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OXIDE SCALE
FORMATION OF
STAINLESS STEEL IN
TRANSITION OF
ANNEALING AND
REHEATING TOWARDS
FOSSIL-FREE METHODS

UNIVERSITY OF OULU GRADUATE SCHOOL;
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**OXIDE SCALE FORMATION OF
STAINLESS STEEL IN TRANSITION
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Abstract

After continuous casting, stainless steel production continues with high temperature heating of slabs in reheating furnaces to ensure a sufficient temperature of slabs for hot rolling. Final annealing is the high temperature heating process for cold-rolled stainless steel strip, restoring its mechanical properties after cold rolling. Combustion of natural gas is a typical method for furnace heating, leaving an oxidizing gas atmosphere inside the furnace due to using excess oxidant to sustain the burning reaction. High temperature exposure to a furnace gas atmosphere causes oxidation on the surface of the steel, known as oxide scale. Oxide scale must be removed after heating processes to produce a clean and corrosion-resistant surface for the final stainless steel product.

The transition towards utilizing hydrogen as fuel gas or electricity for steel heating in the furnace enables to decrease CO₂ emissions that now originate from the combustion of fossil fuels. Another co-development in the path to more efficient heating processes is the transition from air-fuel to the oxyfuel method, enabling better efficiency of combustion. Both changes affect the furnace gas atmosphere and heating conditions influencing the properties of oxide scale.

In this work, different austenitic and ferritic stainless steel grades have been heated in simulated reheating and annealing furnace conditions to investigate how changing the heating method alters the structure, composition and amount of oxide scale formed during heating. By comparing the annealing of austenitic grades using the current methane-air method, the onset of breakaway oxidation happened earlier and at lower temperatures for AISI 304 compared to high levels of silicon containing AISI 309, while breakaway oxidation was not observed for ferritic grades. The transition of heating toward the greener hydrogen-oxygen method promotes earlier onset of breakaway oxidation both in annealing and reheating conditions, in which ferritic grades were found to be more suitable for the transition compared to austenitic grades. A significant difference in suitability was also observed between austenitic grades in reheating conditions, in which the transition increased the oxidation four times for AISI 301 but barely two times for AISI 304.

Keywords: annealing, hydrogen, natural gas, oxidation, reheating, stainless steel

Airaksinen, Susanna, Ruostumattoman teräksen hilseen muodostuminen hehkutuksen ja aihionkuumennuksen siirtymässä kohti fossiilivapaita menetelmiä

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Tiivistelmä

Jatkuvavalun jälkeen ruostumattoman teräksen tuotannossa aihiot kuumennetaan korkeassa lämpötilassa aihionkuumennusuunissa varmistaen aihion riittävän lämpötilan kuumavalssaukseen. Ruostumattoman teräksen loppuhehkutus on kylmänauhan korkealämpötilakuumennusta, joka palauttaa sen mekaaniset ominaisuudet kylmävalssauksen jälkeen. Maakaasun poltto on tyypillinen menetelmä uunin kuumennuksessa, mikä jättää hapettavan kaasuatmosfääriin uuniin johtuen palamisreaktion ylläpitämisestä hapetinylimäärällä. Korkealämpötila-altistus uunin kaasuatmosfäärissä aiheuttaa teräksen pinnan hapettumisen, jota kutsutaan hilseeksi. Hilsekerros täytyy poistaa kuumennusprosessien jälkeen, jotta ruostumattoman teräksen lopputuotteelle saadaan tuotettua puhdas ja korroosiokestävä pinta.

Siirtymällä kohti vetypolttoaineen tai hyödyntämällä sähköä teräksen kuumennuksessa on mahdollista vähentää CO₂-päästöjä verrattuna fossiilisten polttoaineiden polttoon. Toinen rinnakkainen kehityssuunta tehokkaampiin kuumennusprosesseihin on siirtymä polttoaineen ilmapoltosta happipolttoon mahdollistaen paremman polttotehokkuuden. Molemmat muutokset vaikuttavat uunin kaasuatmosfääriin ja kuumennusolosuhteisiin, mikä vaikuttaa hilseen ominaisuuksiin.

Tässä työssä eri ruostumattomia austeniittisia ja ferriittisiä teräslaatuja on kuumennettu aihionkuumennus- ja hehkutusuuneja simuloivissa olosuhteissa tutkittaessa, kuinka kuumennusmenetelmän vaihto muokkaa muodostuvaa hilseen rakennetta, koostumusta ja määrää. Hehkutuksessa nykyisellä metaani-ilma-menetelmällä austeniittisten teräslaatuojen oksidikerroksen hajottavan hapettumisen alkaminen tapahtui aiemmin ja matalammassa lämpötilassa AISI 304:llä verrattuna korkea piipitoiseen laatuun AISI 309, kun taas hajottavaa hapettumista ei havaittu ferriittisillä laaduilla. Kuumennuksen siirtymä kohti vihreämpää vetyhappi-menetelmää edistää hajottavan hapettumisen alkua sekä hehkutus - että aihionkuumennus olosuhteissa, joissa ferriittisten laatuojen havaittiin soveltuvan siirtymään austeniittisia paremmin. Merkittävä ero soveltuvuudessa havaittiin myös austeniittisten välillä aihionkuumennuksessa, jossa siirtymä kasvatti hapettumista nelinkertaisesti AISI 301 -laadulla, mutta vain kaksinkertaisesti AISI 304 -laadulla.

Asiasanat: aihion kuumennus, hapettuminen, hehkutus, maakaasu, ruostumaton teräs, vety

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Oulu, 12.6.2024

Susanna Airaksinen

Abbreviations

AISI	American iron and steel institute, identification for stainless steel grades
bcc	Body-centered-cubic
BSE	Backscattered electrons
EDS	Energy-dispersive X-ray spectroscopy
fcc	Face-centered-cubic
FESEM	Field emission scanning electron microscope
e.g.	exempli gratia
GDOES	Glow discharge optical emission spectroscopy
HO	Hydrogen-oxygen combustion
IA	Induction with air
i.e.	Id est
IN	Induction with nitrogen
MA	Methane-air combustion
MHO	Methane-hydrogen-oxygen combustion
MO	Methane-oxygen combustion
SOFC	Solid oxide fuel cell
TG	Thermogravimetry

List of original publications

This thesis is based on the following publications, which are referred to throughout the text by their Roman numerals:

- I Airaksinen, S., Tuovinen, T., Laukka, A., Vuolio, T., Heikkinen, E.-P., Riekk, E., Manninen, T., & Fabritius, T. (2020). Effect of simulated annealing conditions on scale formation and neutral electrolytic pickling. *Steel Research International*, 92(3), 2000449. <https://doi.org/10.1002/srin.202000449>
- II Airaksinen, S., Tuovinen, T., Vuolio, T., Laukka, A., Heikkinen, E.-P., Riekk, E., & Fabritius, T. (2022). Oxide scale formation of EN 1.4622 and EN 1.4828 stainless steels during annealing and descaling behavior in neutral electrolytic pickling. *Steel Research International*, 93(1), 2100366. <https://doi.org/10.1002/srin.202100366>
- III Airaksinen, S., Laukka, A., Heikkinen, E.-P., Riekk, E., & Fabritius, T. (2023). From fossil-fueled to hydrogen-fueled annealing furnaces: Effects on the oxidation of stainless steels. *Steel Research International*, 94(5), 2200305. <https://doi.org/10.1002/srin.202200305>
- IV Airaksinen, S., Haapakangas, J., Laukka, A., Heikkinen, E.-P., & Fabritius, T. (2023). Oxide scale formation of stainless steels with different heating methods – Effect of hydrogen as fuel. *Steel Research International*, 95(1), 2300334. <https://doi.org/10.1002/srin.202300334>

The contribution as the primary author for all the publications was the following: research design, literature review, and the major proportion of the writing. In Publications I–III, experimental work and analysis of the results concerning annealing experiments, and in Publication IV, the major proportion of the reheating experiments and analysis of the results.

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1 Introduction

Stainless steel production has increased eightfold over the past 40 years. In 2022, global stainless steel production was 55.3 Mt including Europe's share of 6.3 Mt. Total emissions per a produced ton of stainless steel depends on the amount of used recycled scrap as raw material, with an example of 2.45 tons of CO₂ emitted from using 50% scrap and 1.25 tons of CO₂ emitted from using 85% scrap. (Worldstainless, 2022a, 2022b, 2023)

Depending on the end product, a stainless steel production route includes multiple process steps for heating of cast and rolled materials such as reheating and final annealing processes. After continuous casting, the reheating step is used to elevate the temperature of steel slabs to an appropriate value, as demanded by the downstream hot rolling process, and steel grade requirements. At the other end of the coil manufacturing, a final annealing is located after cold rolling and its purpose is to restore the mechanical properties of the cold rolled strips.

The target of the European Union is to limit global warming to 1.5 °C and to achieve climate-neutrality by 2050 (European Commission, 2019), which demands large-scale changes to the current processes for significant reduction of CO₂ emissions. Nowadays, natural gas and propane gas are commonly used fossil fuels with excellent in terms of heating value, but combustion of fossil fuels for producing heat inside the industrial furnaces produces fossil-based CO₂ emissions. By changing fossil fuels to a greener alternative like H₂, or electrifying the reheating and annealing furnaces, it is possible to eliminate CO₂ emissions from these unit processes, if green hydrogen or renewable electricity is used (Capurso et al. 2022; Pfeifer, 2017). However, the transition of heating methods with these alternatives requires investments and development of industrial furnaces. Furthermore, the cost to produce green hydrogen is still high, but a cost-effective production method is currently being studied and the utilization of hydrogen fuel could become more portable depending on the price of natural gas, electricity, and carbon for emitted CO₂ (Ishaq et al., 2022; Capurso 2022; Marocco et al., 2023).

High temperature heating of stainless steels generates an oxide scale on the surface of the steel. The physical and chemical properties of the oxide scale; structure, composition, and amount, are the consequence of the heating process itself as well as the steel grade's own composition. The main factors influencing the oxidation process are temperature, exposure time, and gas atmosphere inside the furnace, as well as properties of the steel grade such as alloying elements, microstructure, and grain size. Thus, changes in a furnace's heating operations and

fuels affect the specific oxidation of steel grades and the following processes for the removal of the oxide scales. Removal processes are important in terms of steel product quality, e.g. the remaining oxide scale on the surface of the steel slab after reheating can roll-in the steel matrix in the hot-rolling process causing surface defects on the intermediate as well as final product surface. Likewise, problems in oxide scale during the removal process after final annealing causes surface defects and can tarnish stainless steels' namesake by decreasing the main function of it: corrosion resistance. Not only do the surface defects reduce corrosion resistance properties, but they also affect the appearance of the product.

Previous research on oxide scale formation for stainless steels has varied from long-term corrosion studies to short-term exposures to high temperatures. However, the previous studies have focused on using different free oxygen contents or differing amounts of water vapor in the gas atmosphere, whereas comparison of different post-burn atmospheres has been studied less. Knowledge of oxide scale formation during current industrial high temperature manufacturing processes with different steel grades is quite minor, and future new fossil-free heating methods bring new aspects in process development and optimization in terms of oxide scale.

The objective of this thesis was to provide information for the behavior of oxide scale formation of different stainless steel grades upon CO₂-free heating method development. The starting point for the study was combustion between air and natural gas, which consists mainly of methane (CH₄). The approach of the thesis was to simulate heat treatment conditions by producing a simulated post-burn reheating and annealing furnace atmosphere for stainless steel material using a laboratory furnace, and thus, to observe the effect of furnace atmospheres and heating conditions, like temperature and time, on oxide scale formed during heating. The studied heating processes were divided into a short annealing process of cold rolled material and a longer reheating process for slabs. The following research questions were set for this thesis:

1. How do the changes in heating conditions affect oxide scale in the current gas atmosphere formed in CH₄-air combustion?
2. How do the oxide scale formations of different steel grades differ from each other in CH₄-air combustion?
3. What kinds of effects does the transition from air-fuel to oxyfuel have on the oxide scale formation?

4. How does the replacement of natural gas with hydrogen affect the oxide scale formation, and which steel grades would be suitable for the transition of fuel gases?

Research in the original publications was connected to the objective of the thesis as follows:

Publication I: Effect of annealing conditions i.e. temperature and time of AISI 304 in the CH₄-air atmosphere.

Publication II: Effect of time and temperature of annealing on oxide scale formation of steel grades for high temperature applications, AISI 309 and EN 1.4622.

Publication III: Annealing of austenitic and ferritic stainless steels in different furnace gas atmospheres including simulated atmospheres based on CH₄-air, CH₄-oxygen, and H₂-oxygen combustions.

Publication IV: Reheating of austenitic and ferritic stainless steels in different combustion-based simulated atmospheres including CH₄-air, CH₄-oxygen and H₂-oxygen and comparing combustion heating to the simulation of induction heating.

2 Stainless steel production

The process route of stainless steel production is presented in Fig. 1. Molten steel is continuously cast in the melt shop and the cast strand is cut into slabs. Reheating of slabs is performed before hot rolling and oxide scale formed during continuous casting and reheating is removed by hydraulic descaling using high-pressure water sprays. The heating operations of reheating and final annealing are located in the rolling mills. After hot rolling, annealing, and cooling, oxide scale of hot rolled strip can be removed by mechanical descaling and chemical and/or electrochemical pickling processes. Final annealing is performed after cold rolling, and oxide scale of cold rolled strip can be removed by pickling processes.

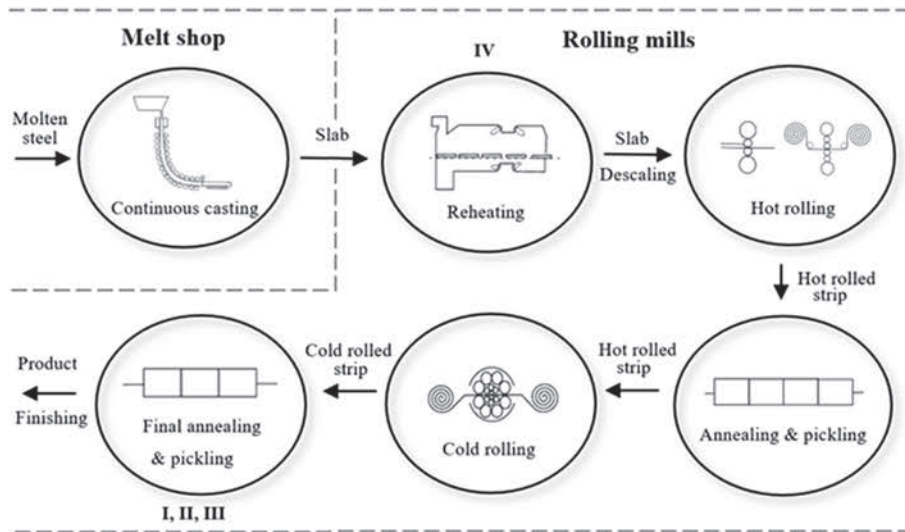


Fig. 1. Process route of stainless steel related to Publications I – IV.

2.1 Reheating of slabs

Stainless steel slabs produced by continuous casting are typically 14 m in length, up to 300 mm in thick and 1620 mm in width, with a maximum weight of 30 t (Outokumpu Stainless AB, 2013; Hautala, 2015). Slab reheating is performed in a walking beam-type reheating furnace to ensure the slabs' suitable and uniform temperature for hot rolling process. The reheating furnace has preheating, heating

and soaking zones. The heating temperature varies from the ferritic steel grades' 1150 °C to the austenitic grades' up to 1300 °C and the total heating time is around 2–3 hours (Gao, 2008; Kim, 2007; Kodukula et al., 2021; Osei et al., 2021). Reheating furnaces are usually heated by methane or propane combustion with air which produces water vapor and carbon dioxide in the furnace gas atmosphere. To ensure complete combustion of the used fuel, excess air is utilized as the oxidizer in the combustion, providing free oxygen in the furnace. A sufficiently oxidizing atmosphere produces a removable oxide scale on the surface of the slab for the descaling process. The successful removal of oxide scale prevents the rolling of the oxide scale into the steel matrix during the hot rolling process causing surface defects (Kizu et al., 2001).

2.2 Final annealing of cold-rolled strips

By cold rolling, the thickness of a stainless steel strip is reduced in a temperature that is below the recrystallization temperature of the steel, and its microstructure is deformed causing the hardness of the steel to increase. Typically, the thickness of cold-rolled stainless steel ranges from under 1 mm to a few millimeters (Outokumpu Stainless AB, 2013). The final annealing is used to restore softness, ductility, and corrosion resistance for the strip (Chandler, 1994). It is performed in an annealing furnace e.g. in a continuous annealing and pickling line by heating the strip to a high temperature characteristic of steel grades. Austenitic stainless steels require higher heating temperatures, up to 1200 °C (Outokumpu Stainless AB, 2013), compared to ferritic stainless steels, around 1000 °C (De Abreu et al., 2006). The total time of the strip in the annealing furnace is only a few minutes until it achieves the annealing temperature, after which it is rapidly cooled. Depending on the carbide precipitate rate of steel grade, fast cooling must be done using water quenching, blast, or still air. (Davis, 1994)

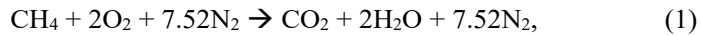
2.3 Pickling

For stainless steels, the oxide scale and chromium-depleted layer from the surface of the strip is removed by electrolytic pickling and mixed acid pickling after final annealing. The chromium-depleted layer is formed during annealing due to chromium content of the steel underneath the oxide scale decreasing by chromium diffusion towards surface to oxidize. Electrolytic pickling uses a neutral sodium sulphate electrolyte and electric current to dissolve oxide scale by an

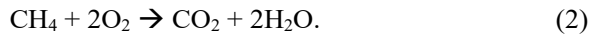
electrochemical reaction. The mixed acid pickling usually utilizes HNO_3 and HF acids to remove the chromium depleted layer and remaining oxides. The clean surface after pickling enables passive layer formation ensuring corrosion resistant for surface of the final product. (Li & Celis, 2003)

2.4 Heating methods of industrial furnaces

Generally, industrial reheating and annealing furnaces are heated by combustion of a gaseous fuel with air. The most commonly used fuel is natural gas, which consists mainly of methane gas. In the combustion reaction (1) of methane with air



carbon dioxide and water vapor are formed in the furnace atmosphere. The traditional air-fuel method also requires energy to heat inert nitrogen, of which accounts for 79% of air (von Schéele, 2009). By changing the oxidant gas from air to oxygen, unnecessary heating of nitrogen gas is avoided, and the volume of flue gas and heat loss in it is decreased by 75% compared to the air-fuel method (Kiriishi et al., 2009). Without nitrogen, the relative water vapor and carbon dioxide contents of furnace gas atmosphere from oxyfuel combustion of methane is increased compared to the air-fuel method. The oxyfuel combustion of methane is presented with the reaction (2) below



The oxyfuel method increases the flame temperature and reduces fuel consumption for the same amount of heat energy (Baukal Jr, 2010; Kiriishi et al., 2009, Hu et al., 2019). Lower consumption of fuel results in decreases CO_2 emissions in the process, whereas a higher content of CO_2 in flue gas simplifies its capture (Ditaranto & Oppelt, 2011; Kiriishi et al., 2009; Koohestanian & Shahraki, 2021). The oxyfuel method significantly decreases thermal NO_x formation compared to the air-fuel method, because nitrogen from air is not available for formation. However, higher flame temperatures can promote NO_x formation from in-leakage air in the furnace, resulting from momentarily or continuous under pressurization. Utilization of the flameless oxyfuel method reduces that amount of NO_x compared to conventional oxyfuel. (von Schéele, 2009; Kiriishi et al., 2009) The purpose of the flameless oxyfuel method is to decrease the maximum temperatures of burning using an invisible flame, which can be produced by dilution of flame using recirculated hot

furnace flue gases or by injecting fuel gas and oxygen separately at high velocity (von Schéele, 2008).

