Characterisation of aluminium diffusion coatings elaborated on austenitic stainless steels and on ferritic-martensitic steels

Claire C. Boulesteix, Fernando Pedraza

► To cite this version:

Claire C. Boulesteix, Fernando Pedraza. Characterisation of aluminium diffusion coatings elaborated on austenitic stainless steels and on ferritic-martensitic steels. *Surface and Coatings Technology*, 2018, 339, pp.27-36. 10.1016/j.surfcoat.2018.01.086 . hal-02467115

HAL Id: hal-02467115

<https://hal.science/hal-02467115>

Submitted on 4 Feb 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Characterisation of Aluminium Diffusion Coatings Elaborated on Austenitic Stainless Steels and on Ferritic-Martensitic Steels

Claire Boulesteix, Fernando Pedraza

Laboratoire des Sciences de l'Ingénieur pour l'Environnement (LaSIE, UMR-CNRS 7356),

Université de La Rochelle, Avenue Michel Crépeau, 17042 La Rochelle Cedex 1, France

claire.boulesteix@univ-lr.fr ; fernando.pedraza@univ-lr.fr

Abstract. Slurry aluminide coatings were elaborated on IN-800HT and HR3C austenitic stainless steels (ASS) and on P92 ferritic-martensitic steels. The thermal treatments conducted in Ar enabled the melting of Al and the high temperature synthesis with the substrate elements to result in an aluminium diffusion coating. Whether for the ferritic-martensitic or the austenitic stainless steels, the coatings were formed by the simultaneous Al inward diffusion into the steel matrix and the outward diffusion of Fe (and Ni for the ASS) on both steel substrates. As a result, the coatings exhibited a B2-(Fe,Ni)Al phase for the ASS and B2-FeAl phase for the P92 substrate. A reduction of the grain size after annealing was noticed for the ASS but their microstructures remained mostly austenitic. However, a significant increase of the grain size occurred in the P92 steel with a transformation from the initial tempered martensitic structure to an austenitic structure. The microhardness of the ASS did not change significantly whereas for P92, a large increase occurred.

Keywords: Austenitic steels, Ferritic-martensitic steels, Aluminium diffusion coatings, Characterisation.

1. INTRODUCTION

In order to achieve higher efficiencies and to decrease the CO₂ emissions in the power generation industry, the operating temperatures and pressures have to be increased [1, 2]. The new generation of ultra-supercritical power plants (USC units) operate with steam temperatures up to 600-650°C and pressures from 25 to 30 MPa [3, 4]. In these plants, austenitic stainless steels are commonly employed in superheaters and reheaters of steam boilers whereas ferritic martensitic steels are preferred for larger components like tubes and pipes [5-7]. Due to their high temperature oxidation and corrosion resistance combined with their high strength, the HR3C and the IN-800HT austenitic stainless steels (ASS) can be employed in USC units [8, 9]. With a density of 8 mg/cm², IN-800HT is a modified version of IN-800 containing more Ni,

Si, Mn and Ti [10, 11]. This material is well-known to resist to stress corrosion and like for the HR3C steel, the presence of chromium in these alloys allows the formation of a protective oxide layer while the presence of nickel improves the stability of the oxide formed [8, 10, 12]. The nitrogen in the interstitial sites of the matrix contained in the HR3C alloy combined with 0.4Nb, 25Cr and 20Ni (wt%) additions represent an effective measure of the enhancement of creep strength [8, 13]. The P92 ferritic martensitic alloy is one of the most commonly employed high Cr creep resistant steels in large components of USC units because of its high creep rupture strength, its excellent mechanical properties, its good weldability, its low thermal expansion, its high thermal conductivity and its adequate corrosion resistance [8, 14-17]. However, despite the good properties of these three alloys, they need to be coated in order to enhance their lifetime at higher temperatures and pressures. In severe atmospheres encountered in USC units, SiO₂ can dissolve and Cr₂O₃ can form volatile Cr oxy-hydroxyl species [18, 19]. Thus, Al₂O₃ is the only oxide ensuring the lifetime increase of the components. This external protective Al₂O₃ scale can grow from Al diffusion coatings [20]. In particular, slurry aluminising offers the possibility of coating large components [21] and is considered as low cost and easy-to-apply process [22]. Slurry coatings can be applied to a metallic substrate by brushing, spraying or by dip-coating [23]. Slurries are suspensions of aluminium micro-particles on a binder-solvent system [22]. In our case, the solvent is water, thus making our coatings environmentally friendly [24]. Once the Al slurry has been sprayed, the subsequent thermal treatment pyrolyses the binder and makes the molten aluminium to react with the substrate to form an aluminide intermetallic phase [21, 23, 25]. These coatings have shown their excellent resistance even after 2000 hours in steam at 650 or 700°C, for respectively P92 and IN-800HT and for the HR3C alloy [25-27]. Experiments conducted by Agüero et al. have shown the good behaviour of another kind of aluminium slurry deposited on P92 ferritic-martensitic steels for 41 000 hours in steam, at 650°C [28]. In addition, they can be repaired [29] and the potential cracks can be sealed [30]. However, although the high temperature behaviour of these aluminides has been discussed, there is no real description of the slurry coatings themselves in the open literature, let alone in what the aluminising treatment may affect the microstructure and microhardness of the parent material, which are the main aims of this work.

