Corrosion behaviour of Ni and nickel aluminide coatings exposed in a biomass fired power plant for two years

Wu, D. L.; Dahl, K. V.; Christiansen, T. L.; Montgomery, M.; Hald, J.

Published in:
Surface and Coatings Technology

Link to article, DOI:
[10.1016/j.surfcoat.2018.12.129](https://doi.org/10.1016/j.surfcoat.2018.12.129)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Wu, D. L., Dahl, K. V., Christiansen, T. L., Montgomery, M., & Hald, J. (2019). Corrosion behaviour of Ni and nickel aluminide coatings exposed in a biomass fired power plant for two years. *Surface and Coatings Technology*, 362, 355-365. <https://doi.org/10.1016/j.surfcoat.2018.12.129>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Corrosion behaviour of Ni and nickel aluminide coatings exposed in a biomass fired power plant for two years

D.L. Wu^{1,2*}, K.V. Dahl², T.L. Christiansen², M. Montgomery², J. Hald²

1. College of Mechanical Engineering, Yangzhou University, Yangzhou 225127, P.R. China

2. Department of Mechanical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

*Corresponding author, email: duoliwu@outlook.com, dlwu10s@alum.imr.ac.cn

Abstract

Ni and Ni₂Al₃ coatings were applied to superheater tubes that were built into a wood-fired boiler with an outlet steam temperature of 520 °C. The present paper evaluates the performance of the coatings after two years of service. The corrosion performance of the coatings is discussed with respect to the temperature histograms and deposit composition and compared to the performance of the coatings after the first year. The Ni coatings showed extremely protective behaviour for 1 year however after 2 years exposure, the Ni coating was chemically attacked, thick NiO was formed and sulphur containing precipitates were present at the base of the Ni layer indicating grain boundary ingress of corrosive species. For the Ni₂Al₃ coatings, localized attack was observed after the first year of exposure, but after two years no intact nickel aluminide coatings were observed.

Keywords

Ni coating, Ni₂Al₃ coating, biomass combustion, power plant testing, fireside corrosion,

1. Introduction

Fireside corrosion of superheaters is a serious concern when combusting biomass in power plants. Corrosive compounds, such as potassium chloride (KCl), hydrogen chloride (HCl) and sulphur dioxide (SO₂) are the main reasons for the high corrosion rate of superheaters [1-3]. In particular, alloys relying on formation of protective chromium rich oxides are not resistant against the corrosive species formed during biomass firing. The chromium rich oxides are attacked by the active oxidation process [4-8] by penetration of Cl species through the oxides or by the formation of non-protective potassium chromate (K₂CrO₄) via the reaction between KCl and oxide [9-12] or a combination of the two mechanisms. The maximum allowable steam temperature is limited by the high corrosion rates resulting in an efficiency that is reduced compared to plants firing fossil fuels [2][13][14]. Laboratory experiments have shown that KCl reacts with Cr₂O₃ to form potassium chromate, however the reaction of alumina with KCl was not observed suggesting that a protective oxide of alumina will be more resistant in this environment [15]. In addition, in situ plant exposures of various materials have revealed that corrosion leads to preferential attack of chromium and iron, while Ni is left behind as a porous substrate, which indicates that Ni has less reactivity in KCl environments and could contribute to a protective coating [14]. Coatings are an option for improving the corrosion resistance of superheater materials and increasing the allowable steam temperature. Based on previous laboratory results by our group and others [16-23] which are discussed in detail in [24], Ni and nickel aluminide coatings were developed.

The current study investigates the corrosion performance of Ni coatings made by electroplating and Ni₂Al₃ coatings made by first Ni electroplating and then pack aluminizing. The Ni and Ni₂Al₃ coated tubes were exposed in a wood firing power plant with an outlet steam temperature of 520 °C for 2 years. The results are compared to the results obtained after 1 year of exposure, which were published in [24]. After 1 year of exposure in two different biomass firing power plants the coatings had performed well in the wood fired plant with 520 °C outlet steam temperature and few start/stop cycles, while the coatings failed in the straw fired plant with intensive thermal cycling and 540 °C outlet steam temperature. The present work reports on the coatings after 2 years of exposure in the wood fired power plant which reveal the presence of degradation mechanisms that were not discovered after 1 year of exposure. In some cases extra analyses of the 1 year samples were conducted to understand the degradation mechanisms that were only observed after 2 years. The performance of the coatings are directly compared to the performance after 1 year of exposure as well as to the performance of an uncoated tube of lean austenitic steel that is presently the material of choice for the actual plant.

2. Experimental procedure

2.1 Uncoated tube

Esshete 1250 (Fe-15Cr-9.5Ni-6.3Mn-1Nb-0.5Si-0.1C-1Mo-0.3V-0.015S-0.035P-0.005B wt. %) was utilized as superheater material in the wood fired power plant located in the Danish city of Randers. Esshete 1250 is one of the steels currently utilized for boiler superheaters in Danish biomass fired power plants. The tube test sections had dimensions of outer diameter 32 mm, inner diameter 19 mm and length 200 mm. Pre-exposure thickness of the tube was $6.34 \text{ mm} \pm 0.032 \text{ mm}$. Both Ni and Ni_2Al_3 coatings were applied to Esshete 1250 tube sections of this size.

