</tr>
<tr>
<td>8</td>
<td>0.3610±4</td>
<td>0.3784±64</td>
</tr>
</tbody>
</table>

It is noticeable that the alloys with the supposedly largest lattice parameter in the reference samples again have the largest lattice parameter after the treatment. A clear proof of generated precipitates could not be recognized by the peak formations.

The recorded carbon content can be calculated mathematically from the determined lattice parameters. The information given here is subjected to the same problems with the already described identification of the lattice plane peaks. Therefore the carbon content is only listed for the once treated samples. The calculated carbon content is listed in Table 3 [3].

Table 3: Carbon content calculated from the lattice expansion

<table>
<thead>
<tr>
<th>sample-no.</th>
<th>1x [at.-%]</th>
<th>dev. ± [at.-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>14.7</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>19.5</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>19.4</td>
<td>0.1</td>
</tr>
<tr>
<td>8</td>
<td>16.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>
In order to determine the magnetization of the samples, they were examined using Feritscope® to determine the equivalent ferrite content in vol%. It was determined that not all samples show magnetization after treatment (Figure 4). The alloy 1.4439 shows no magnetic effects during the whole treatment. For alloys 8, 4 and 5, the magnetic effect increases more in the order listed.

![Figure 4. Equivalent ferrite content](image)

**Fig. 4. Equivalent ferrite content**

In order to visualize the magnetizability, MFM measurements were carried out on the cross section polishes and the surface of the polished sheet specimens (Figure 5). The scaling is shown in degree and stands for the deflection of the measuring arm (cantilever) and results from the magnetic interaction between the measuring tip and the sample surface.

![Figure 5. MFM-measuring on Cross section polishes a) 4-2; b) 5-2](image)

**Fig. 5. MFM-measuring on Cross section polishes a) 4-2; b) 5-2**

The cross section polishes of specimens 4-2 and 5-2 show that only the outermost region of alloys 4 and 5 forms magnetization. Similarly fine fir tree magnetic structures can be seen in both alloys. In order to visualize the magnetic layer areas on a light microscope, experiments with ferrofluid were carried out. A quite good accordance of the layer thickness determined by MFM and
ferrofluid could be found (Fig. 6). The deposited layer thickness can thus serve as a good approximation, although it is subject to some fluctuations such as rinsing effects. This correlation can also be observed in all other samples with a magnetization. On the reference samples, or samples without magnetic effects, no ferrofluid remains on the specimens after rinsing.

![Fig. 6](image1.png)

**Fig. 6.** Treated cross section with Beraha II etching and Ferrofluid layer in magnetic areas

In addition, MFM and ferrofluid measurements were carried out on the polished layer (polished with 1.0 µm diamond suspension) in order to compare the results of the MFM measurement with the ferrofluid examination (Figure 7).

![Fig. 7](image2.png)

**Fig. 7.** Comparison of polished sheet metal surfaces 5-3 a) AFM-measuring (topography) b) MFM-measuring with magnetic domains c) magnetic domains visualized with Ferrofluid

In order to exclude topographic effects that could influence the deposition of the ferrofluid, a measurement with an Atomic Force Microscope (AFM) was carried out before. The AFM measurement shows that the topography of the sample does not allow any correlation with the formed ferrofluid pattern. After the rinsing process, a distinct domain structure remains due to deposited ferrofluid particles, which corresponds very well to the MFM measurement. In both investigation methods, a correlation of magnetic orientation and grain orientation can be detected, which is in good accordance with other investigations [4].

## 4 Discussion

An increase of the layer thickness could be shown with each treatment cycle by means of reflected light microscope and hardness gradients.
Since the alloys with lower hardness and lattice expansion do not form magnetizability, it can be assumed that a critical lattice expansion/carbon absorption is necessary. This can also be seen from the MFM and ferrofluid investigations, which show that only about half of the layer formed can be magnetized in the area of the greatest lattice expansion. A similar relationship could also be observed at a low temperature nitriding of 1.4401 (ALSi316) [5].

By a depth profile analysis of the carbon content (GDOES) and the magnetic layer thickness determination by MFM, the minimum necessary carbon content for the formation of magnetizability could be determined. This is approx. 9.5 at.% C for the sample 8-3 and approx. 12.5 at.% C for the sample 5-3. The critical nitrogen content in similar investigations with the alloy 1.4401 (ALSi316) show a ferromagnetic effect in the range of approx. 0.375 nm caused by minimal nitrogen content of around 14 at.%. The formation of ferromagnetic effects due to low temperature carburization has not yet been observed and is explained by the low solubility of carbon and the associated low possible lattice expansion. [5][6].

Furthermore, the investigated sample size suggests that the formation of ferromagnetic effects is associated with the alloying elements. A first clue is provided by the Schaeffler diagram (Fig. 8). The carbon absorbed by the process was not taken into account in the alloys entered here. It can be seen that the less high-alloyed austenitic stainless steels do not develop a magnetization while the higher-alloyed austenitic stainless steels have a distinct magnetization. The increase in the chromium equivalent is largely caused directly by the higher chromium content. Since chromium has a very high carbon affinity, this is one reason for the increased carbon storage. In addition, the substitution of the lattice atoms by molybdenum or, for example, manganese, can produce a much more distorted initial lattice (larger atom diameters), which in conjunction with the absorbed carbon contributes to a larger lattice tension.

![Schaeffler diagram](image)

**Fig. 8.** Schaeffler diagram

Whether the alloy also influences the critical carbon content, above which this effect occurs, will be clarified in subsequent investigations. Furthermore, the other alloying elements of an alloy that are not considered in the Schaeffler diagram can have an additional influence of the magnetization.
4.1 Summary

By means of metallurgical preparation and hardness profiles an increase in layer depth could be detected with all alloys and each additional treatment. The maximum hardness could not be increased. In spite of the observed layer formation, not all austenitic stainless steels tend to form magnetic effects after low temperature carburization. The lower alloyed stainless steels show no formation of magnetic effects, while the lattice expansion also lags behind the alloys with magnetic effects. The hitherto valid assumption that austenitic steels do not achieve the necessary lattice expansion to form magnetization due to their limited carbon absorption could be refuted. The carbon content necessary for the formation of ferromagnetic effects is in the range of 8.5 at.% to 12 at.% and seems to be alloy dependent. On the basis of the Schaeffler diagram (chromium and nickel equivalent), an influence of the alloying elements could be determined. It is shown that the chromium and nickel content contribute to the magnetization. Mainly the chromium and nickel equivalents are increased by the chromium and nickel content itself.

In addition, MFM and ferrofluid investigations revealed a dependence on magnetization and grain orientation. The use of ferrofluid for the determination of the magnetic layer thickness has proven itself and could deliver comparable results to the MFM measurements. Whether the pure lattice expansion is responsible for the formation of the magnetic effect, or is additionally influenced by micro precipitations, must still be clarified by further investigations. In addition, TEM and SANS measurements will be carried out to detect possible precipitations or cluster formations.

References

NEW DEVELOPMENTS IN HIGH TEMPERATURE SOLUTION NITRIDING OF STAINLESS STEELS

Abstract

The present contribution seeks to provide an overview of the concepts of high temperature solution nitriding (HTSN) of stainless steel and the state of the art of the technology. It is illustrated how HTSN can be applied to different classes of stainless steels. New developments involving HTSN are presented, in particular the combination of low temperature surface hardening (LTSH) and HTSN is addressed. HTSN is an excellent “pre-treatment” for LTSH for austenitic, duplex, ferritic and martensitic stainless steels.

Keywords

High temperature solution nitriding; martensitic stainless steel; austenitic stainless steel; duplex stainless steel; ferritic stainless steel; low temperature surface hardening; expanded austenite

1. Introduction

Stainless steels are used in many different applications owing to their favorable properties where corrosion resistance is - obviously - a key feature. Different classes of stainless steel have been developed in order to meet different requirements, i.e. austenitic, duplex (ferritic and austenitic), ferritic, martensitic and precipitation hardenable classes. One of the shortcomings of stainless steels is the lack of wear resistance and general poor tribological behavior, e.g. they suffer from galling/adhesive wear. In order to improve the (wear) performance of stainless steel, thermochemical surface engineering can be applied. Historically, this has entailed conventional “ferritic nitriding”, which relies on formation of chromium nitrides in the surface, albeit with drastic loss of corrosion resistance [1]. More recently new methods were developed which entail formation of a supersaturated solid solution of nitrogen (and or carbon) in the stainless steel resulting in both increased hardness and unaltered or even improved corrosion resistance: In the mid-1980s low temperature surface hardening (LTSH) based on carbon and/or nitrogen was developed [2,3]. LTSH is carried out at temperatures below, say, 450°C for nitrogen and 520°C for carbon and results in a supersaturated solid solution of carbon and/or nitrogen in austenite or martensite, i.e. expanded austenite and expanded martensite, respectively. This results in a very high surface hardness, e.g. up to 1400-1500 HV, but the case depth is typically limited to, say, 20-30 μm. Moreover, LTSH is strongly influenced by the surface “condition” of the stainless steel, e.g. the presence of deformation-induced martensite in an austenitic stainless steel is highly detrimental for the final corrosion performance of the treated part [4]. In the beginning of the 1990s a new type of process was introduced by Berns [5,6] which in some ways resembles LTSH but in other ways is the immediate opposite. The process entails high...
temperatures and dissolution of nitrogen under equilibrium conditions (at the processing temperature) and was coined high temperature solution nitriding (HTSN). Contrary, to LTSH, HTSH exploits existing knowledge of nitrogen solubility in stainless steels in a new way, whereas, the development of LTSH relied on the “discovery” of extreme supersaturation of nitrogen/carbon in stainless steel at low temperatures [7]. HTSN of stainless steel is in many aspects the “stainless” analogue to classical carburizing/case hardening of steels. The process involves the dissolution of nitrogen in stainless steel at temperatures above, say, 1050°C, from an atmosphere consisting of molecular nitrogen at a particular partial pressure. Austenitic, ferritic, duplex and martensitic stainless steels can all be high temperature solution nitrided. In general there are two different motivations for performing HTSN: i) to obtain a nitrogen-enriched austenitic case on austenitic, duplex and high Cr ferritic stainless steels for improved corrosion (and cavitation erosion) performance, or ii) to obtain a nitrogen containing martensitic case on martensitic and low Cr ferritic stainless steels for improved wear, fatigue and corrosion performance. Hitherto, the HTSN process has been somewhat niche in industry owing, in part, to the high temperatures involved and in particular to the inherent challenges associated with the process and the resulting microstructures.

The present contribution gives an overview of concepts of HTSN for different classes of stainless steels and presents new developments in the optimization of the HTSN process. This also includes the combination of HTSN and LTSH. Experimental details and background information are provided in the figure captions.

1.1. High temperature solution nitriding

The basic idea behind HTSN can be illustrated by the use of a time temperature and transformation (TTT) diagram for a hypothetical austenitic stainless showing the lower stability limit of nitrogen rich austenite and the transformation of austenite into other phases, i.e. Cr$_2$N and CrN, see Figure 1.

![Figure 1. Time-temperature-transformation diagram of hypothetical austenitic stainless steel containing different amounts of nitrogen.](image-url)
Hence, it is analogous to classical TTT diagrams for Fe-C steels. At high temperatures austenite containing nitrogen is the thermodynamically stable phase; for increasing N contents in austenite the lower bound of the austenite stability range is shifted upwards (see also isopleths in the next section). It is in this region that nitrogen is introduced in the HTSN process, i.e. solution nitriding. At intermediate temperatures, say, around 900°C, Cr2N will form rapidly (firstly at grain boundaries and subsequently homogenously within grains). Higher nitrogen contents and hence large supersaturation during cooling will promote the formation of Cr2N; this transformation can be of the order of a few seconds. In the lower part of the TTT diagram formation of CrN occurs instead of Cr2N. At temperatures below, say 500-450°C formation of CrN is extremely sluggish as substitutional diffusion is largely suppressed. In this temperature regime low temperature surface hardening can be performed, which is associated with a large supersaturation, i.e. nitrogen contents in the range 4-8 wt%. It should be noted that such high nitrogen contents are not depicted in the schematic TTT diagram in Figure 1.

From the TTT diagram it is evident that in order to maintain nitrogen introduced by HTSN into solid solution, quenching is required to avoid formation of Cr2N. Industrially, quenching is performed using high pressure gas quench with N2 (or Ar) with pressures up to 20 bars.

The source of nitrogen at high temperature is molecular nitrogen, which normally is considered inert (for low-alloyed steel). Molecular nitrogen will dissociate on metallic surfaces at temperatures above, say, 750-800°C, forming atomic nitrogen. This occurs according to the following equilibrium:

\[
\frac{1}{2} N_2 g = [N]_s
\]

where the equilibrium constant of reaction 1 is written as:

\[
K_N = \frac{a_N}{\sqrt{p_{N_2}}} \sqrt{\frac{p_{N_2}^0}{p_{N_2}}} = \frac{f_N x_N}{\sqrt{p_{N_2}/p_{N_2}^0}}
\]

The activity coefficient, \(f_N\), relates the nitrogen activity, \(a_N\), to the atomic fraction of dissolved nitrogen in the solid state, \(x_N\); \(p_{N_2}^0\) is the reference pressure (usually 1 bar). In an iron-based alloy the activity coefficient will deviate from unity according to:

\[
\ln f_N = \ln f_N^0 \sum f_N^j x_j
\]

where \(\varepsilon\) is the interaction parameter of nitrogen and the \(j\) the alloying element with atomic fraction \(x\).

Assuming equilibrium between nitrogen in the solid state and in the gas:

\[
\mu_N^0 = \mu_N^s
\]

it then follows:

\[
\frac{1}{2} G_{N_2}^0 - RT \ln p_{N_2} = G_N^0 + RT \ln a_N
\]

After rewriting and substituting terms:

\[
\ln x_N = \ln \left( \frac{p_{N_2}}{p_{N_2}^0} \right) - \frac{\Delta G_N^0}{RT} - \ln f_N
\]
Hence, it follows directly that the “process parameters” governing the nitrogen solubility in the stainless steel are partial pressure of nitrogen gas, \( p_{N_2} \) and temperature, \( T \). It follows straightforwardly from Eq. 6 that increasing the partial pressure of \( N_2 \) leads to a higher nitrogen content in the solid state. For a fixed \( p_{N_2} \) an increase in temperature results in a lower nitrogen concentration.

The chemical composition of steel also has a large influence on the amount of nitrogen that can be dissolved, as it expressed by the \( \ln f_N \) term, which includes the interaction of nitrogen and alloying elements (cf. Eq. 3). A negative interaction parameter of an alloying element and nitrogen implies affinity between the elements, resulting in enhanced nitrogen solubility. Elements such as Cr, Mn, Mo will enhance the solubility while Ni will reduce the nitrogen solubility. Strong nitride formers such as Ti, V and Nb obviously have negative interaction parameters, but are not suitable for obtaining a solid solution of nitrogen in austenite. Due to the low solubility product of the corresponding nitrides they will form nitrides at low nitrogen concentrations. Cr is a key element in the process as it gives rise to a significant nitrogen solubility in austenite at high temperatures, provided that the concentration of Cr is higher than, say, 9-10 wt%, i.e. stainless steels. As mentioned above the quenching from the HTSN temperature occurs in high pressure \( N_2 \); it follows directly from Eq. 6 that this procedure is problematic as the high \( p_{N_2} \) in the (short) cooling stage potentially can raise the nitrogen content in the surface region. Practically this implies that for a steel that is solution nitrided to a high nitrogen content (in the austenite region), relatively close to the solubility limit, a strong propensity to form surface and grain boundary nitrides exists in the surface adjacent region. This is a combination of the high nitrogen content itself (cf. the shift of the “nose” of TTT diagram) and the high \( p_{N_2} \) in the quench that further enhances the nitrogen content. Hitherto, this “problem” has largely been overlooked and means that the full potential of the HTSN treatment has not (always) been realized; there is a fine line between improvement of corrosion properties and deterioration of the material. A recent remedy to the problem is to use inert gas, viz. argon, in the quench state; this implies a \( p_{N_2} \) equal to nil, thus avoiding the formation of detrimental surface nitrides [8].

In the following different classes of stainless steels will be discussed with respect to HTSN.

2. Austenitic & duplex stainless steels

The isopleths of 3 different hypothetical austenitic stainless steels, with a composition close to AISI 316, are given in Figure 2. From the isopleths it is clear that the composition strongly influences the stability range of austenite and affects the solubility of nitrogen in austenite. HTSN is typically carried out at temperatures from 1050°C and up to 1150-1175°C; for the 16Cr alloy depicted in Figure 2 the material is stable austenitic up to 1235°C whereas the 20Cr alloy will be duplex in the same temperature interval. When nitrogen is introduced to the surface nitrogen stabilized austenite is obtained. Substitution of Ni with Mn is seen to increase the solubility of nitrogen in austenite and for a fixed \( p_{N_2} \) increase the nitrogen content, see Figure 2B. Commercial stainless steels, such as AISI 304 and AISI 316 will normally be stable austenitic at the applied HTSN temperature. Isobars are shown for different \( p_{N_2} \) and for the different isopleths for the alloys. Here it is evident that a higher \( p_{N_2} \) increases the nitrogen content - and the nitrogen content in austenite. It is also clear that the nitrogen solubility
increases in austenite as a function of temperature, but will require higher \( pN_2 \) (for a fixed \( pN_2 \) the nitrogen content decreases with increasing temperature).

Figure 2. ThermoCalc. Isopleths for hypothetical stainless steels. A) Variation of Cr content: 16Cr10Ni2Mo (16Cr), 18Cr10Ni2Mo (18Cr) & 20Cr10Ni2Mo (20Cr). B) Partial substitution of Ni with Mn: 18Cr10Ni2Mo (0Mn), 18Cr8Ni2Mo2Mn (2Mn) and 18Cr4Ni2Mo4Mn (4Mn). Isobars for \( pN_2 = 0.1 \) and 0.5 bar are shown in both diagrams.

The microstructural evolution in HTSN for an austenitic stainless steel is schematically depicted in Figure 3A. The initial austenitic microstructure is maintained at the HTSN temperature (although cold worked parts will recrystallize) and will experience grain growth. Concomitantly, nitrogen is dissolved in the austenitic surface leading to typical nitrogen contents in the range 0.1 - 1.0 wt% (see also isopleths and solubility of nitrogen in austenite in Figure 2). For most technical parts the high temperatures are associated with loss of strength due to removal of cold work, but this can to a large degree be compensated by the solid-solution hardening by nitrogen in the nitrogen rich austenite case. Moreover, the grain hardening effect (Hall-Petch relationship) becomes more prominent with increasing nitrogen alloying in austenite, which further mitigates the loss of strength by removal of cold work. The main effect of adding nitrogen to austenite is strongly enhanced corrosion performance, provided that nitrogen remains in solid solution during processing! Also cavitation erosion performance can be improved by HTSN. Another benefit is that nitrogen alloying does not have a negative impact on the ductility of the material.

Figure 3. A) Schematic illustration of solution nitriding of austenitic stainless steel and the combination of solution nitriding and low temperature surface hardening (microstructure).
B) Conceptual hardness depth profile of HTSN+LTSH treatment of austenitic or duplex stainless steel.

The combination of HTSN and LTSH has recently been introduced as a commercial process [9] and exploits the benefit of having a thick load bearing case with excellent corrosion properties and without the presence of deformation-induced martensite (from cold working); the presence of deformation-induced martensite is highly detrimental for LTSH processes. The concept is schematically shown for an austenitic stainless steel in Figure 3A and the resulting hardness depth profile of HTSN combined with LTSH is schematically shown in Figure 3B.

For duplex stainless steels some of the same concepts apply as for austenitic stainless steels: a nitrogen stabilized austenitic case is desired. The difference is the core microstructure, which is still ferritic and austenitic for the duplex stainless steel; for austenitic stainless steels it remains austenitic. This concept is illustrated in Figure 4.

![Figure 4: Schematic illustration of solution nitriding of duplex stainless steel. The surface is transformed into a case of nitrogen stabilized austenite. See schematic hardness depth profile in Figure 3.](image)

The introduction of nitrogen will stabilize the austenite, which is also clear from the isopleth for the duplex stainless steel SAF2205 shown in Figure 5. At the HTSN temperature, e.g. 1150°C, the material without added nitrogen is ferritic-austenitic, but when nitrogen is introduced during HTSN, stable austenite is achieved due to the strong austenite stabilizing effect of nitrogen. The austenitic nitrogen-rich case formed has a relatively high content of nitrogen; for SAF2205 up to 1 wt% can be realized. Obviously, such high nitrogen contents in solid solution give rise to an increase in hardness (cf. Figure 3B) and, more importantly, a significant improvement against localized corrosion as pitting and crevice corrosion can be obtained, provided that nitrogen stays in solid solution. The stabilization of austenite by interstitial nitrogen also entails redistribution of substitutional elements, which tend to partition in austenite and ferrite (ferrite formers Cr and Mo in ferrite and austenite stabilize Ni and Mn in austenite). This redistribution takes time and compositional inhomogeneity on the substitutional lattice can be observed in “youngest” part of the austenite case.

The microstructures of SAF2205 solution nitrided at 1150°C for 1 hour at two different partial pressures of nitrogen, pN₂= 0.5 and 0.7, are given in Figure 6. The isobars are also indicated in Figure 5; 0.5 bar is within the austenite phase field, whereas 0.7 exceeds the limit for nitrogen solubility and should lead to formation of Cr₂N. From Figure 6 the nitrogen stabilized case is evident and the core still consists of ferrite and austenite. Due to the presence...
of two phases, grain growth in the duplex part of the material is largely hindered; grain growth does occur in the single phase austenite region (hardened case). Even for the high pN$_2$ of 0.7 bar there are no signs of Cr$_2$N formation in the surface region, as predicted from Figure 5. This can be attributed to the dynamic situation present for the growing layer where the equilibrium nitrogen content is not realized due to continued inward transport of nitrogen and/or slow surfaces kinetics leading to flux controlled growth.

![Figure 5. ThermoCalc. Isoplets for duplex stainless steel SAF2205. Isobars for two different partial pressures of nitrogen, pN$_2$=0.5 and 0.7 are indicated in the figure.](image)

Electrochemical polarization measurements in chloride containing solution show highly improved corrosion performance of the HTSN treated SAF2205 (not shown).

As for austenitic stainless steels the HTSN treated duplex materials can be combined with LTSH, i.e. formation of expanded austenite in the outermost surface of the nitrogen stabilized austenite case. However, care must be taken to avoid “475°C embrittlement” as a consequence of the thermal impact of the LTSH treatment.

