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Surface phase transformation in austenitic stainless steel induced by cyclic oxidation in humidified air

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Abstract

The formation of α' martensite at the surface of an AISI 304 stainless steel subjected to cyclic heating in humidified air is reported. The α' martensite formed during the cooling part of the cyclic tests due to local depletion of Cr and Mn and transformed back to austenite when the temperature again rose to 650 °C. The size of the α' martensite region increased with increasing number of cycles. Thermodynamical simulations were used as basis for discussing the formation of α' martensite. The effect of the α' martensite on corrosion is also discussed.

Keywords: Stainless steel, Thermal cycling, SEM, Oxidation, High temperature corrosion

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1. Introduction

To meet the demands of tomorrow's energy production, power plants need to be more flexible in the consideration of fuels and operation conditions. The materials used in the next generation of power plants will be exposed to higher temperatures and pressures, more corrosive environment and many start-and-stop cycles [1, 2].

The widely used austenitic stainless steel AISI 304 exhibits good oxidation resistance at elevated temperatures in dry air due to the formation of a protective Cr-rich $(\text{Cr, Fe})_2\text{O}_3$ scale [3]. However, at temperatures above 600 °C the addition of water vapour has a detrimental effect on the protectiveness of the Cr-rich $(\text{Cr, Fe})_2\text{O}_3$ [4, 5, 6, 7, 8, 9, 10, 11, 12]. This because the water vapour reacts with the Cr-rich oxide which eventually causes Cr depletion due to vaporization and non-protective breakaway oxides [3, 4, 5, 6, 7, 8, 9, 10, 11, 12] according to the following reaction [9, 12]:

Thermal cycling with the addition of water vapour accelerates the onset of breakaway oxidation [13, 14]. The formation of non-protective breakaway oxides and the protectiveness of the Cr-rich oxide depend on the ratio between the Cr depletion and the supply of Cr by diffusion from the alloy [5, 15, 9, 11]. There are different approaches to improve the supply of Cr to the protective scale, where increased Cr content is a common solution [6, 16, 13]. Another possible solution is grain refinement at the surface, using, for instance, nanocrystalline coatings [11, 14] or plastic deformation techniques

[17] to improve the supply of Cr to the protective oxide scale. The grain refinement produces a large number of grain boundaries that increase the diffusion of Cr to the surface [18, 19, 20].

The surface properties clearly govern the corrosion process. The surface properties of AISI 304-type stainless steels are influenced by the formation of α' martensite (BCC) that forms from austenite (FCC) at the surface during cooling from elevated temperature [21, 22, 23, 24]. The α' martensite formation in AISI 304-type stainless steels has previously been attributed to Cr depletion at grain boundaries through carbide formation [21] and the subsequent increase of the temperature of martensitic transformation (M_s) [21, 23, 24]. Mukhopadhyay et al. [22] have shown, using acoustic emission, that the formation is martensitic, as opposed to diffusion controlled transformation. The α' martensite formation also occur at other locations than grain boundaries; Susan et al. [23] have reported formation of α' martensite at the surface when cooling to room temperature after oxidation at 1000–1100 °C in a low pO_2 environment. The α' martensite formation at the surface occurs due to depletion of Cr, Mn and Si which increases the M_s temperature making the formation of α' martensite above room temperature possible [23]. La Fontaine et al. [24] showed that Cr depletion from oxidation during thermal cycling up to 970 °C in air was responsible for α' martensite formation which gave intergranular corrosion causing intergranular cracking as a consequence. However, the influence of thermal cycling in a water vapour environment on the formation of α' martensite is not yet fully understood. Consequently, more research needs to be conducted to investigate the influence of α' martensite at the surface on corrosion.

The purpose of the present study is to investigate the formation of α' martensite at the surface of an AISI 304 stainless steel during thermal cycling in a water vapour environment. The influence of cyclic oxidation on formation of α' martensite is discussed using thermodynamical simulations. The effect of the α' martensite on corrosion is also discussed.