2.2 Ni coating

The Ni coating was prepared using the electroplating method. The samples to be coated were pre-treated with ethanol washing, anodic degreaser and chemical activation. Prior to final nickel-plating, a pre-plating process was performed in a Woods nickel strike bath (5 minutes with a current density of 6 A/dm^2). The final Watts nickel-plating was performed at 45°C with a current density of 6 A/dm^2 for 100 minutes. After plating, the Ni coated samples were cleaned with ethanol and dried.

2.3 Ni_2Al_3 coating

The Ni_2Al_3 coatings were prepared by a two-step process where nickel was first electroplated followed by low temperature pack aluminizing. The nickel electroplating process was the same as for the Ni coating. Prior to pack aluminizing, the Ni plated tubes were heat-treated in argon for 2 hours at 650°C to strengthen the bonding between the steel and the nickel layer. Pack cementation of the Ni-coated tubes was undertaken in a tube furnace with an argon protective atmosphere. The Ni coated tube sections were embedded in pre-mixed pack powders (10 wt. % Al + 8 wt. % AlCl_3 + 82 wt. % Al_2O_3) and heated to 650°C and held there for 6 h. After aluminizing, the Ni_2Al_3 coated tubes were thoroughly cleaned with ethanol. To make the tube sections ready for welding, the coating was removed by machining from a 2 cm wide area from both ends of the Ni_2Al_3 coated tubes.

2.4 Power plant testing

Two Ni coated, two Ni_2Al_3 coated and one uncoated reference tubes were welded into a leading superheater tube of the Randers biomass fired combined heat and power (CHP) plant in Denmark, as presented in Figure 1. The fuel fired in the power plant was composed of 90 wt. % wood chips and 10 wt. % wood pellets.

The test tubes were located where the surface metal temperature of the tubes was presumed to be the highest based on assessment of flux and steam temperatures, and the plant owners observations. The test tubes were installed during the yearly overhaul in the summer of 2015. One set of tubes was removed by cutting from the middle of the uncoated tube during the summer overhaul in 2016 with the results of investigations reported in [24] and the other set of tubes was removed during the summer overhaul in 2017 with results reported in the present paper. A schematic of all the tubes is given in Figure 2.

Figure 1: Photograph of the test tubes, which were welded into a leading superheater tube of the biomass boiler. (a) Ni coated tube, (b) Ni_2Al_3 coated tube, (c) uncoated Esshete 1250 tube, (d) Ni coated tube and (e) Ni_2Al_3 coated tube.

Figure 2: Schematic of all the test tubes exposed in the Randers biomass fired boiler.

The average outlet steam temperature of the biomass-fired power plant was 520 °C and the total operation time ($T > 450^\circ\text{C}$) was approximately 7100 h in 2015-2016 and 6850 h in 2016-2017. Temperature measurements from the outlet of the tube where coatings were applied revealed that the operating conditions for heating season 2015-2016 and 2016-2017 were largely similar (Figure 3). For both heating seasons, the power plant had one cleaning stop, however in 2016-2017, the steam temperature was more volatile after the cleaning outage compared to after the stop in 2015-

2016. Since the measured temperature decreased as the tubes were subjected to operation and then increased after cleaning, this would indicate that deposit build-up leads to lower temperatures. The two heating seasons had similar temperature as shown from the histograms for the individual years, and the cumulative histogram for the two years (Figure 4), and the arithmetic mean temperature for the 2016-2017 heating season was 503°C compared with 507°C for 2015-2016 season, resulting in an arithmetic mean temperature of 505°C for the two years.

Figure 3: The outlet steam temperature data for the exposure period in 2015-2017.

Figure 4: Temperature histograms for the exposure period in 2015-2016 and 2016-2017.

2.5 Sample preparation and characterisation

After two years of plant exposure (described in section 2.4), tubes d (Ni) and e (Ni_2Al_3) as well as the remaining part of tube c (untreated Esshete 1250) were removed from the boiler in 2017. From all the tubes removed, rings were cut (around 1 cm) from the middle of each tube section. The cut was undertaken in dry conditions and the tube rings were embedded in epoxy resin in order to prepare cross-sectional samples. Grinding and polishing processes were performed according to normal metallographic techniques but using absolute ethanol as lubricant to reduce dissolution of water-soluble compounds. Deposit was removed from the Esshete 1250 tube using a scalpel, embedded in epoxy and prepared without lubricant to a 4000 grit finish. For microstructural and chemical analysis, the samples were analysed with a scanning electron microscope (FEI Inspect S) equipped with energy dispersive X-ray Spectroscopy (Oxford Instruments 50mm² X-Max silicon drift detector) or a JEOL JSM-5900 Scanning Electron Microscope (SEM) with Energy Dispersive Spectrometer (EDS). Prior to SEM characterization, a thin layer of carbon was sputtered on the sample surface using a Q150R Rotary-Pump Sputter. Image acquisition was performed in back-scattered electron (BSE) mode with high vacuum. The corrosion morphology was also examined with reflected light microscopy using an Olympus BH-2 optical microscope. The residual metal thickness or intact coating thickness was measured around the circumference of the tube using reflected light microscopy Olympus BH-2. The metal loss or coating loss was compared to the original tube/coating thickness and the results obtained after 1 year of exposure in order to follow the performance with respect to time.

