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The effect of aluminium addition on the high-temperature oxidation behaviour and Cr evaporation of aluminised and alumina-forming alloys for SOFC cathode air pre-heaters

Kun Zhang ^a, Ahmad El-Kharouf ^{a, *}, Jong-Eun Hong ^b, Robert Steinberger-Wilckens ^a

^a Centre for Fuel Cell Hydrogen Research, Chemical Engineering, University of Birmingham, Birmingham, B15 2TT, UK

^b Fuel Cell Laboratory, Korea Institute of Energy Research, 152 Gajeong-ro, Yuseong-gu, Daejeon, 34129, Republic of Korea

ABSTRACT

The corrosion behaviour and Cr retention ability of SS309, aluminised SS309, and AluChrom 318 have been investigated at 850 °C in air with 3% H₂O. The SS309 samples failed the specifications for application as cathode air preheater (CAPH) material due to a high Cr evaporation rate and massive scale spallation. The surface aluminisation dramatically decreased the Cr evaporation rate of SS309, but not in the long-term due to breakaway oxidation induced alumina scale spallation. The AluChrom 318 formed a γ -Al₂O₃/ α -Al₂O₃ layer scale and demonstrated the highest Cr retention ability and oxidation resistance among the tested alloy samples.

Keywords: A. FeCrAl alloy; B. Denuder technique; B. TEM; C. High temperature oxidation; C.

Cr evaporation

1. Introduction

Solid oxide fuel cell (SOFC)-based micro combined heat and power (μ CHP) is beginning to penetrate the residential heating market with 100 000 units already sold commercially (making use of government subsidies) in Japan. This application reduces the dependence on fossil fuels and minimises CO₂ and noxious pollutant emissions in the residential building sector [1]. As the ceramic materials of a solid oxide fuel cell (SOFC) stack are sensitive to rapid temperature variations, the reactant gases fed to the stack are generally pre-heated to a temperature high enough to prevent such thermal stress [2]. Within the Balance of Plant (BoP, the sum of all auxiliary components in a fuel cell system, apart from the fuel cell stack), the cathode air pre-heater (CAPH) has the role to heat the inlet air up close to the operation temperature (e.g. 750 °C) by utilising the thermal energy recovered from the high temperature exhaust gas of the SOFC systems. The CAPH is the second most expensive BoP component (next to the SOFC stack itself) as limited materials can be used for the requirements imposed by high temperature operation, namely; strength, machinability, long-term creep, corrosion resistance, as well as cost effectiveness [3]. The requirements here differ from those of metallic SOFC interconnects as the necessity to match the thermal expansion coefficients (TECs) of other SOFC components and to form electronically conducting coatings does not apply to CAPHs. The conventionally employed (relatively brittle and expensive to machine) ceramic materials [4] are rapidly losing their reputation to metal based CAPH (mostly stainless steels). The application of stainless steels permits the design of ultra-thin CAPH plates to decrease the bulk size and weight of the CAPH stacks, also reducing the manufacturing cost. Candidate stainless steels normally contain a high Cr concentration to offer oxidation resistance by forming a continuous protective layer of a Cr-

containing oxide scale (Cr_2O_3 or $(\text{Cr}, \text{Mn})_3\text{O}_4$ spinel) under SOFC environments, in particular exposed to high temperature oxidative atmosphere [5]. However, when the Cr-containing oxides of metallic CAPHs react with steam and oxygen the oxide scales are more susceptible to chromium evaporation which produces volatile Cr species such as gaseous CrO_3 and $\text{CrO}_2(\text{OH})_2$ [6,7]. The volatile chromium species induce a poisoning effect on cathode materials, which has been extensively studied and summarised in Jiang and Chen's review work [8]. The Cr evaporation rate of high-Cr alloys forming various outer oxide scales was compared by Stanislawski *et al.* at 800 °C [9]. They found that a Cr retention of more than 99.9% was observed for AluChrom YHf that formed an alumina outer layer. The capability to suppress Cr vaporisation on AluChrom YHF is superior to other steels forming pure Cr_2O_3 (0%) or Cr-Mn-spinels (60-70%) and even better than that applied with Co_3O_4 (90%) as a protective layer, suggesting that the alumina scale is a very effective chromium barrier layer [9].

High-Cr stainless steel alloys containing a small amount of aluminium exhibit good high-temperature oxidation resistance and Cr retention capability by forming an $\alpha\text{-Al}_2\text{O}_3$ scale with a low defect concentration [10]. Alumina grows at a rate slower than chromia due to its extremely low defect concentration [11]. Furthermore, alumina offers a significantly higher degree protection than chromia in the presence of steam at high temperatures. Opila *et al.* have proved that alumina volatility by $\text{Al}(\text{OH})_3$ formation is not expected to be an issue below 1300 °C for long-term applications [12]. However, the ductility of alumina-forming alloys is poor when the critical Al concentration reaches over 5 wt.%, which may cause serious metallurgical processing problems [13]. To avoid this issue, a protective alumina layer can be applied on the chromia-forming alloy (without Al addition to the alloy itself) by

coating the alloy surface with pure aluminium and subsequently oxidising. Aluminising offers superior high temperature oxidation resistance for the Al-free alloys by forming the protective alumina layer similar to alumina-forming alloys do without affecting the mechanical properties of the materials in the core. Sharafi and Farhang confirmed that surface aluminising significantly increased the oxidation resistance of HH309 stainless steel oxidised in air at 1100 °C [14]. Stanislawski *et al.* [15] have proven that the Cr retention capability of aluminised alloys is as efficient as that of alumina-forming alloys while the corrosion resistance of aluminised steels in long-term exposure has not yet been investigated. It is, therefore, necessary to perform a comparison of the Cr evaporation and long-term corrosion behaviour between aluminised and alumina-forming alloys. The purpose of this study is to quantitatively measure the Cr species evaporated from uncoated stainless steel 309 (SS309), aluminised SS309 and AluChrom 318 with a low Al content of 3.58 wt.% by means of the denuder technique at the temperature of 850 °C. This research also investigated whether the corrosion resistance and Cr evaporation performance of SS309 can be improved by surface aluminising. In addition, the suitability of aluminised and alumina-forming high-Cr alloys for CAPH application concerning the reduction of Cr evaporation will be discussed.

2. Materials and methods

2.1 Sample preparation

Two commercial high-Cr stainless steels were selected for this research. The samples were cut into coupons of the dimensions 15×15×0.3 mm³. The alloy compositions for these materials in wt.% are shown in Table 1. Additionally, SS309 was also aluminised on both

sides in order to compare the high temperature corrosion behaviour with uncoated SS309. A 1 µm thick aluminium layer was applied by Teer Coating Ltd using a proprietary physical vapour deposition (PVD) process. All samples were exposed in as-received condition after having been cleaned in acetone and ethanol using an ultrasonic bath.