When produced with fossil-free energy, hydrogen gas is a fossil-free alternative for the heating of industrial furnaces. Combustion of hydrogen gas with oxygen does not result in any carbon dioxide formed within the furnace gas atmosphere as seen in reaction equation (3)



and the result of an ideal combustion process is only water vapor. However, the more extensive utilization of hydrogen gas as the fuel in the heating of industrial furnaces requires the development of heating practices and burners, while in larger Power-to-X scale, the development regarding the production, transportation, and storage of hydrogen. A completely CO₂-free heating method based on green hydrogen would mean the production of which only renewable energy and electricity would be used (Capurso et al. 2022; Li et al., 2022; Oliveira et al., 2021; Schmitz et al., 2021; Wulf et al., 2020).

Other ways to utilize hydrogen gas as fuel in the heating of industrial furnaces would be to replace it with natural gas partially or totally in the air-fuel method. For example, it is already possible to blend a certain proportion of hydrogen in natural gas fuel in current CH₄-air burners. Palacios & Bradley (2021) argued that the amount of replaced natural gas would be 20%, and Luzzo et al. (2021) suggested 30%. In terms of emissions of combustion heating, an 80% substitution of natural gas with hydrogen is required to cut CO₂ emissions in half, but as the amount of hydrogen fuel increases, the amount of NO_x emissions also increases. Higher NO_x emissions are the result of a rise in a burner's flame temperature. However, NO_x emissions can be decreased by flameless burner technology compared to air-staged burners. (Mayrhofer et al., 2021) Furthermore, the need for the development of new burner systems is also caused by hydrogen's lower volumetric energy density compared to natural gas. For the same heat release rate in a combustion system, a higher volume of hydrogen gas is used which demands higher jet velocity or pipe diameter from burners compared to natural gas. (Palacios & Bradley, 2021)

Another way to develop the heating of an industrial furnace toward CO₂-free methods is induction heating. This effect can even be promoted by using renewable electricity (Pfeifer, 2017; Schmitz et al., 2021). Induction heating is a contactless electric heating process, which transfers heat from an electric current in induction coils to the product via electromagnetic waves (Rapoport & Pleshivtseva, 2006;

Rudnev et al., 2017). Induction heating methods are divided by type of induction coils according to the direction of magnetic flux formed in relation to the movement of the steel slab or strip. The longitudinal method produces flux for parallel direction, while the transverse method produces flux vertically through the material. (Davies, 1989)

Induction heating is a more energy efficient heating method and it has the potential for faster heating of stainless steels with the possibility of better furnace atmosphere control compared to combustion heating in gas fired furnace. Faster heating and atmosphere control causes a decrease in oxide scale formation during the heating process. (Rudnev et al., 2017) Heating rate and penetration depth of the current density in the material are dependent on properties of heating method, for example power and frequency, and properties of heated material such as geometry, electric resistivity and magnetic permeability (Morandi & Fabbri, 2016). For example, the requirement of temperature uniformity of stainless steel material in reheating process requires significant optimization of the induction heating system. In comparison to combustion heating, induction heating has its own restrictions, and the change in combustion methods to hydrogen would demand less adjustments and it would therefore be more easily implemented than transition to induction heating (Gomes, 2024).

3 Oxide scale formation during heating processes

The general oxidation mechanism of metals is described as follows: oxidation starts by chemical adsorption of oxygen molecules from the surrounding atmosphere on the surface of the metal. At the gas-metal interface, the molecules split to the atoms, and oxygen spreads by diffusion over the entire surface area, forming a layer with thickness of one atom. Nucleation of oxide scale begins at the grain boundaries and dislocations. Growth of nuclei occurs laterally along the surface, connecting to each other and eventually forming a continuous oxide layer. (Hauffe, 2012; Kofstad, 1988)

The continuous oxide scale layer prevents the continuation of oxidation directly between the metal matrix and the atmosphere. Hence, oxidation requires mass transfer by the diffusion of species through the oxide layer, and those species are more commonly ions than atoms (Revie & Uhlig, 2008). In diffusion, metal ions transfer toward the oxide-gas interface and oxygen ions toward the oxide-metal interface. Depending on the direction of diffusion, the oxide scale layer grows outside or inside. (Tunturi, 1988)

Diffusion of ions through the oxide layer occurs either through a lattice structure or a utilizing line and surface defects. Lattice diffusion happens via point or lattice defects, which are vacancies, interstitial ions, and impurities. Latter diffusion mechanisms happen via grain boundaries, dislocations, surfaces, or cracks, which enables higher diffusion rates compared to a more densely packed lattice structure due to smaller activation energy. (Khanna, 2002; Khanna, 2005; Tunturi, 1988; Kofstad, 1966) Thus, defects of the oxide layer have an influence on diffusion rates of ions and based on which different oxide layers are divided into protective and non-protective. For example, the protective chromium oxide layer has a compact structure while the non-protective iron oxide layer is porous and has lots of defects. (Tunturi, 1988)

The thickness of the oxide scale layer increases as oxidation continues, which causes the formation of voids and microcracks in it. Voids and microcracks enable higher diffusion rates, and thus the oxide layer grows faster. Eventually, macrocracks can form, causing the oxide layer to lose its protective qualities. (Kofstad, 1988) When the oxide scale layer no longer protects the surface of the metal, the oxidation rate and the amount of oxide scale start to increase significantly. Water vapor promotes oxidation by accelerating mass transport from the gas atmosphere into the oxide scale. The mass transport can be divided into gas species

transport via pores, gaps, and cracks, while molecular species transport via grain boundaries, and hydrogen dissolution into oxide scale. (Young, 2016)

Oxidation kinetics is described by rate laws for diffusion. The most important rate laws at high temperatures are parabolic and linear laws. The parabolic rate law is followed when diffusion controls mechanisms for oxidation. Based on this, the oxidation rate decreases while the oxide layer thickens, increasing the diffusion distance. Thus, the parabolic law describes the growth of the protective oxide layer effectively. Linear rate law is an interface-controlled mechanism, in which the rate of oxidation remains constant during oxidation. Oxidation follows linear rate law, for example, when a non-protective oxide layer forms or volatilization of the oxide layer keeps the thickness of oxide layer constant during oxidation. (Khanna, 2002; Kofstad, 1966) Furthermore, combinations of rate laws are typical in high temperature oxidation. For example, the initial oxidation can be interface-controlled linear and change as oxidation progresses to diffusion-controlled parabolic. When the protective oxide layer loses its protection, the rate law changes back to linear. (Kofstad, 1966; Khanna, 2002)

3.1 Structure of oxide scale for stainless steel

For stainless steels, the initially formed continuous oxide scale layer is typically chromium oxide (Cr_2O_3) due to the lower partial pressure of oxygen it requires compared to other alloying elements and iron. The oxide layer is formed by outward diffusion of chromium ions to the surface of the steel, and a chromium depleted layer is formed below it. (Tunturi, 1988; Khanna, 2002) The protectiveness of the chromium oxide layer is based on its dense structure and the decrease of the ions' diffusion rate through it (Visnapuu et al., 1994). Even so, iron and manganese are diffused through the protective layer to form a sublayer in the oxide-gas interface. The composition of the sublayer is $(\text{Fe,Cr,Mn})_3\text{O}_4$ spinel formed by reaction of diffused elements, oxygen and chromium oxide. (Basu & Yurek, 1991) The chromium content of the steel grade affects the protectiveness of the layer at high temperatures, and it has been presented that Cr content of approximately 20% forms a stable, well-protective continuous layer (Tunturi, 1988). If the heating atmosphere contains water vapor, the required critical Cr content increases even more in comparison to dry atmosphere (Ueda et al., 2013). Furthermore, some alloying elements, such as silicon, aluminum, and nickel, can improve the high temperature resistance of protective layer (Tunturi, 1988). For example, silicon alloying could increase the resistance if it forms a continuous Si-

oxide layer (SiO_2) between chromium oxide and steel surface, also reducing diffusion rate of ions through it (Basu & Yurek, 1991).

Loss of protection for the chromium oxide layer occurs when the chromium content of the depleted layer drops below a critical level further defined by the surrounding atmosphere. Hence, as oxidation continues, outward diffusion of chromium ions is not sufficient to upkeep the growth of the layer or repair the formed cracks. (Lai, 2007) Loss of protection enables fast diffusion of iron ions through the oxide layer to the oxide-gas interface forming iron oxides, part of which transforms to Fe-Cr spinels ($\text{Fe(Fe,Cr)}_2\text{O}_4$) due to chromium oxide having solid solubility to iron oxide. (Tunturi, 1988) Internal oxidation happens below the oxide-metal interface-forming subscale, when inward diffusion of oxygen is faster than outward diffusion of metal ions. The metal forming the most stable oxide is oxidized in internal oxidation. (Khanna, 2002; Cheng et al., 2006) Hence, internal oxidation of silicon and chromium is more favorable than iron and nickel.

Oxidation after loss of protection for the chromium oxide layer is called breakaway oxidation. The formation of iron oxides is the sign of the onset of breakaway oxidation. Breakaway oxidation proceeds from the formation of iron oxide-containing nodules to the spread of iron oxide as a thick layer for the whole surface. (Shen et al., 1997) During the iron oxide formation on the surface of the steel, internal oxidation happens below the oxide-metal interface. Internal oxidation occurs in the chromium-depleted layer, which usually produces Fe-Cr spinel and can leave behind unoxidized metallic particles inside the oxide scale. For example, those unoxidized particles are nickel-rich for austenitic stainless steel grades. (Zeng et al., 2014; Laukka et al., 2017; Su et al., 2022)

Especially, presence of water vapor in the heating atmosphere and its partial pressure has significant effect on loss of protection for the chromium oxide layer in high temperatures compared to dry atmosphere (Cheng et al., 2006; Qian et al., 2023). Mechanism for the effect of water vapor on oxidation is proposed in literature, for example, by Issartel et al. (2011). The suggested oxidation mechanism starts by dissociated H_2O i.e. H^+/OH^- diffuse through the protective chromium oxide layer due to their short radii. Diffused species react with iron in chromium depleted layer, forming FeO , which react with chromium oxide to form FeCr_2O_4 . Outward diffusion of iron ions forms iron oxide at oxide-gas interface. Additionally, a new chromium oxide layer and Cr-depleted layer is possible to form at oxide-steel interface as oxidation reaction continues.

3.2 Factors influencing the formation of oxide scale

Oxide scale formation studies for austenitic and ferritic stainless steels can be divided into long-term corrosion studies and short-term oxidation studies. In the context of this thesis, long-term studies are considered to include studies of oxidation of steel surface up to hundreds of hours, while the oxidation time of short-term studies is considered to be from minutes to hours. Based on this classification, the oxidation occurring in the industrial processes such as annealing and reheating can be considered as short-term oxidation.

Long-term corrosion studies for stainless steels are typically aimed to study the in-use characteristics of the produced steel and are performed at lower temperatures (<1000 °C) compared to the steel manufacturing process temperatures themselves. Thus, these studies indicate corrosion of the steel surface, revealing the suitability of specific steel grades in conditions of different applications. For example, interconnectors of solid oxide fuel cells (SOFC) and automotive exhaust gas systems have been generally studied applications for corrosion studies of stainless steels. The studied temperatures of SOFC vary between 800 to 1000 °C, and atmospheres that include dry air and different moist atmospheres like humid air, H₂, or O₂. (Chandra-Ambhorn et al., 2007; Issartel et al., 2011; Sachitanand et al., 2015; Wongpromrat et al., 2015) In an automotive exhaust gas system, corrosion tests are performed with isothermal or cyclic heating including O₂, H₂O, and CO₂ containing atmospheres based on the fuel used in the intended internal combustion engine and temperatures of around 1000 °C (Kado et al., 1978; Wei et al., 2018a; Wei et al., 2018b; Zhan et al., 2021; Faivre, 2013).

For ferritic steel grades, oxidation behavior has been studied at different temperatures and times in air atmosphere (Fujikawa et al., 1983; Sabioni et al., 2014; Brady, 2012, Srisrual et al., 2009; Fan et al., 2020), atmospheres with different oxygen partial pressure (Chen et al., 2014; Alnegren et al., 2016; de Fátima Salgado et al., 2019), atmospheres with different water vapor content (Parry et al., 2018; Srisrual et al., 2019), and CO₂ atmosphere (Promdirek et al., 2014). The effect of different alloying elements on the oxidation behavior of ferritic stainless steel has also been studied in long-term conditions. These studied elements were, for example, chromium (Caplan & Cohen, 1952; Sanchez et al., 2009), molybdenum (Shu et al., 2012), zirconium (Moroishi et al., 1979), niobium and titanium (Moroishi et al., 1979; Toscan et al., 2004), and cerium (Li et al., 2014).

Austenitic steel grades have been studied in long-term corrosion conditions, mainly between temperatures of 800-1000 °C using air atmosphere (Tanabe &

Imoto, 1979; Lille & Jargelius-Pettersson, 2000; Hayashi et al., 2016; Wang et al., 2013; Karimi et al., 2008; Wonneberger et al., 2019; Sabioni et al., 2012; Riffard et al., 2002), CO₂ atmosphere (Evans, 1983; Zeng et al., 2014), O₂ atmosphere (Col et al., 2017; Asteman et al., 2004), and O₂ atmosphere with water vapor (Yu et al., 2017; Asteman et al., 2004; Pour-Ali et al., 2019). Different studied elements for austenitic stainless steel in long-term conditions were, for example, silicon (Evans, 1983; Pettersson et al., 2005; Paúl et al., 2001; Paúl et al., 2007), molybdenum (Buscail, 2008a; Buscail, 2008b), aluminum (Yu et al., 2017; Xu et al., 2011), and sulfur (Pascal et al., 2015).

For long-term corrosion studies, chromium evaporation has been observed to decrease the protectiveness of the chromium oxide layer especially in a water vapor-containing atmosphere (Young, 2016; Asteman et al., 2000; Young & Pint, 2006). The principal volatile species were CrO₂(OH)₂ at lower temperatures, and formation of CrO₃ occurs at higher temperatures (Opila et al., 2007; Yamauchi et al., 2003; van Leeuwen et al., 2023). For example, the amount of volatile chromium oxide is determined to be 1.93 mg·cm⁻² after 50 hours at 1200 °C in a dry oxidizing atmosphere (Berthod, 2005), and 1·10⁻³ mg·cm⁻² per hour at 900 °C in a humid atmosphere (Quadackers et al., 2009). At 1200 °C, a humid atmosphere containing 2.4% O₂ and 19.7% H₂O was determined to produce mass loss for chromia of about 9 mg·cm⁻² after 28 hours (Yamauchi et al., 2003). Furthermore, evaporation of the chromium oxide layer was presented to decrease by the formation of manganese chromium spinel layer (MnCr₂O₄) on the top of it, because it reduced the activity of chromium (Holcomb & Alman, 2006; Falk-Windisch et al., 2015).

Short-term oxide scale formation is also influenced by factors such as heating process and steel grade. The main factors are the gas atmosphere and temperature profile with respect to time in the process furnace and microstructure, alloying, and grain size in steel grade. The factors for short-term oxidation are presented in the chapters below.

3.2.1 Atmosphere

Due to high temperatures and an oxidizing atmosphere, oxide scales are formed on the surface of stainless steel during reheating and annealing processes. For the current heating practice of reheating and annealing furnaces, an oxidizing atmosphere is the result of natural gas combustion with air. Generally, the corresponding atmosphere used in simulations contains 3% O₂, 16% H₂O, 8% CO₂ and 73% N₂. The atmosphere produces a continuous protective chromium oxide

layer on the surface of the steel at the beginning of the oxidation both for austenitic AISI 304 and ferritic AISI 441 steel grades. (Visnapuu et al., 1994; Issartel et al., 2012)

In the heating of the furnace, excess oxidant gas (air, oxygen) is used to assure the complete combustion of fuel gas and to provide sufficient content of free oxygen in the furnace gas atmosphere. Free oxygen content has a major influence on oxide scale formation of the steel surface and the efficiency of oxide scale removal in the descaling and pickling processes. Typically, free oxygen content is around 2–5% in the furnace so that oxide scale formation is optimal in terms of oxide scale's properties and its removability. If free oxygen content is too low, a protective continuous oxide layer is not formed. In annealing conditions using O₂-N₂ atmosphere at 1200 °C, a protective chromium oxide layer was formed for AISI 304 using 3% oxygen, while a non-protective spinel layer formed using 1% oxygen. However, it is possible to form the protective oxide layer using a lower temperature, 1000 °C, even in a lower oxygen content atmosphere. (Zacchetti et al., 2009)

In the post-burn atmosphere of natural gas, a continuous protective oxide layer was observed for AISI 304, formed at the beginning of oxidation using 2% oxygen content at 1176 °C, while oxide scale formed in <0.2 % oxygen was discontinuous and non-protective (Fernando & Zaremski, 1988). Likewise, oxide scale structure of AISI 304 was changed from protective chromium oxide to non-protective Fe-Cr spinel when free oxygen content was decreased from 5% to 0% in the post-burn atmosphere of natural gas at 1120 °C (Visnapuu et al., 1994). At 1100 °C, the closer limit for free oxygen content of the post-burn atmosphere concerning protective oxide formation was determined. Free oxygen content of 2.56% was observed to form a protective oxide layer for AISI 304, while a near-zero oxygen content produced non-protective spinel. (Ozturk & Matway, 1997)

In reheating conditions, free oxygen content of 3% has been observed to decrease the amount of oxide scale for AISI 304 compared to 0% oxygen in H₂O-CO₂-O₂-N₂ atmosphere (Kinoshita & Oguma, 1979). However, in the atmosphere with high water vapor content, produced by a simulated methane-oxyfuel post-burn method, the oxidation of AISI 304 stainless steel surface was hindered in a case without free oxygen compared to a 3% oxygen containing atmosphere (Laukka et al., 2021). For ferritic AISI 430, free oxygen content of 5% in a simulated natural gas combustion with air saw the oxidation rate decreased when compared to 3% O₂ in isothermal heating of 2 hours at 1150 °C (Osei et al., 2021).

The water vapor content of the furnace gas atmosphere is based on the combustion of fuel gas with oxidant gas, and thus a change in the combustion

process causes a change in the water vapor content. Water vapor is suggested to accelerate the oxidation of stainless steels and bring forward the onset of breakaway oxidation compared to a dry atmosphere (Cheng et al., 2006; Chen et al., 2017) or comparatively lower water vapor content (Qian et al., 2023). An increase in water vapor content in short-term oxidation is observed to increase the thickness of the oxide layer for both austenitic and ferritic grades (Wei et al., 2009; Badin et al., 2014; Cheng et al., 2013). However, if the oxidation time is very short (< 1 min), the effect of water vapor remains minor for AISI 304 by comparing air-fuel and oxyfuel methods (Lindell et al., 2015). Similar results were observed for high oxidation-resistant ferritic grade, in which the oxide scale structure remained layer-like Cr-rich oxide without signs of breakaway oxidation, by increasing the water vapor content in the air using reheating simulating conditions for 2 hours at 1100 °C (Cheng et al., 2013).

3.2.2 Temperature and time

Temperature and time are the main factors along with the furnace gas atmosphere in high temperature oxidation processes for affecting oxide scale formation. Generally, higher temperature increases the oxidation rate, and longer exposure time in high temperatures enables the oxidation to proceed further. The extent to which these factors affect oxidation depends on the steel grade.