3. Results

3.1 Deposit analysis

Deposit analysis after 1 year revealed an adherent deposit consisting of KCl and K_2SO_4 [24]. SEM-EDS analysis of the deposit removed from the tube in 2017 revealed similar deposit composition (Figure 5) indicating the presence of KCl and K_2SO_4 . Manganese and iron corrosion products were seen clearly at the base of the deposit originating from the alloy, however the presence of chromium was not so apparent. The base of the deposit is actually the outer oxide, however Cr normally is present in the inner oxide which is the position far from the base of the deposit.

Figure 5: SEM mapping of deposit adjacent the tube revealing elemental distribution.

3.2 Ni and Ni_2Al_3 coatings before exposure

The Ni coating was approximately 135 μm thick after deposition. The Ni_2Al_3 coating was a double layer, where the outer layer was Ni_2Al_3 with a thickness that varied from 50-70 μm and the inner Ni layer was around 100 μm . Details on the morphology of the coatings before exposures were reported in [24]. After exposure, the original Ni_2Al_3 coating consists of several nickel aluminide phases due to interdiffusion as described in [23], and the entire coating will therefore be referred to as the nickel aluminide coating.

3.3 Reference tube and coatings after exposure

3.3.1 Uncoated Esshete 1250 reference tube

The metal loss of the uncoated tube was measured in 24 positions around the circumference of the tube (Figure 6). The position 12:00 marks the flue gas direction. The tubes after 2 years exposure exhibited more attack around the circumference compared to 1 year with an increased amount of grain boundary attack, but the maximum depth of attack did not increase.

Figure 6: Residual metal thickness after 1 and 2 years exposure (red data points from 1 year exposure [24]).

Typical cross-sectional microstructure of the uncoated reference tubes after 1 year (2015-2016) and 2 years (2015-2017) boiler exposure are presented in Figure 7. The corrosion morphologies consisted of an outer Fe rich oxide and an inner more Cr rich oxide and Cr enrichment along the grain boundaries. A greater amount of grain boundary attack was observed after 2 years exposure.

Figure 7: Back-scattered SEM micrographs of cross-sections of the uncoated Esshete 1250 reference tubes, (a) 1 year boiler exposure, (b) 2 years exposure. Note the different magnifications.

3.2.2 *Ni coated tube*

The measured nickel coating thickness at 12 positions around the circumference is shown in Figure 8. Since the initial nickel layer was about 135 μm , and after the 1st year the average thickness was 133 ± 4 μm , there was minimal removal of the nickel layer, however after the second year, there was a clear decrease in thickness on the flue gas side and the leeside. The cross-sectional microstructures of the Ni coated tubes after exposure in the power plant are shown in Figure 9. Compared with the 1 year exposure, a much thicker Ni oxide had formed on the coating surface after 2 years exposure. After the second year the Ni coating was still well adherent to the underlying substrate and the substrate was apparently protected. No cracking was identified within the Ni coatings, however the presence of very small “precipitates” (at a depth shown by the double headed arrow) was observed only for the tube exposed for 2 years. These precipitates were clearly visible at higher magnifications (Figure 10).

Figure 8: Comparison of Ni layer thickness after exposure for 1 (data from [24]) and 2 years.

Figure 9: Back-scattered SEM micrographs of cross-sections of the Ni coated tubes, (a) 1 year exposure, and (b) 2 years exposure.

Further examination of the Ni coating near to the nickel-stainless steel interface revealed that there were enrichments of Mn and S at grain boundaries in the Ni layer shown by the arrow (Figure 10a). For the precipitates shown in Figure 10b, some of the surrounding area was also analysed due to the SEM-EDX interaction volume of the analysis, however the indication of sulphur and increased Mn was clear. The measured Mn contents were 5 wt.% which is significantly higher than the 1 wt.% Mn that was measured in the general interdiffusion area next to the precipitates. The Mn+S enrichments were always present within the nickel layer above the nickel-steel interface, probably at grain boundaries in the interdiffusion zone. Pathways from the nickel oxide surface through the Ni-layer could occasionally be observed; however in many cases they were not as evident as in

Figure 10a. Careful re-examination of the tube cross-sections from one year exposure revealed almost no Mn and S enrichments, indicating that their formation primarily occurred during the second year.

Figure 10: Other areas of tube after 2 years exposure a) showing intergranular pathways from oxide and region of precipitates (white double headed arrow), b) higher magnification at the alloy-nickel interface revealing Mn+S rich precipitates with analysis in wt.%.

3.2.3 Nickel aluminide coated tube

The residual thickness of layers around the circumference of the nickel aluminide coated tube after boiler exposure is shown in Figure 11.

Figure 11: Thickness of layers around the circumference of the nickel aluminide coated tube after 1 year (data from [24]) and 2 years exposure.

After 1 year exposure, the nickel aluminide coatings were still present in most positions and only in one position had the coating spalled. In several positions, the nickel aluminide coating was attacked and the attacked part of the coating was converted into corrosion products. After the first year, the underlying Ni layers (with thickness around 110-125 μm) were still attached to the underlying substrate and were not attacked in any of the positions. After 2 years exposure, the nickel aluminide coatings were severely depleted and intact nickel aluminide coatings (diagonal pattern on bar chart) were no longer present. The Ni layer was still adherent to the tube and only slightly attacked at the nickel aluminide coating-Ni interface where the lowest measured Ni thickness was 77 μm .