2.2 Exposure tests

For the Cr evaporation test, the amount of volatile Cr species was measured by isothermally exposing three identical samples of the stainless steels using a denuder technique [16] in a tubular furnace at 850 °C (Fig. 1). The tests were carried out in humidified air (3 vol% H₂O) to simulate an SOFC cathode environment. The air flow rate was controlled to 6000 ml/min which corresponds to a regime where the evaporation rate is flow independent [16]. As shown in Fig. 1, directly upstream of the samples, a porous SiC flow restrictor was placed to obtain a uniform flow pattern. Downstream of the samples, the gas stream was fed through the quartz glass denuder tube, which had an inner diameter of 5 mm. The inner wall of the denuder tube was coated with Na₂CO₃ used for Cr collection. The Cr-containing gas (CrO₂(OH)₂) produced in the simulated SOFC environment reacted with the Na₂CO₃ to produce Na₂CrO₄ on the basis of equation (1) [16]:

After collection, the inside wall of the denuder tube was subsequently washed with 10 ml distilled water, and the dissolved solution was carefully collected. UV-vis spectrophotometer analysis was then applied on the obtained solution to quantify the total amount of Cr

species evaporated from each sample tested. The detailed method to quantify the Cr evaporation was introduced in a previous study [16].

A high temperature oxidation test was additionally carried out by exposing different types of materials simultaneously at the identical temperature (850 °C) and air flow rate (6.0 L/min + 3% H₂O) for a total duration of 2500 hours. The difference between the high temperature oxidation and the Cr evaporation tests is that in the former case stainless steel samples were removed at regular time intervals for gravimetric measurement and characterisation. For the Cr evaporation test, the denuder tubes were replaced without cooling down the furnace, allowing for uninterrupted measurement of Cr evaporation. The Cr evaporation tests for all the three materials were repeated thrice and showed good repeatability confirming the reliability of the denuder technique. For all the exposure tests, the humidified air environment was applied after the samples were heated up to 850 °C in stagnant air in the furnace.

2.3 Microstructural analysis

Gravimetric measurements on the three different materials were recorded as a function of time after each isothermal exposure test by evaluating the mass change for the coupons exposed simultaneously using a high resolution balance capable of measuring six decimal places (Cubis Micro Balance, MSA2.7S0TRDM). The crystalline structure of the oxide scales formed on the steel surfaces was analysed by X-ray diffraction (XRD) (D2 PHASER 2nd generation, Bruker) with a Co-K_α radiation ($\lambda=0.179026$).

The surface microstructure of non-exposed and exposed samples was studied by imaging the samples using a scanning electron microscope/energy dispersive X-ray spectrometer (SEM/EDX) (Tabletop Microscope TM3030, Hitachi-Hitec). Subsequently, the SS309 and aluminised SS309 samples were mounted in epoxy and mechanically polished down to 1µm to conduct cross-sectional analysis using the SEM/EDX technique. Analytical scanning transmission electron microscope (STEM) and EDX studies were carried out to investigate the specific cross-sectional microstructure of the oxide scale grown on the AluChrom 318 sample using a Philips Tecnai F20 micros operated at 200 kV and equipped with an Oxford Instrument ISIS EDX system. Additionally, a convergent beam electron diffraction (CBED) of Jeol 2100 TEM was used to identify the phases of the oxide scale formed on the AluChrom 318 surface. The cross-section TEM specimens for AluChrom 318 were prepared by the in-situ lift-out technique using a focused ion beam/scanning electron microscope (FIB/SEM) (FIB-SEM, FEI Quanta 3D dual beam). A detailed description of this technique can be found elsewhere [\[17\]](#).

3. Results

3.1 Mass measurements

The isothermal oxidation kinetics, represented by the mass gain as a function of time for SS309, aluminised SS309 and AluChrom 318 exposed at 850 °C with 6.0 L/min air (3% H₂O) for 2500 hours are presented in Fig. 2a. Fig. 2b shows the plot of mass gain rate as a function of time. Up to 500 hours, the SS309 showed a roughly parabolic oxidation behaviour with a mass gain of 0.079 mg/cm². However, the sample revealed an abrupt mass loss up to 2500 hours. The aluminised SS309 showed a rapid mass gain of 0.160 mg/cm²

before 1000 hours, displaying a much higher mass gain rate than that of uncoated SS309 due to the fast and direct reaction between Al and O during the initial oxidation. However, the aluminised SS309 started to suffer a mass loss after 1000 hours exposure mainly because of the exfoliation of the formed alumina scale. The AluChrom 318 with 3.58 wt.% of Al content exhibited a continuous mass increase over 2500 hours with an ultimate mass gain of 0.202 mg/cm², with oxidation kinetics following a parabolic law. No mass loss was observed, implying a continuous growth of alumina scale on the alloy surface.

3.2 Cr evaporation

The results of the time resolved Cr evaporation tests are presented in Fig. 2c. Fig. 2d shows the plot of Cr evaporation rate as a function of time. A total value of 0.0078 mg/cm² evaporated Cr was recorded for aluminised SS309 after 168 hours exposure, 0.0028 mg/cm² was obtained for the AluChrom 318, whereas the bare SS309 had a total value of evaporated Cr of 0.064 mg/cm² after the same oxidation time. The aluminised SS309 showed a slight increase in the rate of Cr evaporation with time. This phenomenon was caused by spallation of the formed alumina scale which will be discussed later in the section of microstructure analysis. However, the Cr evaporation rate of AluChrom 318 decreased with time because of the increase of alumina scale coverage on the alloy surface.