2. Experimental procedures

2.1. Oxidation

The samples were made of an AISI 304 stainless steel with the nominal composition (in wt.%): 0.015 C, 0.35 Si, 1.2 Mn, 18.3 Cr, 10.3 Ni, 0.3 Cu, 0.05 W, 0.01 Nb, 0.07 N and Fe balance. The material originates from a tube that was manufactured by hot extrusion–cold pilgering and then solution annealed at 1060 °C for 15 minutes. The used sample geometry was 10 mm x 10 mm with a thickness of 5 mm. After cutting the samples, the solution annealing at 1060 °C for 15 minutes was again applied to the test specimens, followed by grinding on all sides, using a 500 SiC-paper, to remove oxides.

Testing in corrosive environment was performed at 650 °C in a thermal cyclic rig. The specimens rested on a stationary ceramic table and the thermal cycling was accomplished by lowering and rising a furnace over the specimens. Since the specimens rested on the ceramic table, five sides of the specimen were fully exposed to the corrosive medium. All analyses were made on the surface facing upwards. One thermal cycle consisted of a 96 h dwell time at 650 °C followed by natural cooling until the specimens reached 100 °C which took approximately 18 minutes; Fig. 1 shows the cooling curve as measured on one of the specimens. Specimens subjected to 2, 5, 10 and

20 thermal cycles were used in the investigation.

During the hot part of the cycle, water was introduced as an air-water mist which was sprayed into the furnace (not directly onto the specimens). The water mist immediately evaporated as it was sprayed into the furnace and increased the water vapour content in the furnace chamber. The amount of water vapour was controlled by the water-to-air ratio in the water mist and was adjusted to ~ 15 mol%. This was achieved by controlling the water inlet flow into the air stream, as outlined in Fig. 2. Since the furnace was not airtight, a new burst of air-water mist was injected every 3rd minute which evaporated and flushed the furnace through with water vapour.

As a reference, an isothermal oxidation test in laboratory air was performed at 650 °C for 1000 hours.

2.2. Analytical methods

2.2.1. Analytical scanning electron microscopy

For chemical analysis, energy dispersive spectroscopy (EDS) and wave dispersive spectroscopy (WDS) were used. For microstructural investigation, electron channelling contrast imaging (ECCI) [25] and electron backscatter diffraction (EBSD) were employed. Both chemical and microstructural analyses were performed using a HITACHI SU-70 field emission gun scanning electron microscope (FEG-SEM). EDS and WDS were performed at 20 kV acceleration voltage and a working distance of 15 mm. ECCI was performed at 10 kV acceleration voltage and a working distance of 7 mm. EBSD was measured at 15 kV acceleration voltage and a working distance of 20 mm using an OXFORD electron backscatter diffraction detector. The HKL software CHANNEL 5 was used for the microstructural evaluation and

the EBSD-maps were produced using a step size of 0.1 μm .

2.2.2. X-ray diffraction

Grazing incidence (GI) X-ray diffraction (XRD) was used to analyse the crystalline corrosion products. A Philips X'Pert XRD-machine was employed, equipped with grazing incidence beam and a 2x2 mm² crossed slits attachment. CuK $_{\alpha}$ radiation was used and the angles of incidence were 2°, 5° and 10°. The detector measured between $20^{\circ} < 2\theta < 80^{\circ}$.

3. Results

3.1. Oxidation during thermal cycling in humidified air

Various kinds of oxides formed during the thermal cycling in the humidified air. GI-XRD results after 20 cycles showed that M₂O₃ oxides, spinel oxides, BCC and FCC phases were present, see Fig. 3. Fig. 4 shows the element distribution of O, Fe, Cr, Ni and Mn in the oxide scale after 10 cycles. Table 1 lists the chemical composition in at.% from EDS point scans taken at the positions labelled A-F in Fig. 4. Four different regions in the oxide could be discerned after 10 cycles: 1) an Fe-rich outer layer (C and D), 2) a local Cr-rich oxide on the metal surface (E), 3) inward growing mixed Cr-, Ni- and Fe-oxide relatively rich in Ni (A), and 4) a more shallow inward growing Cr-, Ni- and Fe-oxide lower in Ni (F). The development of the oxides during the cycles is shown in Fig. 5, which displays EDS and WDS analyses of the cross-sections; the linescan starts in the middle of the oxides and goes into the bulk material. In Fig. 6, top-views of the oxidised surfaces are shown. Fig. 6 a) shows a specimen isothermally oxidised in lab air as reference. In

lab air, the alloy formed a fine-grained Cr-rich oxide. Fig. 6 b)-d) show surfaces oxidised moist air for various number of cycles. These specimen formed an outer Fe-rich oxide. Fig. 6 b)-d) also show that the Fe-rich outer oxide coarsened with increasing number of cycles.