In Figure 12, the typical morphology of corrosion products observed on the nickel aluminide coated tubes after corrosion exposure in the biomass boiler for 2 years is shown. Figure 12a shows a spalled nickel aluminide coating, which corresponds to position 3:00 in Figure 11. The corrosion attack had completely consumed the coating and it had then spalled at the coating-Ni interface. For most of the area around the circumference ($\sim 90\%$), Figure 12b is a representative micrograph where the nickel aluminide coating was attacked and where corrosion products containing aluminium were still adherent. The composition and the distribution of the corrosion products in Figure 12b is presented in the elemental distribution maps. In this area, the outer layer consisted of K, S and O, presumably K_2SO_4 from the deposit, however from Figure 5, more KCl was present in other areas. Below the deposit, a porous corrosion product containing Al and Ni was identified with O and K also present within this layer. Traces of Cl were observed at the surface of the deposit probably as KCl and at the corrosion front at the left hand side of the micrograph. There were some Ni rich regions within the corrosion product which were analysed to be unreacted metallic Ni.

Figure 12: Back-scattered SEM micrographs of cross-sections of the nickel aluminide coated tubes after 2 years boiler exposure, (a) spallation of the nickel aluminide coating, (b) corrosion attack of the nickel aluminide coating revealed by EDS mapping.

To understand the degradation leading to the complete failure of the nickel aluminide coating after the second year, different stages of local corrosion attack of the nickel aluminide coating after the first year were studied in detail with SEM. Figure 13 shows localised areas after the first exposure year with different degrees of attack ranging from very limited attack in Figure 13a to descaling of the coating shown in Figure 13d. At most locations as described in [24], the nickel aluminide coating exhibited the behaviour shown in Figure 13a with only slight surface attack, which corresponds to the positions on the tube circumference from 10-3 o'clock and at 7 o'clock. In the positions shown in Figure 13b-d the coating was attacked and aluminium depletion of the coating was visible. The worst case location corresponding to the 4o'clock position is shown in Figure 13d, where the nickel aluminide coating reached end of life, and the underlying Ni layer was being attacked. At all locations, the underlying steel was still well protected without sign of corrosion attack.

Figure 13: Back-scattered SEM micrographs of cross-sections of the Ni_2Al_3 coated tubes showing different corrosion stages after 1 year boiler exposure, (a) protective surface, (b) Al depletion and porosity formation, (c) porosity and corrosion propagation, (d) penetration attack and coating spallation (white ellipse showing position of internal precipitation).

Due to the discovery of the Mn and S rich precipitates in the Ni coated tubes in the interdiffusion zone near the Ni steel interface, this was also examined for the nickel aluminide coated tubes after both the second and the first year of exposure. After the second year, similar precipitates could be observed around the entire circumference of the tube within the nickel layer close to the alloy interface. The position is marked with a double headed arrow in Figure 12b. After the first exposure year, precipitates could only be found below locations where the nickel aluminide coating had failed and the corrosion attack had penetrated to the Ni-layer. Figure 14b shows the precipitates found in the area marked by the white ellipse in Figure 13d. The precipitates were rich in Mn+S and sometimes Cr+S. Where the nickel aluminide coating attack ended above the Ni layer and no further penetration was visible (as shown in Figure 13a, b and c), no S enrichments were found (Figure 14a).

Figure 14: Different locations at Ni-steel interface after 1 year's exposure where a) the nickel aluminide coating was protective or not totally attacked and b) area where coating was consumed.

4. Discussion

The plant conditions with respect to temperature and the deposit composition condensed on the tubes were very similar in the two years of testing. Therefore, the present investigation of the tubes exposed for two years follows the time progression of attack of the different coatings without major changes in exposure conditions. In the present case, new degradation mechanisms become apparent after the second year of exposure, making it critical to follow the coating performance through several firing seasons. Based on the lowest residual thickness of coating + alloy or alloy after 2 years exposure, and assuming average initial thickness, the corrosion rate of the alloy and the two coatings was calculated. The metal loss of substrate was then calculated for 100000 hours for three different conditions (see Table 1). Apparently the Ni aluminide coating system has a slightly higher corrosion rate than the Ni coating and possible mechanisms for the better behavior of the Ni coating are discussed in the next section. Considering the limited initial thickness of the coatings of 0.13-0.16 mm, both types of coating would have failed before 100000 hours. However both coatings would result in a much lower metal loss of substrate than the uncoated steel indicating that the coatings chemical composition is generally more resistant than the steel currently used.

Table 1: Extrapolated metal loss of substrate based on 2 years exposure and lowest residual thickness

Material	Metal loss in mm after 100000 hours
Esshete 1250	1.2
Esshete 1250 + Ni coating	0.5
Esshete 1250 + Ni coating + Ni_2Al_3	0.6
Nickel aluminide coating only	failed

4.1. Uncoated Esshete 1250 reference tube

The oxide formed was a duplex oxide with an outer Fe and Mn rich oxide and inner chromium rich oxide with some grain boundary attack. The presence of Mn rich oxide above the Fe oxide relates to both Mn high affinity for chlorine together with MnCl_2 high volatility compared to Cr chloride [2]. The oxide observed was typical of exposure in biomass boilers for Esshete 1250 [25] and similar 18% Cr steels [26]. More widespread grain boundary attack was observed after 2 years exposure compared to 1 year. Since KCl was present as shown in Figure 5, a chemical reaction between chromium rich oxide and KCl can occur to release Cl species [12]. It is also possible that the attack was initiated by the corrosive chlorine species reaching the steel surface along pores or cracks in the oxide [4]. Based on the maximum metal loss measurement, a reduction of 1.2 mm could be extrapolated after 100,000 hour, which would lead to an acceptable lifetime for this tube. It is interesting to note that there was more metal loss on the leeside of the tube, which could be linked to the amount of deposit on the tube. Figure 3 shows that the tube temperature decreased during exposure time and then increased again after removal of deposits; this could be an explanation for increased attack on the leeside which would have less deposit and therefore higher temperature.