3.3 Microstructural investigation

3.3.1 SS309

Fig. 3 shows the results of microstructure evolution on SS309 oxidised for 100 and 1000 hours at 850 °C in air with 3% H₂O. EDX mapping analyses were conducted on the 1000 hour

exposed sample. XRD patterns of SS309 oxidised for 0, 100, 500, 1000 and 2000 hours at 850 °C in air with 3% H₂O are displayed in Fig. 4. Oxide scale spallation was already observed on SS309 after 100 hours of oxidation (Fig. 3a). EDX mapping of SS309 after 100 hours of oxidation revealed that the cracked surface oxides were composed of a high concentration of Cr, Mn and O with traces of Fe. The edges of the spalled areas, which were located below the porous top scale, contained exclusively Cr and O. In Fig. 4, the formation of a MnCr₂O₄ spinel top scale and Cr₂O₃ sublayer was confirmed by XRD after 100 hours exposure. The top scale of MnCr₂O₄ spinel showed a very porous structure, while the Cr₂O₃ sublayer appeared to be relatively dense. An enrichment of Si was observed on the rear side of the exfoliated scale (metal/oxide interface). An EDX study (Table 2) pointed out that the spalled area beneath the oxide scale contained very high amounts of Fe, Cr and Ni, which can be generally described as (Ni, Fe, Cr)-phase. However, the formula of the (Ni, Fe, Cr)-phase cannot be identified by XRD measurement due to insufficient surface coverage. EDX maps on the front and rear sides of the spalled oxides in Fig. 3a showed a layered structure from the alloy/oxide interface to the outer oxide surface: Steel/SiO₂/Cr₂O₃/MnCr₂O₄. With the oxidation progressing to 1000 hours, more oxides spalled off and the underlying (Ni, Fe, Cr)-phase region considerably increased in size compared to the 100 hours sample, as can be seen from Fig. 3b. Point EDX analysis performed on the old spalled area (Table 2) revealed that the (Ni, Fe, Cr)-phase was gradually replaced with (Fe, Cr)-rich oxide with high oxygen intensity. XRD analysis conducted on the sample exposed for 2000 hours confirmed the presence of Cr_{1.3}Fe_{0.7}O₃.

Fig. 5 shows the SEM/EDX maps on the cross-section of the bare SS309 exposed to humidified air at 850 °C for 1000 hours. It suggests that, compared to the steel base, there

were higher concentrations of Cr, Mn and O in the oxide scale, suggesting that the oxide scale mainly consisted of MnCr_2O_4 spinel phase. In addition, there is a clear Cr-rich band at the metal/oxide interface. However, it is difficult to distinguish the Cr_2O_3 from the $(\text{Cr,Mn})_3\text{O}_4$ layer due to the overlap between Cr $K\alpha$ and Mn $K\alpha$. Si was found to be accumulated at the alloy and oxide interface, but the silica layer was discontinuous and porous. It was easily seen that the oxide layer formed on the bare SS309 surface was poorly adherent and discontinuous, which meant that the microstructure analysis on the cross-section was difficult using the mechanically polished specimen [7]. Thus, the cross-sectional structure of the oxide scale on SS309 was benchmarked against the layered structure found on the spalled oxides on the surface micrograph (Fig. 3).

3.3.2 Aluminised SS309

The SEM micrographs of the aluminised SS309 exposed at 850 °C in air with 3% H_2O for 100 and 1000 hours are shown in Fig. 6. EDX maps in Fig. 6 show the element distribution on the micrograph of the aluminised SS309 oxidised for 1000 hours. Fig. 7 displays the XRD patterns of SS309 oxidised in air with 3% H_2O for 100, 500, 1000 and 2000 hours. For aluminised SS309, after 100 hours oxidation, the sample surface appeared to be completely covered by a wrinkled alumina scale with ramiform and polygonal MnO_2 crystals randomly distributed along the scale wrinkles (Fig. 6a), as confirmed by EDX analysis. Heating up in air prompts the aluminium coating to react with oxygen, leading to formation of an alumina scale on the alloy surface. Significant scale spallation was visible in the aluminised SS309 when the oxidation time increased to 1000 hours. There are two types of spalled areas observed in Fig. 6b. One was a (Ni, Fe, Cr)-phase with a number of large pores, and some of the large pores were about to be filled with (Cr, Mn)-spinel oxides as confirmed by EDX in

Fig. 6b-4. Another type of the spalled area (Fig. 6b-3) showed a strong intensity of Cr and Mn in EDX maps, which coupled with XRD results in Fig. 7, illustrating the internal growth of a foam-like (Cr, Mn)-spinel phase which broke out through the alumina scale. Moreover, the EDX maps also disclosed that the residual (Cr, Mn)-spinel oxide was stuck to the rear side of the spalled alumina scale (Fig. 6b-1). Despite this, a substantial amount of Mn migrated to the alloy surface throughout the alumina scale, resulting in a further growth of tree-like MnO_2 . According to the XRD analysis in Fig. 7, the diffraction peaks for spinel oxides and MnO_2 can be easily detected on the spectrum of 2000 hours. This can be explained by the severe delamination of the alumina layer on the aluminised SS309 surface. However, XRD could not clearly identify any alumina phase on aluminised SS309 at different exposure time. This is due to the high intensity alumina peaks overlapping with peaks from σ -FeCr phase, and the low intensity alumina peaks merging in with the background of the XRD patterns. However, both surface and cross-sectional EDX element maps clearly confirm the formation of an alumina scale on the SS309 surface.

The cross-sectional image of aluminised SS309 presented in Fig. 8 was selected at the location where all the features present on the surface can be seen in the SEM image (Fig. 6b). On the top half part of the cross-sectional image, the discontinuous scale containing Al and O after 1000 hours exposure is shown, confirming the presence of the alumina scale. Large Mn-rich oxide grains were present in the external part of the alumina scale, corresponding to a fast outward growth of the tree-like MnO_2 in Fig. 6b. The fast Mn outward diffusion resulted in a void formation underneath the alumina scale. The underlying voids connected to each other, leading to the formation of a gap between the base alloy and the alumina scale. Additionally, the void was found to be filled with (Cr, Mn)-

rich spinel oxides right below the external tree-like MnO_2 . In the middle part, the oxide scale had a duplex structure with an outer alumina scale and an inner (Cr, Mn)-spinel scale, indicating the internal growth of (Cr, Mn)-spinel via oxygen inward diffusion. The bottom half of the scale which corresponded to alumina scale exfoliation was occupied by a Cr and Mn enriched spinel layer, as indicated by EDX mapping. Additionally, the aluminised SS309 showed the formation of polygonal precipitates beneath the oxide scale with a relatively higher concentration of Al and N (Fig. 8), indicating that the precipitation of AlN occurred during the high temperature oxidation. In Fig. 9, the cross-sectional SEM of aluminised SS309 exhibited numerous diamond-shaped features enriched with Ni and Al after 100 hours exposure. Combined with the XRD spectrum for aluminised SS309 after 100 hours exposure, the results suggest that the NiAl precipitates in σ -(Fe, Cr) grains had formed close to the metal and oxide interface after 100 hours of oxidation [18,19].