As established austenitic and ferritic steel grades have been studied over shorter periods of below 30 minutes as well as up to 3 hours in annealing and reheating conditions. In short oxidation times at high temperatures (> 1000 °C), the oxide scale structure of austenitic and ferritic steel grades was layer-like chromium-rich oxide, and minor increases of time and/or temperature only affected the thickness of the layer (Fernando & Zaremski, 1988; Badin et al., 2014; Wei et al., 2012; Cheng et al., 2015a). Layer-like structured oxide scale was formed, for example, when austenitic AISI 304 was heated at 1065–1176 °C for 10–60 seconds using the post-burn atmosphere of natural gas with 7% O₂ (Fernando & Zaremski, 1988) or after ferritic AISI 441 was heated at 1100 °C between 2.5–20 min using argon atmosphere with 5–13% water vapor content (Badin et al., 2014). Other studies also found that weight gain of the sample significantly increased during oxidation by increasing temperature and time (Ozturk & Matway, 1997; Carvalho et al., 2006). Compared to layer-like structured oxide scale, an increase in oxidation time produced a two-layered structure in the form of an outer iron oxide layer and an inner spinel layer after 20 minutes at 1100 °C in a post-burn atmosphere of

natural gas with 5.2% oxygen content (Ozturk & Matway, 1997). In air atmosphere with 3 ppm humidity for 30 minutes, the iron oxide layer was observed to be hematite (Fe_2O_3) at 1100 °C, while the content of magnetite (Fe_3O_4) increased by increasing the temperature to 1200 °C (Carvalho et al., 2006).

For a longer oxidation time (1–5 h), the effect of temperature and time was studied for austenitic stainless steel, especially for AISI 304 grade. In a nitrogen atmosphere containing 8.7% O_2 , a higher temperature noticeably affected the amount of oxide scale after 1100 °C (Lussana et al., 2014). Correspondingly, in air atmosphere (21% O_2), oxide scale formation started to increase significantly as early as at the beginning of the exposure by increasing temperature from 1000 °C to 1100 °C (Su et al., 2022, Zhang et al., 2021). In a steam H_2O -Ar atmosphere for 1 hour, the amount of oxide scale started to increase between temperatures of 1150 and 1200 °C (Zheng et al., 2018).

Oxide scale structure was observed to develop by increasing temperature and time. At 900 °C, the Cr-rich oxide layer only thickened between 1 and 5 hours in air. The Cr-rich oxide layer was also observed after 1 hour at 1000 °C, but an increase in time developed the structure to become multilayered, including $(\text{FeCr})_3\text{O}_4$ spinel. At 1100 °C, the structure of the attached internal oxide layer was more of a network-like structured combination with spinel and metallic phases, and the thickness of the layer grows from below 10 μm to 130 μm by increasing time. However, the internal oxide scale was found to form pocket-like structures at 1200 °C after 1 hour before it developed to continuous internal layer. (Su et al., 2022) Respectively, isothermal oxidation for 3 hours in a 5% O_2 -containing atmosphere (O_2 - CO_2 - N_2) was found to produce an oxide pocket structure at 1100 °C, while the structure developed to two-layered at 1300 °C (Laukka et al., 2017). However, the internal structure of oxide scale was only pocket-type in a simulated post-burn atmosphere of natural gas with air using dynamic heating with target temperatures of 1200–1275 °C (Laukka et al., 2021).

For ferritic grades, the amount oxide scale increased evenly for grade 430 by raising the temperature in 30 °C increments within a temperature range of 1000–1150 °C, when oxidation was performed in humid air (18% H_2O) for 120 minutes. During oxidation, the structure of the oxide scale was formed as layers containing iron oxide and spinel layers. (Cheng et al., 2015b) However, a different effect of temperature on the oxidation of a higher chromium alloyed ferritic stainless steel between 1120 °C and 1150 °C was observed, in which the oxide scale structure remained nodule-like internal oxidation (Cheng et al., 2014). In a post-burn atmosphere of natural gas with 3% oxygen content, structural change of oxide scale

was observed for AISI 430 after 2 hours between temperatures of 1050 °C and 1150 °C, where the oxide scale nodules developed to a two-layered structure (Osei et al., 2021).

3.2.3 Steel grade

Microstructure has an effect on the oxide scale formation of stainless steels due to higher diffusion rate of chromium in ferritic grades in comparison to austenitic grades. This enables the maintenance of protectiveness of the chromium oxide layer during oxidation (Young, 2008). Either austenitic (face-centered-cubic, fcc) or ferritic (body-centered-cubic, bcc) crystal structure is formed depending on the amounts of different alloying elements in steel. For example, nickel, carbon, manganese, and nitrogen are austenite-forming elements, whereas chromium, molybdenum, niobium, and titanium are ferrite-forming elements. (Davis, 1994) When heated, pure iron is transformed from bcc to fcc at temperature of about 910 °C (Basinski et al., 1955; Kaufman et al., 1963), but by alloying with ferrite-forming elements, ferritic stainless steels retain their ferritic structure even when heated. Ferritic stainless steel grades with higher carbon content, such as AISI 430 (0.2% C), still have austenite structure in parallel to ferritic structure during heating. However, lower carbon containing ferritic grades, such as AISI 441 (0.02% C), have been stabilized with e.g. titanium, and they have ferritic structure at all temperatures. (Davis, 1994)

High temperature oxidation between steel grades is significantly dependent on alloying elements. Chromium is the main element for corrosion resistance of stainless steel. Concerning the high temperature oxidation, at least 12 wt.% of chromium is required for the formation of a continuous protective chromium oxide layer at 1000 °C. However, the resistance to high temperature oxidation can be increased by increasing the chromium content to over 20 wt.%. (Tunturi, 1988; Khanna, 2002) Alloying silicon can enhance oxidation resistance. During oxidation, a silicon-enriched oxide layer formed on the oxide-metal interface, and it has been presented to act as a diffusion barrier, decreasing the oxidation rate. (Basu & Yurek, 1991) Nickel has been presented to have a positive effect on oxidation resistance. For example, 28 wt.% chromium has similar corrosion resistance properties as 50 wt.% nickel with 10 wt.% chromium in Fe-Cr-Ni alloys at 1200 °C in air atmosphere (Khanna, 2002). Additionally, austenitic stainless steels have a lower resistance to rapid temperature changes compared to ferritic stainless steels, which increase the spalling of oxide scale. Increase of nickel content improves the

resistance of austenitic stainless steels, providing good resistance up to 1150 °C. (Tunturi, 1988)

For ferritic stainless steel grades, AISI 430 had lower oxidation resistance compared to higher chromium content containing steel grades AISI 443 and AISI 445. Additionally, oxidation resistance was even better for AISI 445. It was suggested this was due to higher alloying contents of manganese and molybdenum promoting Mn-Cr spinel layer formation, which reduces the evaporation of chromium and maintains the protection of chromium oxide in a humid atmosphere. Hence, oxidation progressed to only as nodule-like structured oxide scale for AISI 445, while the oxide structure was layered with iron oxide and spinel for AISI 430 and AISI 443. (Cheng et al., 2016) For AISI 430, aluminum alloying was observed to decrease oxide scale formation in simulated reheating conditions (Osei et al., 2020; Osei et al., 2021). For austenitic stainless steel grades, AISI 304 is less oxidation resistant than AISI 316 because it loses its protectiveness in air at 1000 °C after 2 hours compared to 77 hours, respectively (Habib et al., 2011). For austenitic grade AISI 304, microalloying of titanium or boron was observed to reduce oxidation for 3 hours at temperatures of 1200–1250 °C with simulated post-burn atmosphere of natural gas (Laukka et al., 2019). The thickness of oxide scale for molybdenum alloyed austenitic AISI 316L was determined to be greater than austenitic AISI 304 in dynamic heating for 150 seconds at 1120 °C in simulated CH₄-air combustion atmosphere 3% O₂. However, the greater thickness of the AISI 304 sample in short-term heating and thus, a slightly lower heating of the surface has been suggested to be the reason for lower thickness of the oxide scale. (Gonzales et al., 2008).

The grain size of stainless steel also influences oxidation due to differences in the diffusion rates between grain boundaries and a lattice structure. The grain boundary diffusion coefficient was determined to be five orders of magnitude higher than lattice diffusion for AISI 304 at 850 °C in air (Sabioni et al., 2012). For example, small-grained AISI 304 stainless steel (4 µm) formed a continuous chromium oxide layer at 800 °C in air, while large-grained AISI 304 stainless steel (40 µm) only had chromium-rich oxide near the grain boundaries and iron-rich oxide in the central areas of the grains (Baer & Merz, 1980). Correspondingly, grain size has also been found to have an effect on Cr-oxide layer formation for austenitic alloys (Basu & Yurek, 1991). However, the difference between diffusion methods was smaller at high temperatures. Higher temperature increased diffusion rates, and because of the greater overall area compared to grain boundary area, the lattice diffusion transported more ions toward oxide-gas interface. (Khanna, 2005)

The surface finish was observed to affect the formed oxide scale after heating in simulated reheating conditions. The as-cast sample of AISI 430 with one original oxide surface was heated for 120 minutes at 1150 °C using simulated atmosphere formed oxide scale slightly more when compared to the ground surface (Osei et al., 2020). For AISI 304, differently structured Fe-Cr spinel layers were formed on as-cast and grounded surfaces after 4 hours of oxidation at 1230 °C using a simulated 4% O₂ containing post-burn atmosphere for methane with air. The difference in the layer structure was presented to be due to different shapes of austenitic grain between as-cast surface with equiaxed grain and grounded surface with columnar grains. (Pistorius et al., 2003) Furthermore, surface preparation of AISI 316 by mechanical polishing produced less oxide scale compared to electropolishing which was suggested to be due to enhanced chromium diffusion and then, maintaining the protection of the Cr-rich oxide layer (Kuiry et al., 1994).

4 Materials and methods

Oxide scale formation of stainless steels in simulated annealing and reheating conditions was studied in this research. The heating simulations were performed in a laboratory furnace in simulated post-burn atmosphere conditions.

4.1 Steel samples

Stainless steel materials used in this research were supplied by Outokumpu Stainless Oy. The stainless steels were in an as-cold rolled state before final annealing process in Publications I–III and as-cast before the reheating process in Publication IV. The following steel grades were studied in the following Publications: austenitic AISI 304 (I), austenitic AISI 309 and ferritic EN 1.4622 (II), austenitic AISI 304 and ferritic AISI 441 (III), and austenitic AISI 301 and AISI 304 and ferritic AISI 444 (IV). The chemical composition of each steel grade is presented in Table 1.

Table 1. Chemical composition of stainless steel grades concerning relevant elements, in wt.%.

AISI	EN	C	Si	Mn	Cr	Ni	Mo	Ti	Nb	N	Fe	Publ.
301	1.4310	0.10	1.25	1.28	16.3	6.5	N/A ³	N/A ³	N/A ³	0.090	Bal	IV
304 ¹	1.4301	0.04	0.47	1.27	18.2	8.1	N/A ³	N/A ³	N/A ³	0.056	Bal	IV
304 ²	1.4301	0.03	0.43	1.42	18.1	8.0	N/A ³	N/A ³	N/A ³	0.056	Bal	I, III
309	1.4828	0.05	1.9	≤2.00	19.3	11	N/A ³	N/A ³	N/A ³	≤0.11	Bal	II
441	1.4509	0.02	≤0.7	≤0.7	17.6	≤0.5	N/A ³	N/A ³	N/A ³	N/A ³	Bal	III
444	1.4521	0.014	0.47	0.37	17.7	0.2	2.01	0.13	0.34	0.012	Bal	IV
-	1.4622	0.02	0.45	≤0.80	21.0	N/A ³	N/A ³	0.15	0.25	0.02	Bal	II

¹ as-cast, ² as-cold rolled, ³ not available

The thickness of as-cold rolled state materials was 1.5–2 mm. The materials were cut from the 200 x 200 mm² plates to samples with dimensions of 30 mm in height and 25 mm width. For reheating tests, as-cast material was cut with dimensions of 2 mm thickness, 30 mm height, and 20 mm width. The cutting was performed with water cooling using a Struers Secotom-10 precision cutting machine. The alumina cut-off wheels 30A15 and 30A20 were used for cutting.

For heating tests, a 2 mm-diameter hole was drilled into the top of the sample. The surface area of the samples was measured by a digital caliper with an accuracy of 0.01 mm for thermogravimetric tests. The measurements were taken at three

points on each side to get averages of sides. Before heating tests, the surfaces of the samples were cleaned with ethanol and/or acetone.

4.2 Experimental procedure

The laboratory furnace was a vertical tube furnace. The sample was heated in the furnace by hanging from analytical balance in thermogravimetry measurements (TG) (Publications III, IV) or hanging from an elevator system in short annealing heating (Publications I–III). Schematic figures for configurations of the furnace are illustrated in Fig. 2. The simulated post-burn gas atmosphere was fed in the furnace using a continuous flow rate of 2 L/min with CO₂, N₂, O₂ gases and air, as required, were fed through mass flow controllers and a preheater to the furnace. A peristaltic pump was used for controlling the amount of water fed to the system. Water vapor was injected into the gas line, which was pre-heated to a temperature of around 300 °C to ensure evaporation of the water. The temperature (electric heating coil) and gas atmosphere (mass flow controllers and peristaltic pump) of the furnace were controlled by a computer by a pre-defined programs set to specific set-points for temperature and gas composition. The experiments with different gas atmospheres in the furnace were named by combinations of simulated combustion of fuel gas, methane (M) or hydrogen (H), and oxidant gas, air (A) or oxygen (O) with a free oxygen content (1, 3 or 5%) if necessary to separate atmospheres. For induction simulations in reheating, the naming was performed by combinations of induction (I) and used atmosphere air (A) or nitrogen (N). For example, MA-1 indicates methane combustion with air, producing 1% free oxygen content in the furnace gas atmosphere. The compositions of atmospheres are presented in Table 2.

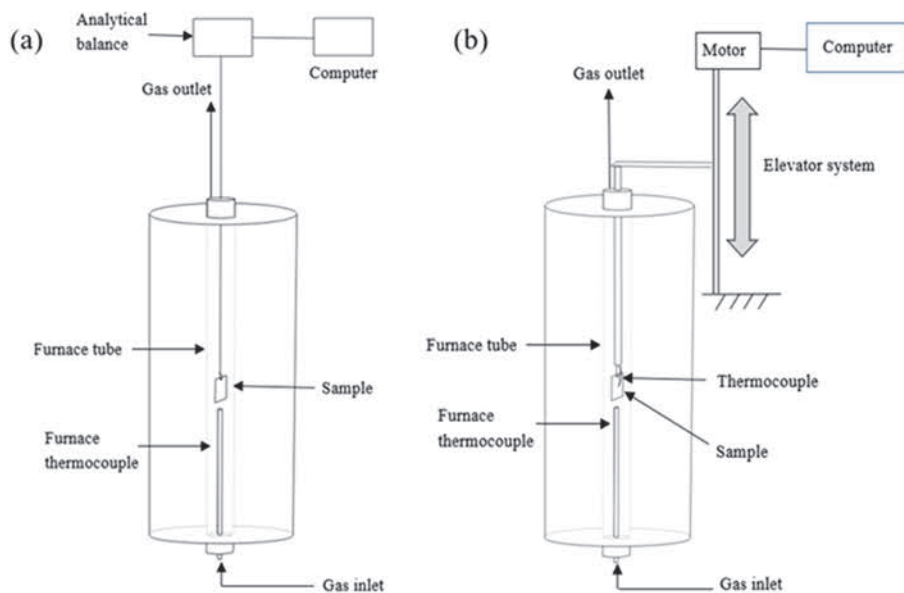


Fig. 2. Schematic figure of the laboratory furnace: a) Thermogravimetry (TG), and b) Furnace equipped with the elevator system. (Modified with permission of Wiley-VCH GmbH from Publication I © 2020 Wiley-VCH GmbH).

Table 2. Composition of the furnace's gas atmosphere. (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023).

Heating simulation type	Gas atmosphere				Gas composition (vol.%)				Publication
	ID	Fuel gas	Oxidant gas	Excess of oxidant gas (vol%)	CO ₂	H ₂ O	N ₂	O ₂	
Combustion	MA-1	CH ₄	air	0.6	9.1	18.1	71.9	1.0	III
	MA-3	CH ₄	air	20.0	8.1	16.1	72.6	3.2	I-IV
	MA-5	CH ₄	air	34.5	7.2	14.5	73.3	5.0	III
	MO	CH ₄	O ₂	5.0	32.3	64.5	-	3.2	II-IV
	MHO	CH ₄ /H ₂	O ₂	5.0	19.4	77.7	-	2.9	IV
	HO-3	H ₂	O ₂	6.7	-	96.8	-	3.2	III, IV
	HO-5	H ₂	O ₂	10.5	-	95.0	-	5.0	III
Induction	IA	-	-	-	-	-	79.0	21.0	IV
	IN	-	-	-	-	-	100	-	IV

Both heating type experiments were performed by hanging the sample inside the furnace from the drilled hole near the edge using a platinum wire. Before each test, nitrogen flow was kept in the furnace to removal moisture and to prevent oxidation of the sample during temperature equilibration. For the elevator system, the sample was hung from a platinum hook in the system and the vertical position of the sample was changed in the furnace to provide the heating profile. The computer-controlled motor is responsible for moving the sample to the desired positions in the furnace. The sample's position changes based on different temperature zones of the furnace from the coolest part at the open top to the hotspot at the vertical center of the furnace. Initially, a calibration curve was measured from the furnace in different temperatures to formulate a specific temperature in sample's position function inside the furnace. The motor is then instructed by a test program to follow a vertical position path to mimic a pre-defined industrial annealing furnace temperature curve. The furnace temperature was measured by a thermoelement at the vertical center of the sample. Examples of heating profiles for annealing simulations for Publications I–III are presented in Fig. 3a. The temperature of the furnace was between 1000 to 1200 °C for annealing. The heating times of the profiles were 1–5 min meaning the time after the preheating zone to the starting point of cooling. The heating conditions of experiments are presented in Table 3.

Table 3. Heating conditions of experiments.

Heating	Steel grade	Furnace temperature (°C)	Time (min)	Pickling	Publication
Annealing	AISI 304	1100, 1125, 1150, 1175, 1200	1, 3, 5	X	I
	EN 1.4622	1000, 1050, 1100	1, 3, 5	X	II
	AISI 309	1100, 1150, 1200	1, 3, 5	X	II
	AISI 441	1000, 1100	1, 5		III
	AISI 304	1100, 1200	1, 5		III
Reheating	AISI 301	1225, 1275	87, 180		IV
	AISI 304	1225, 1275	87, 180		IV
	AISI 444	1150	87, 180		IV

For TG experiments, the samples were hung from an analytical balance in a hotspot of the furnace. Previous calibrations tests showed with the same furnace that the temperature change in the hotspot was about 3 °C from the bottom level of the sample in the furnace to the middle level of the sample (1.5 cm). The distance of sample from the top of the furnace was kept the same for each sample to minimize the temperature difference between them. The TG experiments were performed either in isothermal conditions or dynamically by changing the furnace temperature

according to the desired heating profile. Utilizing the dynamic heating curve to control the temperature of the laboratory furnace itself in longer reheating tests enabled the collection of weight change data, as opposed to the more rapid annealing tests where the dynamic curve was achieved by altering the samples' vertical location. The isothermal experiments were performed for as-cold rolled state material to investigate the differences in mass change between steel grades and heating conditions (Publication III). The heating time was 15 minutes and heating temperatures and atmospheres were similar to the ones used in annealing experiments in Publication III. Dynamic experiments were performed for as-cast material to simulate the slab's surface temperature during the industrial reheating process in Publication IV. The heating profiles for reheating simulations are presented in Fig. 3b. The target heating temperatures were between 1150 to 1275 °C. The holding time in dynamic conditions was 180 min for the combustion simulations and 87 min for the induction simulations. The heating conditions of experiments are presented in Table 3. After heating experiments, the samples were removed from the furnace and allowed to cool down to room temperature in ambient air.