4.2. Ni coated tube

After 1 year of exposure at Randers, there was minimal attack of the nickel layer, and there was no clearly visible oxide [24], but after two years a distinct NiO layer could be observed. It would be expected that there was a NiO layer of a few microns after 7100 hours exposure based on measurements at 500 °C, where a 1 μm layer was formed after 136 hours in O_2 [27], however at temperatures around 500 °C, the effect of surface finish, grain size and presence of impurities can also influence oxidation rates [27][28]. A possible explanation for the protective behaviour observed during the first year could be the presence of a very thin sulphur rich layer formed during the initial exposure stages. The following results from literature can support this theory. Lillerud and Kofstad [29] noted that there was lower weight gain for Ni coated with Na_2SO_4 in an O_2 +4% SO_2 gas, and concluded that the Na_2SO_4 acted as a barrier. This is comparable to the deposit build-up of K_2SO_4 in the present case. A decrease in oxidation of Ni may be due to sulphur chemisorption on active surface sites thus decreasing the activity of Ni and therefore its oxidation [30][31]. For γ' - Ni_3Al exposed in a O_2 +0.1% SO_2 atmosphere, there were indications of a sulphur rich layer consisting of an outer 20 nm thick layer of NiS and an inner 90 nm NiO layer even after exposure only for 12 hours at 150°C [32]. The stability of NiO, NiSO_4 , Ni and NiS in SO_2 gas has

been investigated with respect to time at 540 °C, which showed that NiS was the stable compound while the other corrosion products decreased over time [33]. Another possibility is that a thin sulphur rich protective layer is the result of the nickel coating process, since nickel sulphate is one of the reagents in the nickel coating process. Thus sulphur species either from the combustion environment or the coating process could lead to a sulphur rich nickel layer which would reduce oxidation in the 1st year. Since this layer would be very thin, it was not observed with SEM of cross-sections and therefore validation of this hypothesis would require further investigation with other more advanced characterization methods. It must be noted that the presence of sulphur usually results in thicker less protective oxides [34], so will not be ideal for long term corrosion protection.

The corrosion exposure after two years reveals that the protective behaviour after one year was not sustainable and the progression of attack during the second year resulted in intergranular attack and migration of sulphur species into the Ni layer towards the steel interface. When the initial protective layer failed, a thick NiO layer grew which was probably less protective and allowed corrosive species to migrate through, leading to enrichments of manganese (originating from the steel) and sulphur close to the Ni-steel interface. This is discussed in more detail in Section 4.4.

4.3. Nickel aluminide coated tube

Previous laboratory assessments revealed good performance of model Ni-Al alloys and nickel aluminide coatings [20][21][23] [35]. In the first year of plant testing, the nickel aluminide coating was protective on the majority of the circumference (Figure 13a), however after 2 years, there was no remaining protective nickel aluminide coating. The breakdown of the coating can be followed in Figure 13b-d. Initially the attack progressed along grain boundaries and the Al was selectively removed and porosity was formed, likely via the formation of volatile aluminium chloride. In the later stage, the whole Ni₂Al₃ layer was attacked and depleted in aluminium, as the corrosion propagated to greater depths (Figure 13c). Finally, the inner nickel aluminide intermetallic phases were also penetrated (Figure 13d) and descaling from the Ni layer occurred. With longer exposure time of 2 years, the Al in the coating was fully consumed and the corroding species penetrated into the Ni layer (Figure 12b), also resulting in internal attack of the Ni coating further described in Section 4.4.

The nickel aluminide coating relies on the ability to form protective aluminium oxide to provide corrosion protection at high temperatures. Aluminium generally has high reactivity in dry chlorine-containing gas and above 200 °C, pure aluminium instantly ignites and aluminium chloride forms

[36]. In the pack aluminizing process utilised to coat the tubes, the volatility of aluminium chloride was exploited to form the coating [36]. However, if the reverse reaction can occur during plant exposure, aluminium will be removed from the coating via the formation of volatile aluminium chloride as observed by Galetz et al. [37]. The aluminium chloride would then be transformed into non-protective outer aluminium oxide similar to the active oxidation reactions often reported for Cr and Fe [4]. When both oxygen and chlorine are present in the corrosive atmosphere, it would depend on the local partial pressures of oxygen and chlorine in the gas phase as to which compounds will form, chlorides or oxides. Where a continuous layer of aluminium oxide was established, a protective surface was formed as shown in Figure 13a. If the oxygen partial pressure was very low, the alumina oxide could either fail to establish on the surface or break down with time and the corrosion attack would be further propagated (Figure 13b-d). The α - Al_2O_3 polymorph is known to be more protective than the other alumina polymorphs (γ , θ , δ) also against KCl attack and this has shown promising results against KCl attack in the laboratory for FeCrAl alloys [22][38], however thermal cycling was shown to result in cracks and failure [38]. Since the superheater peak steam temperature at Randers was about 520 °C (Figure 4), the presence of α - Al_2O_3 is not expected. Laboratory testing at 600 °C for 1 week in 5% O_2 +40% H_2O + N_2 with KCl deposit of the nickel aluminide coating used in the power plant exposure revealed that there was reactivity between KCl and the Al_2O_3 oxide formed on the coating [35]. The reaction rate observed in the laboratory exposures was very low, but the reaction would still lead to release of chlorine species that could with time propagate the corrosion attack observed in the plant exposed samples. As shown in the Cl EDX map of Figure 12, chlorine species were present on both sides of the K and Al rich oxide making the release of chlorine species from a reaction between KCl and alumina a valid hypothesis. The further inward migration of the chlorine species and formation of volatile aluminium chloride then consumed the coating. Preoxidation to form α - Al_2O_3 could possibly increase the corrosion resistance of the aluminide coating, however it would require high temperature, which would affect the underlying steel and the alumina layer would still be susceptible to cracking from thermal cycling.