Fig. 7 shows light optic microscopy (LOM) images on cross sections near the surfaces. Inward oxidation, caused by isothermal oxidation in air and thermal cycling in the corrosive environment, and α' martensite (BCC) can be observed. The oxides are not visible in the LOM images due to the contrast settings; the inward oxidation is indicated in Fig. 7 by arrows. The inward growing oxides increased in area with increasing number of cycles, consuming the bulk material. The FCC matrix was more heavily attacked than the BCC regions.

3.2. Formation of α' martensite

In Fig. 8 the typical microstructure of solution heat-treated and grind material is shown. No oxides were present since the specimens had not yet undergone the corrosion tests. Fig. 8 b) also displays an inversed pole figure (IPF) EBSD-map and a low angle grain boundary (LAGB) EBSD-map. The deformation introduced during the grinding can be seen. In Fig. 8 c), a phase identification EBSD-map shows that the microstructure at the surface only consist of FCC (red color). Since the microstructure in Fig. 8 c) only consists of austenite, it shows that the grinding process did not form any strain-induced martensite.

After isothermal oxidation at 650 °C for 1000 hours in air, a α' martensite (BCC) layer with an approximate thickness of 1-2 μm was observed at the surface of the specimen, as shown in Fig. 9 where FCC corresponds to the

red color and BCC corresponds to the blue color. The BCC layer was also observed at the surfaces of the cyclically tested specimens in the corrosive environment at 650 °C. Fig. 10 shows the development of the BCC layers at the surface after 2 cycles in Fig. 10 a) and c), and 5 cycles in Fig. 10 b) and d). After 2 cycles, a layer thickness of approximately 3 μm was present and increased to approximately 2-5 μm and 2-10 μm after 5 and 10 cycles respectively (as seen in Fig. 10 and Fig. 11). The layers consisted of several BCC grains and the BCC grains were smaller than the FCC grains in the bulk material, as shown in Fig. 9, 10 and 11. In the overview image of the area, shown in Fig. 12, the BCC region could be observed by ECCI as well as light optical microscopy. The BCC structure in Fig. 12 was confirmed using EBSD, showed in Fig. 12 d), where BCC correspond to the blue color. The BCC was also observed internally at the grain boundaries where carbides formed, see Fig. 12 b) and e) for such an area. In Fig. 13 a) the typical element concentration of O, Cr, Fe, Ni, Mn and Si over a BCC region (Fig. 13 b)) after 10 cycles is given using a EDS line scan. The BCC region showed Cr and Mn depletion. This can also be observed in Fig. 5 c) and e); below the Cr-rich oxide, a Cr and Mn depleted area can be observed. This was also confirmed by EDS and WDS point scans of the BCC region after 10 cycles, using WDS for Mn and EDS for all other elements. The average chemical composition from 12 point scans in wt.% was found to be:

Si 0.41 ± 0.04 , Mn 0.6 ± 0.14 , Cr 11.56 ± 1.08 , Ni 12.73 ± 0.81 and Fe 74.24 ± 0.82 , where the given scatter equals one standard deviation. In Fig. 5 c) and e), the increase of the BCC thickness with the number of cycles can also be seen.