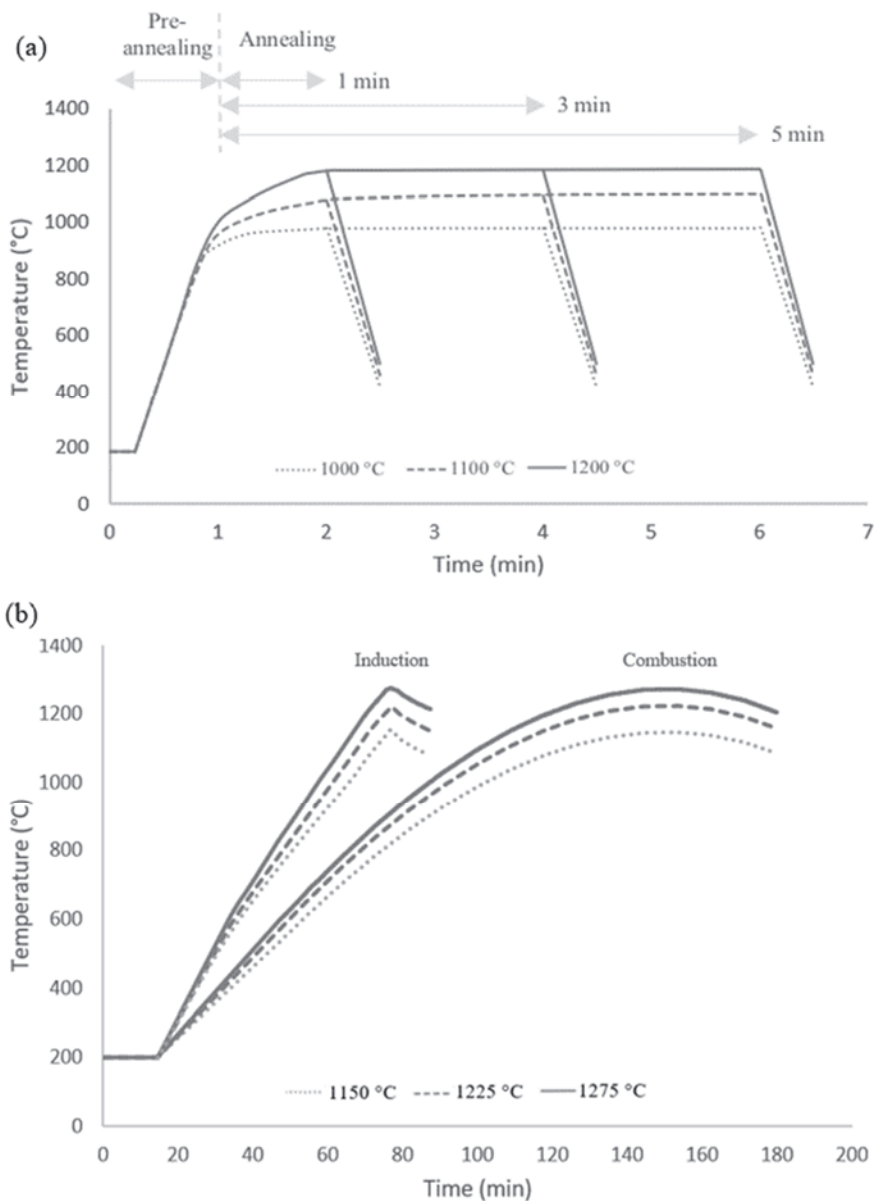


Fig. 3. Schematic target heating profiles: a) Annealing, b) Reheating. (Modified with permission of Wiley-VCH GmbH from Publication III © 2022 Wiley-VCH GmbH and under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

4.3 Characterization

For field emission scanning electronic microscopy (FESEM) analysis, annealed and reheated samples were mounted in epoxy and impregnated using a Struers CitoVac vacuum chamber, cut in half crosswise, and polished. The crosscutting was made in the middle of the sample. The polishing was performed with a Struers LaboPol-6 machine using grinding papers and surfaces. Polished surfaces were coated with a thin carbon layer to provide sufficient electrical conductivity for the FESEM.

The structure, composition and thickness of oxide scale were investigated in the sample from cross-sections using a Zeiss Ultra Plus FESEM equipped with an energy-dispersive X-ray spectroscopy (EDS, Oxford Analytics). Backscattered electrons (BSE) were used for image formation in the FESEM. For the analysis of thickness and elemental depth profiles of the attached oxide scales, a glow discharge optical emission spectroscopy (GDOES, Spectrums GDA750) was used. Determination limits for the oxide scale thickness from the profile were an oxygen content of 5% for annealed samples and 100 ppm for reheated samples due to the prevailing oxide scale layer evenness being vaguer in the annealed samples, limiting a larger area's accuracy in determining where the oxide layer ends, and metal substrate begins.

5 Results

5.1 Annealing results

Annealing experiments were performed using steel grades' own annealing temperature range for the annealing furnace of strip material. Thus, the studied temperature ranges were lower for ferritic grades (1000–1100 °C) and higher for austenitic grades (1100–1200 °C). Differences in oxidation progression were also studied between different steel grades. In terms of steel grades, AISI 304 has good corrosion resistance, and it is one of the most used austenitic stainless steel grades. Austenitic AISI 309 is designed for high temperatures alloying more silicon, chromium, and nickel in comparison to AISI 304. The studied ferritic grades are stabilized and have good corrosion resistance, in which EN 1.4622 alloys more with chromium than AISI 441. (Outokumpu Stainless AB, 2013)

5.1.1 *Effect of annealing time and temperature*

For all studied steel grades, a longer annealing time and higher annealing temperature individually promoted further progress of oxidation. The main research matrix for investigation of annealing time and temperature was for AISI 304 with methane-air gas atmosphere with 3% oxygen content (MA-3) (Publication I), in which temperatures from 1100 °C to 1200 °C were studied with 25 °C intervals and times of 1, 3, and 5 minutes. The annealing produced oxide scale structures which are divided as follows: thin chromium oxide layer, Fe-oxide-containing nodules, Fe-oxide-containing nodules with inner oxidation, large Fe-oxide nodules with network-like structured inner oxide pockets, and a two-layered oxide-containing Fe-oxide layer and network-like structured layer. The examples of each oxide scale structure of AISI 304 are shown in Fig. 4, and the elemental composition of EDS points are presented in Table 4. A thin oxide layer formed at the lowest annealing temperature of 1100 °C, and for one minute annealing at temperatures of 1125 and 1150 °C. The composition of the oxide layer was mainly Cr-rich as seen in point 1 in Fig. 4a. When the oxide layer loses its protectiveness, the onset of breakaway oxidation is observed as formation of the Fe-oxide containing nodules on the surface of the stainless steel as seen after 5 minutes at 1125 °C in Fig. 4b. The outer part of the nodules consists of iron oxide, while the inner part of the oxide nodules consists of chromium-rich oxide. In Fig. 4c, internal

oxidation below the nodules is formed after 5 minutes at 1150 °C, at the onset of which enrichment of nickel is observed. Enrichment of nickel in the non-oxidized steel areas is based on the decrease of Cr and Fe contents because of oxidation. After even more demanding annealing conditions for 3 minutes at 1200 °C, oxide scale nodules grow significantly larger and internal oxidation is structured network-like, as seen in Fig. 4d. Additionally, this kind of structured oxide scale could also be found partly combined as a two-layer-like appearance. Under the most demanding annealing conditions, 5 minutes at 1200 °C, the oxide scale structure was only found in two-layer-like form, in which the upper layer was iron oxide, and the inner layer was a network-like structured oxide layer as seen in Fig. 4e. A closer look at the inner network-like layer is shown in Fig 4f, in which the more iron-rich Fe-Cr oxide layer was at the interface of internal and iron oxide layers (point 2). In point 3, the darker gray phase is composed of Fe-Cr oxide, and the lighter gray phase is metallic iron and nickel (point 4). Iron and chromium containing oxide can be defined as a spinel based on the literature.

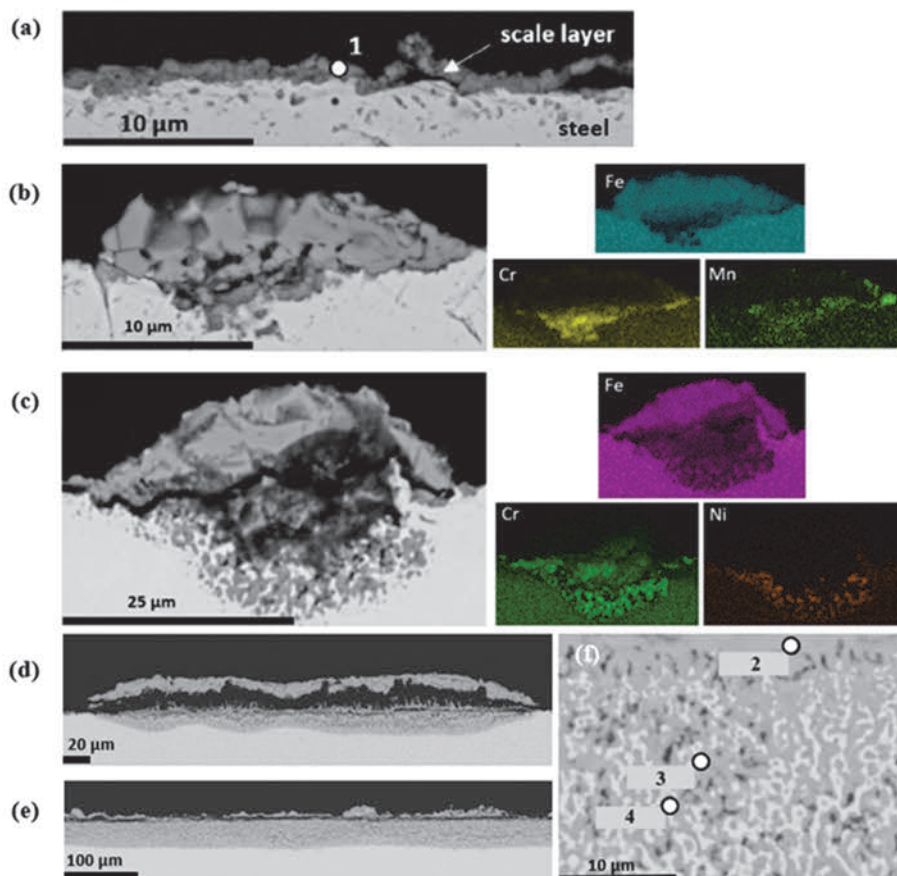


Fig. 4. Oxide scale structures of AISI 304 in CH₄-air gas atmosphere (MA-3) using different annealing conditions: a) Cr-oxide layer at 1100-5min, b) Fe-oxide containing nodule at 1125-5min, c) Fe-oxide nodule with internal oxidation at 1150-5min, d) Large Fe-oxide nodules with network-like internal oxidation at 1200-3min, e) Two-layered oxide at 1200-5min, and f) Enlargement of network-like structure. (Modified with permission of Wiley-VCH GmbH from Publication I © 2020 Wiley-VCH GmbH).

Table 4. Elemental composition of EDS points from Fig. 4–6, in wt.%.

Point	Fe	Cr	Ni	O	Si	Mn	Ti	Nb
AISI 304								
1	9.4	57.6	-	31.0	0.2	1.8	-	-
2	59.2	13.1	-	25.9	0.5	1.3	-	-
3	37.3	34.2	-	26.7	0.3	1.4	-	-
4	57.6	8.8	26.5	6.9	0.2	-	-	-
AISI 309								
5	8.2	58.0	0.8	29.7	0.7	2.6	-	-
6	68.2	18.6	11.9	-	1.3	-	-	-
EN 1.4622								
7	3.0	61.3	-	29.3	0.4	-	0.4	0.8

For austenitic grade AISI 309, three annealing temperatures are investigated (1100, 1150, and 1200 °C) in Publication II. The oxide scale structures for AISI 309 are presented in Fig. 5. Steel grade AISI 309 has higher silicon content than AISI 304, which significantly affects the structure of formed oxide scale and the progress of oxidation in the CH₄-air gas atmosphere (MA-3). Results show by comparing Fig. 4 and 5 that the amount of silicon-enriched oxide formed during annealing is measurably greater for AISI 309 than AISI 304. Silicon-enriched oxide can be seen after every annealing condition as dark phases inside the steel matrix, as the EDS maps in Fig. 5d and 5h illustrate. Silicon oxide enrichment happens mainly in the grain boundaries for steel grade AISI 309, whereas nothing similar was observed for AISI 304.

In addition to silicon enrichment, thin Cr-rich oxide layers are formed on the surface of the steel grade AISI 309 as seen in the EDS maps in Fig. 5d and EDS point 5 in Fig 5f, which is presented in Table 4. Only in the most demanding annealing condition (1200-5min) did the progress of oxidation produce a Fe-oxide-containing nodules as a sign of breakaway oxidation, as illustrated in Fig. 5g and 5h. In the mildest annealing conditions with 1 min at 1100 °C and 1150 °C, the formed uneven surface is seen in Fig 5a. EDS point 6 proves that the material above the smooth surface is steel matrix. Hence, the unevenness of the surface is caused by detaching the steel matrix pieces, which is probably the result of the Si-rich oxide formation inside the steel matrix parallel to the surface level. The corresponding behavior of the surface is also not observed for steel grade AISI 304.

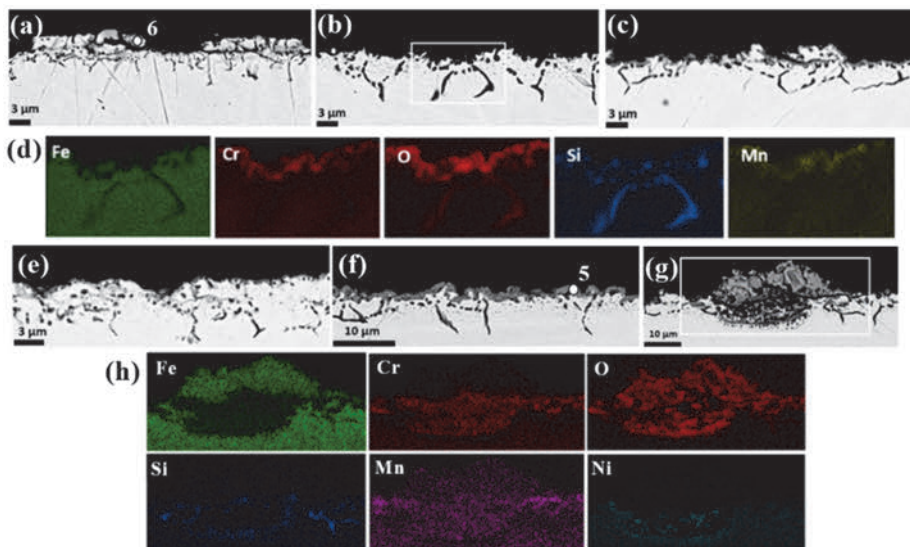


Fig. 5. Oxide scale structures of AISI 309 in CH₄-air gas atmosphere (MA-3) using different annealing conditions. Thin Cr-oxide layer and Si-oxide: a) 1100-1min, b) 1100-3min, c) 1100-5min, d) EDS-maps from part b, e) 1200-1min, and f) 1200-3min. Fe-oxide containing nodules: g) 1200-5min, and h) EDS maps from part g. (Modified under Creative Commons CC BY 4.0 license from Publication II © 2021 Authors).

The oxide scale formed on the surface of ferritic EN 1.4622 (Publication II) in CH₄-air gas atmosphere (MA-3) consisted mainly of chromium-rich oxide, as seen in Fig. 6. The structure of Cr-oxide scale only developed from layer-like to nodule-like in the more demanding annealing conditions. The structure of oxide scale was mainly a thin Cr-rich oxide layer and the onset of a nodule-like formation of Cr-oxide is observed after 3 minutes at 1050 °C. Fig. 6a shows a dark phase of silicon-enriched oxide on the oxide-metal interface under Cr-oxide nodules, as denoted with red arrows after 5 minutes annealing at 1050 °C. Bigger Cr-oxide nodule structures formed after 5 minutes at 1100 °C, as seen in Fig. 6b. EDS point 7 proves that the amount of iron is minimal in the oxide nodule. Based on EDS maps, the lighter areas inside the nodule structure were enriched with iron and niobium.

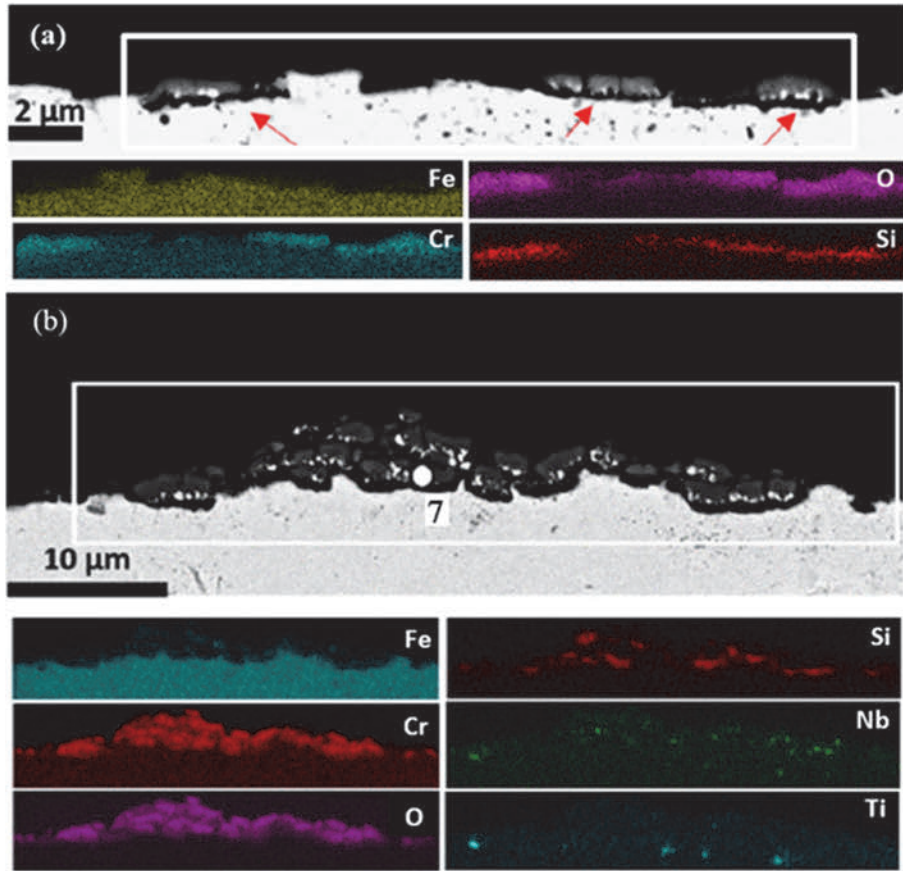


Fig. 6. Oxide scale structures of EN 1.4622 in CH₄-air gas atmosphere (MA-3) using different annealing conditions: a) 1050-5min and b) 1100-5min. (Modified under Creative Commons CC BY 4.0 license from Publication II © 2021 Authors).

For ferritic AISI 441, only two temperatures (1000, 1100 °C) are studied in the CH₄-air (MA-3) gas atmosphere in Publication III. The oxide scale structure for all conditions was the chromium-rich oxide layer. The thickness of the oxide scale layer increased toward a higher temperature and a longer time, and continuous silicon oxide layer is developed in the oxide-metal interface. Oxide scale structures of AISI 441 are presented in Fig. 7.

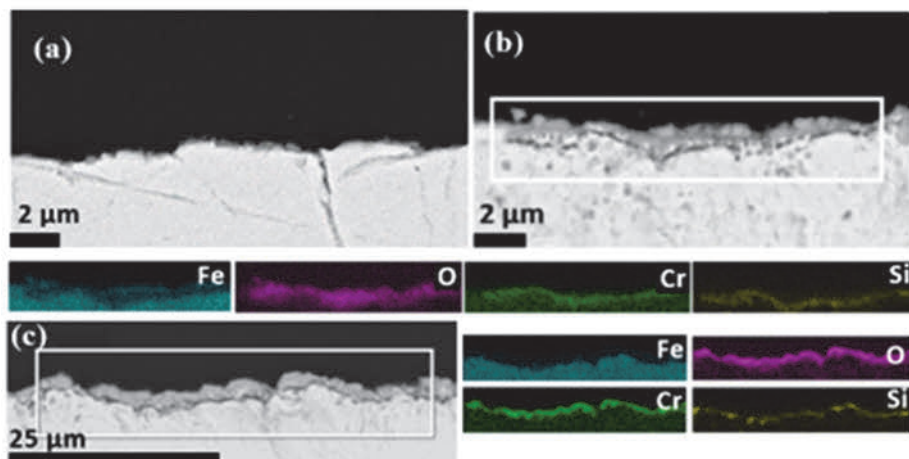


Fig. 7. Oxide scale structures of AISI 441 in CH₄-air gas atmosphere (MA-3) using different annealing conditions: a) 1000-5min, b) 1100-1min, c) 1100-5min. (Modified with permission of Wiley-VCH GmbH from Publication III © 2022 Wiley-VCH GmbH).

