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To cite this article: Stefano Mori, Joy Sumner, Justin Bouvet & Nigel J. Simms (2022) Fireside and steamside performance in biomass power plant, Materials at High Temperatures, 39:2, 106-121, DOI: [10.1080/09603409.2021.2019657](https://doi.org/10.1080/09603409.2021.2019657)

To link to this article: <https://doi.org/10.1080/09603409.2021.2019657>



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Published online: 10 Jan 2022.



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Fireside and steamside performance in biomass power plant

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ABSTRACT

To address the challenge of climate change, the energy sector is developing novel strategies to reduce greenhouse gas emissions. One route is to increase steam temperatures and pressures (above 650°C and 350 bar). Another route is the use of potential net zero emissions fuels, like biomass. Both these routes cause issues for the heat-exchanger materials due to the differences in composition of the combustion environments generated, compared to coal.

This paper characterises candidate superheater/reheater alloys' behaviour (Sanicro 25 and IN740) at 700°C. 1,000 h fireside and 10,000 h steamside exposures were carried out, the first using 'deposit recoat' techniques. Sample cross-sections were analysed using dimensional metrology and SEM/EDX. Fireside results for Sanicro 25 showed degradation throughout the samples' thicknesses. In steamside exposures, Sanicro 25 formed a Cr-rich scale, and Nb rich particles (z-phase). IN740 showed lower metal and sound metal damage than Sanicro 25 for fireside and steam oxidation exposures.

ARTICLE HISTORY

Received 4 July 2021

Accepted 10 December 2021

KEYWORDS

Biomass; fireside corrosion; steamside oxidation; sanicro 25; IN740; dimensional metrology

Introduction

Reducing greenhouse gas emissions is needed to address the challenge of climate change. To address this challenge, current energy systems and future generation methods need to have improved efficiencies and reduced emissions [1–6]. There are several possible routes to address those challenges. For solid fuel combustion plants, two of the main routes can be proposed: one involves an increase in steam system temperatures and pressures, leading to an improvement in plant efficiency (such that greenhouse gas emissions per unit energy drop); the second route is to use 'low-carbon' renewable fuels (such as biomass) to decrease the total carbon footprint [7–10]. Increasing steam temperatures/pressures and firing biomass can lead to a different, and potentially more aggressive environment, for heat exchanger materials. Moving towards 'advanced ultra-supercritical' (AUSC) or 'hyper-supercritical' (HSC) conditions – steam temperatures above 650°C and pressures up to 350 bar – will also place a greater importance on the mechanical properties of the heat-exchangers. To address such requirements expensive high-Ni stainless steels or even more costly Ni-based alloys will be required [11]. These alloys have been studied in such conditions, even if the main focus has been assessing their mechanical behaviour, not providing a comprehensive understanding of the fireside corrosion and oxidation performances of the materials [6,12–17].

AUSC will move towards higher steam temperatures, which will be accompanied with an increase in the heat exchanger metal temperatures. Furthermore,

the use of biomass, which has different chemical compositions and structures compared to coals, will change the chemistry of the combustion environment to which the heat exchanger materials are exposed. Fireside corrosion is usually associated with solid fuel fired systems in which there is a peak (or several peaks) in corrosion damage as a function of metal temperature. Such peaks are dependent on the local exposure environment (i.e. a result of the fuel chemical composition) and the heat exchanger surface temperature. The result of this behaviour, together with differences in the local metal temperatures in the heat exchanger network, implies that some regions of the heat exchangers will have metal temperatures that are hotter than the damage peak temperature, leading to relatively lower damage rates, while other regions will have lower metal temperatures that actually lie towards the damage peak, resulting in higher damage rates [18]. Biomass firing will cause changes in the composition of the combustion gas stream, and therefore in the resulting deposits, forming a potentially more corrosive environment. The chemical composition of the different fuels alters this bell-shaped distribution of damage, as different species could form on the tubes' surfaces [16,19–21]. As such, plants firing biomass may be limited to run at lower temperatures to prevent rapid failure [22].

Steamside operating conditions will also have an impact on the behaviour of the materials. Several papers have characterised the formation of protective Cr oxides on different materials (e.g. Sanicro 25,

IN740) [23–26]. For Sanicro 25 it has been proven that it is possible to produce a protective Cr oxide layer at temperatures below 700°C, while forming an Fe-rich oxide at temperatures of 700°C or above [25]. Further study of this may help to produce a clearer understanding of the ability of this material to be used for AUSC applications.

This paper focuses on characterising the behaviour of two candidate superheater/reheater alloys for the highest temperature parts of AUSC systems (i.e. Sanicro 25 and IN740) in an accelerated laboratory test simulating a biomass combustion environment at 700°C (one of the temperatures at which AUSC heat exchangers should operate in the future), and the corresponding simulated steamside laboratory conditions (i.e. temperatures of 650°C and 700°C). Currently, there is not a clear understanding of the ability of these materials to cope with such biomass-fired conditions (KCl deposits), since those materials were developed to work in coal combustion plants (alkali iron sulphate deposits). Therefore, investigating their behaviour is necessary. It is also necessary to understand the degradation mechanisms taking place in the biomass combustion environment, where the role of Cl could significantly change the attack mechanism on the alloy.

Materials and methods

Materials

The materials used for the work were a highly alloyed stainless steel, Sanicro 25, and a nickel-based alloy, IN740. Sanicro 25 has been chosen since it contains a high amount of Ni and is able to cope with high temperatures. Typical compositions of these alloys are given in Table 1. Table 2 Table 3

The materials were supplied as tubes (38 mm outer diameter) which were cut and then machined into tube segment specimens (Figure 1). The typical dimensions of specimens were ~15 mm long × ~15 mm wide, with a ~4 mm wall thickness. A notch was used as a reference point for the sectioning after mounting in resin. All the surfaces of the specimens were given a UK 600 grit finish.

Exposure condition

Two different sets of tests were carried out to study steamside oxidation and biomass fireside corrosion (Tables 2 and 3): at temperatures of 650°C and

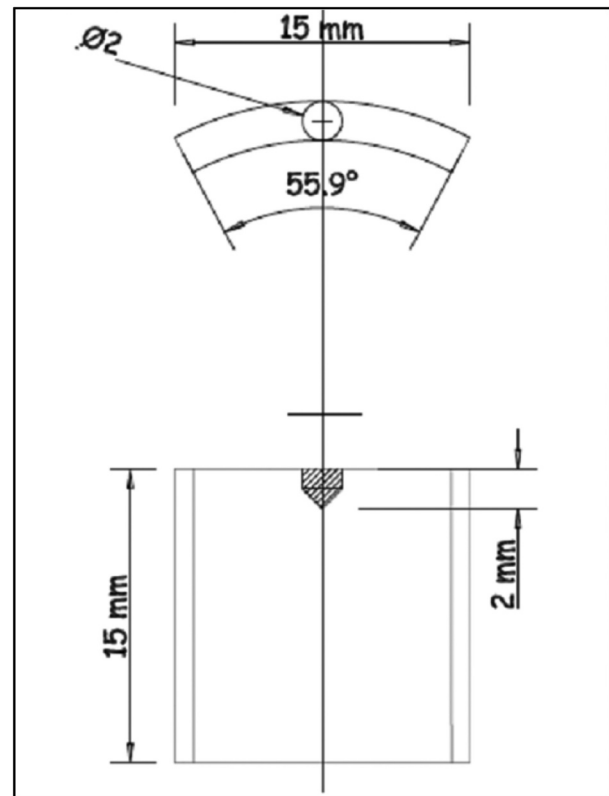


Figure 1. Sample dimensions and shapes [35].

Table 2. List of samples exposed to steamside environment, with exposure times.

	Temperature (°C)	500 h	1500 h	2500 h	5000 h	10,000 h
Sanicro 25	650	1	1	1	1	
Sanicro 25	700	1	1	1	1	1
IN740	700				1	1

Table 3. List of samples exposed to fireside corrosion environment, with exposure times.

	200 h	400 h	600 h	800 h	1000 h
Sanicro 25	1	1	1	1	3
IN740	1	1	1	1	3

700°C for steamside oxidation, and at 700°C for biomass fireside corrosion. The temperature of 700°C is within the range of metal temperatures anticipated for heat exchanger materials in AUSC power plants.

Steamside oxidation

Steam oxidation tests were performed in a horizontal tube furnace, using an alumina-lined stainless-steel reaction vessel. Samples were placed inside the furnace in alumina crucibles. The rig used for this work

Table 1. Typical composition of the alloys used in the work; composition is given in wt% [27,28].