It is important to note that in the present case, breakdown of the nickel aluminide coating was not due to mechanical failure but due to chemical attack presumably after the initial failure of a protective oxide. Therefore, even at the fairly low temperatures in the wood fired plant after a period of 2 years, the nickel aluminide coating was no longer corrosion resistant.

4.4. Mn and S rich precipitates at the Ni steel interface

Enrichments of Mn and S were observed within the nickel layer close to the steel surface after 2 years of exposure, but these precipitates were not present after 1 year of exposure. This indicated the migration of corrosive species through the Ni coating after failure of the protective layer described in section 4.2. Since it was sulphides and not oxides that were observed, it must have been S species migrating through the nickel at grain boundaries and not the SO₂ gas phase molecule. In the interdiffusion zone at the base of the nickel alloying elements can diffuse outwards into the Ni and since Mn has a high affinity to S, this could have resulted in the preferential formation of manganese sulphides within the nickel layer.

Another explanation involves the transport of Cl species through the Ni layer. Similar to sulphur, Cl species (ions or atoms) could migrate through the Ni layer as their ionic radii and atomic radii are slightly smaller than sulphide ions/sulphur atoms. The transport of Cl⁻ ions resulting in corrosion in Cl environments has been previously suggested by Folkesson et al. [39]. Rammer and Galetz [40] suggest the Cl species dissociate and Cl atoms are adsorbed on the surface and then surface diffusion (or in our case grain boundary diffusion) is a fast process. Cl species can also react with Mn (which is the element having the highest affinity for Cl within the alloy) in the interdiffusion zone above the alloy-Ni interface, resulting in formation of gas porosities containing MnCl₂ at grain boundaries, which in turn could react with sulphur resulting in subsequent formation of Mn sulphides. This would release Cl species to again react with alloying elements in the interdiffusion zone. Cl species were not detected in the tubes from Randers investigated in the present paper, however a similar precipitation reaction was observed in the Ni layer below a nickel aluminide coated TP347H tube (by the same process from our laboratory) exposed in the more corrosive Maribo Sakskøbing straw fired plant [41] [24]. The TP347H steel has a lower Mn content (< 2 wt. %), and here both Cr and Mn were found to be enriched in the S precipitations within the Ni coating. In addition metal chloride species were heavily present in the vicinity of the Ni-steel interface. In some areas corrosion products from the TP347H tube were identified above the nickel layer, which is probably due to mechanical breakdown of the layer. Therefore in our previous paper [41], it was not clear how the corrosive species migrated through the nickel and due to the excessive thermal cycling at the Maribo-Sakskøbing plant, mechanical failure of the coating was a possibility. However, in the present study, no mechanical failure of the Ni coating/layer could be observed, indicating that migration of corrosive species probably occurred by diffusion via grain boundaries through the mechanically intact coating. During the first year the Ni coating was intact, since the corrosive species first had to penetrate this layer. Ansey and Ahrens [42] showed that electroplated Ni applied in waste incineration plants suffered intergranular attack, which they ascribed to the

presence of Fe impurities originating from the plating process. Based on observations from this paper, another explanation could be that Cl species migrated through the Ni layer to the Ni coating-carbon steel tube interface, reacted with Fe from the underlying carbon steel forming metal chlorides which then volatilised and oxidised at the surface of the coating. This would result in the presence of Fe oxide at grain boundaries near the surface of the Ni coating as described by Ansey and Ahrens [42].

The presence of sulphur rich precipitates within the nickel just above the Ni-steel interface was also observed around the total circumference for the nickel aluminide coating after 2 years exposure. The nickel aluminide coating exposed for 1 year revealed that where the nickel aluminide coating was present, no sulphur rich precipitates were observed (Figure 14a). Mn+S enrichments were present only where the coating had been penetrated and descaling was observed (Figure 13d lefthand side). This implies that the sulphur found within these precipitates could not have originated from the plating process but must come from the combustion environment. When the nickel aluminide coating was consumed with resulting formation of AlCl_3 , this would then have resulted in migration of both Cl and S species through the remaining Ni-layer as previously described.

The reported corrosion rate of the Ni coating was based on the reduction of the Ni layer compared with the original thickness. However, the presence of corrosive species at the Ni-layer steel interface could with further progression be envisioned to lead to exfoliation of the layer and therefore a faster failure of the layer compared to that predicted by the reported corrosion rate.