![Figure 6. LOM SAF 2205 duplex stainless steel solution nitrided for 1 hour at 1150°C. A) pN$_2$=0.5 bar. B) pN$_2$=0.7 bar. From [10].](image)
3. Martensitic and ferritic stainless steels

HTSN of martensitic and ferritic (including ferritic/martensitic) stainless steels is somewhat different from austenitic and duplex stainless steel. Instead of forming a case of nitrogen stabilized austenite the purpose is to form a case of nitrogen containing martensite. Hence, the attainable surface hardness is significantly higher than for the austenitic and duplex stainless steels.

For the martensitic stainless steels the materials are fully austenitic at the HTSN temperature, which is slightly higher than the typically recommended austenitisation temperature, due to the presence of carbon. Nitrogen is added to austenite similarly to the concept of austenitic stainless steels. Upon cooling the case is - ideally - transformed into nitrogen-containing martensite and the core becomes the usual carbon-containing martensite. The concept is visualized in Figure 7A. The process is normally associated with grain growth, leading to relatively large austenite grains prior to quenching. However, the presence of primary (stable) carbides can prevent grain growth to a certain extent. In order to refine the grain structure a second hardening cycle (HTSN treatment) can be carried out, which essentially is a re-austenitization followed by quenching. There is a limit to the amount of nitrogen that can be added to the material, because nitrogen will lower the martensite start temperature, Ms. This poses a restriction as the nitrogen that can be added to the material depends strongly on the composition of the alloy. For high-carbon or high-chromium and medium- to low-carbon martensitic stainless steels only minor amounts of nitrogen can be added. The consequence of adding too much nitrogen is the stabilization of relatively soft retained austenite, that cannot be transformed into martensite, although cryogenic treatment can, to some extent, mitigate this problem [11].

![Figure 7A](image1.png)  
![Figure 7B](image2.png)

Figure 7. A) Schematic illustration of the microstructure of HTSN of martensitic stainless steel. B) Schematic illustration of (idealized) hardness depth profiles of HTSN of martensitic and ferritic stainless steel.

For ferritic stainless steels the core remains stable ferrite during HTSN and the introduction of nitrogen to the surface brings about a transformation of ferrite into austenite due to the austenite stabilizing effect of nitrogen. Hence, an austenite case develops which will transform to nitrogen martensite upon cooling; a schematic illustration of a hardness depth profile compared to a martensitic stainless steel is shown in Figure 7B. The ferritic material
will experience significant grain growth in the core and will be softer than the martensitic stainless steel. However, the nitrogen-containing case on ferrite can be relatively hard, but typically not as hard as the nitrogen- and carbon-containing case obtained for carbon-containing martensitic grades.

An example of the microstructure of HTSN treated martensitic stainless steel AISI 410 is shown in Figure 8A, where a nitrogen containing martensitic case has formed and the core consists of carbon martensite. The gradient in the nitrogen content is reflected in the gradual transition of the microstructure, i.e. the nitrogen containing part etches less severely due to improved corrosion performance. As already mentioned above, HTSN can be combined with LTSH, which is also possible for martensitic stainless steels; such an example is shown in Figure 8B. The LTSH (nitriding) process results in formation of 35-40 µm thick case (atop the pre-existing HTSN case) consisting of expanded martensite with a hardness reaching 1400 HV at the surface; see hardness profiles of the HTSN and HTSN+LTSH treatment in Figure 9. The LTSH treatment also functions as tempering of the martensite formed from the HTSN treatment. For the specific LTSH treatment shown in Figure 9 the thermal impact leads to a slight increase in hardness in the core of the material (without nitrogen), which can be attributed to secondary hardening. The secondary hardening effect is more pronounced for the nitrogen rich martensite (from HTSN) where a significant increase is observed after LTSH (thermal impact). This provides high load-bearing capacity for the outmost hard case formed from low temperature nitriding. It is also possible to temper the material prior to LTSH at a temperature higher than the LTSH temperature. The combination of a very hard surface zone consisting of expanded martensite with nitrogen in solid solution supported by a thick case of hard nitrogen-rich martensite provides highly improved wear and corrosion performance. The incorporation of nitrogen by high and low temperature processes also leads to formation of compressive residual stresses, which are beneficial for the fatigue performance of the material.

![Figure 8. Light optical microscopy of surface hardened AISI 410. HTSN: 1110°; pN₂= 3 bar for 10 minutes followed by pN₂= 2 bar for 10 min. LTSH: gaseous nitriding in flowing NH₃ for 30 hours at 390°C. A) HTSN; Kalling’s reagent. B) HTSN+ LTSH, Vilella’s etchant.](image)
Figure 9. Hardness depth profiles of surface hardened AISI 410. See corresponding micrographs and process conditions in Figure 8.

4. Summary and outlook

HTSN of stainless steels has hitherto experienced a niche role, but is gaining ground as an industrial process that can be applied to improve the performance of most classes of stainless steels. For austenitic stainless steels nitrogen can be incorporated and lead to a further stabilization of the austenite, hence the steel remains fully austenitic (and non-magnetic) during (severe) deformation. It also strongly enhances the resistance of the steel against localized corrosion. The application of HTSN could also play a major role for 3D printed austenitic stainless steel parts, where the large diffusion depth of nitrogen could be used to add strength whilst homogenizing the material. For duplex stainless steels further improvements in corrosion performance can be achieved due to the possibility of having very high contents of nitrogen in solid solution in austenite. Moreover, the concept also implies that the core structure can have the mechanical benefit from the duplex structure while the case is fully austenitic. The full benefit of corrosion performance from nitrogen in solid solution can be gained upon quenching in inert gas instead of nitrogen. The analogy to classical case hardening (carburizing) of non-stainless materials is evident for ferritic and martensitic stainless steels: essentially HTSN can be considered the “stainless” version of this process. Designing the nitrogen “load” in the case combined with optimized sub-zero treatment and tempering can lead to highly improved materials performance. The possibility of combining LTSH (carburizing, nitriding and nitrocarburising) with HTSN can give properties that so far have not been achievable in stainless steels, as for example very high wear- and corrosion resistance combined with high load bearing capacity and high endurance limit. It is thus anticipated that HTSN will gain more and more ground in industry in the years to come.

References:


EVERS HELGA, PASQUINI ABOLI

DATA DRIVEN CONTINUOUS QUALITY MONITORING IN ROLLING MILLS

Abstract

Over the past decades, huge volumes of quality data collected through continuous and regular monitoring of individual processing lines from the rolling industry have been accumulated. Now is the time to reap returns on past investments made in expensive and precise quality measuring equipment. These data await being put to better use.

Any anomalous or divergent quality data require an action to be taken by the monitoring personnel. This action may be repairing, rerouting or in the worst case scenario, scrapping a coil resulting in losses. A huge amount of time and effort is typically invested in pin-pointing the exact cause of the defect(s).

This paper talks about finally pulling out these hidden or unused yet, available data for the purpose of continuous quality improvement. The data is scoured for previously unseen correlations using one or more classification algorithms. When relations are found, the data is arranged in relational trees. These trees can then be converted into new rules that are implemented immediately and further help in predicting and detecting errors and defects at an earlier stage on the processing line. The newly inducted rules thus help in generating better quality data. These newly generated and more precise data are again fed to the data correlator, which in turn comes up with newer and better correlations, which can be converted into even more intelligent rules based on a great deal of past experience as well as current, improved data. These rules continue to improve the quality of the output coils while at the same time allowing for an easier and earlier root cause analysis of a problem. The feedback based system contributes to bettering itself, thereby resulting in continuous quality improvement

Keywords: Data integration, genealogy, data analyses, quality monitor, digital twin

Introduction

Even today, in many rolling plants, quality grading is not an automated process. A great deal of time and effort is invested in quality supervision on human level. The total extent of time and effort invested often varies based on skill and experience of individual operators.

To help rid the system of such variations and its consequences, one of the important steps is to introduce an automatic coil quality grading system. The automatic grading system makes use of extensive data – past as well as current – which can be employed by the system at any point of time in the process. Extensive data is available – except, it remains hidden or unused. This kind and volume of data is an extremely powerful tool when made available for
immediate and continuous use through its integration and then put to work in automated coil quality grading.

What makes the whole process even more beneficial is the added capability to analyse data on demand to provide further improvement suggestions. These help fine-tuning the system. As an example, a quality rule can be defined that allows a certain number of light scratches on a coil to pass without sending the coil to be reviewed or without blocking the coil. However, the moment the system spots these light scratches clumped in a very small area, it sends the coil to be reviewed or blocks it, depending on the density with which the scratches appear.

Another very useful side effect of an automated coil grading system is that it frees up the IT personnel to resolve and maintain real IT issues because automatic coil grading software can be handled by non-IT personnel. At any point in the process, an engineer may notice an anomaly and correct or introduce one or more logical rule(s) defining quality standards that will rectify the problem.

Concept

The following sections talk about how, in the automated coil grading system, the different tools work in sync with one another to achieve continuously improving quality supervision and therefore, high quality product(s). These tools use the following concepts to achieve this goal:

- **data integration** - integrating all available data on all past and current coils
- **quality rule translation, modification and definition** - translation of existing quality rules into the new system and introduction of new precise, logical quality rules to define desired quality standard
- **automated quality monitoring** - allows reliable, automatic quality supervision
- **genealogy** - storing and maintaining every possible traceable datum on a coil
- **correlating data and feedback** - identification of patterns in process and quality status in a given set of products, that are converted into suggestions for changes in or addition of brand new quality rules
- **quality improvement** - prevention of bad coil production using the feedback

Once the suggested rule modifications are adapted or the newly suggested rules are inducted into the system, the performance of the system (automatically) goes up. Within the
parameters of the quality rules, the system grades the coils flawlessly and leaves operators with more time to concentrate on deviations in a detailed manner rather than going through every single coil. All this while the system continues to perform the functions stated above in a continuous loop.

**Data Integration** There are two main aspects to integration of data:

1. Many a time, a complete overview of all current data within any single application is absent due to technical difficulties in connecting the many diverse systems. Often, this absence is due to connections incompatible with one another. Integration of all data bridges the gap between all data and makes all of this data available at one glance. The data can now freely interact with each other.

2. The second aspect of data integration allows the user to view all of the past data, so far unused, in addition to current, continuously incoming data. It is now connected to and brought together in a way that enables all previous and current process and quality status data to interact with each other.

![Figure 2: Data Integration](image)

In case of sensitive data or to avoid the hazard of unintentional modification or loss of data, access can be restricted based on user roles. The highlight of integration however, lies in its power to be used as a great pool of data which can be used to study previous behavioural patterns. The data makes it possible for the right algorithms to trace back the lineage of problematic coils and find common factors that led to the defective coil.
**Quality Rule Translation, Modification and Definition** Using integrated data, all of the existing quality (logical) rules can be translated into the new system with ease. Existing complex rules can be simplified and/or modified to make them more efficient. The fact that all data is now available for interaction makes it possible to define new quality rules that are far more superior and complex than their forefathers. Better rules help catch problems before they turn hazardous and thus, contribute to continuous quality improvement.

**Genealogy** Data integration achieves the purpose of connecting the user with all data on hand. However, analyses of problems can be a challenging feat while dealing with a very large volume of data. This is where the concept of genealogy comes to the rescue. A complete, meticulous record of every single coil is stored and maintained in the system, right from its perception or in other words, the roots of every single coil are traced back to its origins and a digital twin of the coil is created, stored and maintained (to reflect any further changes) in the system. This means that a full track record of all the raw material that went into the making of this coil and including every single process that each of the contributing material underwent, is stored and maintained in the system. This includes records of all intermediate processes that were applied to the material from the point it was introduced. Eventually, this makes possible a quick and precise analysis of the cause of a problem.

![Genealogy Diagram](image)

**Figure 3: Genealogy**

**Correlating Data and Feedback** Using genealogy for every coil, different algorithms can be put to work to plot behavioural patterns and find out different correlations in the material and processes of coils with the same output quality. The results of such correlations can help spot trends in parameter values measured that were, for instance, within tolerance limits but affected the quality of coils at a later stage. Once such behaviour is made available descriptively or visually, it is very easy to fix the problem by modifying an existing rule with greater than acceptable tolerances or to introduce new rules altogether. The results of the correlation analyses work on creating and proposing such rules that can be directly taken over. This means that it is no more required of the personnel that they spend time and thought into
actually creating a new rule and feeding it into the system – they can simply take over the suggestion.

Usually, the necessary data is prepared, exploration criteria defined and then, data analysis performed. The resulting relations can be viewed in different ways. Fig. 4 shows the usual steps involved in analyses of data.

![Figure 4: Data Analysis](image)

**Quality Improvement** The correlation and feedback system continues to work with past and incoming data to further figure out how to continuously further improve the quality of already acceptable coils. Proactive quality supervision allows deviations in process lines to show up (and therefore, to be rectified) before they can affect the quality of a coil at a later point.

**Conclusion**

Automatic coil grading is the need of the hour. Introducing automatic grading reduces the involved human time and effort. Integrating data makes all data easily reachable and comparable. Organisation of this integrated data based on its entire life cycle (genealogy) allows this large volume of data to be put to good use through analyses. Correlating data using these algorithms helps spot common behaviours and trends in the production process and helps analyse the root cause of a problem (defective coil).

The goal here is not only to avoid delivery of one or more bad products to the customer, but more importantly to ensure that such defects do not occur at all by making certain that conditions leading up to defective production are identified and eliminated.

What is also important to note here is that such a system greatly reduces the downtime in a plant, thereby not only contributing to continuously improving quality, but also to production volume and therefore, revenue.
Fabrication, forming and welding
Nd-YAG LASER PULSED WELDING: EFFECTS ON THE SUPERDUPLEX STAINLESS STEEL UNS S32750

Abstract

The use of superduplex stainless steels in industry increases due to their characteristics that combine good mechanical properties and resistance to corrosion. The study of super duplex stainless steels is very important due to the development of activities in the area of oil and natural gas, mainly with the recent discovery of the pre-salt oil in Brazil. These industries operate in critical atmosphere, because of the presence of seawater and oil. The UNS S32750 consists of a biphasic structure with volumetric fractions of 50% ferrite and 50% austenite. Therefore, the development of techniques for improving welding of super duplex steels is necessary in order to ensure that phase balance and properties of the material are not severely damaged in the process. The objective is to characterize joints of UNS S32750 duplex stainless steel welded with the Laser Nd-YAG (Neodymium-Doped Yttrium Aluminium Garnet) pulsed process. Welds were performed in the autogenous condition, varying the heat input introduced by the process. Then, an analysis of the base metal, the weld beads and the heat affected zone, were performed through optical microscopy (OM), corrosion tests (CPT), SEM (Scanning Electron Microscopy), and EDS (Energy Dispersive Spectroscopy). The results obtained were related to the welding parameters used. The success of the research provides knowledge parameters and properties in the welded joints of this superduplex stainless steel.

Keywords


1. Introduction

The study of super duplex stainless steels is very important due to the development of activities in the area of oil and natural gas, mainly with the recent discovery of the pre-salt oil in Brazil. These industries operate in critical atmosphere, because of the presence of seawater and oil.

In the oil and natural gas industry, super duplex steels are subjected to welding processes that result in microstructural changes, unbalancing the phases’ fractions in welded joint and in its surroundings, reducing the mechanical and corrosion resistance in those regions. [1] This is due to thermal cycles involved in the welding process, with localized heating and cooling, and expansion and contraction. [2, 3]
The mechanical strength and corrosion resistance of super duplex steels come from their biphasic microstructure, with approximately identical ferrite and austenite fractions. Thus, the UNS S 32750 super duplex alloy is an excellent cost and performance alternative because it has high resistance to corrosion from chlorides, making it ideal for application in marine industry. [4, 5]

This study aims to characterize Pulsed Nd-YAG Laser weld beads performed in the super duplex steel UNS S32750.

2. Experimental

The base metal used was 3.0 mm thickness sheets of the stainless steel duplex UNS S32750. Table 1 shows the nominal chemical composition of the base metal. The base metal has elongated grains in the rolling direction of the material. The average balance of the ferrite/austenite phases in the base metal was around 50%. In addition, the estimate of the weight percent of the alloying elements analyzed by EDS in the base metal confirmed the manufacturer's information.

<table>
<thead>
<tr>
<th>Table 1 - Nominal chemical composition of UNS S32750.</th>
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<td>C</td>
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<td>0,018</td>
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In order to evaluate the influence of the heat contribution on the characteristics of the weld bead, the joints were welded in the autogenous bead on plate condition. Welding speed was 1 mm/s and frequency was 3 Hz in all cases, promoting an overlap around 70%. The welds were performed in an argon gas atmosphere with a flow of 12 l/min. Table 2 shows the welding conditions analyzed.

<table>
<thead>
<tr>
<th>Table 2 - Pulsed laser welding parameters.</th>
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<td>Bead N°</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
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<td>3</td>
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<td>4</td>
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</table>

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After the welding process, the samples were metallographically prepared for analysis of the weld beads cross section by grinding and polishing. The sections were cut along the length of each weld bead to analyze the variability of the parameters of width and depth. Then, all samples were etched with Beraha reagent (85ml H$_2$O – 15ml HCl – 1g K$_2$S$_2$O$_3$).

The analysis of the ferrite/austenite balance in the weld and the metal were carried out on images obtained through a digital camera coupled with the microscope. Image processing was done through ImageJ, a public domain image editing software based on the Java platform.

The Critical Pitting Temperature (CPT) determination was performed in the bead 7 and in the base metal, following the ASTM G150 standard.

3. Results and discussion

A characterization of the as received base metal was performed through the analysis of the volumetric fraction of ferrite and austenite. The OM and SEM observation revealed a typical microstructure of a duplex stainless steel, with the ferrite matrix with elongated austenite islands (Fig. 1) and volumetric fraction around 50% each.

![SEM micrograph of base metal showing near equal amounts of austenite (light etched regions) and ferrite (dark etched regions).](image)

Then, the geometries of the weld beads were analyzed. In Fig. 2 the influence of Temporal Width (ms) and Peak Power (kW) on the width(a) and depth(b) of the weld bead are shown. Fig. 3 presents the parameters and the obtained macrostructure of each weld bead section.
Fig. 2 – Influence of Temporal Width (ms) and Peak Power (kW) on the width(a) and depth(b) of the weld bead.
As expected, the sections reported in Fig. 3 confirm that the geometry of the weld bead is directly related with the variations of the parameters involved in the laser welding process, mainly with the heat input. The depth and the width present a small variability along each bead, considering standard deviation values.

These imperfections can be explained by the fact that the laser welding process begins by the incidence of light on a very thin surface layer, where the thermal conduction will form a liquid pool. Due to the high intensity of the laser, the surface temperature exceeds the vaporization temperature of the steel. This causes the formation of a channel (keyhole) that is filled by the plasma, allowing the passage of the beam into the interior, causing an increase of absorptivity, since the incident light will bounce off the walls of the formed channel [6-8].

The microstructure in the weld beads is constituted of primary ferrite whose orientation follows the direction of extraction of heat during the welding (Fig. 4). These characteristics are in accordance with the descriptions of Mohammed [9]. He states that in materials with high Cr/Ni ratio, the solidification in the melting pool occurs only with the formation of ferrite, followed by the nucleation of austenite at grain boundaries of the already solidified ferrite and by its growth as plates to the interior of the grains, promoting the aspect known as Widmanstatten. The weld metal has a ferritic matrix microstructure, with less amount of austenite than the base metal. Also, in the Fig. 4 is possible to notice bands of austenite due the overlap laser pulses.

Comparing weld beads made with close heat input values, there's no significant geometry differences, which means that for this range of values (2-3 kW peak energy), temporal width and peak energy, isolated, are not determinant parameters to weld beads geometry, confirming that only the heat input is effective. Furthermore, imperfections such as porosities and loss of material in the bead surface, were noticed when increasing the peak energy values to 3,5 kW. (Fig. 5)
Fig. 4 – SEM micrographs of molten zone and base metal at beads 1, 7 and 14.
The high welding energy values for the short time of the laser pulse did not keep for longer enough the material at the required temperature to provide the full transformation from ferrite to austenite. So, in all beads, the austenite volumetric fractions were less than 1%. The high ferrite volumetric fraction found in the weld metal of the samples may result in the weakening of the region, which may be detrimental to corrosion and mechanical resistance.

The CPT for the base metal was 91°C, while for the bead 7 was 27°C, confirming the reduction of corrosion resistance in the weld bead (Fig. 6) due the ferrite high volumetric fraction.

4. Conclusions

The main results can be summarized as follows:

- The observation of the weld beads along their length showed that the increase in the heat input produces wider and deeper welds with a depth varying between 0.81 and 2.37 mm and width between 0.99 and 1.59 mm. It seems better to perform autogenous welding on both sides and with a moderate heat input when applied to the union of thicker sheets, such as the one of this study, which is 3 mm thick.
- We observed a very small fraction of austenite in the molten zone, because the high
welding energy values for laser pulse short time did not keep the material at the required temperature for enough time to provide the full transformation from ferrite to austenite. In all beads the austenite volumetric fractions were less than 1%. The high volumetric fraction of the ferrite phase may result in the weakening of the region, which is detrimental to corrosion and mechanical resistance.

- The CPT test confirmed the reduction in the corrosion resistance, since the CPT was 27°C in the weld bead 7, while in the base material it was 91°C.
- In the weld metal the Widmanstatten austenite and the characteristic of the solidification of the primary ferrite have been detected, as during the welding the cooling rate promoted the formation of the austenite in ferrite grain boundaries, as observed in the pseudo-binary diagram 70 % Fe-Cr-Ni for the UNS S32750 steel composition.
- The material presented no HAZ due the fast cooling rate, making this zone indistinguishable.
- Values of peak energy equal or above 3 kW could cause porosities and loss of material in the weld beads due the material vaporization.

References
ELI JORGE DA CRUZ JUNIOR¹, ARTHUR MORAES E VIDEIRA², CLAUDIO GENNARPI, IRENE CALLIARIP, VICENTE AFONSO VENTRELLA⁴

COMPARISON BETWEEN AUTOGENOUS WELDING AND WITH ADDITION OF NICKEL ON Nd:YAG PULSED LASER WELDED UNS S32750 DUPLEX STAINLESS STEEL

Abstract

Duplex stainless steels (DSS) have a biphasic microstructure with equal proportions of austenite and ferrite, which gives them excellent mechanical strength and corrosion resistance compared to austenitic stainless steels. Nd:YAG pulsed laser welding affects the microstructure of DSS resulting in unbalanced microstructure which compromises their properties. As way to obtain a balanced microstructure we have the addition of austenite forming elements, such as nickel or nitrogen. The present work reports the effect of nickel addition on the microstructure and microhardness of UNS S32750 duplex stainless steel welded by Nd:YAG pulsed laser. Two conditions were used: autogenous welding and with addition of nickel (electrolytic nickel foil with 30 µm thickness placed on the contact surface of weld joint). The addition of nickel affected both the microstructure and microhardness resulting in equal proportions of austenite and ferrite in the weld bead and decreased the microhardness in comparison to autogenous welding.