4. Discussion

4.1. Formed oxides

From Fig. 4 and Table 1, mainly four different types of oxides were observed. Together with the GI-XRD results in Fig. 3 and EDS/WDS line scans in Fig. 5, the main oxides are most likely: 1) the outer oxide is Fe_2O_3 or an Fe-rich $(\text{Fe}, \text{Cr})_2\text{O}_3$, 2) at the metal surface there is a Cr-rich $(\text{Cr}, \text{Fe})_2\text{O}_3$, 3) the inward growing oxides are presumably a Ni-rich $(\text{Cr}, \text{Fe}, \text{Ni})_3\text{O}_4$ and 4) a Ni-poor $(\text{Cr}, \text{Fe}, \text{Ni})_3\text{O}_4$ spinel oxides. The ECCI-image in Fig. 14 indicates the locations of the four main oxides. The observed oxides are essentially the same as Halvardsson et al. [12] observed in an AISI 304 subjected to isotherm heating at 600 °C in a water vapour medium. The work by Croll and Wallwork[26] supports the presence of a Ni-rich and a Ni-poor $(\text{Cr}, \text{Fe}, \text{Ni})_3\text{O}_4$, since they shows that Ni is fully soluble in a Fe-Ni-Cr spinel with Cr-content below 14 at.% and arbitrarily Fe/Ni ratio. Other possible oxides that are present include the spinels $\text{Mn}_{1.5}\text{Cr}_{1.5}\text{O}_4$, NiCr_2O_4 and FeCr_2O_4 . The presence of $\text{Mn}_{1.5}\text{Cr}_{1.5}\text{O}_4$ is supported by the EDS/WDS results shown in Fig. 5 a). The other two spinel oxides have not been observed but their XRD peaks are close to those of $(\text{Cr}, \text{Fe}, \text{Ni})_3\text{O}_4$ and are therefore hard to discern; their presence have been reported by others [14].

In Fig. 3, as the angle of incidence increases from 2° to 10°, different oxides and phases appear in the spectrum. Since the oxides are thick after 20 thermal cycles in humidified air, only the strongest peaks from the bulk material (FCC) and the α' martensite (BCC) are observed at 10° incidence angle.

4.2. Formation of α' martensite

As for previous studies, α' martensite was observed internally at grain boundaries, and presumably formed through previously described mechanisms of carbide formation at grain boundaries [21, 22, 24]. The more extensive α' martensite formation observed at the specimen surface is considered to be caused by Cr depletion through a combination of carbide formation and oxidation [21, 23, 24]. Fig. 13 and Fig. 5 c) and e) show a similar depletion of Cr and Mn where the α' martensite layer was found, as reported by others [23, 24]. The reason for the presence of the FCC area between the oxide and the BCC region in Fig.13 is believed to be the higher level of Ni that suppress α' martensite formation [27]. It should be noted that the relatively even Cr level in the Cr depleted area, where the α' martensite layer formed, suggests a high Cr diffusivity in this region; otherwise, a Cr gradient through the α' martensite layer would have been observed. Since the α' martensite layer consists of several grains and these grains are considerably smaller than the grains of the FCC matrix, the number of grain boundaries is much higher in the α' martensite layer compared to the FCC matrix. Since the diffusivity of Cr is much faster in grain boundaries compared to bulk diffusion [28, 20] this will cause a relatively even Cr level instead of a gradient in the Cr depleted area.

The α' martensite layer is growing thicker with increasing number of cycles, see Fig. 10 - 11. This is attributed to the Cr depletion at the interface between the bulk material and the α' martensite layer during the hot part of the cycle. This Cr depletion will generate a small area with a chemical composition that enables transformation to α' martensite during the cooling.

To serve as basis for the discussion, a number of Thermo-Calc [29] and Dictra [28] simulations were performed to find plausible mechanisms for α' martensite formation and growth at the specimens surface. The initial stages of the tests were modelled in a few different ways. A number of simplifications were necessary; the following points describes the model assumptions:

1. Prior to oxidation, the material was exposed to a heat treatment. During this heat treatment, Cr depletion was assumed to occur at the outermost part of the FCC grain due to carbide formation. The influence of oxidation was neglected during the first cycle.
2. Since C diffusivity, D_C^{FCC} , is much higher than Cr diffusivity, D_{Cr}^{FCC} , in FCC-Fe, the C content at the surface during the heat treatment was assumed to remain close to the nominal value of 0.015 wt.% due to outward diffusion from the FCC grain. A Thermo-Calc simulation suggested that the Cr content in the FCC phase at the outermost part of the grain should then drop to ~ 5.2 wt.%. Inserting this in Fick's second law, see Eq. 2, gave the Cr profile after the heat treatment as shown in Fig. 15. This Cr profile was used as input for the oxidation modelling.

$$\frac{C_s - C_x}{C_s - C_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2)$$

3. During oxidation, carbide formation was neglected since: 1) the α' martensite layers observed at the specimen surface were larger than those observed internally at grain boundaries, indicating that oxidation dominated at the surface, and 2) oxidation in lab air gave considerable

lower Cr depletion, again indicating that Cr removal due to oxidation dominated in moist air.