3.3.3 AluChrom 318

Fig. 10 demonstrates the surface microstructure of the AluChrom 318 exposed at 850 °C in air with 3% H_2O for 100 and 1000 hours. The XRD spectrums for AluChrom 318 exposed at 850 °C for 100, 500, 1000 and 2000 hours are shown in Fig. 11. It can be seen that a relatively thin oxide film was observed containing numerous white spots randomly distributed on the surface of AluChrom 318 after 100 hours exposure (Fig. 10a). The surface of AluChrom 318 with the exposure time of 1000 hours revealed two distinct alumina zones in Fig. 10b, chequered with globular and long-ridged alumina with dark grey colour and plain (flat) alumina with light grey colour, while a small amount of the fine-size white particles were still found to penetrate the oxide scale and mostly were distributed on the top of the ridged alumina scale. EDX line scanning (Fig. 10b-3) showed that the ridged oxides contained

extremely high concentration of Al and O, indicating that a dense surface scale of Al_2O_3 was formed. The concentration of Al and O in the plain region was found to be lower than that in the ridged region but still with higher concentration than all other elements, which means that the plain region was covered with a relatively thinner alumina scale. Unexpectedly, the alumina phase could not be detected on the XRD spectrums for AluChrom 318 obtained by either XRD (Fig. 11) or GI-XRD (not shown). The presence of a Fe_2Nb Laves phase in the steel was confirmed by XRD.

Fig. 12 shows the STEM and EDX results measured on the cross-section of AluChrom 318 oxidised for 1000 hours at 850 °C in humidified air, which was prepared using a FIB in-situ lift-out technique [20]. The oxide scale formed on AluChrom 318 had a duplex structure with aluminium as dominant cation in both layers, and the outer scale made up about 90% of the total thickness. Moreover, the thick outer layer with a semi-circular shape corresponded to the ridged alumina detected on the surface SEM images (Fig. 10b). The EDX mapping showed a narrow and straight Cr-rich band in the inner oxide layer, just below the interface to the bottom oxide. Apart from Cr, this band was also enriched with Fe. Quantitative STEM/EDX line scans obtained from the oxide scale are shown in Fig. 12b. EDX point analysis on the indicated spots in Fig. 12a is shown in Table 3. The line scan result exhibits four different regions in the scanned area. Region I was situated close to the gas/scale interface and contained a high level of Al (37.98 wt.%) and O (58.85 wt.%) (Spot 1). Region II has relatively higher in Cr (3.42 wt.%) and Al (40.79 wt.%) levels which corresponded to the Cr-rich band (Spot 3) and inner alumina scale (Spot 4), respectively. Region III was located at the Laves phase and contained a high level of W (47.47 wt%) and Nb (18.65 wt.%), with some Fe (22.62 wt.%) and Cr (8.21 wt.%) (Spot 6). The cross-section TEM bright field image

of AluChrom 318 is displayed in Fig. 13. Again, two distinctive alumina scales can be easily observed. The Fe_2Nb particles were found to penetrate the inner alumina scale and move up to the gas/oxide interface. In order to determine the phase composition of both layers, which consisted of oxide grains on the nanometre scale, convergent beam electron diffraction (CBED) was carried out on both oxide scales. Unfortunately, neither CBED could confirm the phase composition of the alumina scales formed on AluChrom 318. The undetectable diffraction phase of both inner and outer alumina scales could be potentially caused by two reasons: 1) the oxide grains in both inner and outer scales are amorphous; 2) the oxide grains in both inner and outer scales have an extremely small size. The research carried out by the Swedish High Temperature Corrosion Centre (HTC) reported the effect of water on the oxidation status of the FeCrAl alloy Kanthal AF [20–22]. Kanthal AF was exposed at 900 °C for 1, 24, 72 and 168 hours in both dry O_2 and $\text{O}_2 + 40\% \text{H}_2\text{O}$. The TEM CBED results obtained indicated that the oxide scales showed a double-layered structure including an inward-growing bottom layer of $\alpha\text{-Al}_2\text{O}_3$ and an outward-growing upper layer of $\gamma\text{-Al}_2\text{O}_3$ with Cr-rich band in the middle, indicating the original metal/gas interface. The well-developed two-layered scale structure observed after 1000 hours exposure in the research reported here was quite comparable to the multi-layered oxides obtained by researchers from HTC. Therefore, in the current work, it is assumed that the outer and inner oxide layers formed on AluChrom 318 surface are $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$, respectively.

4. Discussions

4.1 Corrosion and Cr evaporation of SS309

In this study, the corrosion behaviour of SS309 in oxidising environment with the presence of water vapour can be directly correlated to the Cr evaporation and scale spallation. The relatively low parabolic mass gain of bare SS309 before 500 hours, in comparison to all the investigated materials can be accredited to Cr loss because of the steam induced Cr volatilisation in the form of $\text{CrO}_2(\text{OH})_2$. The parabolic trend before 500 hours corresponds to a greater oxidation rate than the Cr evaporation rate. The mass loss by Cr volatilisation can be rapidly compensated by the oxidation of a larger amount of Cr diffused outwards from the alloy, resulting in a balance of mass gain. The large amount of continuous chromium loss could be a possible reason for the formation of a porous MnCr_2O_4 top layer on the SS309 surface. However, Sachitanand *et al.* [7] reported that a higher concentration of Mn alloying element in the alloy results in a lower Cr evaporation rate due to the formation of a compact and thick spinel layer of MnCr_2O_4 . By comparing the obtained data with the aforementioned work [7], the SS309 in this research exhibited a Cr evaporation level which is comparable to the E-brite steel with 0.08 wt.% Mn (the lowest Mn content of the investigated alloys in their work) which had the highest Cr leakage under the exactly same exposure condition. Thus, it can be inferred that stainless steels containing Mn in a critical range of 0.3-0.5 wt.% develop a well adhering MnCr_2O_4 spinel top layer above the Cr_2O_3 layer at 800 and 850 °C, and that the rate of Cr vaporisation for those alloys is 2 to 3 times lower than for alloys that form a non-continuous MnCr_2O_4 top layer. In this research work, the transportation of chromium through the porous MnCr_2O_4 spinel scale with high defect concentration [23] formed on the SS309 surface was fast, meaning that the vaporised Cr