Keywords

Microstructure, Microhardness, Laser Welding, Nickel addition, Duplex stainless steel.

1. Introduction

Duplex stainless steels (DSS) have a biphasic microstructure, with equal volumetric fractions of ferrite and austenite, which gives them excellent mechanical strength and corrosion compared to austenitic stainless steels [1,2]. Due to their excellent properties, these steels have a wide range of applications in the petrochemical, chemical, pulp and paper, oil and gas, offshore and marine industries [3].

When subjected to welding processes, DSSs present an unbalanced microstructure, predominantly ferritic, which compromises their properties, especially local pitting corrosion resistance and toughness [4]. The Nd:YAG pulsed laser welding process offers some advantages over conventional processes namely process accuracy, complex shape welding, short cycle time, low heat input and narrow heat affected zone. However, low heat input and high cooling rates, typical of the process, favour the formation of ferrite, resulting in an unbalanced microstructure [3]. To obtain a balanced microstructure, it is necessary a post-weld heat treatment, or add austenite-forming elements, such as nickel or nitrogen.

Some authors have studied the effects of nickel and nitrogen addition on the phase balance for certain welding processes [5-9], however related to the Nd:YAG pulsed laser

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process it’s hard to find results [10]. Due to the importance of the phase balance in the DSS properties and its applications, this project investigates the effect of the use of electrolytic nickel as addition metal on the microstructure and microhardness of superduplex stainless steels welded by the Nd:YAG pulsed laser process.

2. Experimental

The base material used was an UNS 32750 duplex stainless steel, in sheets of 1.5 mm thickness. The Table 1 presents the nominal chemical composition of the material. The welds were performed using a Nd:YAG solid state laser system, in pulsed condition.

Table 1. Nominal chemical composition of UNS S32750

<table>
<thead>
<tr>
<th>Base material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
<th>N</th>
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<tr>
<td></td>
<td>0.018</td>
<td>0.29</td>
<td>0.63</td>
<td>0.02</td>
<td>&lt;0.0003</td>
<td>25.61</td>
<td>3.84</td>
<td>6.97</td>
<td>0.15</td>
<td>0.269</td>
</tr>
</tbody>
</table>

Two conditions were evaluated, autogenous welding (AW) and welding with nickel addition (NiW), both with the same welding parameters. Single-pass welding was applied. The welding parameters were: a peak power of 2.0 kW, a pulse duration of 5 ms, a frequency of 9 Hz, and a welding speed of 1.0 mm/s. Electrolytic nickel foil with a 30 µm thickness was used as the addition metal placed on the contact surface of the weld joint, as present on Fig 1. The shielding gas used for both conditions was pure Ar with 20 l/min of flow.

![Fig. 1 - Schematic diagram of the butt weld joint with 30 µm thick nickel foil](image)

Beraha reagent was used to reveal the microstructure, and the volumetric fractions were calculated by SEM micrographs and ImageJ software. Microhardness profiles were obtained through an ultramicrodurometer.

3. Results and discussion

Figs. 2 (a and b) show the microstructure of the transition region between the base material and the fusion zone for the autogenous (AW) and with nickel addition (NiW)
conditions, respectively. It is possible to notice that the nickel affected the formation of austenite both qualitatively, modifying its morphology, and quantitatively, affecting the volumetric fraction.

![Fig 2 - SEM micrographs of transition region between base material and fusion zone for (a) AW condition and (b) NiW condition.](image)

In DSS weld metals, austenite forms in three modes: allotriomorphs grain boundaries, Widmanstätten, which originates within the ferrite grain from the allotriomorphs grain boundaries and intragranular austenite [11]. In the micrograph of the AW condition, there is little presence of austenite in the allotriomorphs grain boundary and intragranular acicular form. The resulting microstructure is quite unbalanced, with the predominating presence of ferrite. In the micrograph of the NiW condition is visible the presence of austenite in the three forms and in greater quantity in relation to the AW condition, resulting in a visibly phase balanced microstructure.

The volumetric fractions of austenite and ferrite for the base material and the fusion zone for each of the conditions are presented in Table 2. The results were obtained by image analysis in several regions of the bead and base material.

<table>
<thead>
<tr>
<th></th>
<th>VOLUMETRIC FRACTIONS</th>
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<tbody>
<tr>
<td></td>
<td>FERRITE %</td>
<td>AUSTENITE %</td>
</tr>
<tr>
<td>BASE METAL</td>
<td>50,1 ± 0,2</td>
<td>49,9 ± 0,2</td>
</tr>
<tr>
<td>AW</td>
<td>92,7 ± 0,2</td>
<td>7,3 ± 0,2</td>
</tr>
<tr>
<td>NiW</td>
<td>46,8 ± 0,3</td>
<td>53,2 ± 0,3</td>
</tr>
</tbody>
</table>

The addition of nickel increased the proportion of austenite from approximately 7 % (AW) to 53 % (NiW). This effect was a consequence of the addition of nickel when all other welding parameters were exactly the same. As already mentioned, the phase balance in DSS is very important for the material to maintain its mechanical properties and corrosion resistance [4].

The micrographs of fusion zone for the conditions AW and NiW are shown in Fig. 3 (a and b respectively). It possible to observe that nickel not only increased the volumetric
fraction of austenite, but also modified its morphology. In the NiW condition, there is a large presence of intragranular austenite in the acicular, lamellar and Widmanstätten forms.

![Fig. 3 - SEM micrographs of fusion zone for (a) AW condition and (b) NiW condition.](image)

The allotriomorphs grain boundary and the Widmanstätten austenite form at high temperatures, while the intragranular austenite at low. In DSS welding, austenite originates from a solid state transformation, which is highly affected by the cooling rate and the heat input [12]. Under high cooling rates and low heat input, characteristics of the Nd:YAG pulsed laser welding process, there is not enough time for austenite formation, resulting in a predominant ferritic microstructure, as seen in the micrograph of condition AW. The great amount of intragranular austenite in the NiW condition resulted from the thermal cycle (high cooling rate) associated with the austenite formation potential of nickel. The effect of nickel in promoting the formation of austenite overlapped the effects of the thermal cycle after the phase balance was reached.

It is also observed that the balanced microstructure along the fusion zone was very uniform for NiW condition, as can be observed in Fig. 4, which shows a micrograph with a smaller magnification of the weld bead.

![Fig. 4 - SEM micrographs of weld bead for NiW condition](image)

At the fusion line, the austenite fraction is slightly lower than in the weld center, it occurs because the cooling rate is higher in this region without enough time for more austenite formation.
To confirm the absence of secondary phases, Figs. 5 (a and b) show SEM in backscattered electron on the weld bead for the AW and NiW conditions, respectively. In this case, the samples were not chemically attacked. Secondary phases should appear as a lighter spot located between ferrite grains and at austenite–ferrite phase boundaries, while chromium nitrides should appear as dark chains at ferrite/ferrite grain boundaries, effect not observed on the micrographs.

Secondary phases can precipitate in a temperature range between 600°C and 950°C [3]. The low heat input associated to the high cooling rate of Nd:YAG pulsed laser welding does not favor the formation of secondary phases for both conditions.

**Fig. 5** - Back-scattered electron micrograph of the weld bead for (a) AW condition and (b) NiW condition.

The microhardness profiles for AW and NiW condition are shown in Fig. 6 (a and b, respectively).
Fig. 6 - Microhardness profile for (a) AW condition and (b) NiW condition.

The mean value of microhardness in the fusion zone for the AW condition was $400.13 \pm 1.32$ HV, while for the NiW condition it was $365.07 \pm 8.54$ HV. As the AW condition presented a predominantly ferritic microstructure the microhardness in the fusion zone was higher. The increase of the austenite proportion decreases the hardness as observed for the NiW condition.

Although for NiW condition the volumetric fractions are very close to those of the base material, the hardness was approximately 20% higher. The large amount of intragranular austenite and its arrangement along the fusion zone created dislocations thus raising the hardness, an effect also observed [8].

4. Conclusions

- The addition of nickel affected the formation of austenite both quantitatively and qualitatively, modifying its morphology and volumetric fraction.
- In the NiW condition, volumetric fractions of austenite and ferrite of approximately 50% were obtained, resulting in a balanced microstructure.
- The nickel austenite forming effect overlapped the effects of the thermal cycle, once the phase balance was reached
- In the NiW condition a lower hardness was obtained than in the AW condition due to the higher amount of austenite
- In the NiW condition, although the volumetric fraction of austenite in the fusion zone was close to that of the base material, the hardness was higher, since the morphology and arrangement of the austenite along the fusion zone affected the hardness of the region.

References

AN APPROACH FOR PREDICTION OF COIL SPECIFIC FORMING LIMIT CURVES

Abstract

Forming limit curves (FLCs) are widely used for predicting failure in sheet metal forming operations. FLCs are determined in the laboratory according to ISO 12004-2 using the Nakajima test. The testing procedure involves stretching a series of dog-bone shaped blanks with a hemispherical punch until failure occurs. This measurement procedure is extremely time-consuming. Consequently, a variety of statistical models have been proposed for predicting FLCs based on tensile test data. Unfortunately, practically all existing models are targeted for carbon and alloy steels, and thereby these models cannot be directly applied to stainless steels. In the present study, an approach for prediction of coil specific forming limit curves is developed. Predictive equations are derived based on statistical correlations between measured FLCs and steel properties. The application of the method to prediction of FLCs of stabilized ferritic stainless steels is described.

Keywords

Forming limit curve, FLC, ferritic stainless steel.

1. Introduction

Forming limit diagram is widely used for predicting failure of sheet metals and diagnosing production problems in sheet forming operations. Analysis of forming processes by means of forming limit diagram assumes that the failure can be predicted by inspecting the values of major and minor principal strains in the end of the forming process. The principal strains are plotted as a series of points in the principal strain space, i.e. in a coordinate system having the minor strain as the abscissa and the major strain as the ordinate. The points are then compared with a forming limit curve (FLC). The FLC marks the borderline between safe and unsafe regions in the principal strain space. As long as the principal strains are below the FLC, the material can be deformed without developing localized necking and incipient failure. [1,2]

Although forming limit diagram is widely used for evaluating sheet metal formability, it has been shown already in the 1970’s that the approach is valid only for proportional loading conditions [1–5]. Proportional loading refers to cases where the ratio of major and minor principal strains remains constant throughout the forming process and the strain paths are linear in the principal strain space. In practice, the path-dependency of forming limits is often neglected. The ratio of major and minor principal strains is usually nearly constant in the first step of sheet metal forming processes and the first step is often the most critical one. The path-

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dependency cannot, however, be ignored in the analysis of multi-stage forming processes involving redrawing and flanging dies [2,3]. In this kind of forming processes, strains far below the conventional FLC may sometimes lead to failure and sometimes strain levels far above the conventional FLC are safe [2]. Motivated by this problem, a number of path-independent forming limit criteria have been proposed. Paul made a comparison of all common strain path independent forming limit criteria and concluded that all studied methods were indeed path-independent [6]. Path independent forming limits are generally determined using conventional strain-based FLC as input data. Thereby conventional strain-based FLCs will be needed for analyzing sheet metal forming operations, even if the more advanced path-independent methods gain popularity.

FLCs are commonly determined according to ISO 12004-2 using the Nakajima test. In this testing procedure, a series of dog-bone shaped blanks is stretched with a hemispherical punch until failure occurs. Optical strain measurement is used for determining the strain field in the sample. The limit strains are then calculated based on an objective mathematical criterion. This measurement procedure is extremely time-consuming. Therefore, a variety of statistical methods have been proposed for predicting FLCs based on parameters that can be measured with relative ease. The empirical model proposed by Keeler and Brazier [7] in 1977 is still widely used for predicting FLCs of drawing grade mild steel. In this method, the lowest point of the FLC is at the plane strain axis and is given by

$$FLC_0 = \ln \left[ 1 + \left( \frac{23.3 + 14.1t}{100} \right)^{\frac{n}{0.21}} \right]$$

where $n$ is the work hardening exponent and $t$ is the sheet thickness is measured in millimeters. The FLC is composed of two straight lines passing through the minimum point with the angles of 45° and 20° on the left- and right-hand side of the forming limit diagram, respectively. After the pioneering work of Keeler and Brazier, many empirical methods have been proposed for predicting the shape of FLCs. Abspoel et al. [8] and Levy at al. [9] present a comprehensive review of published methods. Unfortunately, practically all proposed methods have been developed for carbon steel. Stainless steels have somewhat different forming characteristics compared to typical carbon steels. Thereby predictive equations developed for carbon steel cannot be directly applied to stainless steels.

Extensive theoretical research has been conducted on predicting the occurrence necking and plastic instability of sheet metals [10]. According to the bifurcation theory, diffuse necking is associated with the loss of uniqueness of the solution and a bifurcation of the flow into an elastic region and a shrinking plastic region [11]. In the geometrical imperfection theory, localized necking is due to initial inhomogeneity or geometrical imperfection in the sheet [12–14]. In theoretical models founded on continuum damage mechanics, the nucleation and growth of micro-voids is considered to be central phenomenon in the process leading to the failure of sheet metals [14]. In general, the theoretical analyses have shown that small changes in the work hardening ability, in the shape of the yield surface or in the strain rate sensitivity may have a strong influence on the shape of the FLC. The limit strains decrease considerably if shape of the yield surface becomes less round near the plane strain state [15,16]. The mathematical form of the work hardening law may also have a substantial effect on the limit strains [17].

The mentioned material properties depend on chemical composition, microstructure and processing of the steel. Therefore, it can be argued that trying to predict the FLC for a diverse group of steels with one single empirical model is an overly ambitious target. The success of the Keeler and Brazier model might also be attributed to the fact that the target group, formable mild steels, is sufficiently homogenous in terms of their properties.
In the present work, an alternative approach is proposed for predicting FLCs for stainless steels in the steel industry. The approach consists of the following consecutive steps:

1. A group of sufficiently similar steels is selected.
2. A representative sample is gathered.
3. Properties of sampled test materials are measured.
4. Predictive equations are derived.

As an illustrative example, the proposed approach is applied on a group of stabilized ferritic stainless steels. The test materials are steels with similar physical metallurgy, microstructure and mechanical properties. Empirical equations are developed for predicting the entire FLC for the steel group. The accuracy of predicted FLCs is discussed.

2. Experimental methods

The mechanical properties of the test materials were measured using tensile tests in 0°, 45° and 90° angles to the rolling direction. The tests were conducted according to EN 6892-1 method A223. The Lankford r-values were determined in the strain range from 5% to 15%. The median of three tests was used as a representative value. The average grain size of test materials was measured by the intercept method according to ASTM E112-96. Five measurements were conducted on each sample and the average value was used.

The FLCs were measured using the Nakajima test according to ISO 12004-02. The tests were carried out with Erichsen model 145-60 Universal Sheet Testing Machine. The complex seven-layered lubrication scheme was used in the tests. The punch velocity was 90 mm/min. GOM Aramis digital image correlation system with cameras fixed to the forming machine was used to measure the strain field during the Nakajima tests. The strain measurement was carried out by means of stochastic high-contrast pattern created by spraying white and black paint on the specimen. Images were recorded with the frequency 10 Hz. The limit strains were determined according to the cross-section method using the software supplied with the GOM Aramis. Three lines were analyzed on each specimen.

The geometry of dog-bone shaped specimens is given in Table 1. Three repeats were performed with each test piece. Additional repeats were performed if large scatter was observed. Fig. 1 illustrates the distribution of measurement points obtained with the sample geometries A-E in the principal strain space. The strain measures $\varepsilon_1$ and $\varepsilon_2$ in the coordinate axes are logarithmic principal strains.

The clustering of data points in the principal strain space can be used to estimate the experimental uncertainty of the FLC measurements. Statistical analysis of measurement data suggests that the distribution of points with respect to their center of mass follows normal distribution. The standard deviation was $s = 0.013$ in the major principal strain. Therefore, the experimental uncertainty of major principal strain was approximately 0.025 at the confidence level of 95%.

Table 1. The shaft width of dog-bone shaped test specimens. The outer diameter of circular specimens was 215 mm, the fillet radius 25 mm and the shaft length 40 mm.

<table>
<thead>
<tr>
<th>SHAFT WIDTH (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
</tr>
<tr>
<td>215</td>
</tr>
</tbody>
</table>

390
3. Selection of test materials

An essential feature in the proposed approach is that the materials included in the same analysis need to be sufficiently similar in terms of their physical metallurgy and mechanical properties. The first step in the application of the method is the selection of suitable target group of materials.

As an illustrative example, the method is applied for predicting FLCs of cold rolled grade 1.4509, 1.4521 and 1.4622 ferritic stainless steels. These steels are modern stabilized ferritic stainless steels with similar physical metallurgy and mechanical properties. Thereby these steels form a good target group for the method.

The second step in the analysis is to gather representative sample of test materials. Cold rolling and heat treatment parameters play an important role in the properties of ferritic stainless steels. The following process parameters

a) the total amount of cold rolling reduction,

b) the number of cold rolling steps with intermediate annealing,

c) the amount of cold rolling reduction in each rolling step, and,

d) the grain size produced in the final annealing,

are considered to be the most important process parameters for our target group [18,19]. The thickness of the strip also plays a role and deserves to be included in the important process parameters [8,9].

In order to capture a representative sample for the target group, test materials were hand-picked from the population according to the following principles:

- The total cold-rolling reduction and the final grain size of the material were varied independently in their respective process windows.
- The thickness of test materials was varied within the range used for demanding forming applications.
For technical reasons the thickness cannot be varied completely independently of the cold rolling reduction. Therefore, the thickness variation was included only within certain realistic limits. The variation of the process parameters in the test materials can be summarized as follows: The total cold rolling reduction varied in the range from 60% to 90%, the grain size varied from 5.9 to 10 in the ASTM grain size number scale and the thickness was ranging from 0.5 mm to 2.0 mm.

All test materials were cold rolled sheets with 2B surface finish. The mechanical properties of test materials in the transverse direction are summarized in Table 2. The r-value in the transverse direction is denoted by \( r_{90} \). Typical chemical composition of studied steels is given in Table 3.

### Table 2. Room-temperature mechanical properties and the grain size of test materials.

<table>
<thead>
<tr>
<th>Identifier</th>
<th>Grade</th>
<th>Thickness (mm)</th>
<th>( R_{p0.2} ) (MPa)</th>
<th>( R_m ) (MPa)</th>
<th>( A_y ) (%)</th>
<th>( A_{80} ) (%)</th>
<th>( r_{90} ) (-)</th>
<th>Grain size (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>1.4509</td>
<td>0.6</td>
<td>325</td>
<td>505</td>
<td>19.0</td>
<td>28.0</td>
<td>1.79</td>
<td>9.5</td>
</tr>
<tr>
<td>A-2</td>
<td>1.4509</td>
<td>0.6</td>
<td>337</td>
<td>473</td>
<td>21.0</td>
<td>33.4</td>
<td>2.03</td>
<td>8.0</td>
</tr>
<tr>
<td>A-3</td>
<td>1.4509</td>
<td>0.6</td>
<td>379</td>
<td>545</td>
<td>16.8</td>
<td>27.0</td>
<td>1.55</td>
<td>10.0</td>
</tr>
<tr>
<td>A-4</td>
<td>1.4509</td>
<td>1.0</td>
<td>372</td>
<td>496</td>
<td>16.5</td>
<td>29.7</td>
<td>1.97</td>
<td>7.9</td>
</tr>
<tr>
<td>A-5</td>
<td>1.4509</td>
<td>1.5</td>
<td>351</td>
<td>484</td>
<td>18.0</td>
<td>30.1</td>
<td>1.77</td>
<td>7.2</td>
</tr>
<tr>
<td>A-6</td>
<td>1.4509</td>
<td>2.0</td>
<td>339</td>
<td>464</td>
<td>19.6</td>
<td>34.4</td>
<td>1.80</td>
<td>5.9</td>
</tr>
<tr>
<td>B-7</td>
<td>1.4521</td>
<td>0.5</td>
<td>383</td>
<td>543</td>
<td>18.5</td>
<td>28.9</td>
<td>2.45</td>
<td>8.1</td>
</tr>
<tr>
<td>B-8</td>
<td>1.4521</td>
<td>1.0</td>
<td>404</td>
<td>528</td>
<td>16.1</td>
<td>28.2</td>
<td>1.99</td>
<td>7.3</td>
</tr>
<tr>
<td>B-9</td>
<td>1.4521</td>
<td>1.5</td>
<td>384</td>
<td>542</td>
<td>16.3</td>
<td>29.4</td>
<td>1.67</td>
<td>6.7</td>
</tr>
<tr>
<td>B-10</td>
<td>1.4521</td>
<td>2.0</td>
<td>417</td>
<td>554</td>
<td>15.1</td>
<td>26.3</td>
<td>1.51</td>
<td>7.2</td>
</tr>
<tr>
<td>C-11</td>
<td>1.4622</td>
<td>1.0</td>
<td>364</td>
<td>499</td>
<td>19.8</td>
<td>32.9</td>
<td>2.13</td>
<td>9.7</td>
</tr>
<tr>
<td>C-12</td>
<td>1.4622</td>
<td>1.0</td>
<td>355</td>
<td>497</td>
<td>17.2</td>
<td>28.6</td>
<td>2.24</td>
<td>8.8</td>
</tr>
</tbody>
</table>

### Table 3. Typical chemical composition of studied steel grades.

<table>
<thead>
<tr>
<th>Grade</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>N</th>
<th>Ti + Nb + V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4509</td>
<td>0.02</td>
<td>0.5</td>
<td>0.5</td>
<td>18.0</td>
<td>-</td>
<td>0.1</td>
<td>0.02</td>
<td>0.6</td>
</tr>
<tr>
<td>1.4521</td>
<td>0.02</td>
<td>0.5</td>
<td>0.5</td>
<td>18.0</td>
<td>2.0</td>
<td>0.2</td>
<td>0.02</td>
<td>0.6</td>
</tr>
<tr>
<td>1.4622</td>
<td>0.02</td>
<td>0.4</td>
<td>0.4</td>
<td>21.0</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
<td>0.6</td>
</tr>
</tbody>
</table>

### 4. Definition of complete FLC based on experimental limit strains

The complete FLCs were defined using the method developed by Gerlach et al. [20]. In this approach, the complete forming limit curve is described using the parametrized function

\[
\begin{align*}
\varepsilon_1 &= a_0 + a_1 \varepsilon_2, \quad \varepsilon_2 \leq \varepsilon_0 \\
\varepsilon_1 &= b_0 + b_1 \exp(-b_2 \varepsilon_2), \quad \varepsilon_2 > \varepsilon_0
\end{align*}
\]

The parameter \( a_0 \) can be eliminated by means of continuity requirement at \( \varepsilon_2 = \varepsilon_0 \).

\[
a_0 = b_0 + b_1 \exp(-b_2 \varepsilon_0) - a_1 \varepsilon_0
\]
The remaining parameters $a_1, b_0, b_1, b_2$ and $\varepsilon_0$ are estimated by regularized least squares method and regression analysis.