Trade name	Fe	Ni	Cr	Co	Mo	C	Si	Mn	S	P	Al	Ti	Nb	Cu	N	W
Sanicro 25	Bal	25	22.5	1.5		<0.1	0.2	0.5	<0.015	<0.025			0.5	3.0	0.23	3.6
IN740	0.7	Bal	25	20	0.5	0.03	0.5	0.3			0.9	1.8	2			

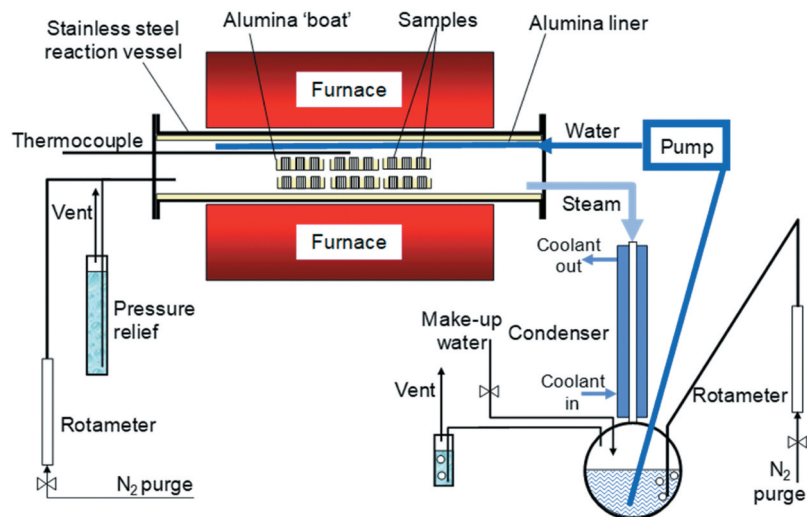


Figure 2. Rig layout for steamside oxidation tests [29].

generated the steam by pumping high purity double de-ionised water, that is continuously de-oxygenised by purging with 'oxygen free nitrogen' (OFN), from a reservoir. The steam passes over the samples/crucibles and then flows into the condenser before the water returns to the reservoir. The system was purged before heating and during cooling for each cycle to ensure that no condensation occurred in the furnace. Exposures were carried out for 250 h periods at 650°C and 700°C.

Prior to their exposure, the samples were cleaned using acetone then IPA (isopropyl alcohol) in an ultrasonic bath for 10 minutes each. Dimensional metrology was carried on the clean samples using a digital micrometre (resolution of 1 μ m). Pre-exposure measurements were collected to allow precise dimension metrology of exposed samples. (Figure 2)

Fireside corrosion

Fireside corrosion tests were carried out in alumina-lined, controlled-atmosphere, vertical tube furnaces. Samples were accommodated in alumina crucibles. Tests were carried on in 200 h cycles up to 1000 h, using the 'deposit recoat' technique [19,20].

Prior to their exposures, samples were cleaned using acetone then IPA in an ultrasonic bath for 10 minutes each. Pre-exposure dimensional metrology was carried on the clean samples using a digital micrometre (resolution of 1 μ m). The cleaned and measured samples were then brush painted with deposit slurries to give coverage of ~ 20 mg/cm² of dried deposit (deposit composition 100% KCl) to simulate deposition in a biomass firing environment (these exposure conditions were deliberately chosen to accelerate the fireside corrosion processes). The deposit was re-

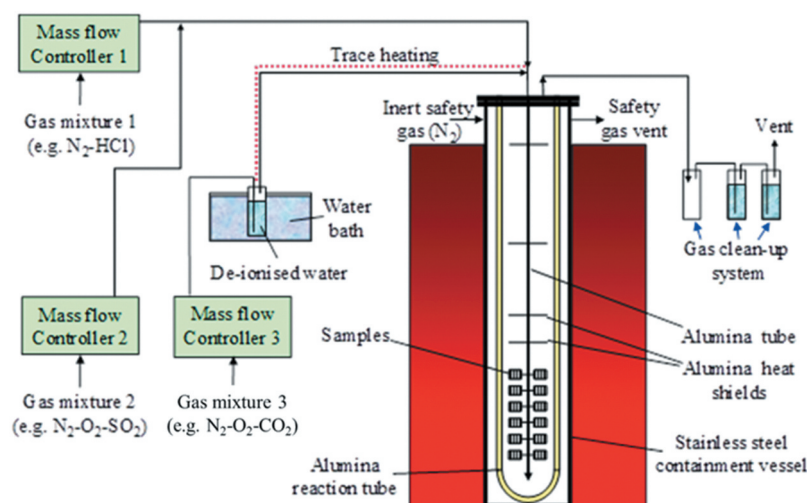


Figure 3. Rig layout for fireside corrosion tests [20].

Table 4. Inlet gas composition used for fireside corrosion tests.

N ₂	O ₂	CO ₂	SO ₂	HCl	H ₂ O
Balance	4.0% vol	12.9% vol	210 vpm	170 vpm	16.4% vol

applied every 200 h. Samples and crucibles were weighed before and after every cycle, as part of this deposit recoat process.

In addition to exposing samples coated in deposit, bare samples (without a deposit) were exposed to provide the baseline reference that is needed for analysis of the dimensional metrology data (details in the following section).

Pre-mixed gases were supplied to the furnace via mass flow controllers, at a flow rate of 100 cm³/min, to achieve the desired gas compositions (Table 4). To add the desired level of moisture, water was injected into the furnace using a peristaltic pump. (Figure 3)

Analytical techniques

Sample cross-sections were prepared for analysis after exposure. Samples were cold mounted to avoid loss of deposit/scale from their surfaces. Cold mounting was performed using glass ballotini beads mixed with low shrinkage epoxy resin, and was then followed by cutting, grinding, and polishing down to 3 µm diamond suspension. All the steps were performed using an oil-based medium, to avoid the contamination and dissolution of corrosion products from the sample cross-sections. The cross-sections were examined by scanning electron microscopy (SEM) to investigate sample microstructures and the scales that had formed on the materials. To

identify the distribution of elements energy-dispersive X-ray spectroscopy (EDX) was used to determine scale growth processes and scale/deposit/gas interactions.

Dimensional metrology was used to generate statistical distributions of corrosion damage data for each exposed sample [30–32]. Sample cross-sections were measured with an image analyser to collect x-y coordinates for the remaining metal and any internal damage. These data were compared to the pre-exposure metrology data collected earlier to determine the alloy performance. This was also done for bare samples (i.e. with no deposit) exposed to same environment to determine the damage caused by the deposit. To produce cumulative probability curves the data were then ordered before plotting. The plots showed damage distributions associated with each material/deposit/gas/temperature combination. A schematic diagram of the process is given in Figure 4.

Fireside induced corrosion damage is presented as ‘metal change’ (negative number showing the amount of material lost) and ‘sound metal change’ (metal change plus any visible internal damage) as a function of cumulative probability. For the samples exposed to steam, a different data analysis method had to be used and the cumulative probability distributions generated show the thickness of the oxide scale on the samples caused by the interaction with the environment (as the oxide scale was too thin for metal change to be used to give a reliable estimate of the oxide thicknesses that had formed on these alloys). These cumulative probability distribution datasets were the key outputs of this study and were produced in line with current standards for high-temperature corrosion assessment [30–32]. Use of these statistical

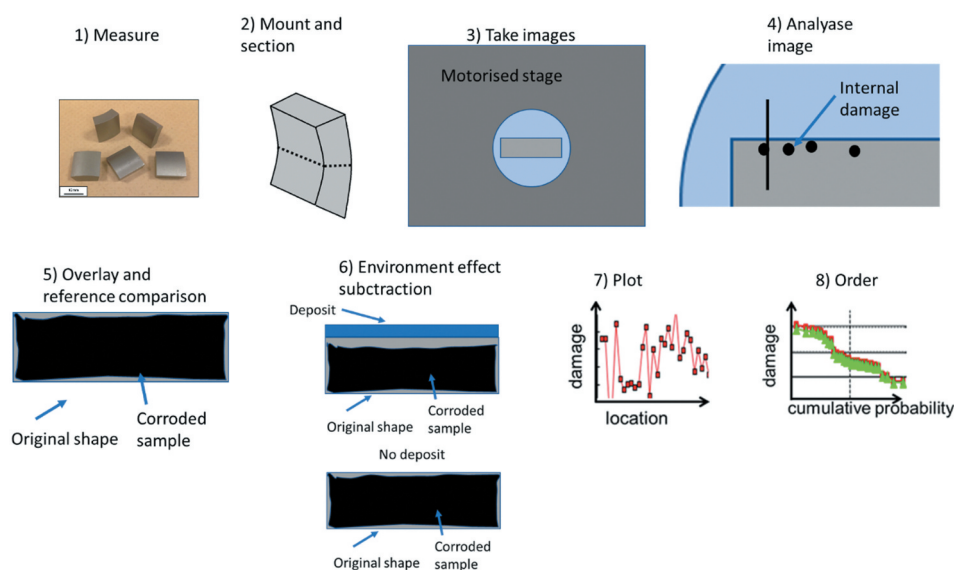


Figure 4. Schematic representation of the dimensional metrology process. The process consists of several steps 1) measurement of samples prior to exposure, 2) mounting the samples in resin, 3) imaging of samples' perimeters, 4) selecting of points at the metal surface and for internal damage, 5) comparison with pre-exposure measurements and reference samples, 6) subtraction of the environmental effect by comparison to a sample without deposit, 7) plot of the resulting change in metal against location and 8) re-order of the data based on cumulative probability.