GDOES results showed that thin chromium oxide layers consisted of sublayers for all studied steel grades, as seen in Fig. 8. These sublayers were manganese- and iron-enriched at the oxide-gas interface, mainly chromium containing oxide at middle layer, and silicon-enriched oxide at the oxide-steel interface. Enrichment of niobium is observed for ferritic grades, and the enrichment layer is located above the silicon oxide layer. Furthermore, depletion of chromium in the steel matrix below the oxide scale is detected for austenitic grades.

The development of oxide scale structure during annealing with different temperatures and times is observed by elemental curves in GDOES profiles and via the increase in the oxide layer's thickness. Typical elemental profile for the oxide scale structure, which mainly contains a thickened chromium-rich oxide layer can be seen, for example, for AISI 309 after 5 minutes at 1150 °C. Due to GDOES provides average information of measured surface, small number of small nodules have only minor effect on elemental profiles. The thickness of the oxide layer increases in more demanding annealing conditions for all steel grades. The GDOES profiles show that the oxide layer for AISI 309 is slightly thicker than oxide layer for AISI 304 after 5 minutes at a 1150 °C annealing temperature. However, oxidation continues further for AISI 304 at 1200 °C, producing significantly greater thicknesses for oxide scales. For ferritic grades, thicknesses of oxide scale are mildly greater for AISI 441 grade in all the tested annealing conditions.

Elemental concentration depth curves for AISI 304 showed that the profile 1200-5min measurably differs from profiles in milder annealing conditions. Chromium enrichment in the Cr-rich layer is not observed which indicates the Fe-Cr oxide containing layer is attached to the surface. Nickel content of the layer levels out after 2 μm from the surface, when nickel-enriched metallic phases appear in the network-like structured layer. For AISI 309, a similar corresponding oxide structure is not observed from GDOES profiles. Additionally, greater silicon enrichment in oxide scale structures is detected for AISI 309 compared to AISI 304 and for ferritic grade EN 1.4622 compared to AISI 441. Otherwise, GDOES curves for ferritic grades mainly describe the evolution of the oxide structure by an increase of in the thickness of the oxide layer on the surface of the steel with all tested situations still showing low Fe content near the gas-oxide interface and, thus, a clear presence of a protective Cr oxide scale.

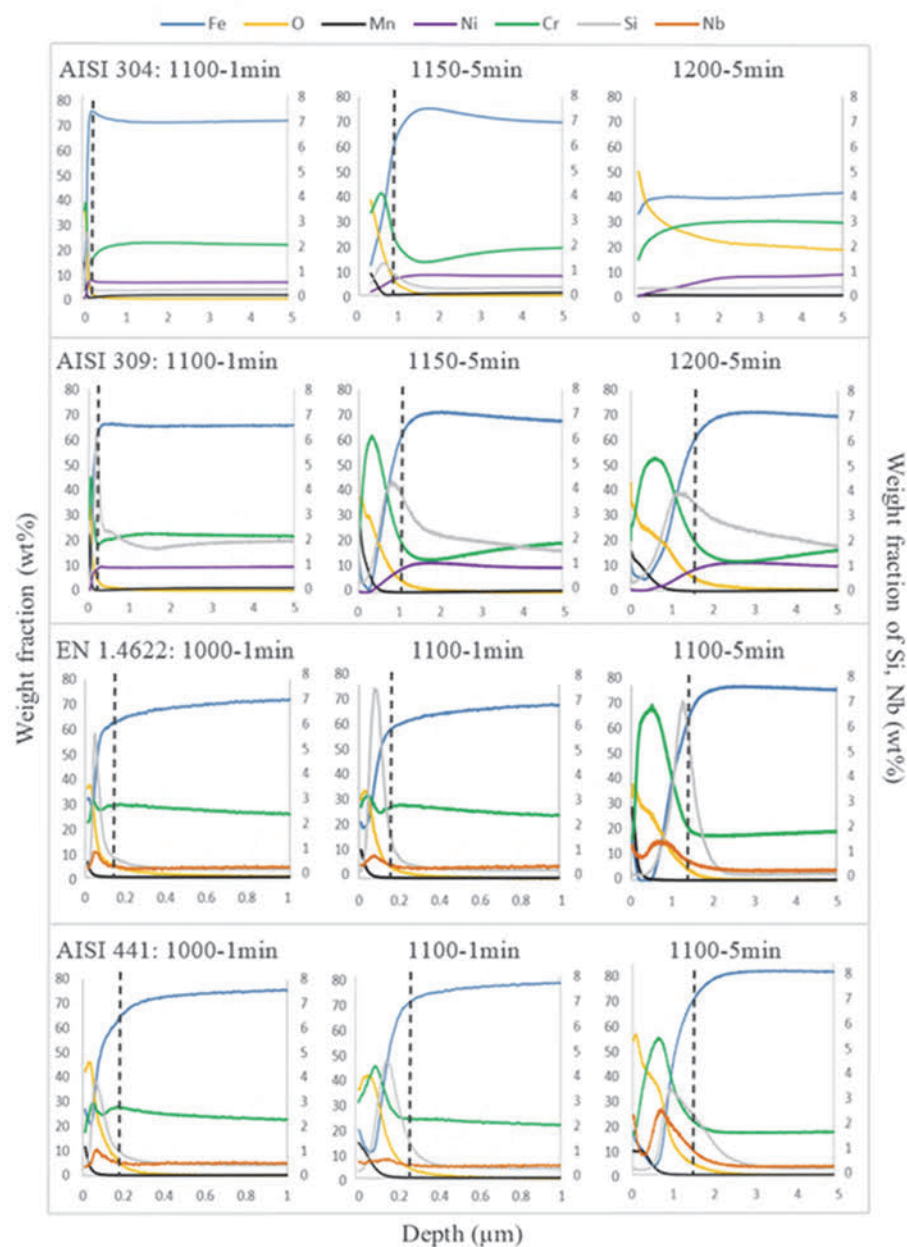


Fig. 8. Development of oxide layers in GDOES depth profiles in MA-3 atmosphere. Vertical dashed line illustrates the thickness of oxide.

5.1.2 Effect of furnace gas atmosphere

The effect of the furnace gas atmosphere for AISI 304 in 1100-5min conditions is presented in Fig. 9. When gas atmosphere is changed from MA-3 (simulating CH₄ burn with air, 3% remnant O₂ in atmosphere) to MO (simulating CH₄ burn with oxygen), the type of oxide scale structure on the surface was developed from the thin Cr-oxide layer to large Fe-oxide nodules with network-like structured inner oxide pockets. Respectively, the difference in the general type between oxide areas in MO and HO-3 (simulating H₂ burn with oxygen, 3% remnant O₂ in atmosphere) methods is not that significant. Instead, in comparison to the MO method, the HO-3 method produced a greater number of those large Fe-oxide nodules, and in addition, inner pocket structures partially combined to form a continuous oxide layer. This would indicate that the oxidation of the surface progresses further with higher water vapor content provided by the atmosphere. The main result of higher free oxygen content of the atmosphere in the HO method is the structural development of the oxide scale. By increasing free oxygen content from 3% to 5%, the internal structure of oxide scale developed a completely continuous internal oxide layer (HO-5), whereas the same structure is only partially continuous with the HO-3 method. Furthermore, the thickness of the attached oxide layer at the surface is determined to have increased from 15 μm to 25 μm by increasing free oxygen content from 3 to 5%.



Fig. 9. Surface of AISI 304 after 5 min annealing at 1100 °C using different atmospheres: a) MA-3, b) MO, c) HO-3, and d) HO-5. (Modified with permission of Wiley-VCH GmbH from Publication III © 2022 Wiley-VCH GmbH).

At a 1200-1min annealing condition, progression of oxidation is also observed on the structures of oxide scales by changing the furnace gas atmosphere, as seen in Fig. 10. For the methane-air method (MA-3), it is typical that only few onsets of oxide nodules are present after 1 minute tests, while Fe-oxide containing nodules are formed with inner oxidation for the methane-oxygen method (MO). The transition between the MO and hydrogen oxygen method (HO-3) shows that nodules grow bigger and internal oxidation extends deeper. The free oxygen content of MA methods slightly increases the amount of nodule onsets for the lowest oxygen content containing MA-1 method, but there are no differences between oxide scale thicknesses or elemental profiles determined by GDOES, as seen in Fig. 11. For HO methods, free oxygen content does not produce a prominent difference between oxide scale structures or the number of nodules.

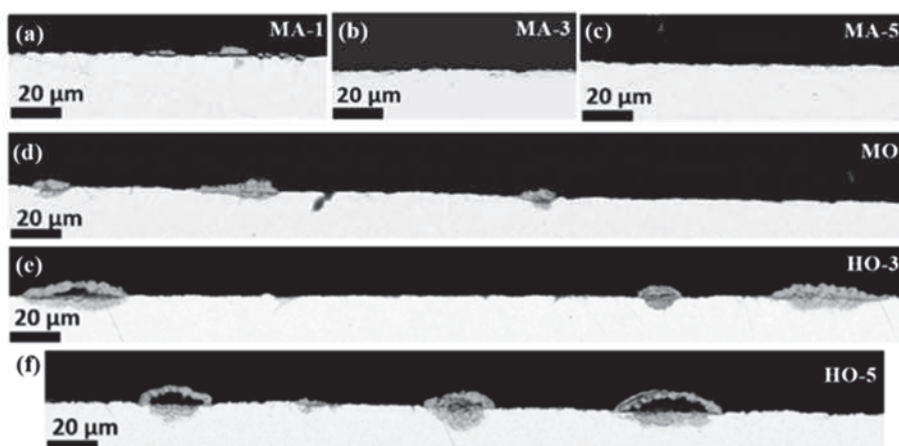


Fig. 10. Surface of AISI 304 after 1 min annealing at 1200 °C using different atmospheres: a) MA-1, b) MA-3, c) MA-5, d) MO, e) HO-3 and f) HO-5. (Modified with permission of Wiley-VCH GmbH from Publication III © 2022 Wiley-VCH GmbH).

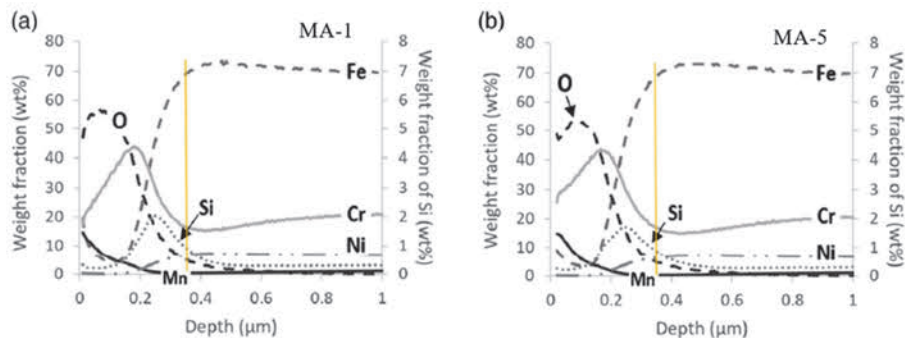


Fig. 11. GDOES depth profiles of oxide scales for AISI 304 after 1 minute annealing at 1200 °C: a) MA-1, and b) MA-5. (Modified with permission of Wiley-VCH GmbH from Publication III © 2022 Wiley-VCH GmbH).

At 1200-5min annealing conditions, the oxidation progressed to a two-layered oxide structure for both methane-air and methane-oxygen methods, as seen in Fig. 12. Thus, the only difference between formed oxide scale layers was the greater thickness of the attached inner oxide layer using oxyfuel method (45 μm) compared to the air-fuel method (35 μm). The thickness of the inner layer is similar in the MO and HO-3 methods, while it was determined to be slightly higher in the HO-5 method's atmosphere (50 μm). The EDS maps of the attached inner oxide layer provide more information about the elemental distribution in the oxide layer, as seen in Fig. 13e. The maps show that there are more silicon enriched oxide phases closer to the oxide-steel interface, while metallic phases are more enriched by nickel further from the same interface.

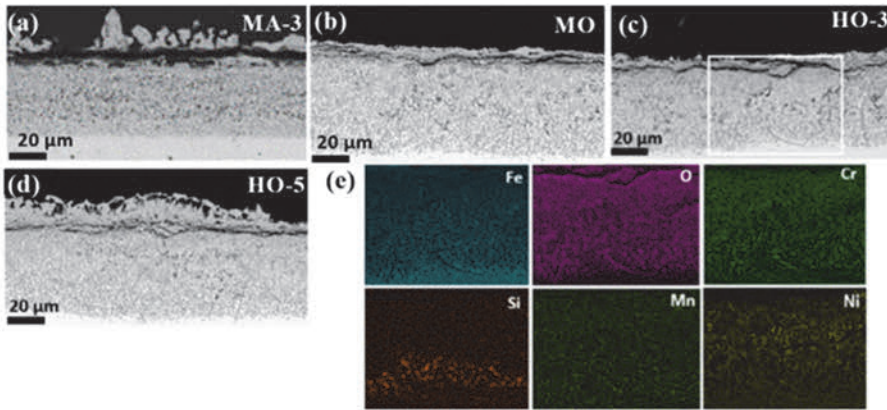


Fig. 12. Surface of AISI 304 after 5 minutes annealing at 1200 °C using different atmospheres: a) MA-3, b) MO, c) HO-3, d) HO-5, and e) EDS maps from part c. (Modified with permission of Wiley-VCH GmbH from Publication III © 2022 Wiley-VCH GmbH).

For AISI 309, the effect of furnace gas atmosphere between MA-3 and MO on the oxide scale structure is more restrained compared to the same atmosphere change for AISI 304. The structure of oxide scale is similar for both oxidants in the studied annealing conditions, but the number of formed nodules is higher for the oxyfuel method in the most demanding annealing conditions, 1200-5min, as seen in Fig. 13.



Fig. 13. Surface of AISI 309 after 5 minutes annealing at 1200 °C using different atmospheres: a) MA-3 and b) MO. (Modified under Creative Commons CC BY 4.0 license from Publication II © 2021 Authors).

For ferritic grade EN 1.4622, the furnace gas atmosphere between MA-3 and MO caused no changes in the structure of oxide scale. Oxidation only proceeds to the point of forming Cr-rich nodule-like oxides using these atmospheres in the most demanding annealing conditions (1200-5min). Differences between the oxide

scales are observed as increased thicknesses, from 1.35 to 1.52 μm , in transition from air-fuel to oxyfuel methods.

For ferritic grade AISI 441, the main change in the structure of oxide scales between methane-air and oxyfuel methods was the development from the Cr-oxide layer to Fe-oxide containing nodules with inner oxidation in the most demanding annealing conditions (1100-5min), as presented in Fig. 14. However, the difference between the MO and HO-3 methods, and between free oxygen contents in the MA and in HO methods, is minor. The development of oxide scale on the surface between heating methods is also observed from GDOES profiles, as seen in Fig. 15. Profiles show that chromium peak indicating the Cr-oxide layer with sublayers of enriched manganese, silicon, and niobium is formed after the MA-5 method, while the Cr-peak is widened, and the oxide layer is thickened by using the HO-5 method.



Fig. 14. Surface of AISI 441 after 5 minutes annealing at 1100 °C using different atmospheres: a) MA-1, b) MA-3, c) MA-5, d) MO, e) HO-3 and f) HO-5.

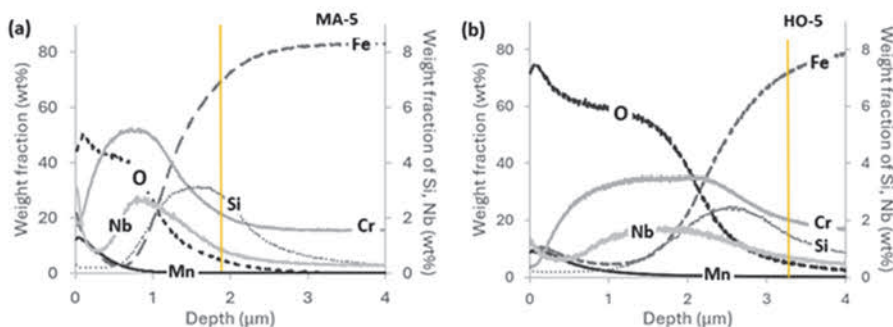


Fig. 15. GDOES depth profiles of oxide scales for AISI 441 after 5 minutes annealing at 1100 °C: a) MA-5, and b) HO-5. (Modified with permission of Wiley-VCH GmbH from Publication III © 2022 Wiley-VCH GmbH).

5.2 Reheating results

Reheating experiments were performed using target temperatures of 1225 °C and 1275 °C for austenitic stainless steel grades AISI 301 and AISI 304. Target temperature of 1150 °C was used for ferritic stainless steel grade AISI 444. For the studied steel grades, AISI 301 has a lower chromium and nickel, but a higher silicon content compared to AISI 304. AISI 444 is molybdenum alloyed ferritic stainless steel grade.

Total sample area normalized weight gain values from TG tests are presented in Table 5. The values show that oxidation in simulated induction atmosphere produced significantly less oxide scale than combustion simulations for both austenitic stainless steel grades. Correspondingly, induction atmosphere simulations also produced less oxide scale for the studied ferritic stainless steel grade, even though the amount of oxidation is minor for combustion simulations compared to austenitic grades. In combustion simulations, the total weight gain values changed differently between steel grades by changing the atmosphere from methane-air (MA) to more water vapor-containing atmospheres. For ferritic grades, the atmosphere produced no difference in oxidation, while for austenitic grades it was a significant factor.

For combustion simulations of austenitic stainless steel grades, two distinct comparisons can be made: increasing the temperature in the same atmosphere or switching the atmosphere at a single temperature. The greatest increase in total weight gain was observed for AISI 304 using hydrogen-oxygen atmosphere (1.9

times), when increasing the target temperature from 1225 °C to 1275 °C. Respectively, the same value was 1.5 times for AISI 301. MA atmosphere had also a similar increase of total weight gain with 1.5 times higher for AISI 301 by increasing the target temperature, which was only 1.2 times for AISI 304.

The greatest increase in total weight gain at a single temperature was observed for AISI 301 at 1225 °C with 4.1 times higher weight gain, when switching atmosphere from air-burned methane (MA) to oxygen-burned hydrogen (HO). The same value for AISI 304 was only 1.2 times. Respectively at 1275 °C, increase in total weight gain from MA to HO was 4 times for AISI 301 and 1.8 times for AISI 304. Furthermore, the increase of the value was almost as high (3.9 times) by switching the atmosphere from MA to MO at 1225 °C for AISI 301, while increase of same value was minor (1.1 times) for AISI 304.