5. Least squares estimation of model parameters

The third step in the method is the application of Tikhonov regularized least squares method [21–23] to estimate the model parameters. Ordinary least squares minimization approach often results in an overdetermined (over-fitted) solution when applied to the full model with five unique parameters $(a_1, b_0, b_1, b_2, \varepsilon_0)$ for each test material. In the Tikhonov regularized least squares method, a regularizing term is added to the target function in order to give preference to solutions with desired properties. Here, the desired solutions are solutions where one or several parameters have the same value for all test materials. The optimal amount of regularization can be determined based on the Morozov discrepancy principle [24,25], which states that the desired level of accuracy is achieved when the standard error of estimation equals to the measurement error in the data.

In the present case, the optimal level of regularization was determined by applying the regularized least squares repeatedly to the same problem. In each round, the number of model parameters included in the regularizing term was increased. The results are summarized in Table 4. The number of data points $N$, the number of independent parameters $p$ and the standard error of estimation $\text{SE} \text{est}$ are also given for each case. It can be concluded four of the five parameters $(a_1, b_1, b_2, \varepsilon_0)$ are effectively constant in this case. The root mean square error (RMSE) obtained for each test material is given in Table 5. For test material B-10, the RMSE is equal to the estimated measurement error with the optimal regularization. The estimated parameters values are summarized in Table 6 and Table 7.

Table 4. Results of iterative Tikhonov regularized least squares solution method. The optimal level of regularization was achieved with $p = 16$ independent parameters.

<table>
<thead>
<tr>
<th>Regularization</th>
<th>$a_0$</th>
<th>$\varepsilon_0$</th>
<th>$b_2$</th>
<th>$b_1$</th>
<th>$b_0$</th>
<th>$N$</th>
<th>$p$</th>
<th>$\text{SE} \text{est}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[-]$</td>
<td>$[-]$</td>
<td>$[-]$</td>
<td>$[-]$</td>
<td>$[-]$</td>
<td>$[-]$</td>
<td>$[-]$</td>
<td>$[-]$</td>
<td>$[-]$</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>812</td>
<td>60</td>
<td>1.54E-02</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>812</td>
<td>49</td>
<td>1.63E-02</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>812</td>
<td>38</td>
<td>1.64E-02</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
<td>-</td>
<td>812</td>
<td>27</td>
<td>1.73E-02</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
<td>812</td>
<td>16</td>
<td>1.82E-02</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>812</td>
<td>5</td>
<td>3.32E-02</td>
</tr>
</tbody>
</table>

Table 5. Root mean square error obtained with the optimal level of regularization.

<table>
<thead>
<tr>
<th>A-1</th>
<th>A-2</th>
<th>A-3</th>
<th>A-4</th>
<th>A-5</th>
<th>A-6</th>
<th>B-7</th>
<th>B-8</th>
<th>B-9</th>
<th>B-10</th>
<th>C-11</th>
<th>C-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.016</td>
<td>0.019</td>
<td>0.015</td>
<td>0.018</td>
<td>0.017</td>
<td>0.022</td>
<td>0.018</td>
<td>0.017</td>
<td>0.014</td>
<td>0.025</td>
<td>0.017</td>
<td>0.016</td>
</tr>
</tbody>
</table>
Table 6. Estimated values of parameters common for all test materials.

<table>
<thead>
<tr>
<th>a₀</th>
<th>ε₀</th>
<th>b₂</th>
<th>b₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.127</td>
<td>0.023</td>
<td>2.778</td>
<td>-0.246</td>
</tr>
</tbody>
</table>

Table 7. Estimated value of parameter b₀ for all test materials.

<table>
<thead>
<tr>
<th>A-1</th>
<th>A-2</th>
<th>A-3</th>
<th>A-4</th>
<th>A-5</th>
<th>A-6</th>
<th>B-7</th>
<th>B-8</th>
<th>B-9</th>
<th>B-10</th>
<th>C-11</th>
<th>C-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.452</td>
<td>0.437</td>
<td>0.431</td>
<td>0.458</td>
<td>0.506</td>
<td>0.515</td>
<td>0.430</td>
<td>0.466</td>
<td>0.496</td>
<td>0.509</td>
<td>0.463</td>
<td>0.481</td>
</tr>
</tbody>
</table>

5. Regression analysis to predict the free parameters

In the proposed approach it is generally found that certain parameters have common constant values for all test materials. The rest of the parameters are identified by regression analysis using measured steel properties as independent variables. It should be noted that certain independent variables, i.e. strip properties, are often correlated with each other. The multicollinearity of data must be taken into account if multiple regression analysis is needed to explain the dependent parameter or parameters.

In the example case studied, simple linear regression analysis revealed that the parameter b₀ can be modelled as a linear function of strip thickness t.

\[ b₀ = 0.408 + 0.055 \left( \frac{t}{t₀} \right) \]  

(4)

where \( t₀ = 1 \) mm. The adjusted R-squared for this regression model was 0.92. The P-values were less than 4.0E-7 for both terms. The root mean square error was RMSE = 0.008 for this linear regression model.
Fig. 2. Correlation between parameter $b_0$ and the regression model.

The RMSE of prediction obtained using the linear regression model for the parameter $b_0$ is shown in Table 8 for all test materials. The RMSE values are lower than or approximately equal to the experimental uncertainty in the measurement data. The accuracy of prediction is therefore on an acceptable level. Fig. 3 shows an example of predicted FLC along with the corresponding experimental data. A visual examination confirms that the predicted FLC is in excellent agreement with the data. It should be noted that the RMSE of prediction for the test material A-1 in Fig. 3 is in the middle of the range of variation for all test materials.

Table 8. Root mean square error of prediction obtained with the linear regression model for parameter $b_0$. 

<table>
<thead>
<tr>
<th>A-1</th>
<th>A-2</th>
<th>A-3</th>
<th>A-4</th>
<th>A-5</th>
<th>A-6</th>
<th>B-7</th>
<th>B-8</th>
<th>B-9</th>
<th>B-10</th>
<th>C-11</th>
<th>C-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>0.019</td>
<td>0.018</td>
<td>0.019</td>
<td>0.023</td>
<td>0.018</td>
<td>0.018</td>
<td>0.015</td>
<td>0.026</td>
<td>0.017</td>
<td>0.018</td>
<td></td>
</tr>
</tbody>
</table>
6. Correction for the biaxial pre-strain

The strain based FLC is valid only for linear strain paths, where the ratio of major and minor principal strains remains constant throughout the process. Recently, it has been observed that the strain ratio is not constant in the Nakajima test [26,27]. Instead, the initial strain is equibiaxial in the Nakajima test. There is always a small biaxial pre-strain before the strain path turns towards the linear path imposed by the sample geometry.

Pre-straining in biaxial tension decreases the forming limits on the right hand side of the diagram and shifts the lowest point to the right from the plane strain axis [1,4]. Therefore, FLCs measured with the Nakajima test need to be corrected to compensate the biaxial pre-straining. The draft international standard ISO/DIS 12004-2:2012 describes guidelines for adjusting individual measurement points to compensate the biaxial pre-straining. In the present case, this adjustment was applied directly to the parametrized mathematical function used for presenting the FLC. The resulting corrected FLC is given by

\[
\begin{align*}
\varepsilon_1 &= a_0 + a_1 \varepsilon_2, & \varepsilon_2 \leq 0 \\
\varepsilon_1 &= a_0 + (b_0 - a_0)(1 - \exp(-b_2 \varepsilon_2)), & \varepsilon_2 > 0
\end{align*}
\]

(5)
The adjustment does not affect equation (3) used to determine the parameter $a_0$. **Fig. 4** shows the FLC of test material A-1 before and after the adjustment discussed above. The adjustment shifts the lowest point to the plane strain axis and increases slightly the forming limits on the right to the axis.

**Fig. 4** The right-hand side of FLC of test material A-1 before (continuous line) and after (dashed line) the correction for the biaxial pre-strain in the Nakajima test.

### 7. Empirical model for the FLC of stabilized ferritic stainless steels

Based on the results presented above, the FLC stabilized ferritic stainless steels in the target group can be described with the following simple model:

$$
\begin{align*}
\epsilon_1 &= 0.203 + 0.055 \left( \frac{t}{t_0} \right) - 1.127 \epsilon_2, \quad \epsilon_2 \leq 0 \\
\epsilon_1 &= 0.203 + 0.055 \left( \frac{t}{t_0} \right) + 0.205 \{1 - \exp(-2.778 \epsilon_2)\}, \quad \epsilon_2 > 0
\end{align*}
$$

(6)

where $t_0 = 1 \text{ mm}$. The derived equation applies for cold-rolled grade 1.4509, 1.4521 and 1.4622 stainless steels produced using the same process route and similar process parameters as the test materials in the representative sample.

Additionally, it should be noted that the FLC in equation (6) does not include a safety margin. Therefore, theoretically speaking, localized necking might occur in 50% of samples at the location of this FLC. A safety margin of 0.025 subtracted from the major strain values calculated with the equation shown above will reduce the probability of necking to 5%.
8. Summary and conclusions

A new approach has been proposed for predicting FLCs of stainless steels in the steel industry. The new method is founded on the proposition that FLCs of different steels can be described with simple empirical equations if and only if the steels are sufficiently similar in terms of their physical metallurgy and mechanical properties.

The first step in the proposed method is selection of suitable target group of materials. The steels in the target group need to have similar physical metallurgy and mechanical properties. In the second step, a representative set of test materials is gathered for the analysis. A representative set captures the variation of the most important process parameters in their respective process windows. In the third step, the FLCs and mechanical properties of sampled test materials are measured. In the fourth step, predictive equations are derived for describing the FLC in terms of steel properties. The data analysis employs Tikhonov regularized least squares analysis for reduction of parameter space. After the least squares analysis, regression analysis is used to model the independent parameters in terms of the strip properties.

The proposed approach was applied for predicting the FLCs of stabilized ferritic stainless steel grades 1.4509, 1.4521 and 1.4622. Predictive equations were derived for describing the FLC for the target group. The root mean square error of predicted FLCs was less than or approximately equal to the estimated measurement error in FLCs. Therefore, the derived equations can be used to calculate FLCs for this group of steels with the same accuracy as that of measured FLCs.

Acknowledgments

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References

MONOBLOCK 4.0: THE NEXT EVOLUTIONARY STEP IN THE STANDARD STAINLESS STEEL COLD ROLLING MARKET

The stainless steel cold rolling market is split in two competing design paradigms: The Monoblock and the split housing 20-High mill. The Monoblock is dominant in standard applications, whereas the split housing Four Column design dominates high quality production. As market pressure is further mounting particularly on standard steel mill operators, the Monoblock 4.0 now emerges as the next evolutionary step. Its main technical improvements are an automated roll change, faster opening, a higher roll grinding range, cheaper support shafts with easy assembly for backup rolls, and proven stability and bending performance. Our analyses show, that these advantages lead to significant financial benefits for standard steel mill operators. So despite the fact that the Monoblock 4.0 still does not match the Four Column performance parameters, it has the potential to become a game changer in the standard stainless steel cold rolling market.

1. Two tracks of cold rolling technology evolution: The Monoblock 1.0 – 4.0 and the split housing.

   The Monoblock design is around since about 100 years. In the early 1930s, Tadeusz Sendzimir invented the 20-High Cluster Sendzimir Mill [1]. The housing was cast in one block and the bore contained all the rolls. One single door provided access to the front side. As any 20-High, the Monoblock was deployed in stainless steel cold rolling as well as in the non-ferrous metals market.

   In the year 1958, the first Four Colum design was patented and launched by Sundwig, now part of Andritz. It was a technical revolution, opening a second track of technical designs in cold rolling technology. The Sundwig Four Column (SFC) was the first deployment of split housing, i.e. the crown was adjusted by wedges that were vertically shifted behind the support saddles. Hydraulic cylinders drove the wedges. At the time, the intermediate rolls were pushed or pulled and so the SFC push-push system was another invention. In addition, the SFC enabled an easier and faster change of intermediate rolls. Additional improvements were made through the invention of hydraulic adjustments in 1988, the simplified back up roll axle design. In 2015, Sundwig launched the world’s first 5 feet precision mill for stainless steel.

   The advantages of the Four Colum design for steel mill operators are still unrivelled. So, the ease and speed of the roll gap opening is measurable: 200 mm for the SFC vs. 13 mm for the Monoblock. The roll grinding range is much higher, e.g. for the work roll it is 45 mm for the SFC vs. 15.5 for the Monoblock. Handling is facilitated through simple back-up roll design and easiest maintenance, a quick roll changing. The back-up roll bending system is fixed in the mill house, actuated by hydraulic cylinders. High speed rolling is enabled through direct oil lubrication for all axial and radial bearings inside the backup/support rolls. The cooling effect of the SFC is 30% higher than the Monoblock design. While the SFC structure is seemingly more fragile than the Sendzimir Monoblock, numerous empirical tests of Andritz have proven this perception to be counter-factual. Due to force equalization, the SFC even shows superior mill housing stiffness of 2.6% vs. 3.9% deformation of the Monoblock. However, the SFC does have the disadvantage of being technically more demanding and thus the manufacturing of a SFC is more costly than a Monoblock. As a consequence, prices for the SFC usually exceed those of the Monoblock design. Most of the major steel mill operators have well recognized...
that the benefits of the SFC more than overcompensate higher prices whenever they have to cover the full scope from simple standard strips to more complex, high end production.

While the high end segment is dominated by the SFC design, the evolution of the Monoblock continued in the standard cold rolling market. So, 14 years after the first SFC, the T. Sendzimir, Inc. iterated the Monoblock housing design to create the **Zero Crown Housing solution**, Monoblock 2.0 so to speak. This reduced the amount of material required for the housing and warranted a uniform deflection across the width of the strip.

Learning from the SFC design, Sendzimir introduced the split housing in 1994. However, also the Monoblock saw technological advances, mainly through licensees of Sendzimir. The licensees have improved the Monoblock 2.0 individually at some points, leading to what might be referred to as **Monoblock 3.0**.

In the year 2019, Andritz Sundwig is poised to take the next step in the Monoblock evolution, introducing the **Sundwig MonoBlock (SMB)** as Monoblock level 4.0, being the best Monoblock ever for the low to mid range cold rolling market.

### 2. Markets change for steel mill operators

In the last decades, market conditions for steel mill operators have worsened significantly, particularly for the standard quality producers. On the one side, the cost of energy and raw material have increased sharply. This means, that energy efficiency starts to be of prime concern. In addition, ever more restrictive environmental protection policies also apply to steel milling, not only in Europe or the US, but also in China and India.

On a global scale, qualified labor is scarce, and thus milling operators need to increase the productivity of their experienced staff. To gain and keep the required staff without further increase in labor cost, the operators have to enhance their employer value proposition by enhancing the attractiveness of the work place. At times, this was considered to be neglectable convenience, more and more it is a bare necessity to stay competitive. Additionally, operators try to avoid higher labor cost by reducing the handlings requirements, thereby enabling less qualified staff to produce the same level of quality output.

While cost are rising in the stainless steel market, revenues are under pressure. The stainless steel production no longer enjoys the growth rates of the past, dropping from a CAGR of 7.4% (2011-2014) to 4.8% (2014-2017) [2]. Excluding China and India, the stainless steel production almost stagnated at 1.3% CAGR since 2011, with a total decline in the EU. China accounted for 53.6% of the world production, but even this single biggest market dropped to just 5.9% CAGR since 2014, roughly 1/3 of the CAGR 2011-2014. And the future perspective is mixed, as the economic slowdown, particularly in the automotive industry will take its toll. Additional challenges loom heavy on the Chinese market since the 2018 trade tariff war with the US has been escalating. Imports of mild and stainless steel – mainly from China – to the US had grown by 36% from 2009 to 2014, imports to Europe even quadrupled in the same period. These figures illustrate the risk for Chinese steel producers if the EU joins the US in shielding its markets against imports from China. So particularly in the low end, the competitive pressure will mount due to overcapacity. On the other side, flexible high end products are needed for many applications in building automation, electric vehicles and their support infrastructure, smart city applications like e.g. smart urban mobility or decentral energy management. So while risks prevail in the low end, the mid to high end of the stainless steel market will see additional opportunities, if operators are able to meet the rising prices move in the wrong direction. From 1/2012 to 12/2018, the price for stainless steel grade 304 nominally declined by 40% [3]. In a long term perspective, it is now only roughly 15%
above the price level of 1967! So if prices were deflated, they would show an average decline of -1.6% p.a. for the last 50 years.

Rising cost in a market with significant over capacity leads to declining margins. However, the effect is not the same in the high end vs. the standard steel milling market. In the high end, additional applications are driving the demand for strips with very low tolerances. As only a limited number of operators are able to deliver this superior quality, they maintain a healthy EBITDA margin of 16% and above, said to be a sustainable level for the long term [4]. The average steel mill only achieved EBITDA margins of 9-12% in 2014, while for some of the standard producers, EBITDA margins are still just barely positive.

To raise EBITDA margins, mill operators have three options: Reduce the over capacity in the market, reduce raw material prices, and raise prices on account of superior quality and flexibility. The first two options are unrealistic, and so mill operators have to move up to higher value production. This is, where technological advances in cold rolling technology can create benefit for mill operators. So the next level of Monoblock cold rolling mills have to meet several criteria that all add to the bottom line of steel mill operators. According to our customer research, the Monoblock 4.0 is requested to enable easier handling and less maintenance, higher flexibility to adjust to quickly changing customer demand, and higher quality to move up the value chain for better prices.

3. Technical advances of the Sundwig Monoblock

The Sundwig MonoBlock could become the next level in the Monoblock evolution as it better meets these market requirements as the conventional Monoblock 3.0. The main technical advances are as follows: An automated roll change, faster opening, and higher roll grinding range, cheaper support shafts with easy assembly for backup rolls, and improved heat transfer.

The automated roll change is a well tested feature of almost all new Sundwig mills in the last couple of decades. A roll change robot allows for a full automation, as compared to the semi-automated clumsy, heavy equipment of e.g. a roll change car which still requires the worker to put hand on the greasy rolls. So the full automation has a very positive impact on the attractiveness of the work place and therefore on the employer value proposition for steel mill operators. In addition, the valuable labor can be focused to do more value added work, thereby increasing labor productivity. Faster roll changes will enable more flexibility in the production program, thereby allowing the operator to address smaller lots in a more efficient way than before, thus enlarging the accessible market.

![Fig. 1: Automated roll change robot of the Sundwig Monoblock in action](image-url)
The same purpose of higher flexibility is also pursued by a faster gap opening. Simulations have shown that the gap opening is 3 times faster.

In addition, the life span of the work roll increases through a much higher grinding range. While the work roll of the Monoblock 3.0 still is at 15.5 mm grinding range, the Sundwig Monoblock will be at 25 mm. This is still a lot less than the SFC with 45 mm, but it is still an improvement of 62% compared to the Monoblock 3.0. Also for all other rolls, the advantage of the Sundwig Monoblock is substantial, as figure 2 outlines. Every steel mill operator immediately realizes that this has a strong financial impact.

Advantage no. 4 for the Sundwig Monoblock are cheaper support shafts with easy assembly for backup rolls. Figure 3 illustrates the difference. The shaft assembly is obviously simpler and in addition, the expensive Teflon rings of the Monoblock 3.0 design are saved.

Finally, the Sundwig Monoblock will keep the proven stability and bending performance of the Monoblock while allowing for up to 30% better heat transfer. This is accomplished through the design of the nozzle plate.
4. Economic benefits of the Sundwig Monoblock for steel mill operators

The technical advances of the Sundwig Monoblock are the basis for the steel mill operator’s economic benefit. How much an operator can grow revenue or lower cost will of course depend on the specific situation. Nonetheless two calculations are provided to illustrate the order of magnitude in change.

We have used one steel mill operator’s data to compute the OPEX improvement for rolls through the improved roll grinding range and backup roll design: It turned out to be a staggering reduction of up to 66%. The lion share of this saving pertains to the work roll, but also the other rolls cost are more than halved. This figure would even be higher, if the faster gap opening was monetarized.

The second major driver of economic benefit to the steel mill operator is the improvement of the heat transfer, which directly translates to 30% less rolling oil for the same production program. Given operator data for the conventional Monoblock 3.0 was 12,000 litres per minute oil supply to the mill with 13,700 l/min. filtration. Our simulation showed that the Sundwig Monoblock will only require 9,600 l/min. oil supply to the mill with 12,000 l/min. filtration. So the need for pumping oil to the mill will be reduced by 2,200 l/min. at 6 bar while the filtration will be reduced by 1,700 l/min at 2 bar. Using the rate of 0.1 € / kWh energy cost and 7,200 hours p.a. operating time, the steel mill operator will save roughly 20,000 € p.a.
5. The Sundwig Monoblock as potential game changer in the standard cold rolling market

Since the inception of the Sundwig Four Column housing design, the cold rolling technology is split in a high end and a standard production end of the market. The performance parameters of the Sundwig Four Column mills are unrivalled. So if a steel mill operator strategically decides to move up to the high end of the stainless steel milling market, he will need the flexibility, quality, and cost efficiency of a SFC to meet market demand.

In the standard cold rolling market however, the 2019 Sundwig MonoBlock proves to be the best Monoblock ever with substantial economic benefit to the steel mill operator. No matter how the stainless steel market conditions will change, in any way it will be imperative to deploy the leading technology to thrive in a commodity market. So operators should not hesitate and wait for signs of a market recovery if at all they see a sufficiently profitable future in standard steel qualities.

Still, history has shown in many markets that the best product does not automatically win the race. In part, this is due to investment policies, in part it may be based on switching and service cost. With regard to investment policies, mill operator will no longer be forced to switch technology in their quest for obtaining performance improvements in standard production. Now they can stay true to their decision to only use the Monoblock design. Operators that consider the switching cost should also not find much of a barrier to use the Sundwig MonoBlock, as all existing backup roll bearings can still be used. Thus a big part of the switching cost is already taken care of. And finally the global Sundwig service organization should discern support issues which may otherwise inhibit the operator to move to the next level in the Monoblock evolution.

So considering the evidence of substantial technical advances, attractive economic benefits, and the lack of any significant switching barrier, the Sundwig MonoBlock is predicted to be a potential game changer in the standard cold rolling market.