4. The Cr profile were used with Eq. 3, from reference [27] where $w_i\%$ is the content of element i , to establish the size of the α' martensite layer that formed during cooling. The minimum temperature of the cycle, 100 °C, was used as a criterion for α' martensite transformation. The influence of Mn, Si and N was neglected.

$$M_s = 1302 - 42w_{Cr}\% - 61w_{Ni}\% - 33w_{Mn}\% - 28w_{Si}\% - 1667(w_C\% + w_N\%) \quad (3)$$

An oxidation–diffusion simulation was performed using the commercial software Dictra coupled with an oxidation routine written in-house. The model has previously been described by Yuan et al. [30]. The simulation was first performed on a FCC grain with an outer BCC region. The result after the first oxidation cycle is presented in Fig. 16 a). While the faster Cr diffusivity in BCC-Fe did give a Cr depleted area, just as observed experimentally, the BCC region also caused inwards diffusion of Ni giving rise to a Ni peak in the FCC region just beneath the BCC region. This Ni peak would prevent the BCC region to grow as Ni enrichment would lower the M_s temperature. Furthermore, the Ni content in the BCC region dropped to levels significantly lower than those observed experimentally. It can hence be concluded that the BCC region transforms back to FCC at 650 °C; this is also supported by the phase diagram presented in Fig. 17 for Fe-12.5 wt.% Ni- x Cr which shows that the material enters the γ -loop at reheating to 650 °C.

Since the relatively even Cr level in the depleted area, observed experimentally in the α' martensite, must have been formed due to fast Cr diffusivity, two other possible mechanisms were tested: 1) the BCC structure is maintained for some time during heating, but eventually transform to FCC, and 2) the BCC transfer immediately to FCC upon heating, but the smaller grains in the α' martensite area give increased Cr diffusivity due to grain boundary diffusion. Dictra simulations were performed in accordance with these assumptions. For the first case, the BCC phase was modelled to remain for 1 hour, but then transformed to FCC; for the second case, Dictra's built-in grain boundary diffusion model was used with a grain boundary width of $5 \cdot 10^{-10}$ m [31] and a grain size of 10^{-7} m.

As seen in Fig. 16 b) and c), letting the BCC transform back to FCC at high temperature removed the Ni peak observed in Fig. 16 a) and gave a better agreement with experimental observations. Adding grain boundaries to the outer layer increased the Cr diffusivity; as seen in Fig. 16 c). The finer grain structure in the outer layer would thus aid chromia formation at the surface and with time become depleted in Cr. Based on the Thermo-Calc and Dictra simulations, it is considered likely that the formed α' martensite layer transforms back to FCC at 650 °C, and that the Cr depleted area observed in the α' martensite layer is formed at 650 °C due to increased Cr diffusivity in the α' martensite layer caused by grain boundary diffusion.

Fig. 18 shows the C profile after 100 hours of oxidation–diffusion; it can be seen that C diffuses from the BCC region inwards into the grain. It should therefore also be possible for further carbide precipitation to occur in the BCC/FCC interface as C is pushed towards that region from the BCC

region. Due to the faster Cr diffusivity in the transformed region, the FCC region, even though far from the surface where oxidation occurs, will continue to be depleted of Cr.