could be rapidly replaced by the quick grain boundary diffusion of Cr from the substrate [24,25], and leaving plenty of cation vacancies in the alloy grain boundaries [9]. During further oxidation, the vacancies within the grain boundaries in the steel base connected with each other to form cracks and even big gaps among alloy grains. Eventually the oxide scale detaches and this results in the cracked surface. The serious mass loss noted for uncoated SS309 after 500 hours is due to a combined action of scale spallation and Cr vaporisation. The main reason for the poor adhesion of the oxide scale can be accredited to the formation of a silica sublayer beneath the $\text{Cr}_2\text{O}_3/\text{MnCr}_2\text{O}_4$. EDX maps of the reverse side of the spalled scale (Fig. 3a) show a high intensity of Si at the metal/oxide interface, indicating the internal precipitation and oxidation of Si. Silica has a much lower TEC than Cr_2O_3 and steel, which is recognised as detrimental for scale adhesion. A poor adherent $(\text{Cr,Mn})_3\text{O}_4$ spinel scale was also detected on AISI 441 in Grolig *et al.*'s study due to the insufficient amount of Nb-enriched Laves phases to bind silica [26]. Spallation of oxide scales allows air (oxygen) access to the underlying Ni-enriched and Cr-depleted alloy. In the spalled region, internal oxidation of Ni-containing (Fe, Cr, Ni)-spinel oxides was evidenced by EDX. With the oxidation continuing, the fast-outward Fe and inward O diffusion led to the transformation from the non-protective (Fe, Cr, Ni)-spinel oxides to the stronger Fe-enriched $\text{Cr}_{1.3}\text{Fe}_{0.7}\text{O}_4$ as healing layer. This was detected in the EDX maps (Fig. 3b) and XRD (Fig. 4).

4.2 Corrosion and Cr evaporation of alumina formers

4.2.1 Alumina formation

As mentioned before, the oxidation of AluChrom 318 leads to the formation of an oxide that consists of two subscales with a Cr-band which separates the top and bottom parts of the scale. The high mass gain rate in the initial stage corresponds to the rapid growth of the top metastable alumina by Al outward diffusion during the furnace heat-up process. Meanwhile, this initial oxidation is accompanied with decomposition of the hydroxylated air-formed oxide film to form the mixture of chromium oxide and iron oxides which indicates the original steel surface [21,22]. The formation of the bottom $\alpha\text{-Al}_2\text{O}_3$ layer in AluChrom 318 seems to have been favoured by the isostructural corundum-type oxides (Cr_2O_3 and Fe_2O_3) produced in the metal/oxide interface by acting as nucleation sites where Al can incorporate [21]. During this oxidation period, Al diffuses outwards, nucleates on the isostructural corundum oxides, and then rapidly turns into the dominant cation to form a continuous alumina layer (stable stages) on the surface [22]. The position of the Cr-rich band in the outer part of the lower oxide suggests that the $\alpha\text{-Al}_2\text{O}_3$ grains have nucleated close to the original sample surface and have grown predominantly inwards. When a dense layer of $\alpha\text{-Al}_2\text{O}_3$ is formed, the outward growth rate of the outer $\gamma\text{-Al}_2\text{O}_3$ is expected to dramatically slow down since the outward diffusion rate of aluminium cation decreases [27]. This oxide growth pattern of AluChrom 318 is also in agreement with the parabolic relation found for the gravimetric analysis. As mentioned earlier, the Fe_2Nb particles were found to penetrate the inner $\alpha\text{-Al}_2\text{O}_3$ scale and stay on the top of the ridged alumina. Meanwhile, this barrier penetration process of Fe_2Nb particles may generate pores in the inner $\alpha\text{-Al}_2\text{O}_3$ scale. Hence, the aluminium from the steel base was found to erupt from the pores to the scale/gas

interface in all the directions to react with oxygen and build the thick outer alumina scale. The eruption path for aluminium outward diffusion is still clearly visible over the Fe_2Nb particles that already broke through the inner alumina scale in Fig. 13. This volcanic eruption growth pattern results in the formation of alumina in globular shape. Subsequently, the adjacent globular alumina scale grew larger and joined together to form the long ridged alumina, as detected in Fig. 10b. As discussed above, the $\gamma\text{-Al}_2\text{O}_3$ in the outer oxide layer is assumed to be metastable and is thus expected to transform to $\alpha\text{-Al}_2\text{O}_3$ with time when exposed to oxygen. However, the presence of water vapour was found to stabilise the $\gamma\text{-Al}_2\text{O}_3$ phase, thereby inhibiting its phase transformation to the stable $\alpha\text{-Al}_2\text{O}_3$ and, resulting in the formation of a duplex structure of a thick $\gamma\text{-Al}_2\text{O}_3$ scale over an extremely thin $\alpha\text{-Al}_2\text{O}_3$ scale [21,22].

However, the third element effect of chromium oxide for $\alpha\text{-Al}_2\text{O}_3$ nucleation on aluminised SS309 is not yet clear. The growth mechanism of the alumina scale on aluminised SS309 clearly differs from the observed duplex alumina scales formed on AluChrom 318. During exposure, the aluminium coating on the alloy surface evolves in the following process: (1) quick reaction with oxygen to form a continuous alumina layer accompanied with Al inward diffusion to the inner substrate and (2) Al outward diffusion to form and/or re-heal the alumina scale. For the former case, the fast oxidation of Al in the initial stage of exposure with a relatively fast parabolic rate corresponds to the rapid-growth of metastable alumina scale to produce a continuous layer due to the low temperature requirement for growth [28]. The inward diffusion of Al into the substrate combines with Ni, thereby promoting the formation of the intermetallic compound NiAl. The formation of NiAl can be accredited to the low diffusivity of Al in the alloy, confirming the typical reservoir behaviour for

maintaining the supply of Al for the further growth of the alumina layer [19]. For the latter case, the further thickening of the outer alumina scale takes place at the expense of the NiAl precipitates close to the alloy/oxide interface [29]. The decrease in the oxidation rate during further oxidation is probably associated with the prolonged diffusion path for the dominant Al outward transport to the gas/scale interface due to the continuous alumina scale thickening. However, Fig. 8 shows that the NiAl denuded zone beneath the scale layer was no longer detectable after 1000 hours oxidation, in comparison with a large amount of NiAl denuded zones detected after 100 hours oxidation in Fig. 9. This confirms that the NiAl precipitates underlying the denuded zone were not able to maintain the supply of Al to the oxidation front, resulting in the termination of the alumina scale thickening after 1000 hours exposure. In addition, comparing the cross-section for the 100 hours (Fig. 9) and 1000 hours (Fig. 8) exposure, it shows that the AlN precipitates had grown remarkably in size with the increase of exposure time. Therefore, it can be suggested that the aluminium in the NiAl denuded zone which were supposed to contribute to the growth of the outer alumina scale had been preferentially captured by the nitrogen impurity (0.11 wt.%) to form AlN in the inner zone of the alloy.