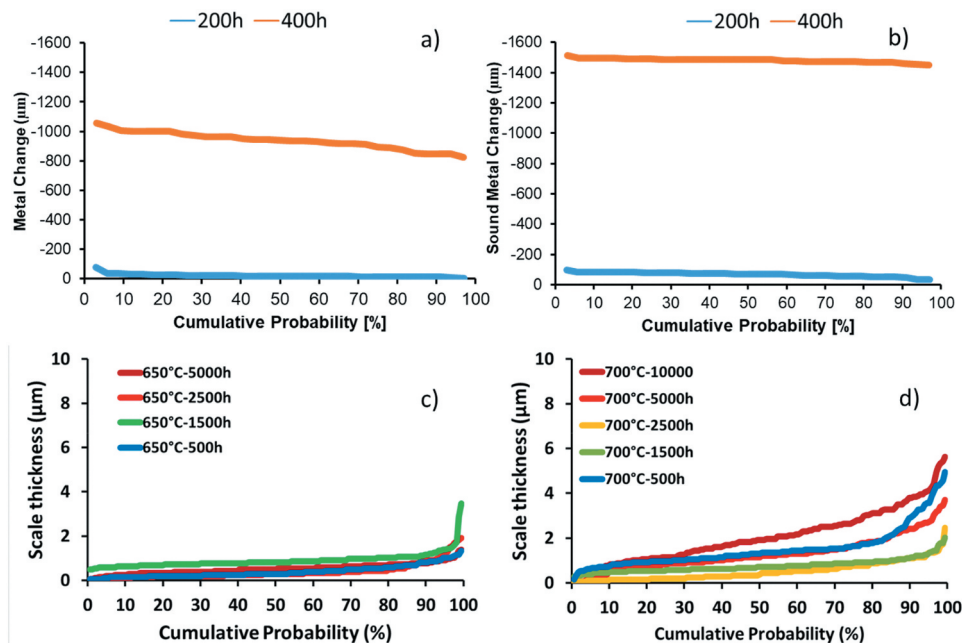


Figure 5. Fireside distribution plots for a) metal change, b) sound metal change, and steamside scale thicknesses at c) 650°C and d) 700°C for Sanicro 25.

methods for analysing corrosion data is becoming more widespread and provides a good basis for corrosion model development and validation [33,34].

Results and discussion

Dimensional metrology

The results from the dimensional metrology analysis are reported in this section. Data for Sanicro 25 are given in Figure 5. The distribution plots show the probability of having a certain amount of damage to the surface of the sample. They are divided into metal change (the amount of metal lost from the thickness during the exposure) and sound metal change (which includes the internal damage, underneath the surface). The data taken from the images were re-ordered to give a cumulative probability of damage for the fireside exposures (Figure 5a and b), the slope of the distribution then indicates the homogeneity of the corrosion damage on the samples' surface. In the case of steamside exposure the oxide thickness has been plotted against standard deviation (Figure 5c and d). A distribution of data approximately parallel to the x-axis indicates a homogenous distribution of the corrosion damage (Figure 5b, orange line), while the higher the slope becomes the more the corrosion damage is distributed inhomogeneously.

Figure 5a shows the distribution of damage for Sanicro 25 after 200 h and 400 h, as metal change. At 200 h the distribution showed damage lower than $-100\ \mu\text{m}$, while after 400 h an increase of 10 times the amount of damage is observed at 200 h. Similar behaviour is shown for the sound metal change, Figure 5b, where the amount of change in sound metal increase

drastically from 200 h to 400 h exposure. The same type of behaviour can be seen for median values of the distribution plots, as well as for the zone showing the highest metal change (left-hand side of graphs in Figure 5a and b). In all cases the samples exposed for longer times showed damage across the entirety of the samples' cross-section in all cases. Images of the samples after 800 h and 1000 h are shown in Figure 6. The image shows a detachment of the corrosion products from the metal surface. Sanicro 25 samples showed similar features after 600 h exposure.

In Figure 5c and d the scale thickness for exposure at 650°C and 700°C, respectively, in steamside environment is shown. From the distribution plot it can be seen that the thickness of the oxide formed on the samples exposed to steam is less than $5\ \mu\text{m}$. From the negligible slopes of the distributions, it can be seen that the thickness of the oxide is homogenous all over each sample. It is worth noting that all the data recorded in Figure 5c and d from various samples are within a $5\ \mu\text{m}$ range, which is within the measurement errors, so no clear conclusion could be made for the temporal behaviour of these samples. Figure 7a and b, c

The data for IN740 are reported in. The cumulative distribution plots for fireside corrosion metal and sound metal changes are in. As can be seen in, for all the exposure times, the distributions of the values for 'metal change' are quite close to each other, with median values around $-100\ \mu\text{m}$. The difference between the exposure times is in the spread of the metal loss values. By increasing exposure time, the maximum damage found on the surface increased (up to $-600\ \mu\text{m}$ for 1000 h exposure) and the amount of a sample's surface damage showing significant increase as well.

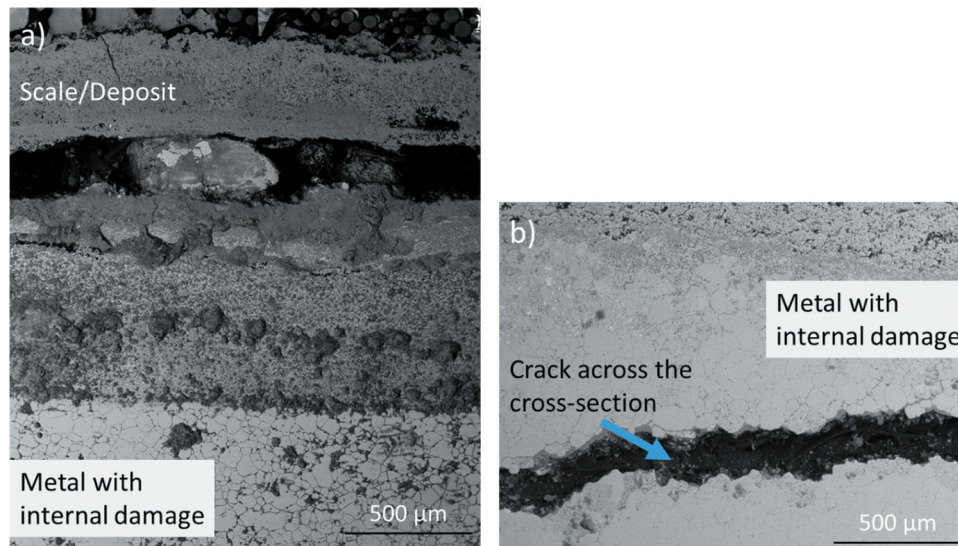


Figure 6. Backscattered SEM micrograph of Sanicro 25 a) after 800 h exposure and b) 1000 h exposure in fireside environment. In image b) a crack can be seen within the sample's substrate metal.

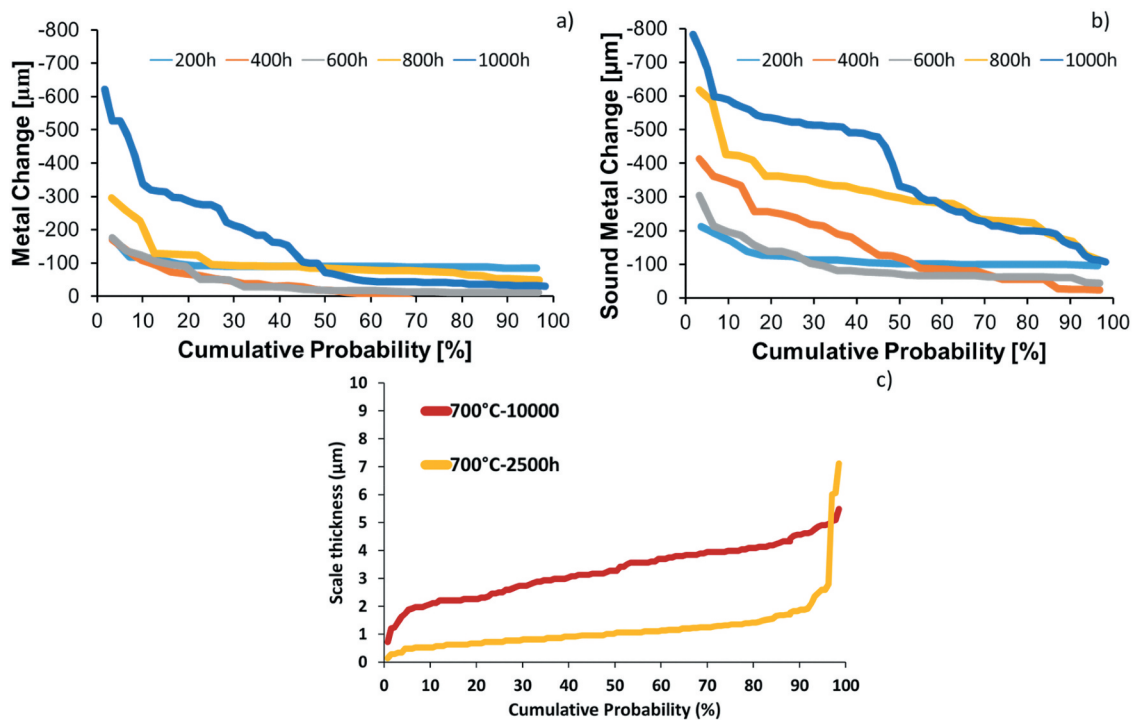


Figure 7. IN740 distribution plot for a) fireside metal change, b) fireside sound metal change and c) steamside oxidation at 700°C.