4.3. The influence of α' martensite on corrosion

The formation of α' martensite at the surface influence the corrosion process, similarly to grain refinement approaches [11, 14, 17]. The α' martensite formation causes an increase in the number of grain boundaries at the surface (see Fig. 9 - 11) and subsequently locally improves the supply of Cr to the protective oxide scale at the surface through grain boundary diffusion. In the microstructure, this is supported by Fig. 19 a) where a Cr-rich protective scale is formed above the α' martensite layer (BCC). This should be compared to Fig. 19 b) where the bulk material is consumed by inwards growing oxides. For this reason, areas that lack the α' martensite are more consumed by inward corrosion than the areas with α' martensite; this can be seen in Fig. 7. Fig. 14 also supports a positive effect of the α' martensite formed at austenite grain boundaries at the surface, showing a thinner Fe_2O_3 scale above the α' martensite region (indicated by arrows) and a Cr-rich $(\text{Cr, Fe})_2\text{O}_3$ formed at the metal surface. However, the formation of α' martensite in this alloy is unintended and not controlled, thus being far from as effective as dedicated grain refinement techniques. The positive effect of the formation of α' martensite on the corrosion resistance is limited to local areas.

5. Conclusion

In the present study, an AISI 304-type stainless steel was exposed to thermal cycling in humidified air in the temperature interval 100–650 °C. The following conclusions could be made:

1. Four main oxide types are formed, they are most likely 1) the outer oxide is Fe_2O_3 or an Fe-rich $(\text{Fe}, \text{Cr})_2\text{O}_3$, 2) at the metal surface there is a Cr-rich $(\text{Cr}, \text{Fe})_2\text{O}_3$, 3) the inward growing oxides are presumably a Ni-rich $(\text{Cr}, \text{Fe}, \text{Ni})_3\text{O}_4$ and 4) a Ni-poor $(\text{Cr}, \text{Fe}, \text{Ni})_3\text{O}_4$ spinel oxide.
2. α' martensite forms during cooling from 650 °C to 100 °C. This is due to Cr depletion caused by oxidation at the surface which locally rises the M_s temperature.
3. The α' martensite grows thicker with increasing numbers of cycles during the thermal cycling.
4. The α' martensite transforms back to FCC at 650 °C during the thermal cycling.
5. The formation of α' martensite will give several smaller grains at the surface, compared to the grains in the FCC matrix. Even though the α' martensite transforms back to FCC at 650 °C, the increased number of grain boundaries will improve the Cr diffusion within this region.
6. A Cr-rich protective scale is formed above the α' martensite layer, due to the reason described in conclusion 5, compared to regions where no α' martensite layer has formed. For this reason, areas that lack the α' martensite are more consumed by inward corrosion and the outer oxide scale is thicker than at the areas with α' martensite. Thus, the

formation of α' martensite is locally decreasing the in- and outward scale growth.

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Figure 1: Temperature curve showing the cooling of the specimens.

Figure 2: The corrosion rig setup. The furnace chamber can move up and down to achieve thermal cycling.

Figure 3: GI-XRD results using angles of incidence of 2° , 5° and 10° after 20 thermal cycles between 100°C and 650°C in $\sim 15\text{ mol\%}$ water vapour.

Figure 4: EDS maps showing the O, Fe, Cr, Ni and Mn distributions after 10 thermal cycles between 100 °C and 650 °C in ~ 15 mol% water vapour.

Table 1: Chemical composition of oxides in at.% from EDS point analyses denoted A-F in Fig. 4. The results are from a specimen exposed to 10 thermal cycles between 100 °C and 650 °C in ~ 15 mol% water vapour.

Oxide	O	Cr	Fe	Ni	Mn
A	46.83	17.93	15.79	18.65	0.71
B	56.47	23.42	12.42	7.29	0.26
C	58.52	0.95	40.24	0.12	0.16
D	58.99	1.53	38.99	0.17	0.30
E	57.76	24.83	12.49	4.11	0.73
F	57.27	19.92	13.72	8.65	0.36

Figure 5: The development of oxides after thermal cycling between 100 °C and 650 °C in ~ 15 mol% water vapour for 2 cycles in a) and b), for 5 cycles in c) and d) and for 10 cycles in e) and f). a) represents an area with more Fe-rich oxide, c) and e) represent areas with more Cr-rich oxide and b), d) and f) represent areas with more Ni-rich and Fe-rich mixed oxide. Mn was detected using WDS and all other elements were detected using EDS.

Figure 6: Top-views of the development of oxides, after 1000 hours static oxidation in air at 650 °C, a), and after thermal cycling between 100 °C and 650 °C in ~ 15 mol% water vapour for: b) 2 cycles, c) 5 cycles and d) 10 cycles.