5. Conclusions

The metal temperatures and deposit composition in the second year were similar to the first year which allows the comparison of performance of the coatings where exposure time is a variable. The corrosion rate at these temperatures is very low, which based on the measurements from the uncoated Esshete 1250 tube after 2 years would amount to 1.2 mm metal loss after 100,000 hours. The initial results after 1 year were positive for both the Ni coating and the nickel aluminide coating. However, despite the low temperatures in this boiler, the Ni coating was attacked after two years and revealed intergranular attack and formation of metal sulphides. The nickel aluminide coating was completely consumed after two years through chemical degradation and subsequent descaling. The exposure in the plant has highlighted chemical mechanisms of degradation which were not apparent from short-term laboratory exposures. The fact that there were differences from 1 to 2 years highlights the necessity for long-term plant exposures.

Acknowledgements

This paper was written under the project EUDP 14-I New Coatings for Biomass Firing. The authors also acknowledge financial support from the FORSKEL project “Biomass Corrosion Management”.

References

- [1] H.P. Nielsen, F.J. Frandsen, K. Dam-Johansen, L.L. Baxter, Implications of chlorine-associated corrosion on the operation of biomass-fired boilers, *Prog. Energy Combust. Sci.* 26 (2000) 283–298.
- [2] M. Montgomery, A. Karlsson, O.H. Larsen, Field test corrosion experiments in Denmark with biomass fuels Part I: Straw-firing, *Mater. Corros.* 53 (2002) 121–131.
- [3] F.J. Frandsen, Ash formation, deposition and corrosion when utilizing straw for heat and power production, Dr. Techn. Thesis, Technical University of Denmark, (2011).
- [4] H.J. Grabke, E. Reese, M. Spiegel, The effects of chlorides, hydrogen chloride, and sulfur dioxide in the oxidation of steels below deposits, *Corros. Sci.* 37 (1995) 1023–1043.
- [5] K. Salmenoja, K. Mäkelä, M. Hupa, R. Backman, Superheater corrosion in environments containing potassium and chlorine, *J. Inst. Energy.* 69 (1996) 155–162.
- [6] R.A. Antunes, M.C.L. de Oliveira, Corrosion in biomass combustion: A materials selection analysis and its interaction with corrosion mechanisms and mitigation strategies, *Corros. Sci.* 76 (2013) 6–26.
- [7] M. Paneru, G. Stein-Brzozowska, J. Maier, G. Scheffknecht, Corrosion mechanism of alloy 310 austenitic steel beneath NaCl deposit under varying SO₂ concentrations in an oxy-fuel combustion atmosphere, *Energy and Fuels.* 27 (2013) 5699–5705.
- [8] S.C. Van Lith, F.J. Frandsen, M. Montgomery, T. Vilhelmsen, S.A. Jensen, Lab-scale investigation of deposit-induced chlorine corrosion of superheater materials under simulated biomass-firing conditions. Part 1: Exposure at 560 °C, *Energy and Fuels.* 23 (2009) 3457–3468.
- [9] J. Pettersson, H. Asteman, J.E. Svensson, L.G. Johansson, KCl induced corrosion of a 304-type austenitic stainless steel at 600 °C; the role of potassium, *Oxid. Met.* 64 (2005) 23–41.
- [10] T. Jonsson, J. Froitzheim, J. Pettersson, J.E. Svensson, L.G. Johansson, M. Halvarsson, The influence of KCl on the corrosion of an Austenitic stainless steel (304L) in oxidizing humid conditions at 600 °C: A microstructural study, *Oxid. Met.* 72 (2009) 213–239.
- [11] S. Enestam, D. Bankiewicz, J. Tuiremo, K. Mäkelä, M. Hupa, Are NaCl and KCl equally corrosive on superheater materials of steam boilers?, *Fuel.* 104 (2013) 294–306.
- [12] J. Pettersson, J.E. Svensson, L.G. Johansson, Alkali Induced Corrosion of 304-type Austenitic Stainless Steel at 600 degrees C; Comparison between KCl, K₂CO₃ and K₂SO₄, *Mater. Sci. Forum.* 595–598 (2008) 367–375.
- [13] A.A. Khan, W. de Jong, P.J. Jansens, H. Spliethoff, Biomass combustion in fluidized bed boilers: Potential problems and remedies, *Fuel Process. Technol.* 90 (2009) 21–50.
- [14] O.H. Larsen, M. Montgomery, Materials problems and solutions in biomass fired plants, *Energy Mater.* 1 (2006) 227–237.