A difference can be seen in the sound metal change, which takes into account the internal damage as well. In this case, the difference between the different exposure times is more evident. At 200 h, the corrosion damage appears to be negligible, with a median value around 0 μm , before increasing to around $-100 \mu\text{m}$ at 400 h and 600 h. At 800 h and 1000 h, the change increases to around $-350 \mu\text{m}$, highlighting the increase in the internal damage with time, although the same trend was not clearly visible for the change in metal.

Looking at the steamside oxidation, scale thickness is reported in. Distribution plot for 2500 h and 10,000 h are reported. As can be seen, the thickness of the oxide scale is below 10 μm at both times, with median values below 5 μm ; orders of magnitude lower than the change in metal due to fireside, which is of the order of magnitude of hundreds of μm . (Figure 8(a)), the median values of the metal and sound metal change distributions are reported for the two materials used in this work. Sanicro 25

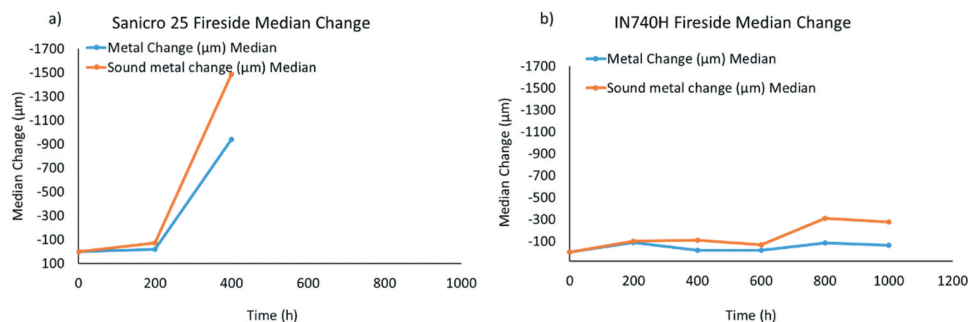


Figure 8. Median values for metal change and sound metal change for a) Sanicro 25, b) IN740.

shows a median dimensional change of $-900\ \mu\text{m}$ after 200 h for the fireside corrosion, which reaches $-1500\ \mu\text{m}$ after 400 h, while for steamside exposure the change due to the formation of the oxide scale is negligible. Similar behaviour has been found for the IN740, where changes reached a maximum of $-100\ \mu\text{m}$ for the metal change and $-300\ \mu\text{m}$ for sound metal change (after 800 h and 1000 h exposure times), values lower than those registered for Sanicro 25. The metal and sound metal change median values for IN740 are comparable with the ones found for the simulation of co-combustion of coal and biomass [35].

The data used in this study were generated from accelerated tests; this is due to the high flux used. The use of this amount of deposit could lead to

corrosion rates and mechanisms that might not appear in a real combustion scenario. Plant data were not generated in this study so a direct correlation cannot be drawn.

Even though oxide surfaces might catalyse the SO_2 to SO_3 reaction, the path experienced by the gas in contact with the samples is negligible with respect to the path inside the ceramic liner.

Microstructure analysis

The following section reports the SEM/EDX microstructural analysis of the exposed samples. The images were taken in point where interesting features were observed. Pictures cannot be related directly to zones with high or median corrosion damage from the dimensional

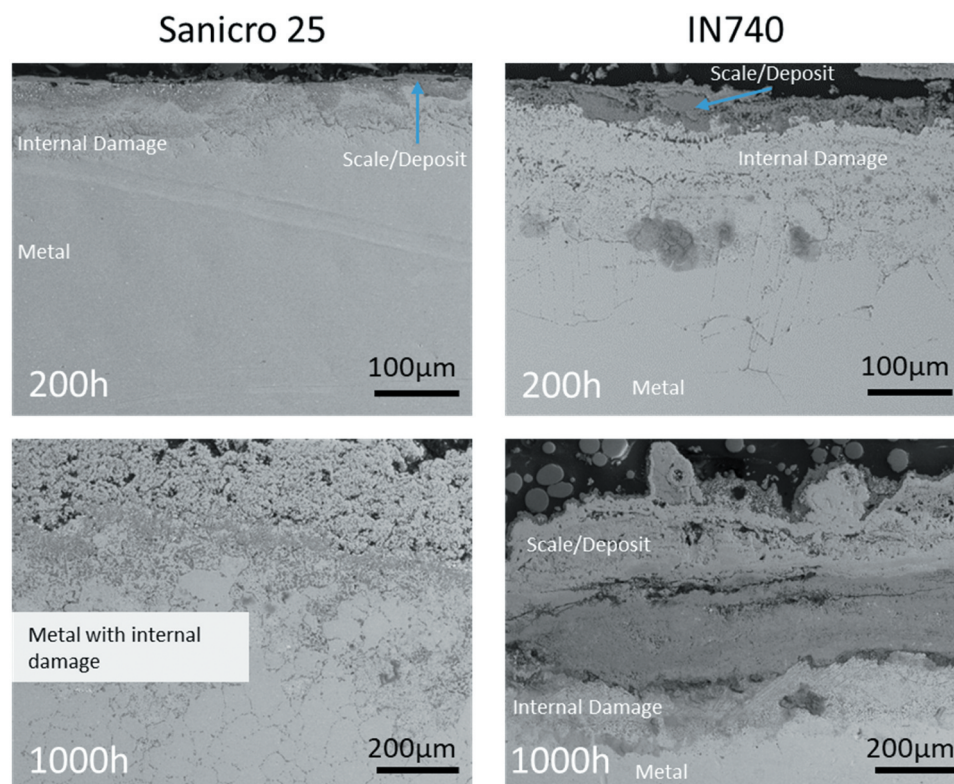


Figure 9. Backscattered SEM micrographs of the two materials exposed to the fireside corrosion environment at 200 h and 1000 h.

metrology data, since these are generated from evenly distributed images around the samples' surface, providing information on the regression of the metal's surface.

Figure 9

shows the microstructure of the two materials. For all materials a low damage level at 200 h increases after 1000 h exposure, as expected. Both materials also show an increase in scale thickness and internal damage after 1000 h exposure. Comparing Figures 6–9, it can be seen how the grains of the Sanicro 25 samples are fully highlighted by the internal corrosion products of the. This kind of behaviour has previously been observed (diffusion cell behaviour) [35]. When grain boundaries are fully surrounded by corrosion products or oxides, further diffusion of alloying elements from the bulk alloy to the grains is

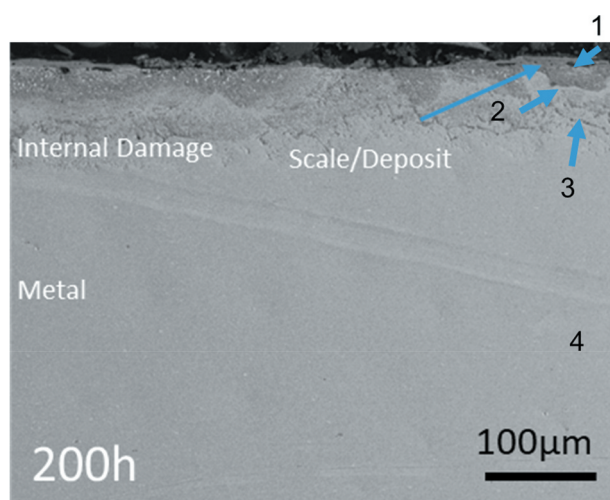


Figure 10. Backscattered SEM micrograph of Sanicro 25 after 200 h exposure. EDX spectra were taken from the points highlighted in the image. Data are reported in Figure 11

compromised, leading to depletion of elements, like Cr, able to form a protective scale above samples' surfaces.