Table 5. Total weight gain values, in mg/cm². (Reprinted under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

Steel grade	Temperature (°C)	Total weight gain (mg/cm ²)					
		IA	IN	MA	MO	MHO	HO
AISI 301	1225	0.4	0.3	14.7	56.7	57.3	59.6
	1275	0.8	0.4	21.7	59.3	65.9	87.8
AISI 304	1225	3.0	0.4	16.3 ¹	17.7 ¹	18.2	19.1
	1275	4.1	0.4	20.0 ¹	22.7 ¹	33.0	35.4
AISI 444	1150	0.3	0.3	1.0	1.0	1.0	1.0

¹(Laukka et al., 2021)

General FESEM images of each steel grade show the cross-section morphology of oxide scale surfaces, as seen in Figs. 16–18. For austenitic AISI 301, a thin oxide layer is formed on the surface after the induction simulation in air at 1225 °C method (IA-1225). Layer-like subsurface oxidation and oxide nodules are observed after induction simulation in nitrogen methods (IN) at both temperatures. After the IA-1275 method, the oxide scale structure contains oxide nodules. Using combustion atmosphere simulating methods, the main oxide scale structure was oxide scale pockets, whose oxide layer above the interface has detached from the surface, which is proved to be Fe-oxide by EDS. The size of oxide scale pockets increased from MA-1225 to MA-1275, and after both methane-oxygen methods (MO), and both oxyfuel methods for methane-hydrogen (MHO-1225) and hydrogen (HO-1225) increased size of pockets even more. MHO-1275 and HO-1275 methods produced a thick two-layered oxide.

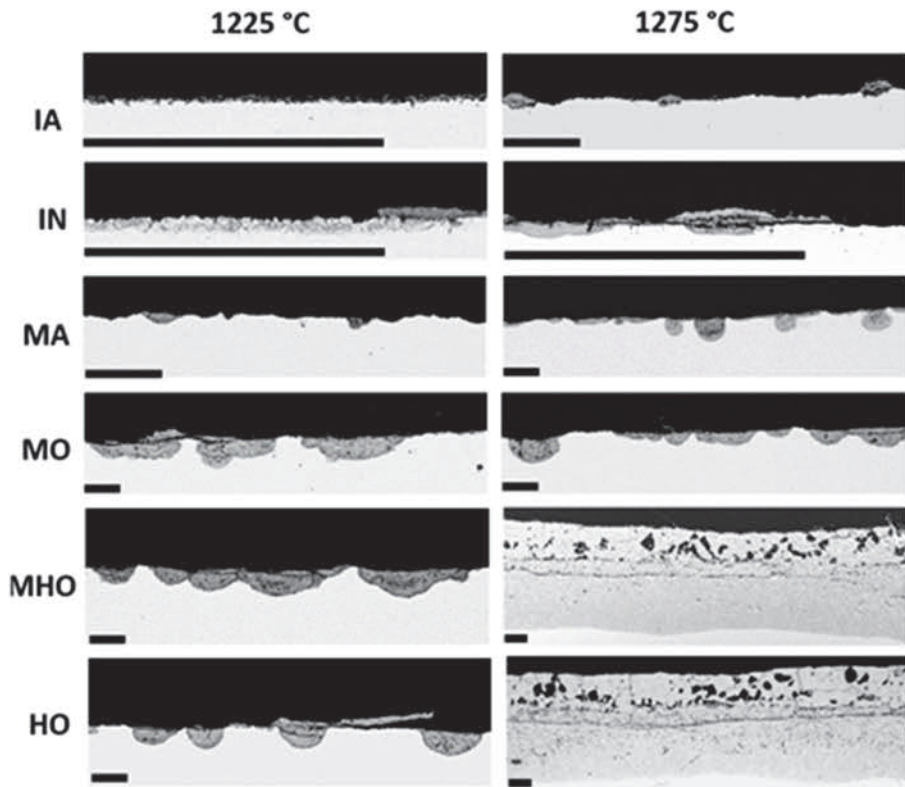


Fig. 16. Oxide scale structures of AISI 301. Scale bar is 200 μm . (Reprinted under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

For austenitic grade AISI 304, IN methods produced a layer-like subsurface oxidation and accumulated the surface oxide. After IA-1225, oxide scale structure was nodule-like, whereas only oxide pockets were observed on the surface after IA-1275. Similar oxide scale pocket structures were observed using MHO- and HO-1225 methods. The size of oxide scale pockets was measurably greater for MHO-1275 and HO-1275 methods, and pockets had combined partially to form a somewhat continuous inner oxide layer structure on the surface.

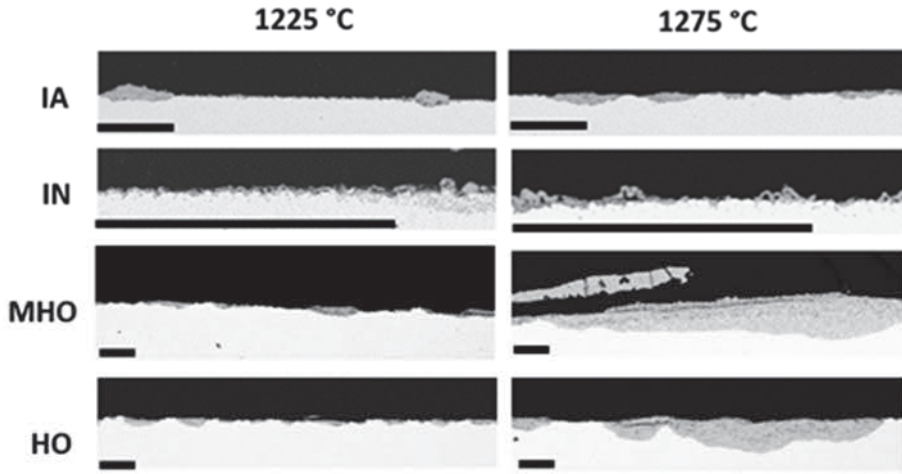


Fig. 17. Oxide scale structures of AISI 304. Scale bar is 200 μm . (Reprinted under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

General FESEM images showed that the oxide scale structure for ferritic grade AISI 444 was an oxide scale layer using all heating methods. The onset of breakaway oxidation is not observed.

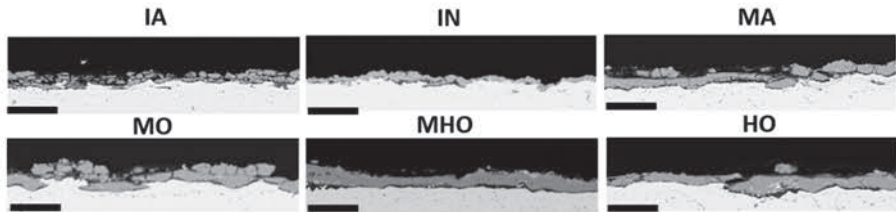


Fig. 18. Oxide scale structures of AISI 444. Scale bar is 20 μm . (Reprinted under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

The chemical composition of oxide scale structures after reheating of AISI 301 is presented in Fig. 19 and EDS points in Table 6. The oxide layer using the induction-air method (IA-1225) consisted mainly of chromium-rich oxide (Fig. 19a), while iron-rich oxide-containing nodules are also formed on the surface using a higher target temperature of 1275 $^{\circ}\text{C}$ (Fig. 19b). EDS points show the distribution of the elements in the nodule, where the upper part is mainly Fe-oxide (point 8) and the inner part is Fe-Cr oxide (point 9). In darker phases, the enrichment of the silicon and chromium content is increased (point 10). For the IN-1225 method, subsurface

oxidation is Cr-rich oxide with manganese enrichment in the darker gray phase and silicon-rich oxide in black phases, as seen in Fig 19c. Oxide scale pockets are formed below the nodules and remain on the surface after outer Fe-rich oxide layer is detached. The composition of the oxide pockets after the MO-1225 method is Fe-Cr oxide, the iron content of which decreases toward the oxide-steel interface, as seen in Fig. 19d. Furthermore, a silicon-enriched oxide is observed at the oxide-steel interface and metallic phases enriched with nickel are closer to the interface. In Fig. 19e, the surface is covered with two-layered oxide after MHO-1275 method. Its upper layer consists of iron oxide (point 11), in which the proportion of chromium increases slightly toward the interface of upper and inner oxide layers, as seen in point 12. Below that interface, internal oxidation consists of Fe-Cr oxide (point 13). A closer look of the internal oxidation shows two phases in Fig. 19f, of which the darker gray is mainly Fe-Cr oxide in point 14 and the lighter gray is metallic phase containing nickel and iron (point 15).

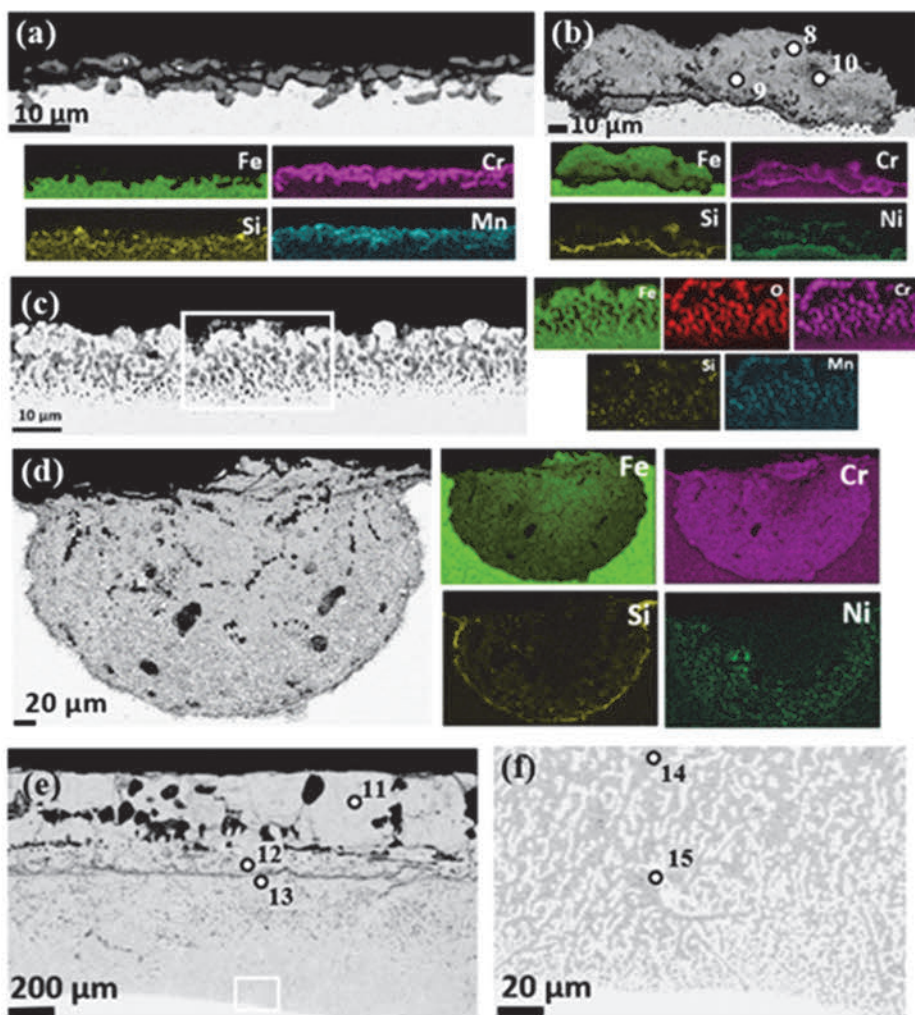


Fig. 19. Composition of oxide scales for AISI 301 after different heating methods: a) IA-1225, b) IA-1275, c) IN-1225, d) MO-1225, e) MHO-1275, f) Enlargement from part e. (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

Table 6. Elemental composition of EDS-points from Fig. 19–21, in wt.%. (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

Point	Fe	Cr	Ni	O	Si	Mn	Nb	Ti
AISI 301								
8	68.25	2.15	-	29.14	-	0.45	-	-
9	33.69	29.65	-	32.93	3.73	-	-	-
10	18.14	36.21	-	37.58	8.05	-	-	-
11	73.55	-	-	25.13	-	1.31	-	-
12	65.46	5.48	-	27.47	0.27	1.23	-	-
13	50.32	20.90	-	27.54	0.14	1.09	-	-
14	43.04	21.02	-	27.85	6.77	1.31	-	-
15	81.81	2.79	15.41	-	-	-	-	-
AISI 304								
16	31.98	35.04	-	29.51	0.50	2.97	-	-
17	37.09	25.17	-	29.21	5.18	3.34	-	-
18	42.39	25.90	1.60	27.21	2.03	0.86	-	-
19	60.32	3.30	36.37	-	-	-	-	-
AISI 444								
20	0.97	64.08	-	34.19	-	-	0.54	0.22
21	43.06	9.15	-	23.62	24.18	-	-	-
22	92.20	6.69	-	-	1.11	-	-	-

Composition of oxide scale structures after various tests for steel grade AISI 304 is presented in Fig. 20. Along with a thick outer Cr-rich oxide layer, nodules containing Fe-oxide formed using the IA-1225 method (Fig. 20a). With the IN-1225 method shown in Fig 20b, the surface oxide layer is Fe-Cr oxide (point 16) and subsurface oxidation had formed Fe-Cr oxides with silicon enriched phases (point 17). For MHO-1225 method, the internal oxide is structured layer-like (Fig 20c), in which darked gray phase is Fe-Cr oxide (point 18) and lighter gray phase is metallic containing nickel and iron in point 19. As oxidation continues further, internal oxide structure is developed to network-like structure using MHO-1275 method as seen in Fig 20d. The composition of the structure's phases is similar to the phases in layer-like structured internal oxidation as seen in EDS maps in Fig 20e.

Ferritic AISI 444 produced a relatively thin layer-like structured oxide after every heating method. An example of oxide scale layer composition is shown in Fig. 21, which is formed using the methane-air method. EDS-results show that the oxide layer has high chromium content (64 wt%) with minor iron content indicating a Cr₂O₃ layer (point 20). The oxide layer also has sublayer as enriched manganese

at the oxide-gas interface and enriched silicon at the oxide-metal interface (point 21). The light phase inside the oxide layer is mainly metallic iron (point 22).

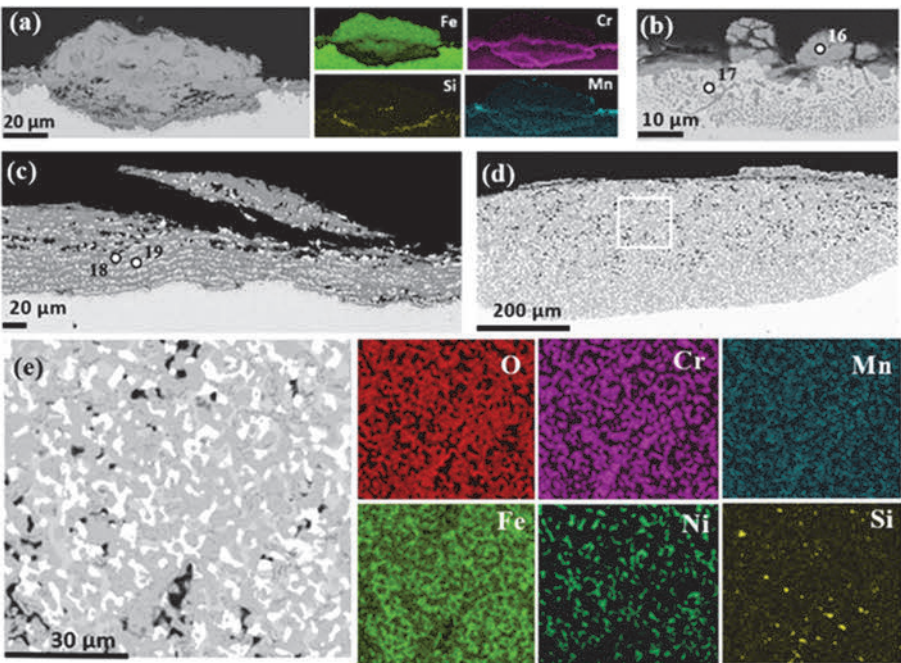


Fig. 20. Composition of oxide scales for AISI 304 after different heating methods: a) IA-1225, b) IN-1225, c) MHO-1225, d) MHO-1275, and e) Enlargement of part d with EDS maps. (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

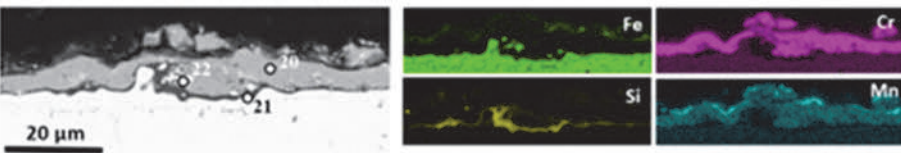


Fig. 21. Composition of oxide scales for AISI 444 after MA-1150 method. (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

GDOES results provide information on the oxide scale layer on the surface of the steel grades after different heating methods, which support the FESEM-EDS

characterization. The examples of the GDOES depth profiles are presented in Fig. 22 and the thickness of oxide scale layers measured by GDOES is shown in Table 7. From austenitic grades, a chromium oxide layer is observed by the increase of chromium content at peak followed by chromium depletion. The methods, whose profiles clearly indicate a Cr-oxide layer, are IA-1225 and IA-1275 for AISI 301, and IA-1225 for AISI 304. If the chromium peak and depletion hollow become more level, the profiles indicate a more Fe-Cr oxide type of layer. For example, IN methods for AISI 301 produce less of a chromium-rich layer and the thickness of the layers remains less compared to induction-air methods. For AISI 304, the decrease in chromium enrichment is observed from the presented methods HO-1225, IA-1275, and IN-1275 compared to the IA-1225 method, which correlates with the oxide scale structure determined by FESEM-EDS. The thicknesses of oxide scale layers showed that the amount of attached oxide scale is within the same magnitude (around 40 μm) after the higher temperature IA method than lower temperature combustion methods (MHO-1225, HO-1225), corresponding to observations of the overall cross-sections from oxide scale surfaces. Furthermore, the difference in the profiles between austenitic steel grades after the IA-1275 method showed more progression of oxidation for AISI 304.

For ferritic AISI 444, the shape of GDOES profiles is similar after every heating method. The structure based on profiles is the Cr-oxide layer, where the enrichment of manganese and silicon in sublayers especially stands out. The thickness of the oxide scale layer increases slightly from the induction-nitrogen method to the induction-air method and to combustion methods (MA-HO).

Table 7. Thickness of attached oxide scale (μm). (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

AISI 301	Thickness	AISI 304	Thickness	AISI 444	Thickness
IA-1225	13	IA-1225	33	IA-1150	11
IN-1225	11	IN-1225	9	IN-1150	8
IA-1275	37	MHO-1225	45	MA-1150	14
IN-1275	14	HO-1225	38	MO-1150	13
		IA-1275	39	MHO-1150	15
		IN-1275	27	MO-1150	15

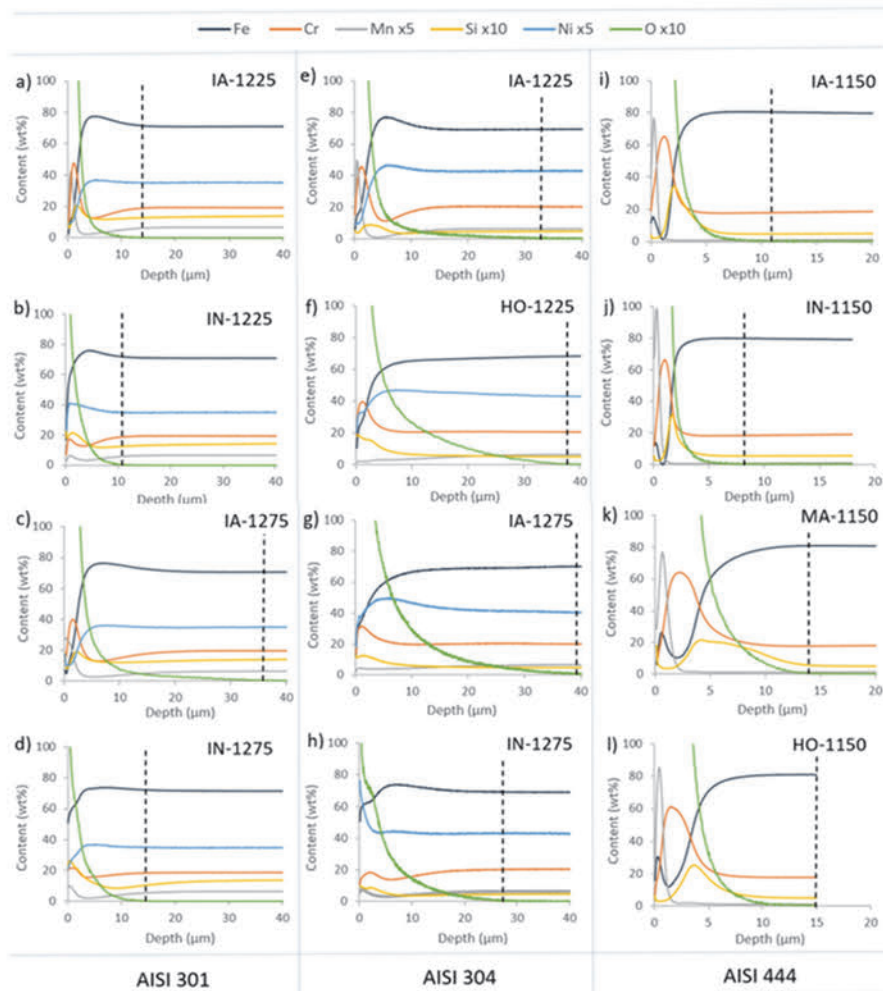


Fig. 22. GDOES depth profiles of elements after different heating methods for AISI 301 (a–d), for AISI 304 (e–h) and for AISI 444 (i–l). (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

6 Discussion

The suitability of stainless steel grades in the transition of furnace heating toward fossil-free methods has been examined in terms of oxide scale formation. The focus in Publication I was on the optimization of current heating method (MA-3) with a comparison of the annealing surface on the subsequent electrolytic pickling efficiency in 17 wt.% sodium sulfate (Na_2SO_4) to clean the annealed surface, whereas Publications II–IV were more focused on the comparison of the heating methods. The number of different annealing samples was 77, the number of short-term isothermal heating samples was 24, and there were 26 reheating samples, which produced extensive information about the connection of oxidation between steel grades and heating conditions.