4.2.2 Chromium evaporation

The AluChrom 318 and aluminised SS309 showed 95% and 88% reduction in Cr evaporation compared to the bare SS309, respectively. This confirmed the excellent Cr retention ability of the formed alumina scale acting as an effective Cr barrier. The alumina scale restrained the surface chromium evolution through restraining the ionic mobility of chromium and oxygen through the alumina grain boundaries [30], thus causing a significant reduction in Cr evaporation. In the first 24 hours of Cr leakage detection, AluChrom 318 showed a higher Cr

evaporation rate than the aluminised SS309. For AluChrom 318, the high Cr evaporation rate in the first 24 hours was derived from the transient Cr_2O_3 formed in the initial stage at the gas/metal interface, leading to the slightly higher chromium evaporation before the eventual development of the continuous alumina layer takes over [3]. The rapid formation of the alumina scale on the aluminised SS309 by direct reaction between the aluminium coating and oxygen accompanied by the inward diffusion of aluminium into the alloy matrix resulted in a lack of exposure of Cr_2O_3 crystals, thereby leading to low Cr evaporation in the initial stage. However, the denuder technique revealed that the alumina scale formed on AluChrom 318 possessed a better Cr retention ability compared to that formed on the aluminised SS309. Fe^{3+} and Cr^{3+} are not expected to diffuse into the oxide scale after the formation of a continuous Al_2O_3 scale. The solubility of Fe^{3+} and Cr^{3+} in $\alpha\text{-Al}_2\text{O}_3$ is considered to be extremely low at temperatures below 1000 °C [31]. The results showed that no chromium was detected on spot 1 and 2 in Fig. 12 by STEM/EDX. However, the relatively higher concentration of Fe in the outer $\gamma\text{-Al}_2\text{O}_3$ can be accredited to its presence in the divalent state [21]. Meanwhile, based on the XRD measurement, the alumina scale formed on aluminised SS309 surface was mostly in metastable phases. The metastable alumina phases are cation-deficient [15] and are therefore considered to possess a lower Cr retention capability than the duplex alumina structure formed on the AluChrom 318 surface. Furthermore, the alumina scale on the aluminised SS309 surface grew with pores and cracks along the wrinkles due to the thermal stress which caused scale volume change. Thus, it can be deducted that Cr transport through the wrinkled alumina scale with accelerated speed led to the increased trend of Cr evaporation rate, as can be seen in Fig. 2d. Furthermore, the serious scale spallation with the depletion of the NiAl reservoir which occurred on aluminised SS309 will definitely provoke the Cr evaporation rate to an exponential growth

during extended exposure. Meanwhile, the Cr evaporation rate of AluChrom 318 in Fig. 2d decreased with time. This can be explained by the slightly higher surface Cr concentration on the thin alumina region which contributed to the initial evaporation process, whereas after the ridged alumina had formed, the Cr vaporisation process in the ridged alumina oxide was governed by the Cr diffusion via alumina grain boundaries. Once the dense and ridged oxides expanded over the entire surface the Cr evaporation rate stayed approximately constant.

5. Conclusions

The oxidation and Cr evaporation behaviour of SS309, aluminised SS309 and AluChrom 318 were investigated at 850 °C in a flow of 6.0 L/min of air with 3% H₂O. The bare SS309 did not satisfy the requirements for a successful application as CAPH material due to the formation of a porous multi-layered SiO₂/Cr₂O₃/(Cr,Mn)₃O₄ scale giving rise to serious scale spallation and substantial Cr evaporation. The Cr evaporation measurements showed that the Cr evaporation rate of aluminised SS309 was one order of magnitude lower than that of SS309, indicating that surface aluminising is an efficient way to minimise the Cr evaporation. Furthermore, the aluminised SS309 exhibited a comparable Cr evaporation level as AluChrom 318 which exhibited the best Cr retention ability over 168 hours. However, the alumina scale formed on aluminised SS309 suffered spallation during oxidation. It was observed that a high Mn outward flux and O inward diffusion throughout the alumina scale led to the breaking out of the internally formed (Cr,Mn)-spinel oxides. The difference in the Cr evaporation kinetics between both alumina formers was due to a different oxide formation mechanism. The AluChrom 318 formed a γ -Al₂O₃/ α -Al₂O₃ layered scale with the

aid of the isostructural Cr_2O_3 , and the inner $\alpha\text{-Al}_2\text{O}_3$ could effectively prevent the Cr^{3+} from outward diffusion at 850 °C. In contrast, the aluminised SS309 formed **an alumina scale** with a large amount of cracks and voids formation which led to an accelerated Cr evaporation rate. Thus, the AluChrom 318 demonstrated the an outstanding Cr retention ability and the alloys formed will be useful for overcoming the Cr evaporation in SOFC balance of plant components, in the case inspected here specifically the cathode air pre-heater.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data forms part of an ongoing study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] A. Arsalis, A comprehensive review of fuel cell-based micro-combined-heat-and-power systems, *Renew. Sustain. Energy Rev.* 105 (2019) 391–414. <https://doi.org/10.1016/j.rser.2019.02.013>.
- [2] P. Costamagna, The benefit of solid oxide fuel cells with integrated air pre-heater, *J. Power Sources.* 69 (1997) 1–9. [https://doi.org/10.1016/S0378-7753\(96\)02386-5](https://doi.org/10.1016/S0378-7753(96)02386-5).
- [3] L. Ge, A. Verma, R. Goettler, D. Lovett, R.K.S. Raman, P. Singh, Oxide Scale Morphology and Chromium Evaporation Characteristics of Alloys for Balance of Plant Applications in Solid Oxide Fuel Cells, *Metall. Mater. Trans. A.* 44 (2013) 193–206. <https://doi.org/10.1007/s11661-012-1492-y>.
- [4] J.L. Córdova, H. Heshmat, Development of a ceramic heat exchanger for application as solid oxide fuel cell cathode air preheater, in: *Am. Soc. Mech. Eng. Power Div. POWER*, American Society of Mechanical Engineers (ASME), 2016. <https://doi.org/10.1115/POWER2016-59333>.
- [5] Z. Yang, K.S. Weil, D.M. Paxton, J.W. Stevenson, Selection and Evaluation of Heat-Resistant Alloys for SOFC Interconnect Applications, *J. Electrochem. Soc.* 150 (2003) A1188–A1201. <https://doi.org/10.1149/1.1595659>.
- [6] K. Hilpert, D. Das, M. Miller, D.H. Peck, R. Weiss, Chromium vapor species over solid oxide fuel cell interconnect materials and their potential for degradation processes, *J. Electrochem. Soc.* 143 (1996) 3642–3647.
- [7] R. Sachitanand, M. Sattari, J.-E.E. Svensson, J. Froitzheim, Evaluation of the oxidation and Cr evaporation properties of selected FeCr alloys used as SOFC interconnects, *Int. J. Hydrogen Energy.* 38 (2013) 15328–15334. <https://doi.org/10.1016/j.ijhydene.2013.09.044>.
- [8] S.P. Jiang, X. Chen, Chromium deposition and poisoning of cathodes of solid oxide fuel cells - A review, *Int. J. Hydrogen Energy.* 39 (2014) 505–531. <https://doi.org/10.1016/j.ijhydene.2013.10.042>.
- [9] M. Stanislawski, J. Froitzheim, L. Niewolak, W.J. Quadackers, K. Hilpert, T. Markus, L. Singheiser, Reduction of chromium vaporization from SOFC interconnectors by highly effective coatings, *J. Power Sources.* 164 (2007) 578–589. <https://doi.org/10.1016/J.JPOWSOUR.2006.08.013>.