Sanicro 25 fireside

In Figure 10, a SEM micrograph of a Sanicro 25 sample after 200 h exposure is shown. In the figure the points where EDX was performed are highlighted (data are reported in Figure 11 and Table 1). From the data it can be seen that there are different compositions through the sample's thickness. As can be seen from the data, the scale on the sample's surface is mainly composed of Cr and O. Going away from the surface (spectra 2 and 3) it can be seen that the sample shows elements typical of the alloy composition. It has to be noted that the amount of Cr is significantly lower (by around a quarter for spectrum 2 and a third for spectrum 3) with respect to the nominal value of the alloy. This area also shows internal damage, coupled with the depletion of Cr. Spectrum 4 shows a composition similar to that of the unexposed alloys (see Figure 11 and Table 1).

In Figure 11 the compositions of the points highlighted in Figure 10 are shown (in weight percents). This shows that the scale (point 1, Figure 10) is mainly composed of Cr (around 60 wt%), which is then lowered in what can be seen as a depletion area, which extends the length of the observed internal damage area (about 51 μm) (points 2 and 3, Figure 10). After that the Cr quantity returns to the typical alloy concentration (point 4, Figure 10). Signs of oxidation were found only in the scale and damaged area (points 1 and 2, Figure 10), indicating that the scale is exploiting its protective function over the alloy. The other two main elements of the alloy (Fe and Ni) were found in the scale composition. The damaged area (point 2, Figure 10)

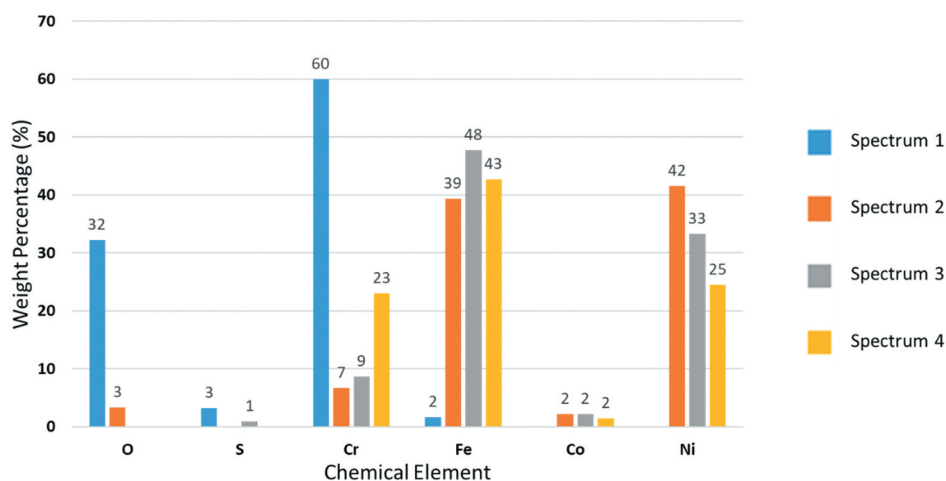


Figure 11. EDX composition of representative elements (weight percentage) from points highlighted in Figure 10

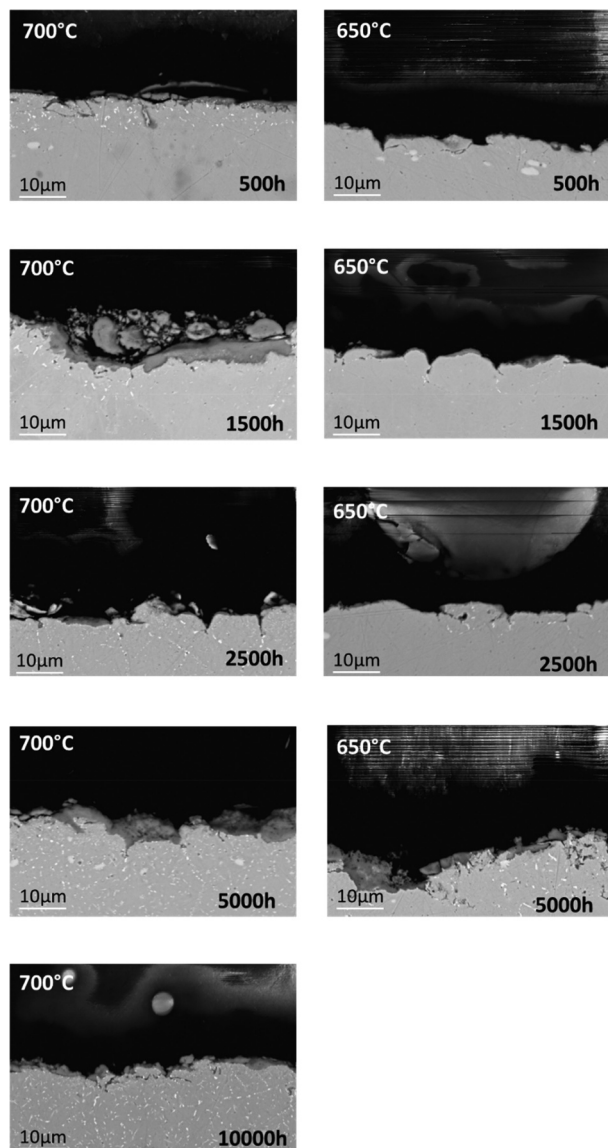


Figure 12. SEM micrographs of Sanicro 25 steamside oxidation samples after different exposure times.

seems to be enriched in Ni (around 40 wt%), with Ni concentration returning to the typical alloy composition in point 4, Figure 10 (around 25 wt%).

Sanicro 25 steamside

In Figure 12 SEM micrographs for Sanicro 25 samples exposed to steam are shown for different exposure times and temperatures. In the images the presence of precipitates below the metal surface of the samples can be seen. From the pictures it appears that the presence of these precipitates increases with time and temperature, reaching a maximum for the samples exposed for 10,000 h at 700°C.

Figure 13 shows a backscattered SEM image and EDX maps of Sanicro 25 exposed for 10,000 h at 700°C. Two types of precipitates are present: big clusters (identified previously as z-phase [23,25]) and grain boundary precipitates which are smaller in size and more concentrated. The Nb map shows that the

precipitates formed are rich in Nb. This was noted earlier in the literature, with the Nb-rich particles corresponding to Nb-rich nitrides (Z-phase) [23,25]. Also observed were the presence of the small grain boundaries precipitates, which are linked in the literature to the presence of Cr-carbides [23,25]. The presence of a thin oxide layer can be seen from O map at the metal's surface; this appears to be mainly chromia since the chromia scale is thermodynamically favourable with respect to other alloying elements.

IN740 fireside

Figure 14

shows the morphology of IN740 samples at different exposure times. From the images, a deposit/scale layer can be seen (dark area). At low exposure times the thickness of the scale is less than 100 µm, while after 1000 h exposure there is a growth in the scale thickness to about 409 µm. Figures 15–16

Results from EDX analysis are shown in. shows that the most external part of the scale consists of Ni and Co oxides, while the inner part (dark grey area is a Cr-rich scale. In this area a diffusion of S can also be seen, meaning that the external oxide layer could be susceptible to S diffusion. Looking at the compositions from the EDX spectra, Figure 16, the variation at different points can be seen. The elemental compositions reflect what can be seen in the maps, with the external scale layer mainly formed by Ni and Co oxides. Co passes from 26 wt% in point 1 to 1 wt% in point 4. Similarly, Ni is predominant in the brighter areas (points 2 and 3, 71 wt% and 66 wt% respectively). On the other hand, the dark area, corresponding to points 4 and 5, is predominantly composed of Cr (69 wt% and 61 wt% respectively) and O (19 and 23 wt%). In the same region there is an increase of the S content (which rises to 11 wt%).

Figure 17 shows a backscattered image and EDX maps after 1000 h exposure of IN740 in a fireside corrosion test at 700 °C. Data from spectra indicated in Figure 17 are shown in. From the maps it can be seen that the scale is formed of Cr, O and S, while the area of underlying damage shows a depletion of Cr. In the same region, an increase in the Cl content can be seen, which has diffused from the outer surface towards the alloy. In contrast, Ni and Co do not seem to be depleted in the damaged area.