Figure 7: Cross-section LOM images of the development of α' martensite (BCC) regions, after 1000 hours isothermal oxidation in air at 650 $^{\circ}\text{C}$, a), and after thermal cycling between 100 $^{\circ}\text{C}$ and 650 $^{\circ}\text{C}$ in ~ 15 mol% water vapour for: b) 2 cycles, c) 5 cycles and d) 10 cycles.

Figure 8: Microstructure after grinding: a) cross-section, b) crystallographic orientations from an inverse pole figure map, where the white lines correspond to low angle grain boundaries ($1^\circ - 10^\circ$). A high angle grain boundary ($> 10^\circ$) is also present and marked GB. c) shows a phase identification map where red corresponds to FCC.

Figure 9: Microstructure shown on a cross-section after isothermal oxidation in air at 650 °C for 1000 hours, showing an α' martensite (BCC) layer at the surface. In the phase identification map, red corresponds to FCC and blue corresponds to BCC.

Figure 10: Microstructure after thermal cycling between 100 °C and 650 °C in ~ 15 mol% water vapour. Cross-sectioned specimens exposed to: a) 2 cycles and b) 5 cycles. The corresponding phase identification maps are shown in c) (2 cycles) and d) (5 cycles); red corresponds to FCC and blue corresponds to BCC.

Figure 11: Microstructure after 10 thermal cycles between 100 °C and 650 °C in ~ 15 mol% water vapour, showing: a) a cross-section and b) a phase identification map where red corresponds to FCC and blue corresponds to BCC.

Figure 12: Microstructure after 10 thermal cycles between 100 °C and 650 °C in ~ 15 mol% water vapour showing: a) a cross-section with various oxides, b) a LOM image where α' martensite (BCC) can be seen as darker fields, c) a magnification of the area with BCC, d) phase identification maps where red corresponds to FCC and blue corresponds to BCC e) crystallographic orientations from an IPF map and f) a magnification of internal BCC formed due to carbide formation at a grain boundary.

Figure 13: a) EDS line scan results after 10 thermal cycles between 100 °C and 650 °C in ~ 15 mol% water vapour. The α' martensite (BCC) region shows a Cr and Mn depleted area. b) ECCI-image showing the analysed area in a), where the line scan and the BCC region are marked.

Figure 14: ECCI-image of the microstructure after 10 thermal cycles between 100 °C and 650 °C in ~ 15 mol% water vapour. The image shows the effect of grain boundary diffusion of Cr, resulting in a thinner outer oxide layer (presumably Fe_2O_3) indicated by the three arrows at the α' martensite (BCC) regions. Above the α' martensite there is a Cr-rich $(\text{Cr,Fe})_2\text{O}_3$ scale on the metal surface, compared to the inward growing oxides (presumably a Ni-rich $(\text{Cr,Fe,Ni})_3\text{O}_4$ and a Ni-poor $(\text{Cr,Fe,Ni})_3\text{O}_4$ spinel oxides) next to it.

Figure 15: Cr content as function of distance from surface of a FCC grain used as input for Dictra simulation. The curve was established by assuming Cr consumption through carbide formation with a constant C content of 0.015 wt.%.

Figure 16: Modelled Cr profiles for several possible cases: a) BCC was retained as high temperature; b) BCC was retained 1 h at high temperature, then transformed to FCC; and c) BCC was transformed to FCC at high temperature but Cr diffusion was speed up by grain boundary diffusion.

Figure 17: A Fe-12.5 wt.% Ni- x wt.% Cr phase diagram expressed as a function of x . The Cr depleted region of the material entered the γ -loop at heating to 650 °C. Data from Thermo-Calc Software TCFE7 Steels/Fe-alloys database version 7 [32].

Figure 18: The corresponding C profile for the simulation in Fig. 16 c).

Figure 19: ECCI-image of the microstructure after 10 thermal cycles between 100 °C and 650 °C in ~ 15 mol% water vapour, showing: a) a Cr-oxide on top of a α' martensite (BCC) layer and also small particles of Cr-oxide and in b) the consumption of the FCC matrix and formation of inward growing oxides.