- [10] S. Kitaoka, T. Kuroyama, M. Matsumoto, R. Kitazawa, Y. Kagawa, Control of polymorphism in Al₂O₃ scale formed by oxidation of alumina-forming alloys, *Corros. Sci.* 52 (2010) 429–434. <https://doi.org/10.1016/j.corsci.2009.09.031>.
- [11] D.J. Young, Alloy Oxidation III: Multiphase Scales, in: *High Temp. Oxid. Corros. Met.*, 2016: pp. 335–392. <https://doi.org/10.1016/b978-0-08-100101-1.00007-8>.
- [12] E.J. Opila, N.S. Jacobson, D.L. Myers, E.H. Copland, Predicting oxide stability in high-temperature water vapor, *J. Miner. Met. Mater. Soc.* 58 (2006) 22–28. <https://doi.org/10.1007/s11837-006-0063-3>.
- [13] Z. Yu, M. Chen, C. Shen, S. Zhu, F. Wang, Oxidation of an austenitic stainless steel with or without alloyed aluminum in O₂+10% H₂O environment at 800°C, *Corros. Sci.* 121 (2017) 105–115. <https://doi.org/https://doi.org/10.1016/j.corsci.2017.03.015>.
- [14] S. Sharafi, M.R. Farhang, Effect of aluminizing on surface microstructure of an HH309 stainless steel, *Surf. Coatings Technol.* 200 (2006) 5048–5051. <https://doi.org/10.1016/j.surfcoat.2005.05.024>.
- [15] M. Stanislawski, E. Wessel, T. Markus, L. Singheiser, W.J. Quadakkers, Chromium vaporization from alumina-forming and aluminized alloys, *Solid State Ionics.* 179 (2008) 2406–2415. <https://doi.org/10.1016/J.SSI.2008.09.015>.
- [16] J. Froitzheim, H. Ravash, E. Larsson, L.G. Johansson, J.E. Svensson, Investigation of Chromium Volatilization from FeCr Interconnects by a Denuder Technique, *J. Electrochem. Soc.* 157 (2010) B1295–B1300. <https://doi.org/10.1149/1.3462987>.
- [17] K. Kim, FIB serial milling and lifting out of fine inclusions in an intensively melt sheared aluminum alloy, *Mater. Lett.* 117 (2014) 74–77. <https://doi.org/10.1016/J.MATLET.2013.11.083>.
- [18] H. Hattendorf, R. Hojda, D. Naumenko, A. Kolb-Telieps, A new austenitic alumina forming alloy: An aluminium-coated FeNi₃₂Cr₂₀, *Mater. Corros.* 59 (2008) 449–454. <https://doi.org/10.1002/maco.200804126>.
- [19] X. Xu, X. Zhang, X. Sun, Z.P. Lu, Effects of silicon additions on the oxide scale formation of an alumina-forming austenitic alloy, *Corros. Sci.* 65 (2012) 317–321. <https://doi.org/10.1016/j.corsci.2012.08.039>.
- [20] F. Liu, H. Josefsson, J.E. Svensson, L.G. Johansson, M. Halvarsson, TEM investigation of the oxide scales formed on a FeCrAlRE alloy (Kanthal AF) at 900°C in dry O₂ and O₂ with 40% H₂O, *Mater. High Temp.* 22 (2005) 521–526.

<https://doi.org/10.1179/mht.2005.062>.

- [21] F. Liu, H. Götlind, J.-E.E. Svensson, L.-G.G. Johansson, M. Halvarsson, Early stages of the oxidation of a FeCrAlRE alloy (Kanthal AF) at 900 °C: A detailed microstructural investigation, *Corros. Sci.* 50 (2008) 2272–2281. <https://doi.org/10.1016/J.CORSCI.2008.05.019>.
- [22] H. Götlind, A.F. Liu, J.-E. Svensson, A.M. Halvarsson, L.-G. Johansson, F. Liu, Á.M. Halvarsson, The Effect of Water Vapor on the Initial Stages of Oxidation of the FeCrAl Alloy Kanthal AF at 900 °C, *Oxid Met.* 67 (2007) 251–266. <https://doi.org/10.1007/s11085-007-9055-0>.
- [23] D.H. Speidel, A. Muan, The System Manganese Oxide–Cr₂O₃ in Air, *J. Am. Ceram. Soc.* 46 (1963) 577–578. <https://doi.org/doi:10.1111/j.1151-2916.1963.tb14619.x>.
- [24] A. Col, V. Parry, C. Pascal, Oxidation of a Fe–18Cr–8Ni austenitic stainless steel at 850 °C in O₂: Microstructure evolution during breakaway oxidation, *Corros. Sci.* 114 (2017) 17–27. <https://doi.org/10.1016/J.CORSCI.2016.10.029>.
- [25] B.K. Kim, D.-I. Kim, K.-W. Yi, Suppression of Cr evaporation by Co electroplating and underlying Cr retention mechanisms for the 22wt.% Cr containing ferritic stainless steel, *Corros. Sci.* 130 (2018) 45–55. <https://doi.org/https://doi.org/10.1016/j.corsci.2017.10.019>.
- [26] J.G. Grolig, J. Froitzheim, J.E. Svensson, Coated stainless steel 441 as interconnect material for solid oxide fuel cells: Evolution of electrical properties, *J. Power Sources.* 284 (2015) 321–327. <https://doi.org/10.1016/j.jpowsour.2015.03.029>.
- [27] J. Engkvist, S. Canovic, K. Hellström, A. Järnäs, J.E. Svensson, L.G. Johansson, M. Olsson, M. Halvarsson, Alumina Scale Formation on a Powder Metallurgical FeCrAl Alloy (Kanthal APMT) at 900–1,100 °C in Dry O₂ and in O₂ + H₂O, *Oxid. Met.* 73 (2010) 233–253. <https://doi.org/10.1007/s11085-009-9177-7>.
- [28] H. Josefsson, F. Liu, J.E. Svensson, M. Halvarsson, L.G. Johansson, Oxidation of FeCrAl alloys at 500–900°C in dry O₂, *Mater. Corros.* 56 (2005) 801–805. <https://doi.org/10.1002/maco.200503882>.
- [29] L.-F. He, P. Roman, B. Leng, K. Sridharan, M. Anderson, T.R. Allen, Corrosion behavior of an alumina forming austenitic steel exposed to supercritical carbon dioxide, *Corros. Sci.* 82 (2014) 67–76. <https://doi.org/https://doi.org/10.1016/j.corsci.2013.12.023>.
- [30] K. Gerdes, C. Johnson, Surface Scale Formation on Solid Oxide Fuel Cell Proximal