Looking at the elemental compositions in a quantification of the behaviour seen in Figure 17 can be observed. It can be seen that the Cr content is higher in the scale (above 50 wt%) while it decreases in the inner corrosion area (7 wt% and 19 wt%, respectively, at points 3 and 4), falling below the typical alloy composition (25 wt%). Beneath the inner corrosion damage area, the Cr content then approaches the typical alloy composition (26 wt% in point 5). Spectrum 4 shows the composition of the particles

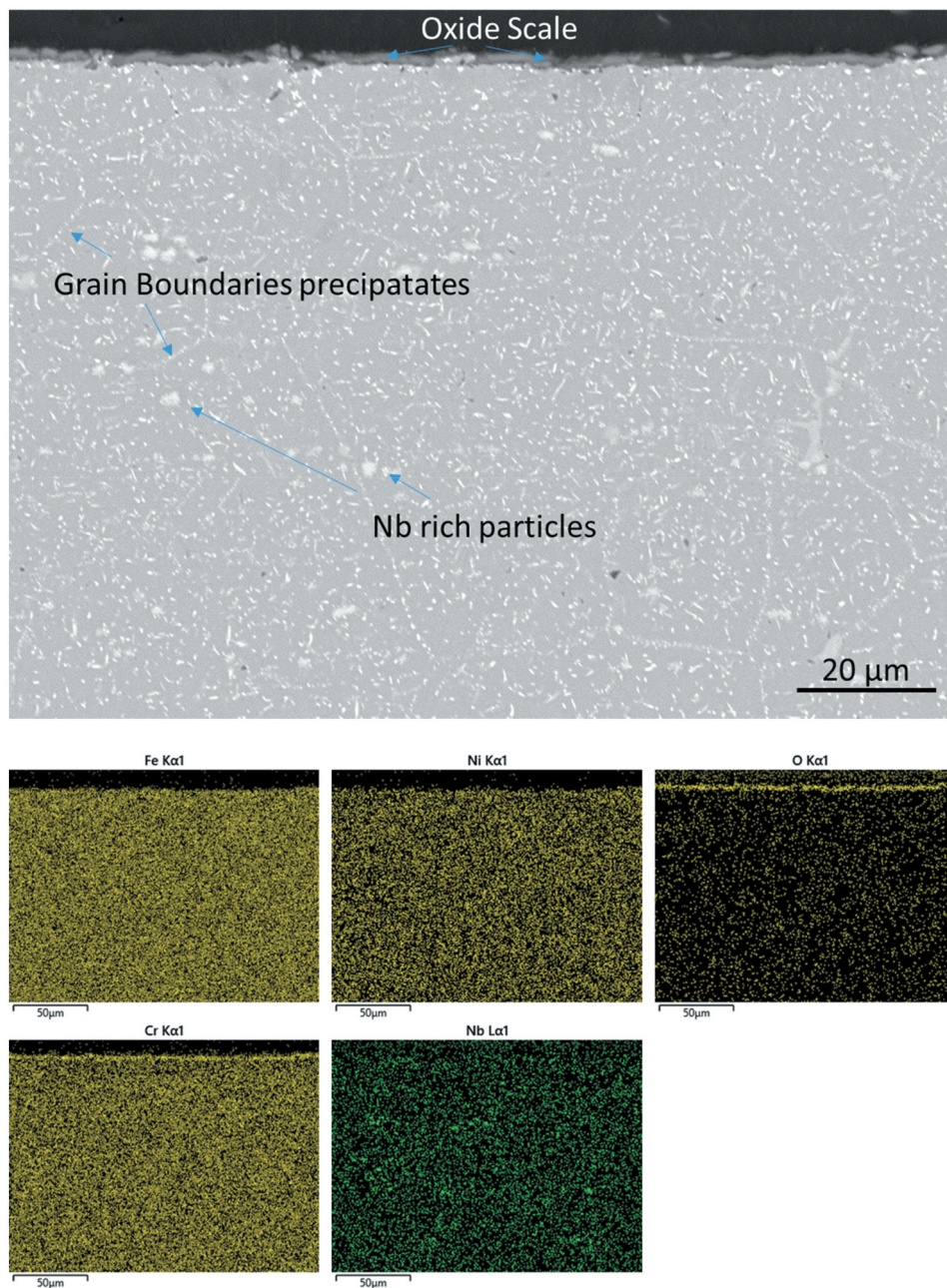


Figure 13. SEM micrograph of Sanicro 25 after 10,000 h exposure at 700°C in the steam environment, with EDX maps.

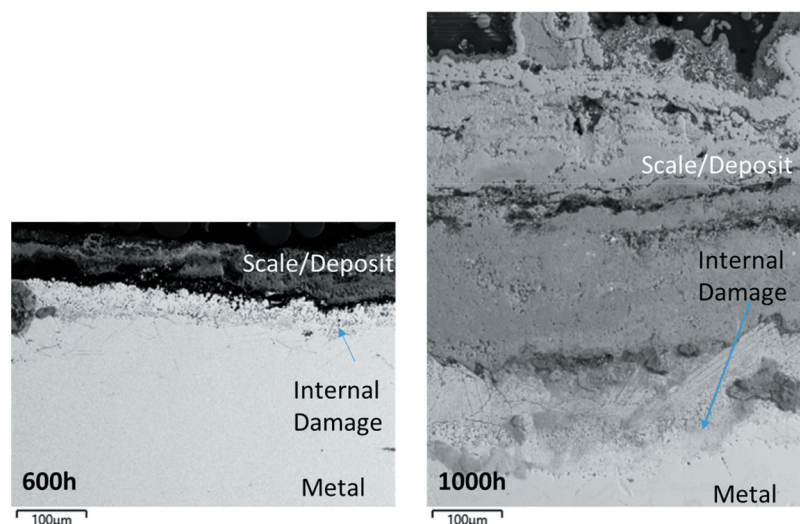


Figure 14. Backscattered SEM micrographs of IN740 undergone fireside corrosion at different exposure times.

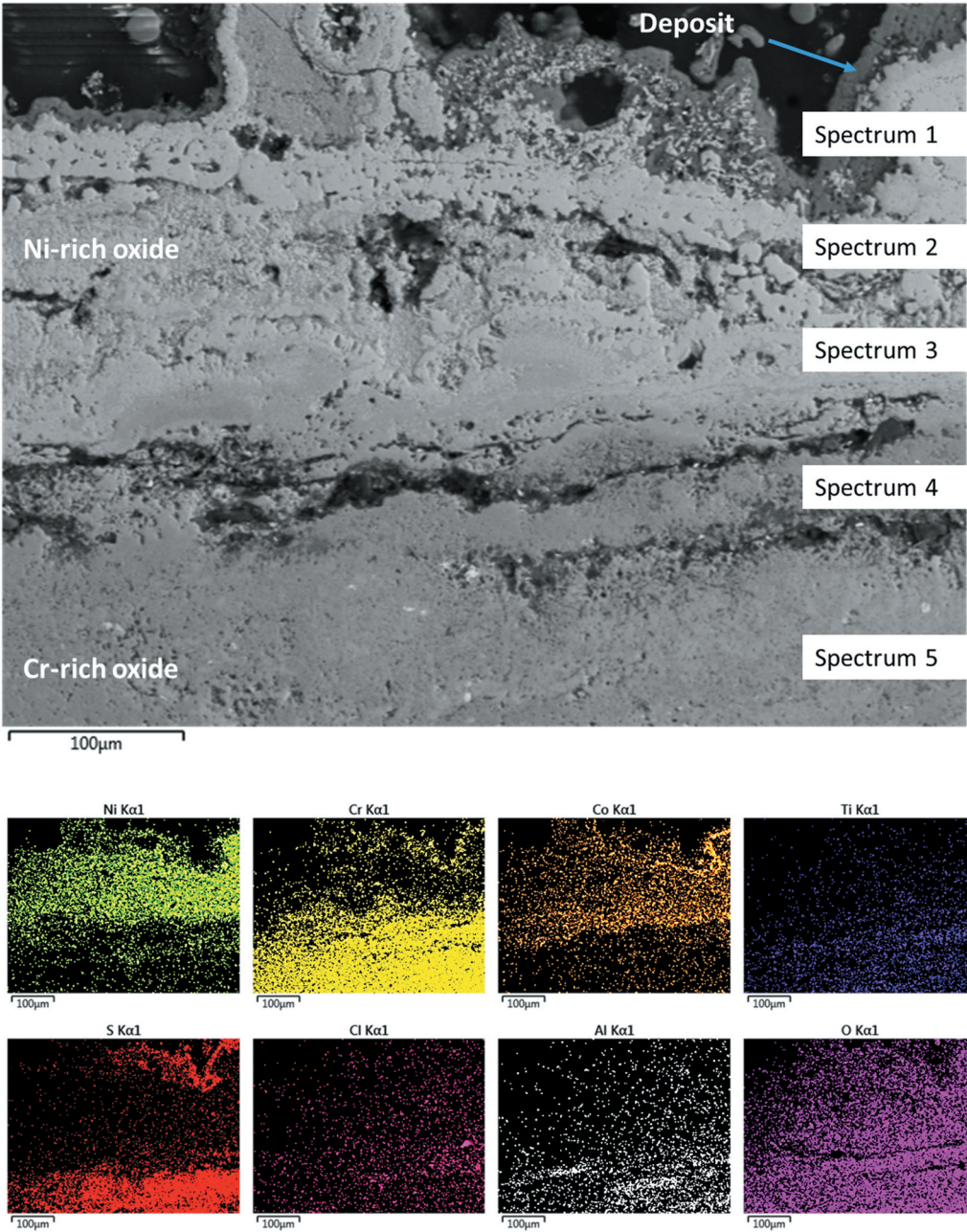


Figure 15. Backscattered SEM micrograph and EDX maps for IN740 after 1000 h exposed in an accelerated fireside corrosion test. Spectrum labels are placed below the areas from which spectra were taken.