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Applications
APPLICATION OF HIGH STRENGTH DUPLEX STAINLESS STEEL WIRE FOR OFFSHORE FISH FARMING CAGES AND GEOLOGICAL PROTECTION SYSTEMS

Abstract

The first part of this work shows the development and application of a new material system using high strength duplex stainless steel wires as net material with environmentally compatible antifouling properties for off-shore fish farm cages. Current net materials from textiles (polyamide) shall be partially replaced by high strength duplex stainless steel in order to have a more environmentally compatible system which meets the more severe mechanical loads (waves, storms, predators (sharks, seals)). With a new antifouling strategy current issues like reduced ecological damage (e.g. due to copper disposal), lower maintenance costs (e.g. cleaning) and reduced durability shall be resolved.

High strength steel wires are also widely used in geological protection systems, for example rockfall protection or slope stabilisation. Normally hot-dip galvanised carbon steel is used in this case. But in highly corrosive environments like coastal areas, volcanic areas or mines for example, other solutions with a high corrosion resistance and sufficient mechanical properties are necessary. Protection systems made of high strength duplex stainless steel wires enable a significantly longer service life of the protection systems and therefore a higher level of security.

Keywords

High Strength; Duplex Stainless Steel; Wire; Fish Farming; Geological Protection

1. Introduction

In the areas of protection against falling rocks and the protection of fish in aquaculture, there are good opportunities for the use of stainless steels to ensure a sustainable use of materials.

As a result of increasing needs and shrinking resources, aquaculture is gaining progressively significance in the recent years. Ecological issues such as negative effects on the ecological system due to the high fish density in the farms, the use of textile/polymer material for the nets and copper as antifouling strategy etc. are very present, particularly regarding the increasing number of fish going to be produced in farms in the future. Current trends focus on larger farms operated offshore. To make these farms working more safe and economical, reliability has to be improved and maintenance costs need to be reduced. Also, alternatives with higher mechanical strength compared to current textile net materials as well as common metal wires might be necessary.

Geological protection systems are very important for the protection of people, streets, railway lines, coast lines and many more. Rockfall barriers or slope stabilization nets are some examples of a wide array of products in this working range. The most used material for
such installations is high strength carbon steel. Hot-dip galvanizing is generally applied for corrosion protection and if necessary amplified with organic coatings. In highly corrosive environments, the service life of these installations can be very short and therefore requires a lot of maintenance.

The following first part shows the development of a new material system for fish farming nets and in a second step the use of this system also for geological protection systems.

2. Development of fish farming net

The detailed process of development is described in different publications [1, 2, 3], so we just give a short summary here with some keywords of the development.

The project for development of the fish farming net was structured in three topics:
- Production Technology
- Selection of Stainless Steel
- Antifouling strategy

The challenge in production of those kind of nets was to adapt the previous manufacturing processes from high strength unalloyed steel to high strength stainless steel. The different material properties of the steels necessitate many adjustments to the manufacturing process. Fig. 1 shows a manufacturing unit for the stainless steel net.

The selection of stainless steel was mainly focused on corrosion resistance, mechanical properties and availability. The corrosion resistance should be good enough for maritime environments. The mechanical properties should allow a high strength up to 1700 MPa through cold working processes. A high availability for wire products should be given. At the end, the two duplex stainless steels 1.4362 (UNS 32304) and 1.4462 (UNS 31803) were used for field tests.

For antifouling strategy, different methods were examined in immersion tests at different sites on the world. Fig. 2 shows a test frame for immersion testing. For example copper cladding or different kinds of layers were used. Finally, none of the tested methods were really practicable. But due to its very smooth surface, the steel wires showed a very much better cleanability than the textile nets. The cleaning can be done with high pressure water jet for example. Due to the poor adhesion of fouling, the cleaning intervals could be increased and the overall cleaning costs therefore be reduced. This was a good compromise for all involved parties.
3. Application of high strength nets for fish farming

A first test for the nets under real conditions was done on the Chilean pacific coast. Chile has a big fish farming industry for salmon. The farms are often build in squares, which is much easier for assembling of the stainless steel nets. Usually, the fish farms are protected with a second net against predators like seals. With a stainless steel net, the second net is not necessary anymore.

In a first testing step, the outer predator protection net was replaced by a stainless steel net. It was necessary to test different mounting options for the nets to the swimming platform because the behaviour of steel nets is quite different to textile nets. Fig. 3 shows the installation of a stainless steel net in Chile.

During test phase some unpredictable corrosion effects occurs. The movement of the net in the current of the sea induces some tribology in the contact points of the nets. In some
cases, depending to water temperature and fouling, corrosion started and damaged the net. In laboratory experiments, the phenomena was investigated and published elsewhere [4, 5].

After the field tests, the decision was made to use only the stainless steel grade 1.4462 (UNS 31803) for further production of stainless steel nets.

![Fig. 3: Installation of stainless steel net at fish farm in Chile](image)

4. Application of high strength stainless steel nets in geological protection systems

High strength steel nets are widely used in protection systems for geological applications, e.g. slope stabilization. In highly corrosive areas such as coastal or volcanic areas and also in the mining industry, the classical corrosion protection systems like zinc or/and organic coatings are reaching their limit. Fig. 4 and Fig. 5 show examples of heavy corrosion in these areas after short time. In these cases, the high strength stainless steel net could be an interesting alternative to the conventional solutions.

One of the first application of a stainless steel net in a coastal area was done in Newquay, Cornwall, UK and is shown in Fig. 6 and Fig. 7. The slope stabilization for a cliff near the Atlantic ocean was carried out with a high strength stainless steel net. The slope stabilization has now been installed for about three years and no corrosion has occurred so far.
Fig. 4: heavy corrosion of zinc coated steel wires after only a few month in volcanic area
Fig. 5: corrosion of zinc coated steel net after 2 years in a coastal area

Fig. 6: Application of stainless steel net in a coastal area
5. Summary

The application of high strength stainless steel nets for fish farming offers new possibilities in aquaculture. Due to the good cleanability of the stainless steel wire, the usage of toxic copper can be avoided. For predator protection, no second net around the fish farm is necessary. The high strength of the wire also offers new ways to go more offshore. Finally, the stainless steel is well-suited for recycling and produces no microplastics.

In geological protection systems the usage of high strength stainless steel nets can be useful in regions with high corrosion rates like coastal or volcanic areas. First applications have shown a good performance during the first years of usage.

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DEVELOPMENT OF FERRITIC STAINLESS HOT-ROLLED STEEL SHEETS FOR EXHAUST PIPE FLANGE

Abstract

The replacement of C-steel sheets with ferritic stainless steel sheets is promoted from the perspective of the initial rust-resistant characteristic of an automotive flange part. However, thick hot-rolled ferritic stainless steel sheets containing Ti with high Cr lack low-temperature toughness compared to C-steel. In this study, from the perspective of low-temperature toughness, Nb-added and Nb and Mo-added 17% Cr hot-rolled ferritic stainless steel sheets have been developed for an exhaust pipe flange. The developed hot-rolled steel sheet 1, namely, NSSC 430R3M, with Nb-added 17% Cr-Low C, N, was shown to be superior to a conventional Ti-added 17% Cr steel sheet in terms of low-temperature toughness and high-temperature strength. The developed hot-rolled steel sheet 2, namely, NSSC 436LNB-M, with Nb and Mo-added 17% Cr-Low C, N, which was required for high heat and corrosion resistance, was demonstrated to be superior to the conventional Ti and Mo-added 17% Cr steel sheet in terms of low-temperature toughness; further, its high-temperature strength was higher than that of steel sheet 1. Furthermore, based on the results of a drop weight test, the flange parts made using steel sheets 1 and parts welded to the exhaust pipe showed superior low-temperature toughness at -40 °C.

Keywords

ferritic stainless steel, rust prevention, heat resistance, high-temperature strength, low-temperature toughness, flange

1. Introduction

Many types of stainless steels have been developed and applied to automobile exhaust parts according to various required characteristics, such as the heat resistance, corrosion resistance, and mechanical properties [1, 2]. The initial rusting of the exhaust parts may be a problem, and there has been a recent trend toward the use of high grade stainless steel as the preferred material for such parts. In addition, the various exhaust parts are connected by fastenings such as flanges; a conversion from C-steel sheets to ferritic stainless steel sheets, along with the application of high-Cr ferritic stainless steel, has advanced in terms of the initial rust resistance, even in flange parts. Fig. 1 shows the results of a test on C-steel and ferritic stainless steels simulating marine transport, in which initial rusting is a problem. The initial rust resistance of 11% Cr-added ferritic stainless steel sheet is superior to that of a C-steel sheet, and that of a 17% Cr-added ferritic stainless steel sheet is even better. Based on these results, it is possible to significantly improve the appearance of exhaust parts, by converting from C-steel ferritic stainless steel. In contrast, thick hot-rolled steel sheets or
plates are often used as exhaust pipe flanges, but are inferior in terms of low-temperature toughness compared with a C-steel sheet or plate, and particularly in the case of conventional Ti-added hot rolled high-Cr ferritic stainless steel sheets, there is a concern regarding brittle cracks during the punching of flange parts during winter, as well as damage by stones when an automobile is in operation. In addition, when fastening a flange on an exhaust gas recirculation (EGR) system that has already been mounted, condensed water and high-temperature exhaust gas have adverse effects, and it is therefore necessary to achieve higher corrosion and heat resistance for such parts. In this paper, we report two types of developed hot rolled ferritic stainless steel sheets that can be used for exhaust pipe flanges, which are excellent in terms of corrosion resistance, heat resistance, and low-temperature toughness [3].

2. Alloy design and evaluation method

2.1 Improved toughness through the addition of Nb

For a ferritic stainless steel sheet with high purity, it is necessary to suppress the intergranular corrosion caused by the Cr depleted zone owing to the formation of Cr carbide and nitride; thus, stabilizing elements such as Ti and Nb combined with C and N are added. It is known that Ti-added steel has a lower toughness than Nb-added steel [4]. In addition, it is also known that the toughness is influenced by various alloying elements [4] as well as the grain size [5] and sheet thickness [6]. Fig. 2 shows the influence of the thickness and stabilizing element on the ductile-brittle transition temperature obtained through a Charpy impact test for V-notched specimens of hot- and fold-rolled 17-19% Cr ferritic stainless steel sheets. When the thickness is relatively low, the vicinity of the crack is in a plane stress state, and the test piece is twisted; thus, no brittle fractures occurs regardless of the stabilizing
element. However, a brittle fracture occurs dose occur when the thickness increases and ductile-brittle transition temperature rises. Comparing the effects of the stabilizing element, Nb-added steel has a lower transition temperature and better toughness than Ti-added steel. Ti (C, N), which is a coarse precipitate, is assumed to affect the origin of a brittle fracture and promote crack propagation of Ti-added steel [7]. In contrast, in the case of Nb-added steel, Nb (C, N) precipitates are finer than Ti (C, N) of Ti-added steel; thus, the effect on the toughness is smaller. Therefore, the developed steel adds Nb as a stabilizing element based on 17% Cr-Low C, N (developed steel 1, NSSC 430R3M). Moreover, for flanges requiring higher corrosion resistance, Mo was also added (developed steel 2, NSSC 436LNB-M).

2.2 Evaluation of low-temperature toughness of flange parts

In general, the ductile-brittle transition temperature is often obtained in the Charpy impact test specified for an evaluation of low-temperature toughness of steel materials. However, in this method, a test piece imparted with a notch is used, and the ductile-brittle transition temperature obtained by this method does not always indicate the low-temperature toughness of the actual part. Therefore, in this work, the drop weight impact test was conducted on the single flange single part and flange-exhaust pipe joint by referring to the secondary workability evaluation method of a cold rolled steel sheet [8]. Fig. 3 shows a schematic of this test. A weight was allowed to fall freely on the flange part exposed to a predetermined temperature, and an impact was applied to the end of the flange part at low-temperature. The occurrence of cracking was observed after the test, and the low-temperature toughness of the actual part was evaluated.

![Fig. 2 Effect of thickness on ductile-brittle transition temperature in Charpy impact tests for V-notched specimens of Ti- and Nb-added ferritic stainless hot- and cold-rolled steel sheets.](image1)

![Fig. 3 Schematic figure of drop weight impact test at low-temperature for the flange part, and the flange part welded to an exhaust pipe.](image2)
3. Characteristics of developed steel

In this section, the characteristics of the two types of developed steels manufactured using a conventional process are compared with conventional steel (Ti added 17% Cr and Ti and Mo added 17% Cr steels).

3.1. Tensile properties

Table 1 shows the tensile properties at room temperature (JIS G 02241) for the developed and conventional steels. Developed steels 1 and 2 have a slightly higher proof strength than conventional steels, but exhibit excellent ductility.

*Table 1 Mechanical properties of developed and conventional ferritic stainless hot-rolled steel sheets at room temperature (6 mmt).*

<table>
<thead>
<tr>
<th>Material</th>
<th>0.2% yield stress MPa</th>
<th>Tensile strength MPa</th>
<th>Total elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Ti-added 17%Cr steel</td>
<td>273</td>
<td>411</td>
<td>39</td>
</tr>
<tr>
<td>Developed steel 1</td>
<td>292</td>
<td>450</td>
<td>38</td>
</tr>
<tr>
<td>Conventional Ti and Mo-added 17%Cr steel</td>
<td>326</td>
<td>452</td>
<td>37</td>
</tr>
<tr>
<td>Developed steel 2</td>
<td>330</td>
<td>478</td>
<td>34</td>
</tr>
</tbody>
</table>

3.2. High-temperature strength

Fig. 4 shows the tensile strength at elevated temperature. The developed steel has a higher high-temperature strength than conventional Ti-added steel. Because steel 1 contains Nb, it is considered that the high-temperature strength is improved by Nb in a solid solution [9]. In addition, the steel 2 shows a greater high-temperature strength than the steel 1 from Mo in a solid solution [9].
Fig. 4 Tensile strength at elevated temperature.

3.3. Oxidation resistance

Fig. 5 shows the increase in oxidation when the developed and conventional steels are subjected to continuous oxidation test at 900 °C in atmosphere for 200 h. The developed steel has almost the same oxidation resistance as conventional steel and shows excellent oxidation-resistance.

Fig. 5 High-temperature oxidation at 900 °C for 200 h in air.

3.4. Corrosion resistance

Fig. 6 shows the results of the pitting potential test (JIS G 0577) on the corrosion resistance of the developed and conventional steels. Steel 1 shows a pitting corrosion resistance equivalent to that of conventional Ti-added steel. In addition, steel 2 is more corrosion-resistant than steel 1 and has a pitting corrosion resistance equivalent to conventional Ti- and Mo-added steel. Fig. 7 shows the results of the investigation through the oxalic acid etching test (JIS G 0571) on the intergranular corrosion susceptibility of a MIG-welded joint between steel 1 and Type 436L using 430Nb as the wire. Because the developed steel contains Nb at an appropriate amount, the welded portion shows a stepped structure.
and the intergranular corrosion resistance of the welded portion is excellent.

Fig. 6 Pitting corrosion resistance after polishing.

Fig. 7 Intergranular corrosion susceptibility of MIG welded zone between steel 1 and SUS436L.

3.5. Toughness

Fig. 8 shows the impact value by the Charpy impact test (JIS G 2242) for V-notched specimens of the developed and conventional steels with a thickness of 6 mm. The developed steel has a lower ductile-brittle transition temperature than conventional steel, and it was confirmed that the developed steels had excellent low-temperature toughness.

Fig. 8 Ductile-brittle transition curves for Charpy impact test (6 mmt).
3.6. Toughness of flange parts

Tables 2 and 3 show the results of a low-temperature drop weight test on a single flange piece and a joined flange-exhaust pipe (Type 436 L) using steel 1 (8 mm thick), respectively. It was confirmed that the flange parts using steel 1 did not crack at -40 °C, and excellent low-temperature toughness and high reliability were also recognized in actual parts.

Table 2: Results of drop weight test at low-temperature for the flange parts of steel 1.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>-80°C</th>
<th>-40°C</th>
<th>-30°C</th>
<th>-20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Developed steel 1</td>
<td>×</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

O: not fracture, ×: fracture

Table 3: Results of drop weight test at low-temperature for flange parts of steel 1 welded to exhaust pipe.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>-80°C</th>
<th>-40°C</th>
<th>-30°C</th>
<th>-20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Developed steel 1</td>
<td>×</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

O: not fracture, ×: fracture

4. Conclusion

Two types of ferritic stainless steel hot-rolled sheets, which have excellent corrosion resistance, heat resistance, and low-temperature toughness, were developed for exhaust pipe flanges. The developed steel 1 (NSSC 430R3M) with Nb addition and developed steel 2 (NSSC 436LNB-M) with Nb and Mo additions based on 17% Cr-Low C, N have excellent corrosion resistance, and heat resistance, and low-temperature toughness in comparison with conventional Ti-added 17% Cr ferritic stainless steels. The low-temperature toughness of the flange and the flange-exhaust pipe joint parts were evaluated using a drop weight test, and it was confirmed that parts using the developed steels have excellent low-temperature toughness.

References

Abstract

In this study, to respond to the automotive exhaust manifold of a high-temperature exhaust gas engine and turbocharger system, the effects of the elements on the high-temperature strength of an austenitic stainless steel sheet were studied. As a result, a new austenitic stainless steel sheet, NSSC 701 (24%Cr-12%Ni-2%Si-0.6%Mo-0.1%C-0.2%N), with excellent heat resistance was developed. NSSC 701 is superior to conventional heat-resistant austenitic stainless steel sheets such as Type 310S (25%Cr-20%Ni-0.5%Si-0.05%C-0.01%N) and SUSXM15J1 (19%Cr-13%Ni-3.3%Si-0.05%C-0.01%N) in terms of the tensile strength, creep properties, high-cycle fatigue, sliding properties, and oxidation resistance at elevated temperatures.

Keywords

austenitic stainless steel, heat resistance, high-temperature strength, creep, high-cycle fatigue, sliding, oxidation

1. Introduction

For mileage improvement and purification of the exhaust gas, a high-temperature exhaust gas and lightweight vehicle body are required [1, 2]. The heat-resistance of austenitic stainless steel is superior to that of ferritic stainless steel for automotive exhaust manifold of a high-temperature exhaust gas engine and turbocharger system at temperatures of above 900 °C. In turbocharger systems in particular, the replacement of austenitic cast steel or Ni-based alloy with austenitic stainless steel sheets may be effective from the perspective of a lighter weight, lower cost, and higher performance of a turbocharger requiring creep and sliding properties at high-temperature [3, 4]. To respond to the automotive exhaust manifold of a high-temperature exhaust gas engine and turbocharger system, a new austenitic stainless steel sheet, NSSC 701 (24%Cr-12%Ni-2%Si-0.6%Mo-0.1%C-0.2%N), having superior heat resistance over conventional heat-resistant austenitic stainless steel sheets such as Type 310S (25%Cr-20%Ni-0.5%Si-0.05%C-0.01%N) and SUSXM15J1(19%Cr-13%Ni-3.3%Si-0.05%C-0.01%N), was developed. In this study, we report the alloy design and excellent heat resistance performance of the developed austenitic stainless steel sheet in comparison with conventional steel sheets [5].
2. Alloy design of developed austenitic stainless steel sheet with excellent heat resistance

Because high-temperature strength is the basic characteristic of heat-resistant steel, the chemical composition was designed from the viewpoint of high-temperature strength. In general, solid solution strengthening is an effective strengthening mechanism at high-temperature [6]. In the case of steel materials, elements with a larger difference in atomic radius or slower diffusion rate in comparison with Fe, such as C, N, Mo, W, and Nb, are chosen for strengthening. It can be expected that austenitic stainless steel with added C and N has a high strength at elevated temperature because the solubility of C and N in the austenite phase is approximately 100 times higher than that of the ferrite phase [6, 7]. The effects of C and N on the 0.2% proof stress at 900 °C in 19%Cr-13%Ni-3.3%Si steel are shown in Figure 1. The high-temperature strength improves with an increase in the amount of C and N. The addition of N is effective in comparison with C because it is presumed that N has a slower diffusion rate and larger deference of atomic radius than C. Figure 2 shows the effects of Si, N, C, Mo, and Nb on the 0.2% proof stress at 900 °C in 19%Cr-13%Ni steel. The enhancement of Si is extremely small, such as 3 MPa per 3%, because of the small size difference. The strength is increased when C, Mo, and W are added for 0.2% N-added steel. In contrast, the enhancement of W is small, such 5 MPa per 0.47%, and the enhancement of Nb is not large. Based on these results and considering the costs involved, we decided to utilize C, N, and a small amount of Mo to improve the high-temperature strength. In addition, for the chemical composition of a new austenitic stainless steel sheet, 24%Cr-12%Ni-2%Si-0.6%Mo-0.1%C-0.2%N was selected as the optimum chemical composition when considering the oxidation resistance and austenitic phase stability [8, 9].

![Figure 1](image1.png)  
**Fig. 1** Effects of C and N on 0.2% proof stress at 900 °C in 19%Cr-13%Ni-3.3%Si steel.

![Figure 2](image2.png)  
**Fig. 2** Effects of Si, N, C, Mo, W, and Nb on 0.2% proof stress at 900 °C in 19%Cr-13%Ni steel.

3. Characteristics of NSSC 701

In this section, the properties of a cold-rolled and annealed sheet manufactured through a commercial process are compared with conventional heat-resistant austenitic stainless steel sheets.
3-1. Chemical composition

An example of the chemical compositions of the developed austenitic stainless steel, NSSC 701, is shown in Table 1. NSSC 701 (24%Cr-12%Ni-2%Si-0.6%Mo-0.1%C-0.2%N) was designed to obtain a better heat resistance than conventional heat-resistant austenitic stainless steel, such as SUSXM15J1 (19%Cr-13%Ni-3.3%Si-C, N) and Type 310S (25%Cr-19%Ni-C, N).