Balance of Plant Components, J. Fuel Cell Sci. Technol. 6 (2008) 011018 1–5.
<https://doi.org/10.1115/1.2971195>.

- [31] P.Y. Hou, X.F. Zhang, R.M. Cannon, Impurity distribution in Al_2O_3 formed on an FeCrAl alloy, Scr. Mater. 50 (2004) 45–49.
<https://doi.org/https://doi.org/10.1016/j.scriptamat.2003.09.044>.

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

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Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Captions

Fig. 1. The schematic diagram of the denuder technique.

Fig. 2. (a) Discontinuous mass measurements and (b) mass gain rates as a function of time for SS309, aluminised SS309 and AluChrom 318 in 3% H₂O humidified air at 850 °C for 2500 hours; (c) Accumulated Cr evaporation and (d) Cr evaporation rates as a function of time for SS309, aluminised SS309 and AluChrom 318 exposed to 3% H₂O humidified air at 850 °C for 168 hours.

Fig. 3. SEM top view and EDX mapping of SS309 exposed at 850 °C in air + 3% H₂O for (a) 100 and (b) 1000 hours.

Fig. 4. XRD patterns of SS309 after oxidation at 850°C in air with 3% H₂O (6.0 L/min) for 0, 100, 500, 1000 and 2000 hours.

Fig. 5. SEM cross-sectional images of SS309 after exposure to humidified air at 850 °C for 1000 hours with the corresponded EDX maps.

Fig. 6. SEM top view of aluminised SS309 exposed at 850 °C in air + 3% H₂O for (a) 100 and (b) 1000 hours. EDX mapping showing the element distribution for Fig. 6b.

Fig. 7. XRD patterns of aluminised SS309 after oxidation at 850°C in air with 3% H₂O (6.0 L/min) for 0, 100, 500, 1000 and 2000 hours.

Fig. 8. SEM cross-sectional images and EDX mapping of aluminised SS309 after exposure to humidified air at 850 °C for 1000 hours.

Fig. 9. Cross-sectional SEM image and EDX mapping of aluminised SS309 after 100 hours exposure at 850 °C in air with 3% H₂O environment.

Fig. 10. SEM top view of AluChrom 318 exposed at 850 °C in air + 3% H₂O for (a) 100 and (b) 1000 hours. EDX linescan along the line indicated in Fig. 10b. EDX mapping showing element distribution on Fig. 10b.

Fig. 11. XRD patterns of AluChrom 318 after oxidation at 850°C in air with 3% H₂O (6.0 L/min) for 0, 100, 500, 1000 and 2000 hours.

Fig. 12. (a) STEM cross-sectional image and EDX mapping of AluChrom 318 exposed at 850 °C in air + 3% H₂O for 1000 hours; (b) EDX linescan along the line indicated in Fig. 12a.

Fig. 13. TEM bright field cross-sectional images of the duplex alumina scales on the AluChrom 318 exposed at 850 °C in air + 3% H₂O for 1000 hours.

Tables

Table 1. The chemical compositions of the stainless steel materials investigated in this study.

(wt.%)	Fe	Cr	Mn	Al	Ni	Si	Nb	W	Co	others
AluChrom 318	Bal.	18.8	0.21	3.58	0.24	0.32	0.73	2.02	--	Hf 0.06; Y 0.07 Zr 0.03; Cu 0.03 C 0.01; N 0.01
SS309	Bal.	22-24	2.0	--	12-15	0.75	--	--	--	C 0.2; P 0.045 S 0.03,N 0.11

Table 2. EDX point analysis on the indicated spots in Fig. 3.

at.%	O	Fe	Cr	Ni	Mn	C	Si	S	P
1	16.03	48.63	14.62	6.99	1.73	9.44	2.36	0.13	0.07
2	39.07	32.54	13.79	4.35	1.46	6.6	2.1	0.09	0
3	57.14	12.19	19.37	1.22	3.59	4.05	1.29	0.08	0

Table 3. EDX point analysis on the indicated spots in Fig. 12a.

Wt.%	1	2	3	4	5	6
O	58.58	56.55	53.45	56.06	-	-
Al	37.98	36.07	32.83	40.79	5.02	0.50
Si	2.08	6.65	9.10	2.66	1.09	2.46
Cr	-	-	3.42	0.17	29.61	8.21
Fe	1.09	0.73	1.20	0.32	64.28	22.62
Nb	-	-	-	-	-	18.65
W	-	-	-	-	-	47.57
Total	100	100	100	100	100	100

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

AUTHORSHIP STATEMENT

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Category 1

Conception and design of study: K. Zhang, J.E. Hong, R. Steinberger-Wilckens;

acquisition of data: K Zhang

analysis and/or interpretation of data: K Zhang, A. El-kharouf, R. Steinberger-Wilckens.

Category 2

Drafting the manuscript: K Zhang

revising the manuscript critically for important intellectual content: A. El-kharouf, J.E. Hong, R. Steinberger-Wilckens.

Category 3

Approval of the version of the manuscript to be published (the names of all authors must be listed): K Zhang , A. El-kharouf, J.E. Hong, R. Steinberger-Wilckens.

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This statement is signed by all the authors

Author's name (typed)	Author's signature	Date
Kun Zhang	KUN ZHANG	14.03.2020
Ahmad El-kharouf	Ahmad El-kharouf	16.03.2020
Jong-Eun Hong	Jong-Eun Hong	13.03.2020
Robert Steinberger-Wilckens	Robert Steinberger-Wilckens	16.03.2020