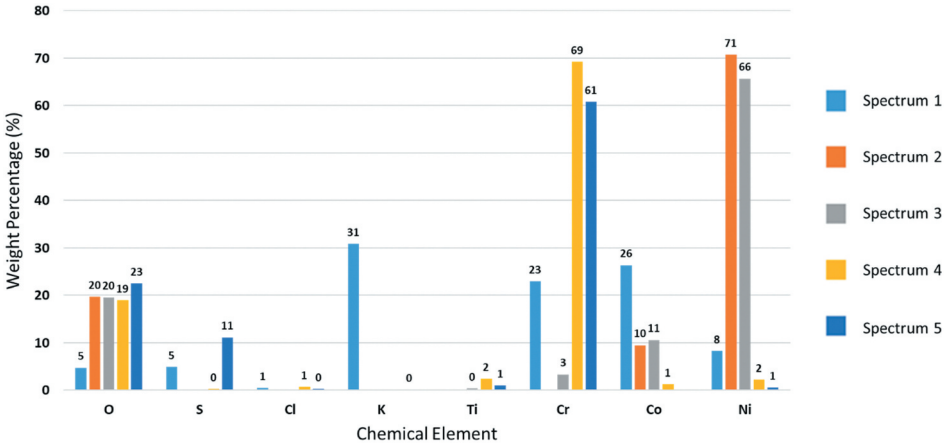


Figure 16. EDX spectra of IN740 fireside after 1000 h exposure, from .

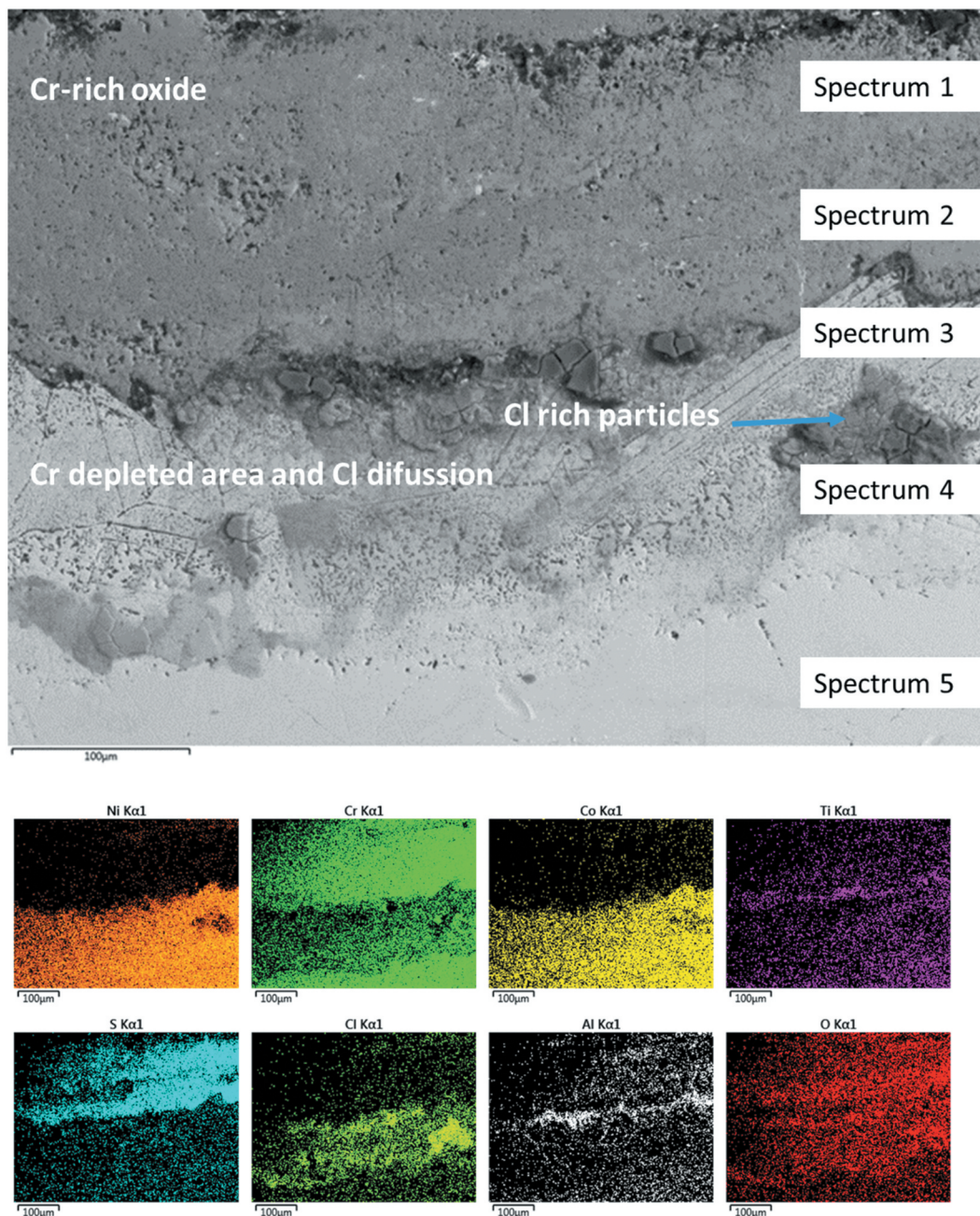


Figure 17. Backscattered SEM micrograph of IN740 after 1000 h fireside corrosion exposure with EDX maps. Spectrum labels are placed below the areas from where spectra were taken.

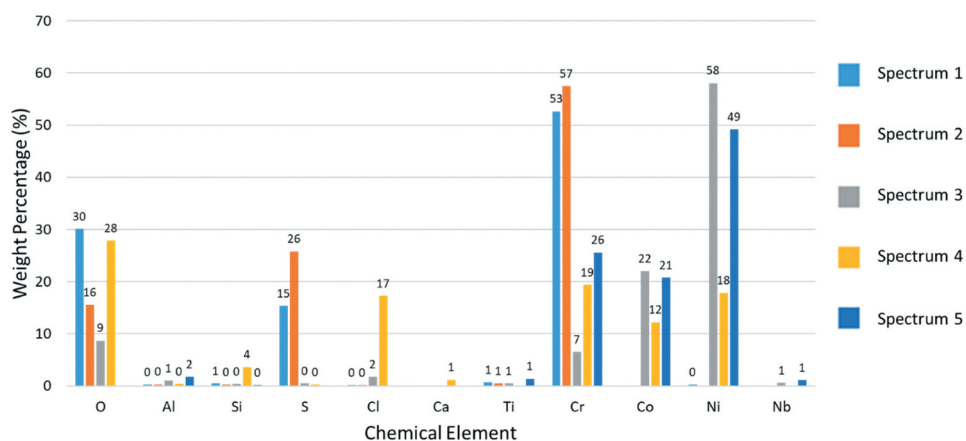


Figure 18. EDX spectra of IN740 fireside after 1000 h exposure, Figure 17.

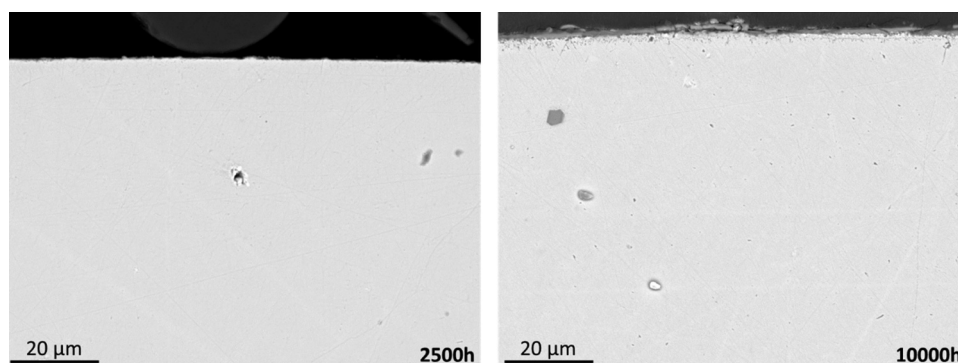


Figure 19. SEM micrographs of IN740 steamside oxidation samples after (a) 2500 and (b) 10,000 hours exposures at 700 °C.