<table>
<thead>
<tr>
<th>Steel Type</th>
<th>Type</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSSC 701</td>
<td>-</td>
<td>0.10</td>
<td>2.0</td>
<td>24.3</td>
<td>12.1</td>
<td>0.6</td>
<td>0.23</td>
</tr>
<tr>
<td>Conventional</td>
<td>SUSXM15J1</td>
<td>0.05</td>
<td>3.3</td>
<td>19.2</td>
<td>13.9</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>Conventional</td>
<td>310S   (EN1.4951)</td>
<td>0.04</td>
<td>0.5</td>
<td>25.1</td>
<td>19.1</td>
<td>-</td>
<td>0.03</td>
</tr>
</tbody>
</table>

3-2. Microstructure and mechanical properties at room temperature

Figure 3 shows the microstructure of a cold-rolled and annealed sheet of NSSC 701. This steel shows an austenitic single phase, and many annealing-twins were observed. Table 2 shows the tensile properties and hardness of NSSC 701 at room temperature in comparison with the conventional steel sheets. The tensile strength of NSSC 701 is approximately 190 MPa higher than that of Type 310S. The elongation of NSSC 701 is 45%, and NSSC 701 has high strength and elongation properties.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Thickness (mm)</th>
<th>0.2% proof stress (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Total elongation (%)</th>
<th>Vickers Hardness (t/2, 1kgf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSSC 701</td>
<td>2.0</td>
<td>461</td>
<td>796</td>
<td>45</td>
<td>214</td>
</tr>
<tr>
<td>SUSXM15J1</td>
<td>2.0</td>
<td>313</td>
<td>708</td>
<td>53</td>
<td>163</td>
</tr>
<tr>
<td>Type 310S</td>
<td>2.0</td>
<td>297</td>
<td>603</td>
<td>42</td>
<td>157</td>
</tr>
</tbody>
</table>

3-3. Strength at elevated temperature

Figure 4 shows the 0.2% proof stress obtained by the tensile test at above 700 °C with a strain rate of $4.8 \times 10^{-5}$ s$^{-1}$. NSSC 701 has higher strength at an elevated temperature from 700 °C to 1,000 °C than Type 310S and SUSXM15J1. For example, the 0.2% proof stress of developed steel is 111 MPa at 900 °C. This proof stress is 1.8 times higher than that of Type...
310S, 2.1 times higher than that of SUSXM15J1, and 4.3 times higher than that of Type 444 (17%Cr-1.8%Mo-0.47%Nb-0.1%Ti-LC, N), which shows the highest heat resistance at a ferritic grade. Moreover, the high-temperature strength of NSSC 701 is higher than that of Ni-based alloy (alloy 718, 53%Ni-19%Cr-17%Fe-3%Mo-5%Nb-5%Ta) at a temperature of above 900 °C. Figure 5 shows the 0.2% proof stress at elevated temperature after aging for 100 h. Even after aging, the developed steel has higher strength than Type 310S and SUSXM15J1. Although M23C6 and a-σ-phase were precipitated on the grain boundaries through aging from 700 °C to 1,000 °C, based on the strength after aging, the solid solution strengthening of C, N, and Mo is thought to be effective in NSSC 701.

![Fig. 4 0.2% proof stress at elevated temperature.](image)

**Fig. 4** 0.2% proof stress at elevated temperature.

**Fig. 5** 0.2% proof stress at elevated temperature after aging for 100 h.

### 3-4. High-cycle fatigue at elevated temperature

Because vibrations are exerted on automotive exhaust parts under a high-temperature environment, plane bending fatigue tests at high-temperature were carried out at a repetition rate of 1,700 cycles/min, and R = -1. Figure 6 shows the S-N curves at 800 °C. NSSC 701 has a higher fatigue limit and longer life than Type 310S and SUSXM15J1 because of the higher strength at elevated temperatures.

![Fig. 6 S-N diagram at 800 °C.](image)

**Fig. 6** S-N diagram at 800 °C.

### 3-5. Creep properties

Particularly in the case of turbocharger parts, the creep characteristic of a material becomes important because minute deformations at high temperature affect the performance of the parts. Figure 7 shows the results of a creep test at 800 °C and 900 °C. In this experiment, a stress from 15 to 60 MPa was applied after holding for 1 h at a predetermined temperature. Figure 7(a) shows the stress–lifetime curves at 800 °C and 900 °C. NSSC 701 has the longest lifetime under these experimental conditions. Figure 7(b) shows the minimum creep strain-rate–stress curves at 800 °C and 900 °C. The minimum creep strain-rate of the
developed steel is equal to or less than that of Type 310S and SUSXM15J1. NSSC 701 with an added high N element has superior creep properties because of the high strength at an elevated temperature. Moreover, a retardation of the dislocation climb at high temperature by solute atoms or I-S pairs, or a lower stacking fault energy, is thought to be effective at improving the creep properties in a developed steel sheet with added high N and Si elements.

![Fig. 7 Creep properties at 800 °C and 900 °C. (a) Stress–lifetime curves. (b) Minimum creep strain-rate–stress curves.](image)

3-6. **High-temperature sliding properties**

There is a component inside the turbocharger that controls the flow rate of the exhaust gas, and this component is required to have high frictional wear characteristics [3, 4]. Therefore, an experiment on the high-temperature sliding properties was carried out using a high-temperature pin on a disc tribometer under dry conditions. A schematic diagram of the sliding wear test at high-temperature is shown in Fig. 8. The same materials were used for the disk and pin. The constant load, sliding velocity, and sliding distance were 0.5 N, 3.3 mm/s, and 20 m, respectively. The tests were carried out after holding at 850 °C for 1 h in air. After a sliding wear test, the depth of the wear mark on the surface of the disk was evaluated based on the average value of six points measured using a laser microscope. Figures 9 and 10 show the

![Fig. 8 Schematic diagram of pin-on-disk sliding wear test at high temperature.](image)

![Fig. 9 Average depth of wear mark after pin-on-disk sliding wear test at 850 °C in air.](image)
average depth of the wear mark and the surface and depth profile after sliding wear tests, respectively. NSSC 701 has the shallowest average depth of the wear mark because the amount of abrasion and adhesion is smaller. In NSSC 701, it is considered that the protective oxidation layer of Cr and Si and the high strength of the material contribute to the excellent sliding properties.

3-7. Oxidation resistance

Figure 11 shows the surface after a cyclic test for 300 cycles at 1,050 °C in air. The heat pattern used in the cycle test is heating for 30 min at the test temperature in the furnace, and cooling for 15 min to room temperature. NSSC 701 does not show any abnormal oxidation or remarkable scale spallation like Type 310S and SUSXM15J1. Figure 12 shows the weight change after a cyclic oxidation test at an elevated temperature. The amount of weight change in NSSC 701 is extremely small in comparison with Type 310S and SUSXM15J1 and shows a superior oxidation resistance because it contains high Cr and Si. Figure 13 shows the weight change after a cyclic oxidation test of the welded parts at 1,050 °C in N2+0.5%O2+7%H2O. The heat pattern in a cycle is heating for 8 min, holding at 1,050 °C for 3 min, and cooling to 200 °C for 9 min. The amount of weight change in NSSC 701 is very small in comparison with SUSXM15J1, and NSSC 701 is also an excellent material for welded parts.
4. Conclusion

A new heat-resistant austenitic stainless steel sheet, NSSC 701 (24%Cr-12%Ni-2%Si-0.6%Mo-0.1%C-0.2%N), was developed for an automotive exhaust manifold and a turbocharger system. This developed steel sheet shows extremely superior characteristics in comparison with conventional steels and is expected to contribute to the development of a high-temperature exhaust gas for improved mileage and a lightweight vehicle body.

References


HOT-CRACK TENDENCY IN THIN-WALLED HIGHLY ALLOYED AUSTENITIC STAINLESS STEEL

Abstract

The paper discusses weldability of highly alloyed 1.4541 grade with the respect to their tendency to hot cracking in heat affected zone (HAZ). Metal Inert Gas (MIG) method was used to perform welding trials on plastically deformed samples (shells). Welded samples were prepared using material with different alloying elements amount (mainly Mo and Cu) in order to reveal correlation between chemical composition and susceptibility to hot cracking. Macro and micro-structure were investigated using optical microscopy. Solidus temperature was determined by means of differential thermal analysis (DTA) both in initial and equilibrium condition. Microstructure changes in heat affected zone were studied using scanning electron microscope (SEM) and energy dispersive x-ray spectrometry (EDS).

Chemical composition analysis revealed that parts made of 1.4541 with higher susceptibility to liquation cracking in HAZ show higher Mo and Cu content. Mo-rich precipitates were detected at grain boundaries, which suggest grain boundary liquation as primary mechanism leading to hot crack formation.

Keywords

Hot-crack, austenitic stainless steel, liquation, welding

1. Introduction

Reduction of fuel consumption is one of crucial factors that drives the interest of automotive industry towards lightweight applications. One of the ways to reduce mass of exhaust systems components is reduction of wall thickness. However, with thinner walls parts become more prone to heat input, particularly during welding process.

Austenitic stainless steel are recognized as one most crucial materials for parts of exhausts systems exposed to high temperature. They exhibit excellent mechanical properties, corrosion resistance, formability. However, one of their disadvantages is susceptibility to hot cracking during welding process.

Hot cracks are typically referred to weld metal, they occur during crystallization (solidification cracks), in so-called high temperature brittleness range (HTB), i.e. between nil strength temperature (NST) and ductility recovery temperature (DRT). In weld metal hot cracks occur typically above solidus temperature, i.e. in solid-liquid mixture. However, hot cracks may also occur in heat affected zone, close to the fusion line, in the area called partially melted zone. Occurrence of partially melted zone is related with segregation of elements that tend to locally decrease melting point, such as C, and impurities (S, P). Additionally, similar behaviour of carbide forming elements was also reported.

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2. Materials & methods

In the paper 1.4541 austenitic stainless steel with different Mo and Cu level were studied. Chemical composition of the base metal were presented in table 1.

<table>
<thead>
<tr>
<th>Part description</th>
<th>Grade</th>
<th>C [%]</th>
<th>Si [%]</th>
<th>Mn [%]</th>
<th>P [%]</th>
<th>S [%]</th>
<th>Cr [%]</th>
<th>Ni [%]</th>
<th>Mo [%]</th>
<th>Cu [%]</th>
<th>Ti [%]</th>
<th>Fe [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell 1</td>
<td>1.4541</td>
<td>0.036</td>
<td>0.48</td>
<td>1.00</td>
<td>0.016</td>
<td>&lt;0.002</td>
<td>17.33</td>
<td>9.28</td>
<td>0.38</td>
<td>0.64</td>
<td>0.37</td>
<td>bal.</td>
</tr>
<tr>
<td>Shell 2</td>
<td>1.4541</td>
<td>0.030</td>
<td>0.42</td>
<td>0.98</td>
<td>0.020</td>
<td>&lt;0.002</td>
<td>17.98</td>
<td>9.13</td>
<td>0.11</td>
<td>0.17</td>
<td>0.33</td>
<td>bal.</td>
</tr>
<tr>
<td>acc. to EN10088-1</td>
<td></td>
<td>Max.</td>
<td>0.080</td>
<td>Max.</td>
<td>1.00</td>
<td>2.00</td>
<td>Max.</td>
<td>0.045</td>
<td>Max.</td>
<td>0.015</td>
<td>-</td>
<td>5xC</td>
</tr>
</tbody>
</table>

Metal Inert Gas (MIG) method with shielding gas 96%Ar + 4%O2 was used to perform welding trials on plastically deformed samples (shells).

The microscopic analysis of the base metal and weld seam, respectively, was performed using the stereo-microscope Nikon SMZ800 and optical microscope Nikon Eclipse LV150. In order to disclose the structure, welded specimens were chemically etched in a 30ml HCl + 10 ml HNO3 + 40 ml distilled water.

Microstructure changes in heat affected zone were studied using scanning electron microscope (SEM) and energy dispersive x-ray spectrometry (EDS).

Differential thermal analysis (DTA) was performed using Setaram 16/18 Setsys equipment, in Ar atmosphere, in temperature range 100-1550°C, with heating rate 10K/min and cooling rate 30K/min.

TEM analysis was carried out using FEI Titan 80-300 microscope. Samples were prepared using Quanta 3D 200i microscope equipped with Focus Ion Beam (FIB).

3. Results and discussion

Metallographic analysis of cracks observed in welded shell 1 revealed typical features of hot cracks, i.e. orientation parallel to weld axis (fig.1), smooth crack edges and oxidized surface that results from presence of liquid phase at the moment of crack formation (fig. 2). It should be noted that cracks were observed in heat affected zone only, which indicates relatively large partially melted zone – from the line of fusion down to inner surface of the shell. Considering morphology and location of the crack, it can be expected that cracks result from segregation of chemical elements towards grain boundaries which decrease solidus temperature and favor local formation of liquid phase. Such phenomenon is referred to as liquation, and cracks caused by this phenomenon as liquation cracking.
Fig. 1. a) Cross section of lap joint made of 1.4541 steel with increased Mo and Cu content. Note visible overheated zone with δ-ferrite in HAZ; b) close-up of crack in heat affected zone.

Fig. 2. a) Oxidized layer on crack surface; b) Tip of the crack, note smooth edges and inter-crystalline propagation typical for hot cracks.

Detailed analysis of microstructure in heat affected zone, particularly near the tip of the crack revealed presence of precipitates at grain boundaries (fig. 3). Their eutectic-like morphology supports the conclusion regarding liquation phenomenon. Moreover, brighter areas in these precipitates observed using BSE indicate presence of heavy elements, presumably Mo. EDS line-scan across grain boundary revealed increasing content of Mo, Ti and C, and decreasing content of Fe, Ni and Cr in direct vicinity of grain boundary (fig. 4). All these elements tend to decrease Fe solution solidus temperature according to binary phase diagrams Fe-Mo, Fe-Ti and Fe-C, whereas influence of C is supposed to be the strongest. No signs of Cu influence were observed.
Fig. 3. Precipitates observed in heat affected zone near the tip of the crack

![Fig. 3. Precipitates observed in heat affected zone near the tip of the crack](image)

In order to reveal segregation of chemical elements in HAZ and identify precipitates at grain boundaries, TEM investigation was performed. Ti₃P was identified which indicates contribution of impurities segregation to liquation (Fig. 5 and 6). However, measured content of P in both shells was significantly lower than allowable limit for 1.4541 (0.016 and 0.020 in shell 1 and 2, respectively), hence its influence on cracking susceptibility is considered negligible. Liquation cracking in analyzed case is more related with MC carbides observed in

Fig. 4. Results of EDS line-scan (SEM) through precipitates on grain boundaries

![Fig. 4. Results of EDS line-scan (SEM) through precipitates on grain boundaries](image)
grain boundaries (fig. 7). EDS mapping was performed in areas where precipitates occurred (fig. 8). They revealed increased content of Ti, C and also Mo which is in agreement with EDS results from SEM. Additionally, Nb was also detected in precipitates. However, no signs of segregation in solid solution around precipitates were observed. While presence of MC-type primary carbides suggests liquid phase formation on grain boundaries in heat affected zone during welding process, no direct evidence on segregation of chemical elements that actually causes liquation can be observed in microstructure of heat affected zone.

![Fig. 5. TEM image and electron diffraction of Ti₃P precipitates on grain boundaries](image)

![Fig. 6. EDS mapping (TEM) of area marked in fig. 5.](image)

In order to explain this phenomenon, differential thermal analysis was carried out in temperature range 1200-1550°C both for samples from shell 1 and shell 2 (fig. 9). Additionally, for each sample two full thermal cycles were performed. Results show clear differences in thermal behavior, both between shell 1 and shell 2, and between 1st and 2nd cycle in case of shell 1. In steel with higher Mo content, two endothermic effects were observed, relatively weak at 1416°C, and strong at 1442°C. Considering microstructure analysis in heat affected zone, the former can be attributed to grain boundary liquation and the later to solidus temperature. It should be noted that during 2nd DTA cycle first effect was no longer observed, and on-set temperature of 2nd effect increased to 1463°C. This change of DTA curve in 2nd cycle explains lack of visible segregation around primary carbides at grain boundaries in heat affected zone. During welding process Ti, Mo and C segregated towards grain boundaries which locally decreased melting point and caused formation of liquid phase.
Then primary MC-type carbides precipitated directly from the liquid. It should be noted that e.g. TiC exhibits some homogeneity range, hence all segregated Ti, Mo and C was used to form carbides, and remaining Fe solid solution was relatively homogeneous, as indicated by EDS results obtained on TEM from area that already went through thermal cycle during welding process. Such microstructure can be considered equilibrated, this is why during 2nd DTA cycle of shell 1 no thermal effects are observed below solidus, and transition from solid to liquid is sharper and shifted towards higher temperature. In steel with lower Mo content no signs of thermal effects below solidus were observed. Also no significant differences between 1st and 2nd DTA cycle were detected, on-set temperature of melting was 1452° and 1460°C during 1st and 2nd run.
4. Summary

Chemical composition analysis revealed that parts made of 1.4541 with higher susceptibility to liquation cracking in HAZ show higher Mo and Cu content. Microstructure analysis of heat affected zone near the crack area revealed presence of primary MC-type carbides at grain boundaries, with increased content of Ti and Mo. However, no of Ti, Mo or C was observed in solid solution around precipitates. DTA analysis revealed that in material with higher Mo content small endothermal peak occurs below solidus temperature, presumably attributed to liquation of grain boundaries. During second DTA cycle this thermal effect disappeared which suggests that elements that caused liquation, i.e. C, Ti, Mo were used to form carbides and remaining content in solidified matrix was not detectable. While DTA measurement does not replicate thermal cycle during welding process due to much lower heating and cooling rates, it indicated differences in thermal behaviour of investigated materials which results from chemical composition. It should be noted that presented results does not relate to general behaviour of Mo as alloying element in austenitic steel, as its segregation was accompanied by segregation of Ti.

References

Environmental aspects
ULRICH MEYN\textsuperscript{1} and Dr. THOMAS KÜHL\textsuperscript{2}

TREATMENT AND DISPOSAL OF CR(VI) CONTAMINATED STEEL PLANT WASTE PRODUCTS

Abstracts

Several disposal options exist for waste products from steelmaking operations. The production of Cr-containing steels requires specific attention since slags and dust generated in melting processes often contain water-soluble Cr(VI). Due to the toxicity of hexavalent Cr landfill options are usually not considered feasible. Regulators apply concentration limits in respective leachates. Important parameter deciding on safe disposal is Cr(VI) which can be manipulated by appropriate treatment concepts and products.

KRONOS ecochem is a supplier of iron salts dealing with environmental issues already since 1974. Besides offering solutions for water treatment the company is strongly involved in the cement industry providing products and expert service for Chromate reduction. With MKN Technologies they expanded their field of Fe-salt use to new applications, namely the metal industry with production of FeCr and Cr-alloyed steels.

Utilising MKN’s stainless steelmaking expertise melting shop processes have been investigated where KRONOS ecochem technology is able to adequately address Cr(VI) issues. After identifying problem zones and determining toxicity levels suitable process steps were developed. Transferring learning points and methodology from cement operations assisted in specifying equipment and procedures needed to facilitate Chromate reduction. This paper discusses how stainless steelmaking dust is successfully treated enabling subsequent safe disposal by landfill. Main focus is given to the sustainability of Cr(VI) conversion, user-friendliness of the process and economical attractiveness of the entire concept.

Keywords

chromate, hexavalent, Cr-oxide, Fe-salts, stainless steel, waste, disposal

Introduction

With the discovery of Chromium in 1797 especially stable trivalent and hexavalent Chromium compounds increasingly became part of our life applied in a number of different areas:

Pigments in paints
Enamel or glass paints
Wood preservatives insoluble in water (Chromium containing salt blends)
Chromium tanning in leather making
Catalysts (ammonia synthesis)
Oxidants (Potassium chromate for alcohol oxidation)
Production of heat- and corrosion resistant alloys (stainless steels).

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Due to toxicity especially of hexavalent Chromate adequate protective measures have to be provided in the work place. In cases their use and application has been restricted if not even prohibited. All Chromium-VI components are considered toxic and carcinogenic. The regulator’s position in this regard is well defined with strict limits for handling of implicated materials. Latest development is for instance the announcement of TRGS 561 for Germany.

Main intake route is via the respiratory tract. The ability to penetrate human skin has been confirmed with water-soluble Chromate, Chromic acid and Chromium tri-oxide respectively. Chromium-VI components not only cause irritation of skin and mucous system but also damage especially kidneys, liver and blood. The degree and consequences of contaminating the skin is often underestimated since pain is hardly ever felt or completely absent.

2 oxidation states of Chromium are relevant for this discussion, namely:

- Non-toxic Chromium-III components that are marginally water-soluble and
- Soluble, toxicologically relevant Chromate (Chromium-VI components).

Keeping this in mind an elemental analysis showing the total Chromium content provides only limited information with regard to toxicity. True risk indication is fully exposed not until differentiating the oxidation state through for instance leaching and separating soluble from insoluble components. Analytical leaching procedures according to DIN 38414-4 or DIN EN 12457-1 refer.

Background

Stainless steel manufacturing is performed at the front end of operations at elevated temperatures. Toxic Chromium-VI components may form in the production process and are most likely to be found in oxidic by-products. As mentioned earlier the true size of the problem with toxic Chromate in steelmaking oxides becomes fully evident only when hydro-metallurgical analysis methods are applied. In this context it makes sense when pyro- and hydro-metallurgists exchange notes when looking for solutions on the steelmaker’s Chromate topic. For many years specialists from the chemical industry have been solving issues with disposal of Cr-contaminated waste products, soil decontamination and similar challenges.

Consequently, a hydro-metallurgy partner for this multi-disciplinary project on Chromate in steelmaking by-products was looked for. With KRONOS ecochem a competent player was found, a supplier of iron salts already since 1974. The company has been heavily involved in environmental clean-up projects for many years. They offer water treatment solutions, deal with Chromate in residues from combustion processes and the like.

A well established and adequate remedy to performing decontamination of Chromate containing materials is Chromate reduction. For this purpose reductants, such as Fe(II)-salts are added to facilitate transformation of water-soluble, hexavalent Chromate to trivalent status with low solubility:

\[
\text{[1]} \quad \text{CrO}_4^{2-} + 3 \text{ Fe}^{2+} + 4 \text{ OH}^- + 4 \text{ H}_2\text{O} \rightarrow \text{Cr(OH)}_3 + 3 \text{ Fe(OH)}_3
\]

According to this formula the stoichiometric requirement of bivalent iron is

- 3 mol Fe(II) per 1 mol Cr(VI) or
- 3.22 mg Fe(II) per 1 mg Cr(VI)/kg material [ppm] respectively.
The theoretical numbers indicate minimum quantities. Real dosing usually means higher consumption and is dependent on Fe(II) salt type and decontamination conditions.

Besides treatment of Cr(VI)-contaminated soil, water and combustion residues Chromate reduction is also utilised in cement and cement making applications. Contamination levels in cement prior to treatment are known to be as high as 40ppm. When guideline 203/53/EG came into effect on 17 January 2005 all European member states were committing themselves to reducing Chromate concentrations in cement and cement making applications respectively.

EG regulations stipulate among others that production, sales and usage of cement or cement-containing products is governed by EG No. 1907/2006:

Cement or cement-containing products may not be produced, sold or used if after hydration the content of soluble Chromium (VI) measures more than 0.0002% (2ppm) in dry cement mass.