6.1 Difference between steel grades

Annealing typically produces a thin oxide layer on the surface of the stainless steel, but the progression of the oxidation is dependent on the steel grade. The summary of formed oxide scale structures using the current methane-air method (MA-3) with different annealing times and at different temperatures is illustrated in Fig. 23. Oxide structures are divided into five categories in order of severity from least to most severe: thin oxide layer, oxide nodules, oxide nodules with internal oxidation, large oxide nodules with network-like structured internal pockets, and two-layered oxide. Fig. 23 shows that oxidation during annealing differs significantly between steel grades. The onset of breakaway oxidation as a formation of iron oxide-containing nodules appeared only for austenitic grades in the studied conditions. Furthermore, the onset of the breakaway oxidation happened earlier and at lower temperatures for AISI 304 than for AISI 309. Thus, oxidation progressed to a two-layered structure for AISI 304, while only a nodule formation is observed for AISI 309 after annealing of 5 minutes at 1200 °C. Oxide scales of ferritic grades are Cr-rich oxides. When oxidation during annealing proceeds to more demanding conditions, those oxides developed into nodule-like shapes for EN 1.4622, while the AISI 441 remained layer-like.

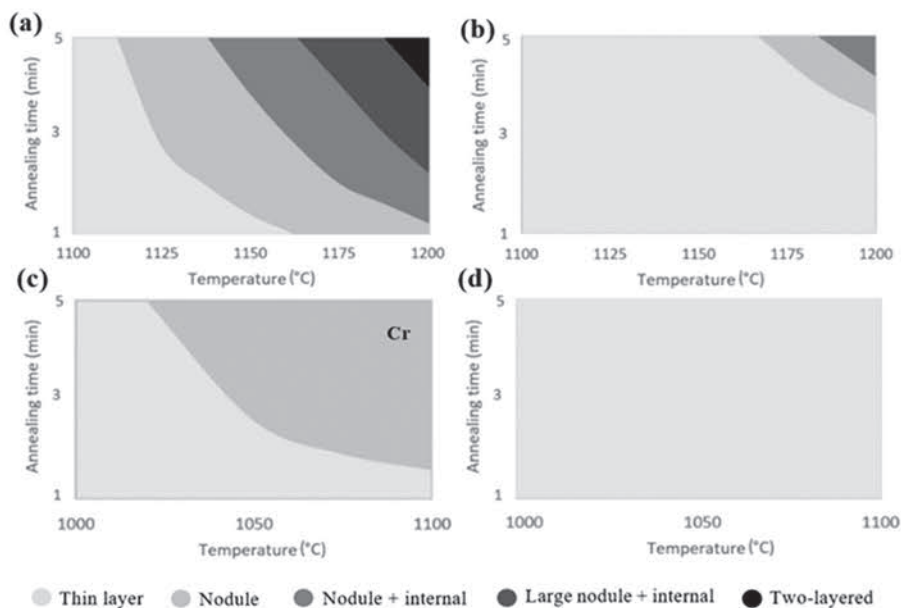


Fig. 23. Oxide scale structures formed in different temperature and duration in CH₄-air gas atmosphere (MA-3): a) AISI 304, b) AISI 309, c) EN 1.4622, and d) AISI 441. In part c), the Cr presents chromium-rich oxide nodules.

Alloying of the steel grades has a major impact on oxide scale formation. When comparing studied austenitic grades, AISI 304 is less alloyed by chromium and silicon compared to AISI 309. Both elements have beneficial effects on increasing oxidation resistance, indicating AISI 309 is more resistant to oxidation than AISI 304, which is proved by the oxide scale results in this study. For AISI 309, higher chromium content promotes the maintenance of the protectiveness of the Cr-oxide layer both for longer periods of time in a single atmosphere and in higher temperatures overall. Thus, the onset of breakaway oxidation requires a higher temperature and/or longer time compared to AISI 304.

Oxidation of silicon is clearly greater for AISI 309 grade, and silicon oxide was observed to form in grain boundaries inside the steel matrix and below the chromium oxide layer in the oxide-steel interface. It is suggested that silicon oxide (SiO₂) formation hinders the oxidation rate. Even the non-continuous silicon oxide layer, as formed on AISI 309, has been found to have this effect, while the continuous layer would be more effective. Silicon oxide formation is mainly observed in grain boundaries because diffusion there is faster than inside the grains,

and thus oxide scale formation happens faster. (Basu & Yurek, 1991) In this thesis, the annealing conditions for oxidation of AISI 304 were too demanding to keep the formed chromium oxide layer as a protective one. Also, silicon oxide content of AISI 304 could be too low to form clear silicon oxide phases like on AISI 309, but the increase of the silicon peak in GDOES profiles proved the enrichment of the silicon on the oxide-steel interface. However, a higher silicon content (0.96 wt.%) of AISI 304 compared to the silicon content of the AISI 304 in this study (0.43 wt.%) and less demanding heating conditions (1000 °C, 2 h, steam atmosphere) has seen SiO₂ being present at the grain boundaries (Zheng et al., 2018). Furthermore, other differences in surface structures are found between steel grades, such as steel matrix pieces on the surface of AISI 309. A similar phenomenon is not observed on AISI 304. Silicon oxide formation inside the steel matrix as parallel to the surface could be the reason for the detachment of matrix pieces because spallation during cooling is possible at the SiO₂-steel interface (Evans, 1983).

The chromium content of studied ferritic grades is different in that ferritic EN 1.4622 has a higher chromium content (21.0 wt.%) than AISI 441 (17.6 wt.%), which could be the first reason for nodule-like chromium oxide formation on the surface. Correspondingly, AISI 441 has been found to form nodule structures of Cr-rich oxides in long-term conditions (Wongpromrat et al., 2015; Parry et al., 2018). Thus, Cr-rich nodule formation is also possible for AISI 441, but it would require milder oxidation conditions i.e. lower temperature with longer heating time.

In reheating studies, AISI 301 has lower chromium content but higher silicon content compared to AISI 304, which does not make the comparison of oxidations as linear as in annealing studies. However, elemental distribution between austenitic steel grades could be the reason for the difference in oxidation rate and oxide scale structure in the MA-3 atmosphere. The combination of lower chromium and higher silicon contents retain protectiveness of the oxide layer better for AISI 301 at 1225 °C, but at a higher target temperature (1275 °C), oxidation already progresses further compared to AISI 304. Correspondingly, silicon has been found to equalize the oxidation differences between steel grades of low and high contents of chromium. At 900 °C, long-term studies in air showed that the amount of oxide scale for high silicon containing AISI 304 decreased from low silicon containing AISI 304 and remained at the level of high chromium AISI 310 (Paúl et al., 2007).

6.2 Progress of oxidation in transition of annealing methods

Use of oxyfuel burners and hydrogen as fuel gas are potential process changes in the target to produce less fossil originated CO₂ emissions from stainless steel heating methods. Hence, oxide scale formation was studied in this thesis between methane-air (MA-3), methane-oxygen (MO), and hydrogen-oxygen (HO-3) heating methods in simulated annealing furnace conditions with 3% free oxygen in furnace gas atmosphere. By changing the oxidant for methane from air to oxygen, the share of water vapor in the furnace gas atmosphere increased fourfold using methane as fuel gas. Also, the transfer of the fuels from natural gas to hydrogen gas increases the water vapor proportion in the furnace gas atmosphere. The increase is 6 times greater between MA and HO, and 1.5 times greater between MO and HO.

The second factor of atmosphere is the free oxygen content, which affects the oxidation of the steel surfaces. Variations of free O₂ content in furnace gas atmosphere in this thesis were in the MA method for 1, 3, 5% O₂, and in the HO method for 3 and 5% O₂. Suitability of steel grades is different for transition of heating methods. Thus, part of the transitions could be possible without altering the oxide layer and thus avoiding changes to the current removal processes of oxide scale.

The effect of the heating method on oxidation cannot be fully deduced from the thickness of oxide scale because oxide scale formed at high temperatures is not always a homogeneous layer-like structured. GDOES is a useful characterization method, especially for thin layer-like oxides, in which it reveals the different sublayers. It provides average data from the depth profile of elements in the burn spot area (2.5 mm in diameter), which is necessary in the evaluation of oxide thickness from the entire surface area. The determination limit for oxygen was 5% from the annealed surfaces, which proved to be a workable method for thin layers, because the peak of the silicon is supposed to be very close to the determined oxide-steel interface. The location of the silicon is specified by FESEM-EDS. However, with thicker and more heterogeneous structured oxide scales such as for determining thickness from thin layer with nodules and possible internal oxidation, GDOES is not as effective. Thus, in the determination of oxide scale thickness in reheating studies, a smaller proportion of oxygen was used, in which case the purpose of the determination would be to reach the maximum depth, where the oxide scale can still be found. In that kind of case, GDOES can only determine the attached oxide scale on the surface, not the whole thickness of the formed oxide after heating simulations.

As previous research has shown (Wei et al., 2009; Badin et al., 2014; Cheng et al., 2013), higher water vapor content of the heating methods increases the amount of oxide formed, and thus, the difference between heating methods can be seen in the thickness and structure of oxide scale in different annealing conditions. The thickness of oxide scales can be seen in Tables 8 and 9. Thicknesses were measured by GDOES up to 5 μm , while the thickness of thicker oxide scales was estimated by FESEM from the attached internal oxide layer. Thickness of oxide scale for austenitic grades is observed to increase by comparing air-fuel and oxyfuel methods of methane with longer annealing times. For example, oxide thickness is increased from 0.56 to 0.98 μm for AISI 304 using 5 minutes annealing at 1100 °C. Respectively, only clear difference between air-fuel and oxyfuel methods of methane for ferritic grades is observed in the most demanding annealing condition (1100 °C, 5 minutes). These observations support the FESEM results in progression of oxide scale by increase the water vapor content of gas atmosphere.

The attained thickness results also support the FESEM results by showing that steel grades alloyed with a higher silicon content (AISI 309) and with a higher chromium content (EN 1.4622) have oxidized significantly less at the more demanding conditions in relation to their less alloyed austenitic and ferritic grades (AISI 304, AISI 441), suffer less in terms of total amount of oxide formed from changing conditions from air-fuel to oxyfuel. The results correlate well with previous studies, in which more alloyed grades have been oxidized less at high temperatures compared to low-alloyed grades. (Cheng et al., 2016; Osei et al., 2021; Paúl et al., 2001)

Table 8. Thickness of oxide scales for austenitic grades in different furnace gas atmospheres (μm).

Annealing conditions	Thickness (μm)							
	AISI 304						AISI 309	
	MA-1	MA-3	MA-5	MO	HO-3	HO-5	MA-3	MO
1100-1min	-	0.17	-	0.22	0.24	0.23	0.20	-
1100-3min	-	0.33	-	-	-	-	0.47	-
1100-5min	-	0.56	-	0.98	15 ¹	25 ¹	0.66	0.69
1125-1min	-	0.23	-	-	-	-	-	-
1125-3min	-	0.47	-	-	-	-	-	-
1125-5min	-	0.60	-	-	-	-	-	-
1150-1min	-	0.26	-	-	-	-	0.27	-
1150-3min	-	0.78	-	-	-	-	0.77	-
1150-5min	-	0.93	-	-	-	-	1.04	1.15
1175-1min	-	0.28	-	-	-	-	-	-
1175-3min	-	0.65	-	-	-	-	-	-
1175-5min	-	7.02	-	-	-	-	-	-
1200-1min	0.36	0.42	0.35	0.36	0.38	0.33	0.41	-
1200-3min	-	1.81	-	-	-	-	1.14	-
1200-5min	-	35 ¹	-	45 ¹	45 ¹	50 ¹	1.58	1.91

¹FESEM

Table 9. Thickness of oxide scales for ferritic grades in different furnace gas atmospheres (μm).

Annealing conditions	Thickness (μm)							
	EN 1.4622		AISI 441					
	MA-3	MO	MA-1	MA-3	MA-5	MO	HO-3	HO-5
1000-1min	0.14	-	0.18	0.18	0.18	0.19	0.18	0.19
1000-3min	0.14	-	-	-	-	-	-	-
1000-5min	0.21	0.26	0.30	0.30	0.28	0.29	0.30	0.29
1050-1min	0.12	-	-	-	-	-	-	-
1050-3min	0.35	-	-	-	-	-	-	-
1050-5min	0.38	0.39	-	-	-	-	-	-
1100-1min	0.16	-	0.34	0.24	0.29	0.36	0.25	0.35
1100-3min	0.78	-	-	-	-	-	-	-
1100-5min	1.35	1.52	1.70	1.44	1.86	4.16	3.76	3.30

A major difference in thicknesses between free oxygen content is observed only in the 5-minute annealing times. For austenitic AISI 304, the thickness of internal oxide scale is greater for the HO-5 method compared to the HO-3 method at both annealing temperatures (1100 °C, 1200 °C). For ferritic AISI 441, the most

significant difference in thickness is observed between MA methods in the most demanding annealing conditions, where the MA-3 method is shown to produce the thinnest oxide scale. A slight effect of free oxygen content is expected after the studied short annealing times based on the research of Ozturk & Matway (1997). This research stated that the higher free oxygen content in a simulated MA atmosphere decreased oxidation of AISI 304, and it required about 5 minutes of isothermal heating to obtain the onset of differences in oxidation between 2.56% and 5.19% contents by TG.

It is well known that overly low free oxygen content changes the oxidation of the surface in comparison to a sufficient content, because the formed oxide layer is not as protective, but a small increase in free oxygen content after that is not as significant. For example, the increase in the amount of oxidation was significant by decreasing content from 3% to 1%, while oxidation increase slightly by increasing content from 3% to 5% after 60 minutes at 1250 °C (Kinoshita & Oguma, 1979). Respectively, isothermal oxidation tests for 15 minutes showed a notable difference for AISI 304 in shapes of TG curves between MA-1 and MA-3 methods, while the MA-5 method did not differ from the MA-3 method as seen in Fig. 24 (Publication III). The shape of the curves was similar to previous research (Ozturk & Matway, 1997). The linear shape of the MA-1 method proved that the free oxygen content (1%) was too low compared to others, where the shape of the TG curves describes oxidation remaining low before the breakdown of the protective layer at the onset of breakaway oxidation. Similar differences between free oxygen contents are not observed for AISI 441 grade, which may be due to ferritic grades having higher diffusion rates than austenitic grades (Young, 2008), enabling similar oxidation in comparison to other MA methods. Secondly, the amount of oxidation is much lower for ferritic grade compared to austenitic grade in the studied time of 15 minutes, so it may be that differences in oxidation between free oxygen contents could be revealed after longer heating times.

By comparing air-fuel and oxyfuel methods, TG oxidation tests showed differences in oxidation for both steel grades. For austenitic AISI 304, the effect of the heating method is observed using both furnace temperatures. The higher water vapor content from oxyfuel methods is highlighted by the immediately increased oxidation rate as the onset of breakaway oxidation, and the difference between MO and HO methods is observed only at a higher heating temperature, at 1200 °C. Furthermore, free oxygen content in HO methods does not show differences in TG tests. For ferritic AISI 441, oxyfuel methods separated from air-fuel methods after 200 seconds at 1100 °C by increasing of oxidation rates, and the amount of oxide

scale increased by increasing the water vapor content of the heating methods, but the difference was not that significant after 15 minutes.

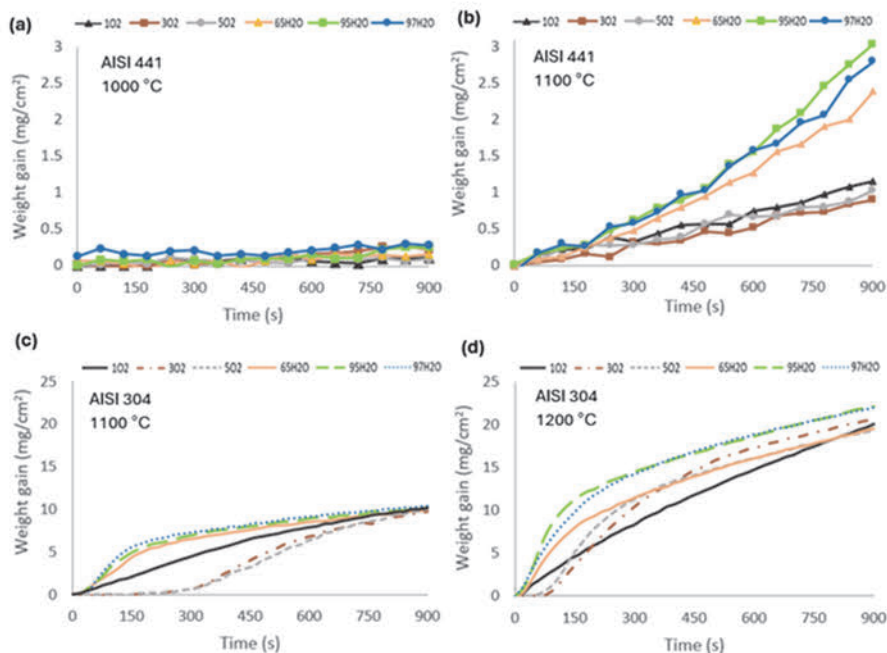


Fig. 24. Oxidation during isothermal heating for AISI 441 a) 1000 °C and b) 1100 °C, and for AISI 304 c) 1100 °C and d) 1200 °C. (Modified with permission of Wiley-VCH GmbH from Publication III © 2022 Wiley-VCH GmbH).

The summary of oxide scale structures formed between different heating methods of annealing for AISI 304 and AISI 441 is presented in Fig. 25. In Publication I, neutral electrolytic pickling efficiency for AISI 304 surfaces after different heating conditions of MA method is studied. The results showed that the efficiency of pickling was connected to different oxide scale structures. The efficiency decreased significantly when the structure of oxide scale developed to nodules with internal oxidation. The greater thickness of the chromium oxide layer also decreased the share of the cleaned surface after pickling.