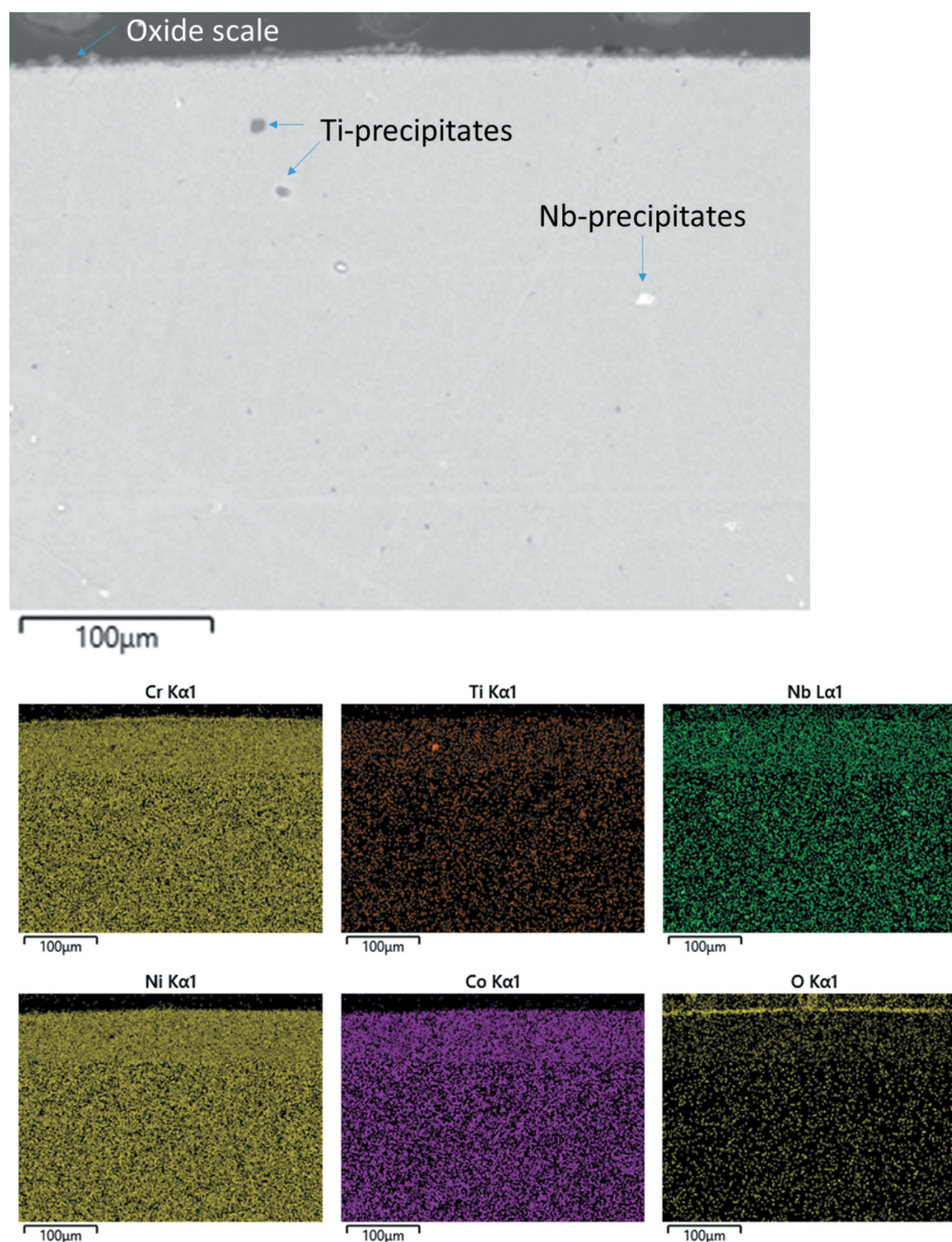


Figure 20. Backscattered SEM micrograph of IN740 after 10,000 h exposure at 700°C in a steam oxidation environment, with EDX maps.

observed in Figure 17, which have a high Cl and O content, as well as the main alloy elements, e.g. Ni, Cr and Co. The metal composition returns to a typical IN740 composition by position 5. Figure 18

IN740 steamside

Figure 19

In SEM images of IN740 after different exposure times at 700°C are shown. From the images it can be seen that, unlike Sanicro 25, there is the presence of fewer precipitates. Also, an oxide scale can be seen after 10,000 h exposure. (Figure 20)

In a backscattered SEM image of IN740 and EDX maps are shown for the sample exposed for 10,000 h. From the backscattered SEM image the presence of two different precipitates can be seen (i.e. dark spots and bright spots). Comparing the SEM image with the EDX maps it can be noted that the dark areas correspond to a Ti rich zone, while the bright area corresponds to a Nb rich zone (as for Sanicro 25). Also, the presence of a thin Cr rich oxide layer on the surface of the sample can be noted.

Summarising, it can be seen that Sanicro 25 is highly affected by internal corrosion damage when exposed to the accelerated simulated biomass firing environment at 700°C. The amount of penetration recorded was high, with internal damage recorded across the entire thickness of the samples after only 600 h of exposure; while samples after 1000 h exposure show cracks across the entire cross-section. On the other hand, the IN740 samples have shown a much lower metal change compared to Sanicro 25, with values similar to those that have been reported for accelerated co-firing conditions [35]. This makes IN740 a good candidate for AUSC biomass-fired power plants in light of coal replacement. A thin oxide scale (median oxide thickness below 5 µm) was found in steamside oxidation exposure experiments for both alloys. The presence of a z-phase has been observed for Sanicro 25, as reported previously, typical of Sanicro 25 microstructure after ageing [17,23].

General discussion

From dimensional metrology of samples exposed to an accelerated fireside biomass corrosion environment (using KCl), it has been seen that, for Sanicro 25 samples exposed for 600 h or higher, damage fully penetrated below the metal surface, throughout the entire cross-section. The damage has developed in the form of grain boundary attack, which could have led to a diffusion cell type of behaviour, limiting the possible diffusion of a potentially protective alloying element, such as Cr, from the bulk alloy to the surface. For this reason, after initial formation of a protective oxide (mainly chromia),

other elements started to oxidise, causing a layered oxide structure that was not able to provide effective protection.

For IN740, it was found that the amount of metal and sound metal change were of the same order of magnitude as the metal and sound metal change found in a previous study looking at the accelerated fireside corrosion of this material under co-firing conditions (median damage around 300 µm [35]). The image metrology performed on the samples exposed to steam oxidation showed an oxide scale below 5 µm for both materials, Sanicro 25 and IN740.

SEM and EDX analysis of the samples exposed to the steam oxidation environment showed the formation of thin and compact Cr-rich oxide layers, for both IN740 and Sanicro 25. The scales formed have been able to protect the materials from further degradation. For Sanicro 25 the formation of Nb-rich particles has been found, corresponding to Z-phase (as already reported in literature [17,23]). For IN740, the SEM and EDX analyses highlighted the formation of two different precipitates, one rich in Ti and the second one rich in Nb, as for Sanicro 25 although in lower quantities. For the fireside environment exposures, Cr depleted regions have been found for both alloys, with Sanicro 25 showing metal changes above 1000 µm. This has been linked with the appearance of internal damage across the entire cross-section after only 600 h exposure. This damage took the form of grain boundary attack, leading to a diffusion cell behaviour, which stopped the diffusion of alloying element from the bulk to the grain fully surrounded by the damage. In the case of the IN740, it has been seen how the scale/deposit was formed by different alloying elements.

Conclusion

In this work steamside oxidation and biomass fireside corrosion exposures have been performed for IN740 and Sanicro 25. The fireside corrosion exposures have been conducted with the deposit re-coating technique, which allows a better simulation and control of the environment. The materials were exposed at 700°C for up to 1000 h in total for the accelerated fireside corrosion exposures (with samples covered with 20 mg/cm² of KCl every 200 h). The steamside oxidation exposures were carried out at 650°C and 700°C for Sanicro 25 and 700°C for IN740, with an exposure time of up to 10,000 h. Samples were then characterised using dimensional metrology and SEM/EDX.

From the findings of this work, it appears evident that, even though Sanicro 25 and IN740 performed in similar ways within the steam oxidation environment, the former alloy is not a suitable choice when it comes to AUSC conditions in biomass-fired power plants,

due to its response to the fireside corrosion environment created with KCl. In fact, it shows how, after only 600 h of exposure time, the internal damage is able to penetrate several millimetres into this alloy, making the Sanicro 25 not suitable for this scenario.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Engineering and Physical Sciences Research Council (EPSRC) – Flexible and Efficient Power Plant: Flex-E-Plant [grant number EP/K021095/1] and EU Research Fund for Coal and Steel Project RFCS-2015/709954 ‘Preparation for Commercial Demonstration Plant for 700 °C Operation’, DP 700 – Phase 1.

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2022-01-10

Taylor & Francis

<https://doi.org/10.1080/09603409.2021.2019657>

Mori S, Sumner J, Bouvet J, Simms NJ. (2022) Fireside and steamside performance in biomass power plant, Materials at High Temperatures, Volume 39, Issue 2, 2022, pp. 106-121