For decontamination treatment a number of salt product options exist: liquid Fe(II)-Chloride solutions are available as much as Fe(II)-Sulphates as dry free-flowable product or where preferred with residual moisture.

MKN-Technologies is the partner in this project with expertise in the pyro-metallurgy field contributing steelmaking know-how to this investigation and ferro-alloy smelting process technology.

It is common knowledge that heat- and corrosion-resistance in steels is provided through Cr alloying: among other elements. Higher alloy content usually means improved protection against oxidation. Getting Chromium into stainless steel typically involves processes such as submerged- and open-arc melting and Oxygen blowing for refining. Only at elevated temperatures metallurgical reactions take place as required. Steelmakers supply heat and in furnace zones with high energy density generate temperatures of several thousand degrees Celsius. Open arc and flame point are hot spots realizing exceptionally high reaction rates.

Under prevailing oxidizing furnace conditions the formation of all oxide types in and near these hot spots is unavoidable. Any available Cr will readily oxidize to highest oxidation state in the presences of excess Oxygen and temperatures measuring more than 2500°C. Oxide products containing among other components also hexavalent Chromate either become airborne and are dragged off by off-gas streams or get integrated in liquid slag.

It is these stainless steelmaking by-products - slag and dust - and their level of Chromate contamination that are of interest to this investigation. What options exist to deal especially with the toxicity of stainless slag and dust?

**Toxic stainless steelmaking by-products**

Before coming up with any bright ideas it makes sense to review how steelmakers have dealt with the topic up to now. From a vast variety of possibilities some of the more common solutions for slag and dust treatment are presented here.

**Liquid slag**

The steelmaker is able to contribute pyro-metallurgical options for as long as Cr-oxides are accessible under high-temperature conditions. Liquid slag contained in ladle, furnace and converter can be modified with suitable reductants to facilitate conversion of Cr-units to lower oxidation and even metallic state.
The reduction of Cr-oxides in liquid slags with Si or Al carriers is common practice in stainless steelmaking. This method is not only aiming at rendering the final slag less toxic but also aims at recovery of valuable Cr alloy units.

If Cr(VI) reduction in liquid slag cannot be fully accomplished then effective Chromate bonding within the prevailing slag chemistry presents an option. For this purpose suitable slag agents are supplied to the bulk mass prior to slag tapping enabling formation of spinel type phases (1). Cr(VI) effectively locked up in the final slag lattice results in sustained stabilization.

Another lock-up mechanism is selected by steelmakers in post-tap hole treatments when liquid stainless or Cr alloy slag is fast-cooled through quenching or granulation. Forced rapid solidification physically ties up Chromate in the slag’s crystal structure.

**Solid slag**

Stainless steelmaking slags in solid form can go into recycling applications, becomes secondary raw material or are permanently dumped as waste. Regardless of the final use regulators stipulate strict tolerance limits concerning the resulting Cr(VI) impact on the environment.

**Slag recycling**

Steelmaking slags are often used in construction and building projects. They are well suited filler materials substituting natural stone. When utilizing contaminated stainless slags in such applications slag user are obliged to manage the risk of setting Cr(VI) free. For the purpose of disabling leaching water contact with the secondary raw material is usually restricted or totally eliminated. Individual smaller pieces or entire batches of toxic slag are sealed inside safe capsule systems. A type of encapsulation is practiced in slagment: a form of cement with contaminated additives where concrete building components take over the safe permanent containment. Big scale capsuling is performed for instance in road construction designs where asphalt covers prohibit water penetrating into layers of contaminated filling material.

**Slag disposal**

Long-term storage of stainless steelmaking slags is closely monitored with regard to Cr(VI) release from dump sites into the environment. Disposal procedures have to adhere to strict legal limits. Water-soluble Chromate renders landfill options usually not feasible. Some stainless producer, however, follow a strategy whereby they dilute toxic slag from their production with sufficient quantities of uncontaminated material. This may sound like a way to go. But is this really sustainable…?

Where landfill disposal is technically, economically or legally not feasible stainless producer usually have to dispose slags with hazardous waste operators. They specialize in providing close system storage sites and toxicity management for waste dumps. In their approach safe storage of contaminated slag may include hydro-metallurgical processing of by-products, water treatment methods etc. Utilizing hazardous waste services is typically much more costly for steelmakers than ordinary landfill options.

In the past European steelmakers have made attempts to managing stainless slag disposal in their own yards. Prior to landfill storage they treated Cr(VI) contaminated slags with Fe-salts. A technical research study by Kühn et al. (1) demonstrated that Fe(II) Sulphates reduce
Cr(VI) to Cr(III). Chromate concentrations in leachate initially went down sufficiently but picked up again after days. With increasing time they returned to original levels. Permanent Cr(VI) reduction in stainless slags by Fe-salts appears to require more attention and research.

Dust

Steelmaking dust presents special challenges in melting shops. After forming airborne fines remain in pyro-metallurgical vessels for very short residence times. Small dust particles are typically fast drawn through the free-board zone by high-velocity off-gas streams. Oxidic components, in stainless operations consisting also of Chromate, get instantly sucked into furnace ducting and are lost to further interaction with the melting process. Attempts of performing immediate Cr(VI) reduction and decontamination are no longer given. After off-gas cleaning the dust is usually collected as dry powder. During subsequent handling and storage generally strict emission control criteria have to be observed.

The literature reports toxicity levels of well over 300ppm Cr(VI) in stainless steelmaking dust. Concentration may vary and depend among others on Cr-alloy levels in melts.

(2) AOD dust of Crucible Steel Inc. New York State, USA 430ppm Cr(VI)

(3) EAF dust Slovenian Steel, Jesenice, Slovenia 370ppm Cr(VI).

Similar to slag as a steelmaking by-product dust is recycled or discarded as waste.

Dust recycling

Stainless dust recycling is mainly practiced for the recovery of valuable alloying elements. Dependent on market situation reclamation of especially Nickel is cost effective. Chromate reduction is also accomplished in the process but not always prime objective. Processes are predominantly based on pyro-metallurgy and significant energy cost is encountered for dust re-melting. Stainless steelmakers in cases (4) re-introduce their dust to their own melts.

In the past steelmakers often selected outsourcing to deal with their stainless dust recycling issue. In dedicated plants external specialists ran tailor-made smelt reduction processes (to name a few):

SCAN-Dust (injection technology)

Rotary hearth furnace processes (INMETCO, FASTMET)

ZEWa-zero waste (re-melting in ladle furnace)

OXYCUP shaft furnace (Küttner)

Steel plant dust is fed as agglomerate where in-bath injection technology for smelt reduction is not feasible. With processing costs exceeding metal reclamation gains in cases steelmakers had to subsidize dust removal. Many dust smelting start-up operations have been discontinued for economic reasons.
In certain scenarios stainless producers pay contractors a lump-sum fee for removing contaminated dust from their steel plant site. External dust processors provide a service and take over responsibility for subsequent use and selection of adequate decontamination. Arrangements like these appear, however, to be locally confined to circumstances and opportunities specific only to certain regions.

**Dust disposal**

When stainless dust recycling is economically not viable steelmaker have to face very similar Cr(VI) long-term disposal issues as with slag. For cost reasons going the landfill storage route would obviously be preferred over options that involve complex hazardous waste management.

One operator (3) was able to demonstrate that landfilling dust from speciality steel production on a Solvay waste bed offered sufficient environmental protection. A liner layer consisting of waste from soda ash production provided an effective shield. Chromate released from stored stainless waste was absorbed and immobilised in this barrier lining.

A great number of stainless producers, however, have no option but to accept costly hazardous waste disposal.

**Objective**

The review demonstrates how diverse and complex the subject is. Dependent on individual plant situations operators develop unique answers to adequately deal with issues. No two operations follow the same strategy. Local conditions with opportunities and restrictions dictate the way forward. To make matters even more challenging proven technology may become obsolete when circumstances change. When regulators decide on stricter environmental protection limits steel producer have to follow up with appropriate schemes.

The stainless steelmaker is constantly requested to modify and look for alternatives to improve processes. With regard to Cr(VI) contaminated slag and dust experts from outside the melting shop arena may offer preferred solution proposals. Competent in Chromate reduction scenarios hydro metallurgists have provided assistance in related applications for many years.

They are comfortable in processing environment where steelmakers would not immediately look for solutions for hot issues.

This project investigates innovative use of proven techniques. In what way can hydro-metallurgy with well-established solutions solve Chromate problems in Cr alloy- and steelmaking? Are there processes in the chemical industry better suited for stainless melting shops; - simpler, more user-friendly and less expensive?
Tests and results
Slags

The project started off with testing Cr(VI) contaminated slags originating from historic dumps of FeCr- and stainless steel-making operations.

It is self-explaining that the release mechanism of water-soluble Cr(VI) is triggered in dry slag through water contact. The resulting pH-value is measurable indicator and driver for setting Cr free under conditions of stimulated Chromate solubility. A number of different test designs were carried out in order to characterize the leaching process itself, and to try different reduction methods with the aim of minimizing the released chromium content. Experimental results show that leaching of Cr(VI) from slag is a function of slag particle size. Different size fraction material including especially ground powder was subjected to leaching (according to EN 12457-4: 100 g material shaking in 1000 ml demineralised water for 24 hours). The smaller the particles are, the larger is the relevant surface area exposed to water. The powder fraction shows the highest leaching level of hexavalent chromium.

Chromate reduction tests with Fe(II)-salts have been conducted with different addition timing to the leachates:

1.) before the start i.e. before the 24 hours shaking time, and

2.) after 23.5 hours of shaking i.e. just 30 minutes before the end of the test.

The results reveal that an addition of Fe(II)-salts at the beginning of the test does not lead to complete reduction of hexavalent chromium. The reason is most likely that Fe(II) is quickly oxidised in competing reactions to Fe(III) which is no longer capable to reducing any more Cr(VI) that is released later in the test. Only the part of contained Cr(VI) that is leached out already at the time of dosing (or shortly after) can be reduced.

A flow-through lysimeter-type cylinder set-up was constructed for long-term leaching tests, enabling controlled and constant circulation of leachate by pumping. The results showed that leaching of hexavalent chromium from slag samples that we investigated is a continuous process, which can go on for weeks. The findings of these Cr(VI) release and reduction mechanisms tie-up with observations from the Kühn study (1).

Dependent on particle size Cr(VI) takes longer to being set free. In the presence of sufficient Fe(II)-salts all available Cr(VI) is converted to Cr(III) and does not revert back to Cr(VI) as our sustainability testing confirmed. Any late released Cr(VI) that is not met with available Fe(II)-salts will lead to increase in Cr(VI) concentrations in the leachate.

Applying single Fe(II)-salt dosing directly to slag heaps appears to have serious limitations. The behaviour points instead to a better option of treating the leachate of the slag heap with Fe(II)-salt. This would have the advantage that in leachate a further raise in Cr(VI) concentration is barred with no more contact to slag. The technical disadvantage is that a leachate drainage system would be necessary. This solution might be impossible or too expensive for existing heaps but appears feasible with future dump developments.

Dust

Compared to steel- and alloy-making slags dust handling is an entirely different waste treatment scenario rather like operating a fluidized bed reactor process. Particle size and kinetic conditions in the freeboard area of the furnace are deciding factors whether by-products report to one or the other material stream. As previously indicated most airborne oxides leave the
metallurgy reactor via the off-gas stream. Other portions are able to penetrate the liquid melt and get captured by slag or metal.

The dust stream escaping from the melting furnace consists of particles small enough to be carried away by prevailing off-gas conditions. The carrying capacity with regard to size and weight of the solids is dependent on gas flow rates in furnace ducting. Gas pressure in the off-gas system is managed by creating primary and secondary suction in-line with dust extraction requirements. Any oversize solid particles that got trapped by the off-gas stream are separated outside the furnace in subsequent dust processing steps for example collected in drop-boxes.

The particle size of typical steelmaking dust ranges from 0 – 1mm. Melting shops operate closed dust handling systems to control environmental pollution and emissions. Off-gas cleaning is predominantly performed by dry de-dusting processes generating powder-type non-metallic solid fines as steelmaking by-product. Melting shop operators typically run central off-gas and dust handling systems providing extraction at relevant points in the process where emissions occur. After intermediate storage in silos dust is removed from production site in batches destined either to waste disposal or recycling.

Where local conditions offer no opportunities to generate gains from stainless dust recycling melting shop operators feel the full impact of disposal costs. Similar to Chromate contaminated slag landfill options are not considered feasible for stainless dust without prior treatment.

Incorporating learning points from our slag investigation we could, however, imagine that there are ways to modify Cr(VI) containing dust to rendering the treated waste material fit for landflling.

**Stainless dust treatment with Fe(II)-salts**

Our slag tests indicated that we are able to demonstrate sustainable reduction of Cr(VI) to Cr(III) with small size solids. Slag ground to powder of less than 1mm was effectively converted with Fe(II) salt additions to material with permanently low Chromate content.

Extending slag trial procedures to stainless dust samples confirmed Chromate reduction behaviour. For this purpose dust from a German special steel producer was collected for investigation. The original waste product showed significant contamination levels in excess of 660ppm Cr(VI).

Based on related processes and experience with cement treatment suitable Fe(II)-salt products were identified and chosen for Chromate reduction tests. The substantially higher level of toxicity in stainless dust had to be taken into account when selecting the appropriate dosing. The decontamination results are presented in figure 1.
Fig. 1: Chromate reduction with FeCl$_2$ (KF) and different types of FeSO$_4$–hydrates (FG20, FG30, KnC).

Subsequent tests with dust from another European stainless-steel production verify initial findings. Although Cr(VI) concentrations at start of treatment were not as high (around 80ppm) the final Chromate content in leachate after adequate Fe(II) salt dosing was sustainably kept at a level of almost zero.

Findings and recommendations

Repeated trials have established that decontamination of stainless dust can be accomplished with described concept. With regard to Chromate the sustained reduction success to non-toxic Cr(III) enables safe disposal of treated material in landfill deposits. Salt products and procedures as applied in cement manufacturing prove to be useful also with this dust management project.

In cement making continuous Fe-salt addition is practiced whereby additives are fed to the dry bulk stream becoming part of the final product mixture. The remaining material handling steps ensure proper mixing and even distribution in finished goods. Similarly one can design continuous Fe salt feeding onto dust conveyor belts prior to intermediate waste storage and transport from site. Dependent on product type salt additives are applied in dry form or sprayed on as liquid. In both cases the application to small size particles provides for adequate dosing results. In other words Fe(II)-salt availability is effectively synchronised with decontamination demands at the time when Cr(VI) is released.

There is no rigid plant design or equipment set-up required to facilitate satisfactory addition and distribution of Fe(II) salts in contaminated dust. Fe(II)-salt product selection,
correct dosing and addition timing has to be decided on individual plant needs. For economic reasons decontamination effort is optimised in-line with toxicity levels in stainless dust.

Decontamination process design and operation criteria

The conversion of the dust decontamination concept into an industrial application follows generic criteria such as:

1. Perform decontamination treatment as close to the source as possible. This aims at minimising the safety risk with ongoing toxicity exposure during necessary dust handling steps. Ideally the Fe(II)-salt is to be brought into the dust stream as soon as possible after de-dusting of furnace off-gas has been completed.

2. For logistic reasons it is preferred to bring the smaller Fe(II)-salt quantity to the bigger bulk mass of contaminated dust. Ideally, we envisage continuous feeding of reductant onto a flowing dust stream. For instance trickling or spraying Fe(II)-salts onto material being conveyed from a de-dusting to storage plant. This provides for even distribution and homogenously mixed material with necessary hand-over and re-packing events of typical dust operations.

3. The decontamination set-up should be universally usable. The Fe(II)-salt feeding apparatus is proven technology, can be retro-fitted into existing dust handling plants as well as integrated in new equipment design. Relevant equipment applied in dust projects may look similar to facilities utilised in cement making.

4. Optimisation of decontamination process results is providing for most economical solution. Contamination levels in dust and conformation with final product specification will be constantly monitored in line with individual operational needs. Services provided by Fe(II)-salt suppliers aim at making customers self-sufficient towards managing their own decontamination process.

5. The removal of decontaminated dust from steel plant to final destination is safer and less cost intensive. Intermediate dust handling activities on-route to recycling plants or disposal dumps is less complex than dealing with hazardous waste transport issues.

Conclusion

Disposal options of slag lumps in waste heaps are selected dependent on individual requirements and in cases proper dump site preparation appears unavoidable. Since long-term Cr(VI) release through leaching cannot be effectively controlled with single Fe(II)-salt dosing it seems that run-off water and leachates need to be collected and treated with appropriate reductants.

Successful Chromate reduction is, however, less problematic for powder-type waste products. Kinetics of Cr release and dust behaviour can be compared to cement applications. In that sense one can use equipment and mimic procedures with appropriate adjustment to dosing strategies for Cr(VI) contaminated steelmaking dust. With proposed technology being simple and user-friendly the steelmaker is able to perform necessary treatment steps already much
closer to furnaces and earlier after Cr(VI) generation. Unique solutions have to be found in cooperation with customers since every operation has different needs.

After Fe(II)-salt treatment steelplant dust conforms to Cr(VI) regulations and in that respect is safe for landfilling. This disposal route (or alternative uses) as decontaminated material ex steelplant is feasible and proposed here as most economical Chromate waste handling solution.

**Literature**


**Acknowledgement**

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ENERGY AND ENVIRONMENTAL SOLUTIONS FOR STAINLESS STEELMAKING: SUCCESSFUL PROJECTS & INNOVATIVE PRODUCTS

Abstract

Environmental protection and energy efficiency have become a decisive factor for steel producers over the recent years. Existing as well as new plants have to comply with the most stringent environmental regulations set by national and local governments. It is a global trend that emission and energy efficiency standards are lowered worldwide.

Primetals Technologies has a vast experience in the area of gas cleaning and waste heat recovery from off-gases to comply with all actual standards for revamp as well as greenfield projects under the constraint of cost efficiency and minimum operational expenses.

The paper discusses the integration of an AOD in an existing steel plant in Slovenia with special focus on the off-gas de-dusting system including a novel gas cooler. Also a waste heat recovery project based on an innovative hot water cycle for internal heat usage of an Italian EAF based steel mill will be introduced. A new innovative bag filter system based on concrete structure which features extremely low dust as well as noise emission levels at minimum ID fan power consumption will be presented.

Furthermore, know-how based solutions which incorporate various energy efficiency measures across the gas cleaning plant and linking the de-dusting operation to the steel production will be introduced. Such digitalization approach either reduces the energy consumption or increases the suction capacity.

Keywords

Gas Cleaning, Dedusting, Revamp Solutions, Waste Heat Recovery, Automation, AOD Dedusting, EAF Dedusting

1. Introduction

Environmental protection and energy efficiency have become a decisive factor for steel producers over the recent years. Existing as well as new plants have to comply with the most stringent environmental regulations set by national and local governments. It is a global trend that emission and energy efficiency standards are lowered worldwide.

Primetals Technologies has a vast experience in the area of gas cleaning and waste heat recovery from off-gases to comply with all actual standards for revamp as well as greenfield project under the constraint of cost efficiency and minimum operational expenses.

In the following sections two best practice examples regarding the revamp of an existing mini mill:

- New gas cleaning system for an additional AOD installation in Slovenia

Primetals Technologies Austria GmbH
- Upgrade of a water cooled hot gas line of an electric arc furnace to waste heat recovery in Italy are presented. Besides those two examples of successful revamp projects recent innovations in the area of gas cleaning are introduced. An innovative filter system based on concrete as structural material instead of steel as well as an intelligent emission control system based on automation upgrades will be discussed.

2. AOD Integration in an Existing Steel Plant in Slovenia

In July 2015 Primetals Technologies was chosen to be the main supplier for engineering, fabrication and delivery of the melt shop upgrade with an AOD converter and a dedusting system including all the auxiliary aggregates like the de-slagging stand, material handling, converter heating, relining and wrecking stand as well as the transfer car by an Slovenian stainless steel plant. The supply of Primetals included also the layout of the melt shop update and the start up. All equipment was delivered according to the time schedule due to strict monitoring and expediting of all suppliers by Primetals.

As for all the brown field projects detailed planning, tight coordination and advanced project management between all parties is necessary to ensure the fulfilment of the project time schedule during installation and commissioning without affection on the running production in the melt shop. Crucial were the installation and commissioning activities inside the steel plant especially in the material handling and AOD converter were the working sequence was planned even on an hourly basis in daily site coordination meetings. With the great experience of Primetals from many other brown field projects together with the good cooperation in planning and execution with the plant operator’s melt shop team a safe project progress with minimum production stops could be achieved. Less than 2 years after the contract was signed the first heat was tapped on the AOD in April 2017. Detailed information on the implementation of the AOD in the existing melt shop can be found in [1].

In order to realize the lowest emission levels inside and outside the plant, advanced primary and secondary dedusting systems have been installed for the new AOD process aggregates, in order to comply with future environmental standards. Moreover to improve the former insufficient dust situation inside the steel plant, the new dedusting also includes suction points for smaller emission sources, such as the existing EAF material handling system, the ladle furnace, the TN stand and the torch cutting machine.

The total suction capacity of the dedusting system is approx. 900,000m³/h which is generated by 2 radial ID fans. Installed electric power of ID fan motors at a nominal speed of 1500rpm is 1,5MW each. For energy efficient operation, depending on the production plan - stainless or carbon steel production – one ID fan is switched off if AOD is not in operation. CO₂ in the primary off gas from the AOD is fully combusted. The main purpose of the dedusting system is proper capturing and cleaning of the off gas.

A picture of the newly installed dedusting line is shown in Fig. 1.
Before cleaning the AOD primary off-gas in the filter plant, the gas needs to be cooled down. The secondary cooling unit after the water cooled hot gas line for the primary off-gas line is realized by a forced draught cooler (FDC). This innovative installed FDC with pending patent in place, is a counter flow heat exchanger where the off-gas is guided in counter-current direction to the cooling air flow. This system has several advantages compared to cross-flow heat exchanger, such as higher cooling efficiency and therefore reduced cooling surface, reduced installation footprint and reduced number of fans required [2], [3]. Hence with the new effective cooler design minimization of dilution air for cooling, minimization of heat flow to the filter and reduction of operational and maintenance cost could be achieved. The very compact design which needs less installation space was a great advantage for the revamping project.

Fig. 1: Additional dedusting system for AOD installation

Fig. 2: Typical 3D model and picture of newly designed FDC
All duct lines (primary, secondary and raw gas ducts) are connected before the off gas is finally cleaned in the state of the art bag filter plant with pulse-jet cleaning procedure. Monitoring of bag filter cleaning is done via Acoustic Expert, an innovation automation solution based on sound analysis for ensured operation and early failure detection. The fabric filter is equipped with 8 chambers. In Fig. 3 the installation sequences of the filter plant area outside the melt shop can be seen.