Neutral electrolytic pickling has been presented to effectively dissolve chromium and manganese containing oxides (Hildén et al., 2000; Li & Celis, 2003). Hence, it is suitable for pickling thin Cr-rich oxide layers formed after final

annealing. The purpose of the process is to improve the efficiency of the final pickling (mixed acid pickling), so that it can dissolve the chromium-depleted layer formed below the oxide scale and thus, remove remained oxide scales on top of it (Li & Celis, 2003). Silicon forms more stable oxide compared to chromium (Basu & Yurek, 1991), and thus it can cause problems in the pickling process. Mixed acid pickling is applicable to dissolving formed silicon oxide by hydrofluoric acid (HF), but electrolytic pickling is not capable of that (Li & Celis, 2003; Ipek et al., 2005; Hildén et al., 2001). This phenomenon is also observed in pickling tests of higher silicon alloyed austenitic grade AISI 309 (Publication II), whose pickling results after annealing were much worse than AISI 304 even if the amount of oxidation was significantly less, respectively.

Based on the pickling results (Publication I), it can be assumed for AISI 304 that the efficiency of electrolytic pickling may reduce in the transition of methods from air-fuel to oxyfuel due to the change of oxide scale structure after 1 minute at 1200 °C. Pickling results can also decrease measurably with longer annealing times at 1100 °C, which can be seen from the structural development of oxide scales in Fig. 25. For ferritic grade AISI 441, the heating method has only a minor effect on the development of the oxide scale structure. Based on electrolytic pickling results in Publication II for EN 1.4622 grade, the efficiency of pickling remains good if heating time is short and the oxide scale structure is a thin chromium oxide layer. Thus, the efficiency may only decrease by oxyfuel methods in the most demanding annealing conditions (1100 °C, 5 min).

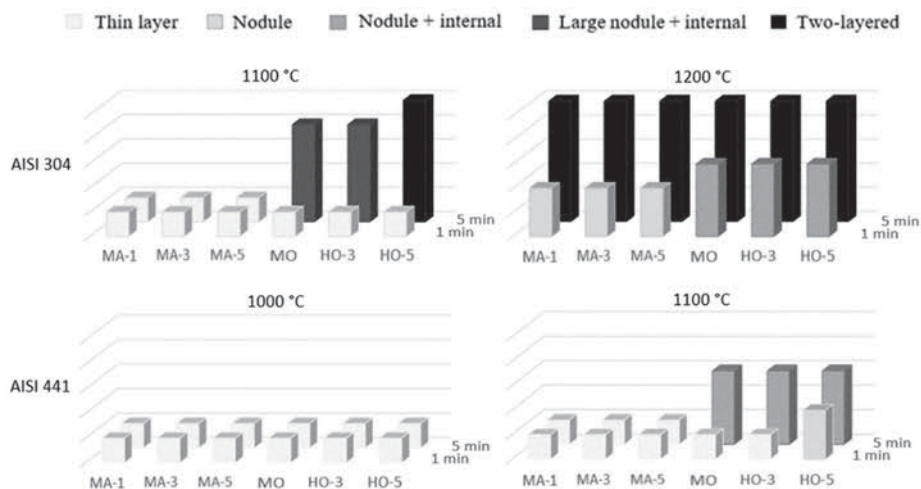


Fig. 25. Oxide scale structures of AISI 304 and AISI 441 using different heating methods. Classification for oxide scale structures: 1) Thin Cr-oxide, 2) Nodules, 3) Nodules with internal oxidation, 4) Large nodules with internal oxidation, and 5) Two-layered oxide.

In summary, the suitability of stainless steel grades on the transition of annealing toward CO₂-free methods varies. The studied ferritic grade, AISI 441, is better able to be heated by annealing methods with higher water vapor content, such as methane-oxygen and hydrogen-oxygen, without a great need to modify the pickling process after annealing compared to austenitic AISI 304. More alloyed steel grades, AISI 309 and EN 1.4622, are more resistant to oxidation and thus the progress of oxide scale structure is more hindered if the furnace gas atmosphere is made more demanding in terms of surface oxidation.

6.3 Progress of oxidation in transition of reheating methods

The effect of reheating methods in the transition toward CO₂-free methods produces measurably different oxide scale structures for austenitic steel grades, as seen in summary in Fig. 26. The amount of oxide scales is lower for induction simulation methods, which is mainly based on shorted heating curves compared to combustion simulation methods. For both induction simulating methods, AISI 301 produced less oxide scale in comparison to AISI 304, and IA methods have less developed oxide scale structure between steel grades, respectively. Hence, the oxidation of AISI 301 remains lower perhaps due to different alloying content of

silicon and chromium, in which silicon is greater and chromium is lower compared to AISI 304.

For combustion reheating methods, the water vapor content of furnace gas atmosphere significantly increased by changing the heating method from air-fuel to oxyfuel. A greater share of water vapor in the atmosphere accelerates oxidation for both austenitic steel grades. Only methane-air methods for AISI 301 have a similar amount of oxidation in comparison to AISI 304, but the transition to oxyfuel methods increases its oxidation considerably more as seen in Fig. 26. Thus, in terms of oxide scale amounts, the suitability of stainless steel grade AISI 304 is better than AISI 301 in a reheating process for oxyfuel methods and for a change of fuel gas from methane to hydrogen. However, shorter heating by induction could be even better for AISI 301.

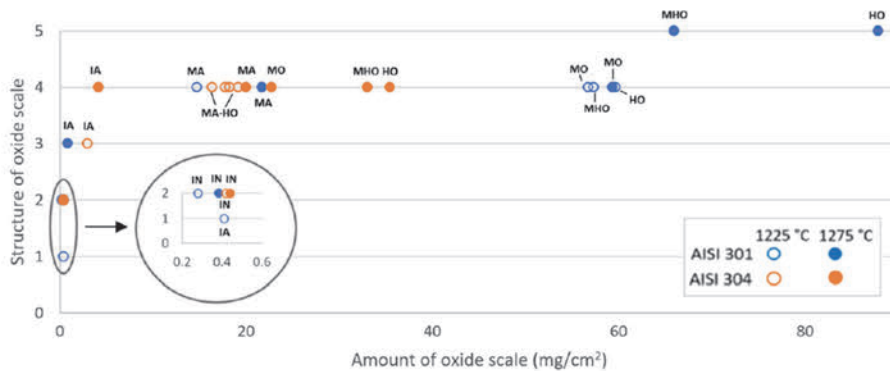


Fig. 26. Summary of oxide scale structures of austenitic AISI 301 and AISI 304 using different heating methods. Oxide scale structures are: 1) Cr-oxide, 2) Subsurface oxide and nodules, 3) Nodules, 4) Oxide pockets, and 5) Two-layered oxide. (Reprinted under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

The difference between air-fuel and oxyfuel methods could be even smaller because the oxyfuel method has a higher heating rate compared to the air-fuel method (von Schéele, 2010), which could enable shorter heating time for the slabs in the reheating furnace. Previous studies estimated that the heating time would be 30% longer for the air-fuel method considering the batch furnace process (Adolfi et al., 2006), while Hu et al. (2019) suggested that the heating time was only 6% shorter for oxyfuel method in a pilot-scale reheating furnace. Correspondingly, the heating time for induction heating could be even shorter, because the heating curve in this study (Publication IV) simulates the situation, where the difference between

temperatures of core and surface for slab was supposed to be kept small (Morandi & Fabbri, 2016).

By comparing the development of the pocket structures, differences can be observed between austenitic steel grades after different reheating methods. For AISI 301, the structure of oxide scale pockets developed by increasing the water vapor content in atmosphere from the network-like structured to uniform structure as seen in Figs. 27a and b. The network-like structure in pockets is observed only after MA methods, while the mildest oxyfuel condition, MO-1225, shows that the development of uniform-like structure starts in the middle part of the pockets (Fig. 19d). This structural difference correlates with the onset of a greater amount of oxidation, as seen in Fig. 26.

In the network-like structure, there is Fe-Cr oxide, Ni- and Fe-rich metallic particles and pores over the whole area, and silicon enrichment nearer the oxide-steel interface. However, in the uniform structure, Ni- and Fe-rich metallic particles have disappeared, and nickel is oxidized, as seen in point 23 in Table 10. Furthermore, a clear chromium-rich oxide layer is formed at the interface (point 24) and enrichment of silicon (point 25 and 26) is observed both at the interface and near it. The Cr-oxide layer is called the healing layer, which can be induced by high silicon content of AISI 301 and thus the formation of continuous silicon oxide layer. Both the healing layer and the silicon oxide layer are observed to reduce oxidation rate (Nguyen et al., 2014; Basu & Yurek, 1991). Col et al. (2017) stated that oxidation of nickel does not occur in the pockets with network-like structure due to the oxygen partial pressure being insufficient. Hence, oxidation of other elements is reduced due to the healing layer and Si-oxide acts as a diffusion barrier, while oxygen partial pressure can be sufficient to enable the oxidation of nickel, disappearing the metallic phases from the pockets. Furthermore, it is suggested that water vapor increases the inward transport of oxygen due to rapid water molecule diffusion through the oxide scale and dissociation into the voids (Young, 2016). This could promote the oxidation of nickel, which together with mass transport of water molecules can reduce the number of voids inside the oxide scale.

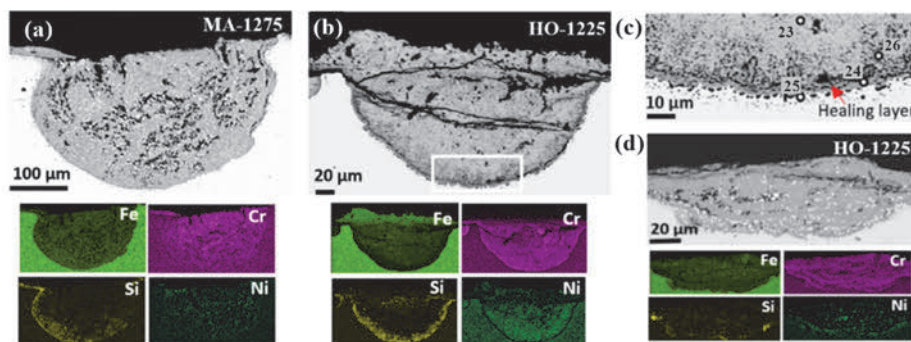


Fig. 27. Structure of oxide pockets: For AISI 301, a) network-like structure after MA-1275, b) uniform structure after HO-1225, and c) healing layer of part (b). For AISI 304, d) multilayered structure after HO-1225. (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

Table 10. Elemental composition of EDS points from Fig. 27. (Modified under Creative Commons CC BY 4.0 license from Publication IV © 2023 Authors).

Point	Fe	Cr	Ni	O	Si	Mn	Ti	Nb
AISI 301								
23	28.40	28.87	12.50	30.23	-	-	-	-
24	6.72	55.95	1.89	35.44	-	-	-	-
25	43.22	8.53	5.86	25.10	17.30	-	-	-
26	21.37	41.53	2.07	30.85	4.17	-	-	-

A similar uniform pocket structure is not formed for AISI 304. Its pocket structure develops from a multilayered (Fig. 27d) to a network-like structured (Fig. 20d) in the studied conditions, from which the network-like structure is only observed at the higher target temperature. Development of the multilayered structure is presented by Cheng et al. (2006) based on the multilayered oxide of AISI 316. When the Cr concentration is not enough for external oxidation of the Cr oxide layer, the oxidation continues by internal oxidation at Cr-depleted layer forming Fe-Cr oxide and Ni-rich phases. A new Cr-rich oxide layer can form after the bulk diffusion of chromium from the steel matrix raises the concentration high enough to enable continuous layer formation. In the network-like structured oxide scale, there are no more corresponding chromium-rich layers left, which can be caused while oxidation continues by solid solubility of chromium and iron oxides to form Fe-Cr spinel.

As a summary of the reheating studies, oxidation of ferritic AISI 444 is not changed by the transition of heating methods, so it is better suited for that transition in terms of the current descaling process compared to austenitic grades. Change in oxidation for austenitic grades might have an influence on the efficiency of the descaling process due to different amounts and structures of oxide scale. It has been stated that the thermal shock and mechanical pressure produced by hydraulic descaling remove oxide scale from the steel surface (Hlaváč, 2015). Thus, the shielding of oxide scale into pocket structures by steel matrix could hinder the efficiency of descaling, especially for rounder pockets of AISI 301. However, the transition to oxyfuel methods makes the shape of the pockets wider and they are less covered by steel, which can promote descaling. In addition to the shape of pockets, the inner structure of oxide scale could affect the efficiency of descaling because oxide scale layers with oxidized nickel could be descaled better than a network-like structure (Mukadi & Pistorius, 2010). Thus, optimization of descaling would be needed after the transition of heating methods.

7 Conclusions

The transition of heating processes toward fossil-free methods affects oxide scale formation on the surface of stainless steel during heating processes. For the annealing of cold rolled strips, the current methane-air heating method in the furnace produced the following results:

- Higher temperatures and longer exposure time in the furnace are observed to develop surface oxidation further.
- Oxide scale structure of steel grade AISI 304 developed from chromium oxide layer to oxide scale nodules, internal oxidation below them and two-layered oxide by changing furnace conditions toward the most demanding: 5 minutes at 1200 °C.
- Greater silicon and chromium contents hindered oxidation of AISI 309 in comparison to AISI 304.
- Onset of breakaway oxidation is not observed for ferritic steel grades.

By changing the methane combustion from air-fuel to oxyfuel, an increased water vapor share in furnace gas atmosphere has the following influences on oxidation:

- AISI 304 experiences no difference between methods under the mildest studied annealing conditions for 1 minute at 1100 °C. Other furnace conditions produced greater amounts of oxidation, and structural differences between oxide scales are observed in conditions for 5 minutes at 1100 °C and 1 minute at 1200 °C.
- Transition between oxidants has less effect on AISI 309 compared to AISI 304 because its only effect was to increase the amount of oxide scale nodules using the longest time at the highest annealing temperature (5 minutes at 1200 °C).
- Only the most demanding annealing condition for ferritic AISI 441, 5 minutes at 1100 °C, produced oxide scale nodules as a sign of breakaway oxidation using the oxyfuel method, while the air-fuel method with milder furnace conditions produced a chromium-rich oxide layer.
- The oxyfuel method causes no structural difference compared to the air-fuel method for ferritic EN 1.4622.

Fuel change from methane to hydrogen in oxyfuel methods significantly increases the share of water vapor in post-burn atmosphere causing surface oxidation as follows:

- For AISI 304, a more continuous internal oxidation layer is formed in 5 minutes at 1100 °C, and more developed nodules are formed in 1 minute at 1200 °C.
- Difference in oxidation is minor for ferritic AISI 441.

Changes in the heating method alter the oxide scale produced, ultimately affecting the pickling process following the final annealing. The transition of heating method in annealing conditions in terms of both oxidant and fuel gases is more suitable for ferritic grades because the effect on oxidation is minor. Correspondingly, oxidation of AISI 309 does not change much between methane combustion methods so that requirements to modify pickling process are minimal, even if the silicon oxide formed inside the steel matrix causes significant problems for electrolytic pickling. However, AISI 304 might require modification in the pickling process, because higher water vapor content in a furnace atmosphere changes the structure and amount of oxide scale, even using the shortest annealing time at 1200 °C.

The transition of heating processes in reheating of stainless steel produced the following results in terms of oxide scale:

- From methane-air to hydrogen-oxygen, oxidation increased by about fourfold for AISI 301 at both temperatures, while these were below twofold for AISI 304.
- Similar conditions in the structure of oxide scale developed from oxide scale pockets to two-layered oxide for AISI 301, but the transition of methods only increase the size of oxide scale pockets for AISI 304.
- Shorter induction heating simulations significantly decrease the amount of oxidation.
- For ferritic AISI 444, the effect of heating method on oxide scale was only minor, and thus, it is more suitable in the transition of heating methods compared to austenitic grades.

8 Industrial relevance and future work

All the experiments presented in this thesis have been planned to simulate the conditions of the industrial heating processes used in steelmaking. It is good to note that while laboratory-scale experiments differ from the industrial-scale processes, they provide vital information on researched theme. In this thesis, oxide scale formation was studied between different combustion heating methods without considering the possibility of shorter heating times based on more efficient methods. For example, the oxyfuel method provides this opportunity. However, continuous process lines in the steel industry can hinder the integration of faster heating process steps because it would also require a change in the process steps surrounding it to optimize the production of process line. Hence, it would be justified to drive heating processes with the same heating time of current system, hindering the heating capacity of new methods.

Transition of combustion heating method from air-fuel to oxyfuel have effect on pressurization of industrial furnaces due to the amount of flue gas decrease without nitrogen carried by air oxidant gas into the furnace. The industrial furnaces are slightly overpressurized to inhibit air leakage to the furnace, increasing the free oxygen content inside the furnace, but in this thesis, pressurization has not been considered in the oxidation tests.

Heating profiles used in oxidation tests simulated the surface temperature of stainless steel material in industrial heating furnaces. Industrial annealing and reheating heating programs have been constructed for each steel grade, considering the thickness of the material and oxide scale formation on heat transfer to the material. Difference with heating profiles for combustion using current heating method have only been considered between austenitic and ferritic steels in this thesis, but the effects on heat transfer could investigate further.

Utilization of hydrogen fuel demands in addition to research for development of its production, also a lot of technical implications concerning on, burner design, storage, supply and safety. For example, overall gas flow rate of hydrogen is higher than natural gas and thus, higher jet velocity or pipe diameter is required. Different fuel ratios between natural gas and hydrogen are also possible to utilize in combustion process. The whole system requires analysis in terms of hydrogen supply possibility and cost to existing facilities.

NO_x emissions are very harmful for the environment by forming acid rain and ground-level ozone. In the heating furnaces, the increase of water vapor content and decrease of flue gas temperature by utilizing hydrogen as fuel could lead

aqueous condensation and dissolution of NO_x to form nitric acid (Hemrick, 2022), which could have effects on refractories, likewise higher water vapor content (Gomes, 2024). Higher flame temperatures of hydrogen fuel and oxyfuel method promotes thermal NO_x formation, which can be decreased by lower flame temperature of flameless oxyfuel burner technology. Furthermore, flue gas recirculation to hydrogen fuel before air combustion decreases the flame temperature.

In future work, further information should be gathered on oxidation in terms of optimizing heating and scale removal processes. New fuels, the oxyfuel method, and electrification of heating require the development of burners, furnaces, and processes, which have specific influences on heating conditions affecting steel surface oxidation. For example, higher heating rates in combustion enable shorter heating times for the process, which can hinder the amount of oxidation and the development of oxide scale structures. If the change of oxidation in relation to the current process is high, it also requires optimization of both descaling and pickling processes.

In the development of heating processes towards CO₂ free heating, there is the possibility to change all or only part of a furnace's burners from air-fuel to oxyfuel. More knowledge about the progress of oxidation could provide background information to optimize it. Hence, progressive oxidation tests to reveal the time-bound structural changes of oxide scale by taking samples out of the furnace after different times during the same heating curve or switching the atmosphere during heating could provide more information. That information could be used to optimize the heating process in combination with different burner types or in hybrid heating methods, such as a combination of combustion and electrification.

More research is also required on the removal of oxide scale, and the research could be extended to duplex grades or the steel grades that are known to be difficult to pickle. Differences between the removal of further progressed oxide scale using new fuels or the oxyfuel method in annealing could be studied with a combination of electrolytic and mixed acid pickling. For reheating, the descaling efficiency of different oxide scale structures remained unclear in this study. Mechanical properties of oxide scale would be possible to study from cooled surface, but more characteristic information would be provided by descaling hot oxide scale after heating with high pressured water.

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- I Airaksinen, S., Tuovinen, T., Laukka, A., Vuolio, T., Heikkinen, E.-P., Riekk, E., Manninen, T., & Fabritius, T. (2020). Effect of simulated annealing conditions on scale formation and neutral electrolytic pickling. *Steel Research International*, 92(3), 2000449. <https://doi.org/10.1002/srin.202000449>
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