- [15] S. Kiamehr, K.V. Dahl, T.N. Lomholt, T.L. Christiansen, M.A.J Somers, High Temperature Corrosion due to Biomass Firing: A study on the reactivity between potassium chloride, ISHOC 2014 Proceedings International Symposium on High Temperature Oxidation and Corrosion 2014, 144-147.
- [16] S.C. Cha, M. Spiegel, Local reactions of KCl particles with iron, nickel and chromium surfaces, *Mater. Corros.* 57 (2006) 159–164.
- [17] T. Jonsson, A. Slomian, T.N. Lomholt, S. Kiamehr, K. V. Dahl, Microstructural investigations of pure nickel exposed to KCl induced high temperature corrosion, *Mater. High Temp.* 32 (2015) 44–49.
- [18] Y.S. Li, M. Spiegel, Internal Oxidation of Fe–Al Alloys in a KCl-Air Atmosphere at 650°C, *Oxid. Met.* 61 (2004) 303–322.
- [19] S. Kiamehr, Materials Solutions to Mitigate the Alkali Chloride-Induced High Temperature Corrosion, Ph.D Thesis DTU Mechanical Engineering, November 2014, p162.
- [20] Y.S. Li, M. Spiegel, S. Shimada, Corrosion behaviour of various model alloys with NaCl-KCl coating, *Mater. Chem. Phys.* 93 (2005) 217–223.
- [21] S. Kiamehr, T.N. Lomholt, K.V. Dahl, T.L. Christiansen, M.A.J. Somers, Application of aluminum diffusion coatings to mitigate the KCl-induced high-temperature corrosion, *Mater. Corros.* (2016) 82–94.
- [22] S.C. Okoro, M. Montgomery, F.J. Frandsen, K. Pantleon, Influence of Preoxidation on High-Temperature Corrosion of a FeCrAl Alloy Under Conditions Relevant to Biomass Firing, *Oxid. Met.* 89 (2018) 99-122.
- [23] D. Wu, S.C. Okoro, K.V. Dahl, M. Montgomery, K. Pantleon, J. Hald, Laboratory Investigations of Ni-Al Coatings Exposed to Conditions Simulating Biomass Firing, 9th Int. Symp. Corros. Prot. Mater. (2016) 1–8.
- [24] D.L. Wu, K.V. Dahl, J.L. Madsen, T.L. Christiansen, M. Montgomery, J. Hald, Effects of different fuel specifications and operation conditions on the performance of coated and uncoated superheater tubes in two different biomass fired boilers, *ACS Appl. Energy Mater.* 1 (2018) 1463-1475.
- [25] P. Henderson, M. Lundberg, Corrosion of superheaters at 600C in biomass-fired boilers, *Proceedings Proc. 9th Liege Conference: Materials for Advanced Power Engineering.* (2010) 1116-1125.
- [26] M. Montgomery, S.A. Jensen, A. Hansson, O. Biede, T. Vilhelmsen, *Proceedings Proc. 9th Liege Conference : Materials for Advanced Power Engineering.* (2010) 1096-1105.
- [27] R. Peraldi, D. Monceau, B. Pieraggi, Correlations between growth kinetics and microstructure for scales formed by high temperature oxidation of pure nickel. II. Growth Kinetics, *Oxid. Met.* 58 (2002) 275-295.
- [28] R. Haugsrud, On the high temperature oxidation of nickel, *Corros. Sci.* 45 (2003) 211-235
- [29] K.P Lillerud, P. Kofstad, Sulfate-induced hot corrosion of nickel, *Oxid. Met.* 21 (1984) 233-270.
- [30] G. Luckman, R.S. Polizzotti, An effect of chemisorbing surface reactions poisons on the transition from internal to external oxidation, *Metall. Mater. Trans. A*, 16A, (January 1985) 133-136.
- [31] M. Blaszcyszyn, R. Blaszcyszyn, R. Meclewski, A.J. Melmed, T.E. Madey, Interactions of sulfur with nickel surfaces: adsorption, diffusion and desorption, *Surf. Sci.* 131 (1983) 433-477.

- [32] X. Liu, C. Bonifacio, J.C. Yang, P. Ercius, B. Gleeson, Effect of environmental sulfur on the structure of alumina scales formed on Ni-base alloys, *Acta Mater.* 97 (2015) 41-49.
- [33] A.K. Roslik, V.N. Konev, A.M. Maltsev, Some aspects of the mechanism of high temperature oxidation of nickel in SO₂, *Oxid. Met.* 43 (1995) 59-82.
- [34] F. Gesmundo, D.J. Young, S.K. Roy, The high temperature corrosion of metals in sulphidising-oxidising environments: a critical review, *High Temp. Mat. Proc.* 8 (1989) 149-190.
- [35] K.V. Dahl, A. Slomian, T.N. Lomholt, S. Kiamehr, F.B. Grumsen, M. Montgomery, T. Jonsson, Characterization of pack cemented Ni₂Al₃ coating exposed to KCl (s) induced corrosion at 600 °C, *Mater. High Temp.* 3409 (2017) 1–8.
- [36] R. Bianco, R.A. Rapp, Pack Cementation Diffusion Coatings, *Metall. Ceram. Prot. Coatings.* (1996) 236–260.
- [37] M.C. Galetz, B. Rammer, M. Schütze, The protection of aluminides by alloying with molybdenum in high chloride containing atmospheres at 1000C, *Oxid. Met.* 81, (2014) 151-165.
- [38] N. Israelsson, K.A. Unocic, K. Hellström, J.E. Svensson, L.G. Johansson, Cyclic corrosion and chlorination of an FeCrAl alloy in the presence of KCl, *Oxid. Met.* 84 (2015) 269-290.
- [39] N. Folkeson, L.G. Johansson, J.E. Svensson, Initial stages of the HCl-induced High Temperature Corrosion of Alloy 310, *J. Electrochem. Soc.* 154 (9), (2007) C515-C521.
- [40] B. Rammer, M.C. Galetz, Kinetics of volatilization of high temperature corrosion products and its application to chlorine corrosion, *Mater. Corros.* 68 (2017) 186-196.
- [41] D. Wu, K.V. Dahl KV, T.L. Christiansen, M. Montgomery M, J. Hald, Microstructural investigations of Ni and Ni₂Al₃ coatings exposed in biomass power plants, *Mater. High Temp.* 35:1-3, (2018) 255-266.
- [42] J.W. Ansey, F. Ahrens, Thick-layer nickel coating as corrosion protection for Components in Steam Generators (in German), *VGB PowerTech* 12 (2003) 106-110.