Fig. 3: Installation sequence of the filter plant area outside the melt shop

Besides analytical calculations also detailed CFD simulations have been carried out to optimize the capture efficiency of the charging hoods for the AOD to minimize diffusive emissions during charging process. Fig. 4 shows a picture of the charging hood as well as results from the CFD simulations.

Fig. 4: Picture of AOD charging hood and results of CFD simulations
3. Waste Heat Recovery Solutions for EAF and AOD

Especially for stainless steel plants waste heat recovery solutions are usually an opportunity to gain a benefit out of waste heat. Hot water systems are a simple and reliable solution and can be applied in combination for EAF and AOD. The hot water can either be internally used for heating purpose or sold to external partners (i.e. municipal heating). Besides solely hot water also low pressure steam can be generated from the hot water and internally applied for processing (i.e. steam injectors for VD plants or finishing lines) or heating of liquids and solids (i.e. scrap drying). Fig. 5 shows a schematic principle of a possible waste heat recovery and waste heat utilization concept for a stainless steel plant.

Fig. 5: Typical waste heat recovery and waste heat utilization concept.

Moreover, the cooling with hot water provides additional advantage regarding dew point corrosion. Due to higher water temperature, condensation of sulphur oxides is avoided. This results in an increased lifetime of the water cooled duct.

As part of the revamp of the electric arc furnace (EAF) at an Italian steel plant it was decided by the customer to upgrade the water cooled hot gas line for waste heat recovery purpose. In Fig. 6 a picture of the electric arc furnace and first section of the waste heat recovery system before start-up is shown.
A novel waste heat recovery solution based on pressurized water for minimum investment costs was implemented to provide steam for internal waste heat utilization. Fig. 7 shows storage system of the novel waste heat recovery solution.

The main advantage of this system is that from operational point of view the concept is similar to the well-known state of the art water cooled hot gas line. Water is circulated in a similar way with only elevated pressure and temperature. Whereas the high water temperature leads to an increased lifetime of the water cooled duct since corrosion can be avoided. Within the water cooled hot gas line no steam is generated. Hence, the same layout requirements as for the existing water cooled duct were be fulfilled.

The recovered energy from the EAF is directly used within the steel plant. A storage system is applied to overcome the idle times of the furnace and to supply a constant amount of steam to the downstream consumers.

With the newly installed system, the entire steam demand of the plant is covered. The hot water is fed to two different pickling lines at a distance of 1.5 and 0.5 kilometer. The large distance between heat recovery system and consumer is covered by long piping throughout the entire steel plant, whereas the pipelines even cross a public road. This specific solutions demonstrates that even long distances throughout the steel plant can be handled.
Steam generators are installed, which are heated by the hot water from the waste heat recovery system. Thus, feed water is fed to the steam generator and is evaporated. In parallel, hot water is cooled down by transferring heat to the water/steam side. The cooled water is fed back to the heat recovery system. The produced steam is enough to substitute the existing gas fired boilers.

A continuous supply of 17 tons of steam per hour are supplied to the three pickling lines. By this upgrade more than 10 million cubic meter of natural gas and 20,000 tons of carbon dioxide per year can be saved per year. In addition, the steam provided by the waste heat recovery system has a much better quality compared to the steam provided by the old gas fired boilers. Hence, the waste heat recovery system even brought an operational benefit for the pickling lines.

During downtimes of the pickling lines, an additional heat exchanger provides proper cooling, in order to allow EAF operation at any time without disturbance.

The whole upgrade from the old water cooled hot gas line to the new waste heat recovery system including also the EAF and the dedusting was done during a world record plant shut-down time of 31 days only.


Kappa Zeron is an IP protected fully integrated filter house in a unique massive concrete panel design, which feature absolute emission tightness (sound and particulate emission). This innovative design and construction allows a compact footprint, close to zero particulate emissions, lowest pressure loss and lowest sound emission levels.

Fig. 8: Zeron project examples – 260.000 Am³/h (left) – 1.300.000 Am³/h (right)

Concrete panels can be produced in 10-times larger dimensions compared to steel sheet based panels. Therefore the sealing edge length is essentially reduced. The flexible sealing material and the unique clamping system results in tightness of the housing unattained so far. Any dust leakage to the clean gas side can be ensured. There are no stiffeners in the bag housing required; thus avoiding scrubbing of the bags when touching any stiffeners.

The massive concrete panels achieve a substantial sound level reduction of 57dB. Filter penthouse and fan house are fabricated from such concrete panels also cleaning pulse noise and fan noise are effectively reduced to a minimum. There is no requirement for any additional sound or thermal insulation cladding as used for steel panel construction. The
special design of the gas inlet and outlet features low gas velocities which result in a moderate flow noise.

The massive concrete elements ensure protection for explosions, fire, corrosion and weather (wind, snow loads and earthquake).

The concrete panel plates can be locally casted. The big dimensions of these panels allow much faster erection of the whole filter system. Even the weight of the panels is high foundation work is limited due to the area loads instead of point loads in case of a steel structure support.

5. Energy Saving Assistant (ESA)

In addition to process technologies to reduce energy consumption and turn waste heat into value, automation systems were developed to reduce the energy consumption and to improve process control for environmental plants. Moreover, all secondary de-dusting systems based on bag filter technology often suffer from non-optimized operation in terms of energy efficiency. Typically, these plants are mostly operated in a trade-off between the following three boundary conditions:

- Productivity
- Energy consumption
- Emission control

The ESA incorporates various measures based on advanced automation solutions. Figure 9 gives an overview on single automation improvements for an integrated steel plant.

![Fig. 9: Typical drawing of a plant dedusting system including automation packages for energy saving](image)

The difference of this system resp. approach compared to other systems is that different automation solutions are bundled and the primary plant operation is taken into consideration. This can be either done as standalone solution based on intelligent measurement devices (video, acoustics, etc.) only requiring some basic process data or by using the primary process...
data in a calculation model for the dedusting system. This general approach is shown in Fig. 10 and described in the following.

**Fig. 10:** General control concept of the energy saving assistant

At first set-points based on experience and know-how for an optimum emission capture efficiency are selected for the plant as a starting point. An intelligent control algorithm based on mass and impulse balances is afterwards applied to define the optimum set-points for the negative pressure before the bag filter resp. for the ID fan speed. This leads to an improvement in terms of energy consumption. Based on these pre-defined or calculated set-points the plant is operated for a few heats and the set-points are validated. Intelligent measurement systems based on video analysis or noise analysis are applied during this time. Based on this additional information the pre-defined set-points can be adapted. Plant operators can always choose if they want to optimize their plant in terms of energy efficiency or capturing efficiency.

The above mentioned approach requires a study of the respective plant, whereas the existing situation is assessed and the feasibility of such measures is evaluated. Afterwards, potential savings or improvements are discussed.

**6. Conclusions**

The actual difficult global market situation arising from oversupply of steel and resulting inadequate product margins, unpredictable raw material and energy prices, political and macro-economic discussions about climate change and carbon footprint reduction of the heavy industry as well as globally stricter environmental regulations related to emissions levels, water scarcity and pressure towards a zero waste production requires immediate action. Consequently main focus to manage these challenges is to implement innovative technologies and measures to optimize production costs while maintaining the environmental issues to stay ahead competition.

The two presented examples for revamp projects has shown that also for brownfield plants upgrades towards reduced emissions and increase energy efficiency are possible without any major interference with the production process and comply with the most stringent environmental standards. Furthermore, innovative technologies like bag filter plants
made of concrete as well as automation solutions can further reduce all kinds of emissions and optimize the energy efficiency of a dedusting plant.

References


EFFLUENT FREE STAINLESS STEEL PICKLING

1. Abstract

A large variety of surface treatment processes is applied in stainless steel pickling. Mixed acid containing hydrofluoric and nitric acid is used as a standard treatment for hot and cold rolled material. The metal-fluorides and -nitrates from the waste acid can be pyrohydrolyzed by the Andritz PYROMARS process. The recovered acid is recycled into the pickling process and the metal oxides are re-used in the steel making process.

In the CAPL (Cold rolled annealing and pickling line) an electrolytic process using sodium sulphate is used. Due to the pH-neutral solution the metals precipitate as metal hydroxides, but chromium(VI) stays in solution (as chromic acid salts). The Neolyte recovery process uses an acidification and a sodium bisulfite addition to reduce Cr(VI) to a harmless Cr(III) hydroxide.

Additionally the new ZEMAP process (Zero Effluent Mixed Acid Pickling) recovers the valuables from the rinse water from the stainless steel pickling line. A neutralization process using ammonia prior to a multi-stage evaporation unit produces a highly concentrated Metal-Fluoride/Nitrate stream, which can be recovered by the a.m. PYROMARS process. The clean condensate can be reused in the rinsing process and the nitrates disposal can be reduced to almost zero.

2. Keywords:

Pyrohydrolysis; Spray Roasting, HF/HNO₃ Mixed Acid; ZEMAP; Neolyte recovery

3. Introduction:

For the last three decades, Andritz has focused on reducing waste streams from SST pickling. Several attempts have been made to develop nitrate free pickling mixtures. Some SST producers are using nitrate free pickling processes; nevertheless, more than 75% of all pickling lines around the world are still using “mixed acid”. This mixture of acids is easy to handle, base material attack is controllable and finished material does not corrode. Material treated with hydrochloric acid as main pickling liquor has been reported to have corrosion issues. Another benefit of the mixed acid pickling process is that the spent acid can be regenerated with the ANDRITZ PYROMARS process, a pyrohydrolysis process developed by Andritz Ruthner in the 1980s.

Disadvantages of mixed acid pickling are the costs for HF, decomposition of nitric acid to NOₓ and nitrate pollution in the effluent streams. With the PYROMARS process, the nitrate output is drastically reduced, but still not enough for today’s limits. Worldwide regulations are
getting stricter on nitrate effluent limits. Besides increasing pressure to reduce costs, SST producers face tougher environmental limits on nitrate pollution.

Since the beginning of the new millennium the Andritz Stainless steel group is focusing their research activities on the nitrate problem in waste water. It was even considered switching the entire stainless steel pickling process to alternative media, like HF and H$_2$O$_2$, HF and H$_2$SO$_4$, HCl and Fe(III) or only HF. However, considering all facts, the Andritz technology team has decided that mixed acid provides the most reliable process for a good surface finish and adequate pickling times.

Around 2005, Andritz developed ZEMAP (Zero Effluent Mixed Acid Pickling), the solution to the nitrate problem ( patented in 2006).

Key-focus was:

- easy to handle,
- easy to control,
- insensitive to changing process conditions,
- space requirement compared to biological nitrate treatment,
- the new unit should be retrofittable into existing lines,
- avoiding effluents,
- total nitrate reduction,
- neutralization with suitable media for further treatments,
- reliability and availability.

4. Pickling lines

The stainless strip pickling processes consists of the following main process steps: electrolytic pickling, mechanical brushing, chemical pickling and rinsing. All these processes consume chemicals, water and power. After rolling and annealing of stainless steel, scale has to be removed from the surface.

Conventionally the first pickling step of this process is the neutral electrolytic pickling, whose main advantage is that the electrolyte attacks scale, without affecting the base material. The principle of this process involves the strip undergoing an alternated polarization by passing through sets of anodes and cathodes, located in a tank filled with aqueous sodium sulphate solution. This leads to chemical reactions, forming gases on the strip surface that literally blast the scale away. The ongoing dissolving of scale leads to precipitation of metals as hydroxides, except Chromium(VI), which stays in solution. The toxic Cr(VI) needs to be removed from the neutral electrolytic pickling liquid before disposal. This can be done in the waste water treatment plant or - even better - in the so called Neolyte recovery plant (detailed explanation in chapter 5).

In a subsequent pickling step a mixture of nitric and hydrofluoric acid, so called mixed acid, is used as a pickling agent. The spent pickling acid contains metal fluorides and nitrates as well as undissolved scale, varying according to the stainless steel composition. The wastes from this stage can be treated in the PYROMARS plant (detailed explanation in chapter 6). The
latest plant generation allows a acid volume reduction of at least 10% along with an increase in concentration, which is necessary to control the overall acid balance.

The third pickling/finishing process for cold rolled strips is electrolytic pickling with nitric acid. All these process steps create a large amount of waste electrolyte, waste acid and contaminated rinse water. After neutralization and filtration the fluorides and metals are found in the filter cake and the nitrates remain in the liquid effluent. The waste water streams containing nitric acid and/or hydrofluoric acid (up to approx. 8g/l HNO₃ and 2g/l HF) are treated in the ZEMAP. In the past, these wastes were completely treated in the wastewater treatment plant.

5. Neolyte recovery plant

During the electrolytic pickling process in neutral electrolyte, 6-valent chromium is enriched in the pickling solution. To stabilize the concentration, a part of the 6-valent chromium must be removed.

6-valent chromium is soluble in acidic as well as in neutral or alkaline solution, thus 6-valent chromium cannot be precipitated as Hydroxide by increasing the pH value. As 3-valent chromium will precipitate at higher pH value, 6-valent chromium must be reduced to the 3-valent form first, before it can be precipitated as chromium hydroxide and removed by filtration.

The 6-valent chromium will react with sodium hydrogen sulfite (NaHSO₃) and sulphuric acid (H₂SO₄) at a pH value less than 2.0. After addition of the necessary amount of sulfuric acid, NaHSO₃ is added to reduce Cr⁶⁺ to Cr³⁺. The completed reduction is indicated by the decrease of the redox potential. After this step, dissolved chromium (III) as well as dissolved nickel is precipitated as hydroxide by additional sodium hydroxide (NaOH).

With the recovery process forming a surplus on sodium sulphate, it is not necessary to add salt in solid form during normal operation to the pickling line. The amount of sodium sulphate, built through the chemical reaction, will compensate the losses from drag out and desludging. In the following diagram all relevant equations are shown.

![Neolyte recovery chemistry](image)

**Fig. 1: Neolyte recovery chemistry**
6. **PYROMARS process (Pyrolytic Mixed Acid Recovery System)**

The first step for the reduction of nitrates is made with the installation of the mixed acid recovery plant, PYROMARS. The process itself is a RUTHNER-type spray-roasting pyrohydrolysis process, adapted to the HF/HNO₃ system. Fig. 2 shows a flow sheet of the process. The waste pickle acid is fed into the pre-evaporator stage. The hot reactor off-gas is quenched and the acid is pre-concentrated. The hot pre-concentrated acid is then sprayed by a nozzle system into the top of the reactor. The reactor is directly heated by tangentially installed burners. While the liquid droplets fall down, water and the free acids evaporate and the metal salts are decomposed into the corresponding metal oxides and acid gases. The nozzle system generates fine droplets, which are homogeneously distributed over the roaster cross section, in order to guarantee sufficient evaporation of the liquid at a low temperature level to minimize the decomposition of nitric acid.

The metal oxide, which is more than 99% pure, is transported from the reactor bottom to the oxide bin and filled into big-bags [2].

![Flow sheet of the PYROMARS process](image)

**Fig. 2:** Mixed acid recovery via the PYROMARS process (latest generation)
The following reactions take place:

Reactor:

**evaporation:**
\[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g) \]  
\[ \text{HNO}_3(aq) \rightarrow \text{HNO}_3(g) \]  
\[ \text{HF}(aq) \rightarrow \text{HF}(g) \]  

**conversion:**
\[ 2 \text{ FeF}_3 + 3 \text{ H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6 \text{ HF} \]  
\[ 2 \text{ HNO}_3 \rightarrow \text{NO}_2 + \text{NO} + \text{O}_2 + \text{H}_2\text{O} \]  
\[ \text{NO}_2 \rightarrow \text{NO} + \frac{1}{2} \text{O}_2 \]  

Absorber:

\[ \text{HNO}_3(g) \rightarrow \text{HNO}_3(aq) \]  
\[ \text{HF}(g) \rightarrow \text{HF}(aq) \]  

**Oxidation column**

**Oxidation**
\[ \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \]  

**Absorption**
\[ 3 \text{ NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{ HNO}_3 + \text{NO} \]  

**Catalytic de-nitrification:**
\[ 2 \text{ NO}_2(g) + \text{O}_2 + 4 \text{ NH}_3(g) \rightarrow 3 \text{ N}_2(g) + 6 \text{ H}_2\text{O}(g) \]  
\[ 4 \text{ NO}(g) + \text{O}_2 + 4 \text{ NH}_3(g) \rightarrow 4 \text{ N}_2(g) + 6 \text{ H}_2\text{O}(g) \]

The recovered acid leaving the absorber column is fed to a storage tank. The gases leaving at the top of the absorber still contain most of the NO\(_X\) formed according to reaction (5). In an additional cooling and oxidation step these NO\(_X\) gases are converted into HNO\(_3\), thus increasing the recovery rate of the process substantially. A part of the condensate from the spray cooler (condensation) is fed to the rinse water storage tank and from the tank to the ZEMAP process, leading to a reduced volume of regenerated acid. A reduction of approximately 10-20\%, compared to the volume of waste acid, guarantees a closed water balance of the entire pickling and acid regeneration process. In pickling lines not only regenerated acid is dosed, also fresh acid is used to keep concentration constant, so it is advantageous to send less regenerated acid volume back to the pickling lines to ensure a balanced acid management.

Reaction (10) shows the process of HNO\(_3\) formation in the oxidation column. The NO formed desorbs from the liquid and has to be oxidized according to reaction (9), which mainly determines the rate of HNO\(_3\) formation. This very important reaction step is strongly improved by an elevated pressure in the oxidation column and cooling with chilled water.

In this process all the valuable components contained in the spent mixed acid, hydrofluoric and nitric acids are recovered in the form of a reusable mixed acid. The metals are converted into oxides, which are recycled in the melting process. This is especially beneficial in view of the high nickel content.

PYROMARS either recovers nitrates in form of nitric acid or decomposes them via NO\(_X\) to nitrogen gases. The process was first installed in 1992 and more than 20 Andritz plants now operate successfully throughout the world [1].
7. **ZEMAP (Zero effluent mixed acid plant)**

**General**

Although the PYROMARS process effectively reduces the amount of metals and nitrates in the wastewater, there is still a small amount remaining in the waste water. This is caused by a certain carry over of the mixed acid in to the rinsing section and depending on the strip dimensions, line speed and the type of the rinse, the amount can vary from 10% to 30% of the total waste acid [2]. Also the latest generation of PYROMARS with volume reduction releases an effluent stream (approx. 10% of plant capacity) with low concentration of nitric acid (approx. 10g/l HNO₃).

Initial target was to minimize mixed acid waste water amounts from the rinsing section of an annealing and pickling line for stainless steel. These wastes are loaded with nitrates (usually 1 to 5g/l NO₃⁻), which are an environmental problem because nitrate-nitrogen drastically affects algae growth in municipal waters. Compared to biological nitrate treatment plants, the space requirements for a ZEMAP system is 15 times lower (approx. 90m² to 1500m²).

ZEMAP itself is a very insensitive system compared to classic biological nitrate treatment plants. The plant is almost resistant to temperature changes, pH fluctuations, or an oversupply of nitrogen sources from nitrate. The bacteria from a biological treatment plant cannot handle such fluctuations and probably die through these changes in their environment.

Also, for ZEMAP the startup and shut down procedure is quite simple by switching on/off steam and vacuum pump.

Basic Layout as follows:

![ZEMAP Diagram](image)

**Fig. 3:** Height requirements approx. 22m area requirement aprox.90m² for a ZEMAP
As the drawing above shows, space requirements are not that demanding, compared to biological treatment and the possibility to fit in a unit into an existing production facility is still possible. Especially for retrofits this is a huge advantage. If possible the ZEMAP should be close to a PYROMARS, as the concentrated sole must be transferred into the waste acid and shorter transfer pipes are always easier to keep free of plugging.

Configuration & results of the first industrial ZEMAP:

ZEMAP is basically a four stage “Lamella Type” falling film vacuum evaporator. The evaporator for rinse water was developed in a cross divisional collaboration together with Andritz Pulp& Paper. The Paper division has been designing and using similar types of vacuum evaporators for several decades to concentrate black liquor [3].

In 2015, Andritz Metals installed the first industrial size ZEMAP in combination with a new PYROMARS. During commissioning the first condensate was high in ammonia (up to 400mg/l) and the fluoride concentration was higher than expected (max. values on fluoride up to 45mg/l), as was the resulting condensate conductivity. Nevertheless, from the first day of operation the steel plant could use the produced condensate in the pickling line without any bad influence on strip quality.

Further optimization was done to improve the condensate quality. Originally the final evaporation should be done in the PAFC vessel (Passive Augmented Forced Circulation). Process principle is overheating and pressurizing of the process liquid with subsequent relaxation. This process step gives an extra boost on concentration and evaporation.

Due to the condensate quality it was necessary to shut down this last process part to reduce the fluoride and ammonia load in condensate. The vessel was operating at a temperature between 108-103°C, decomposition temperature of ammonia fluoride is also in this range so it influenced heavily ammonia and fluoride amount in the condensate.

**Fig. 4:** Falling film lamella evaporator (1 stage type) and close up of a lamella
It was decided to install an additional ammonia stripping system to reduce the remaining ammonia content in the condensate to a target value below 50mg/l. Ammonia content in the beginning of plant start-up: 200-550mg/l NH₄OH depending on incoming rinse water quality and concentration. After installation of the stripping equipment: 10-25mg/l NH₄OH.

At the end of 2018 the plant was accepted by the fully satisfied customer. The very same customer immediately ordered the next ZEMAP unit.

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Table 1: Ammonia content of process condensate before and after installation of stripping equipment

The table shows that the nitrate concentration in the condensate could be reduced effectively. Even nitrate values below 10mg/l are possible.

Fig. 5: Basic flow sheet for optimized ZEMAP
8. Conclusion and Outlook:

PYROMARS is already a well proven and established technology for mixed acid recovery. With our first industrial ZEMAP, Andritz has proven that it is possible to close all waste stream loops in mixed acid pickling. Plants with ZEMAP and PYROMARS can be operated to almost zero effluent, condensate from ZEMAP can be reused without quality losses on strip surface; besides environmental benefits these processes are also financially feasible. If a surplus on steam is available in the factory, a payback time of 1.5 to 3 years for ZEMAP is possible [3]. This potential is reflected by the decision of our first ZEMAP customer to immediately order the second ZEMAP for his wire pickling factory.

Andritz has set a new benchmark for stainless steel pickling with lowest nitrate effluents (mg/l range). Further improvement is in progress and thanks to the good cooperation and satisfaction of our customer, valuable feedback is implemented for future ZEMAP’s.

Nominations & Awards:

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Fig. 6: Award ceremonies ZEMAP
References