1. EXPERIMENTAL PROCEDURE

2. 1 - Materials of Study

IN-800HT coupons of 16 mm diameter and 2 mm thick were ground with SiC#180 paper. The same procedure was conducted with HR3C and P92 coupons of 20*10*2 mm. The nominal compositions of the three studied substrates are given in Table 1.

TABLE 1. Nominal and experimental (EDS) compositions of IN-800HT, HR3C and P92 substrates (wt%).

		Fe	Ni	Cr	C	Ti	S	Others
IN-800HT	Nominal	Bal	30-35	19-23	0.10 max	0.15-0.60	0.015 max	Si: 1 max Mn: 1.5 max Cu: 0.75 max
	EDS	45	29	21	< 1	< 1	-	Si: 1-2
HR3C	Nominal	Bal	17-23	23-27	0.06	-	-	Si: 0.4 Mn: 1.2 Nb: 0.20-0.60 N: 0.15-0.35
	EDS	53.5	20	25	< 1	-	-	Mo: 0.4 Nb: 0.5
P92	Nominal	Bal	0.4 max	8.50-9.50	0.07-0.13	-	0.01 max	Si: 0.50 Mn: 0.30-0.60 Mo: 0.30-0.60 W: 1.5-2 V: 0.15-0.25
	EDS (wt%)	87	-	9	-	-	-	Mn: < 1 Mo: <1 W: 2

Aluminium micro-particles (4-5 μm average size, Hermillon, France) were used to aluminise the substrates. In order to obtain a more precise particles size and their composition, the powders were microscopically analysed. Characterisation of the Al powders and of the slurry were performed by DSC measurements, using a SETARAM Labsys Evo 1600 thermal analysis. The heating and cooling rates of these analyses were $10^{\circ}\text{C}.\text{min}^{-1}$ and the tests were performed under argon (20 mL/min). The Al microparticles were heated up to 1300°C and up to 700°C for the slurry since after the melting of Al no significant event is recorded for the slurry [31].

2. 2 – Aluminisation

All the samples were coated by spraying aluminium slurry containing 43wt% Al micro-particles dispersed in 57wt% of binder (1/10 polyvynil alcohol/deionized water). After drying in ambient air for at least 1 hour [31], the coated samples were annealed in argon ($400^{\circ}\text{C}/3\text{h} + 650^{\circ}\text{C}/3\text{h} + 1000^{\circ}\text{C}/1\text{h}$ or $1100^{\circ}\text{C}/1\text{h}$ for, respectively the ferritic-martensitic steel and the austenitic stainless steels). These coating conditions were based in previous investigations on nickel-

based superalloys [23, 32] but were slightly lowered in temperature and shortened in time for these Fe-based alloys.

2. 3 - Vickers microhardness and evaluation of the grain size

Microhardness values were measured across the additive layer and the interdiffusion zone of the coatings and in the substrate for each coated material. The acquisitions were performed using a Shimadzu Type M tester with a Vickers indenter, with a load of 15 g and for 10 seconds. The average values of microhardness were calculated from 10 indentations performed for each part of the coating/substrate system [33].

The average grain sizes of the coatings and of the steel core materials were evaluated using the ASTM E112 standard test method [34]. The intercept procedure was selected and involves an actual count of the number of grain boundary intersections with a test line per unit length of test line. For each system, 6 lines were plotted in 2 spatial dimensions in order to get a better average.

2. 4 - Crystal Structures Before and After Aluminisation

The crystal structure was determined by X-Ray Diffraction (XRD) using a Bruker AXS D8 Advance (CuK α radiation), in θ -2 θ mode.

2. 5 - Etching

In order to obtain informations about the distribution and the size of the grains, the samples were mounted in resin, polished and etched before microscopic characterisation. The P92 samples were immersed for few seconds in a solution of Nital 5%. For aluminised IN-800HT, an electrochemical etching was realized by immersion for 3-5 seconds in a 10 vol% H₂SO₄ aqueous solution. For the uncoated IN-800HT and for the uncoated and aluminised HR3C, chemical etching was realized with a Kalling n°2 solution (5g CuCl₂ + 100mL HCl + 100mL ethyl alcohol).

2. 6 - Microscopic Characterisation

The etched cross-sections of the uncoated/coated samples were analysed using a Leica DMRM microscope and a LEICA MC170HD camera coupled with the software LAS v4.9 for the

images acquisition. All the samples were also characterised by scanning-electron microscopy (SEM) in a FEI Qanta 200F FEG with an EDAX detector for chemical analyses.

3. RESULTS

3.1 – Aluminium particles and corresponding slurry Preliminary analyses were carried out on the Al micro-particles in order to obtain an average size. Fig. 1. a) highlights the relatively heterogeneous distribution of the particle size. Indeed, some particles can measure up to 12 microns while the smallest ones do not exceed 0.5 microns. The Gaussian plot of Fig. 2. b) shows that average size of the Al particles used in this study is about 3 microns. Oxygen was detected in small quantities ($\approx 5\text{-}8\text{ at\%}$) and Ar was also quantified to less than 1 at%, which arise from the wire explosion method employed to produce the particles [35, 36]. In contrast, no other elements were detected. In order to clarify this point, DSC measurements were carried out with the Al micro-particles. The corresponding thermogram shown in Fig. 2. a) let appear an endothermic event at $657 \pm 1^\circ\text{C}$ which is below the theoretical melting point of Al (660.5°C [37]). This difference of melting temperature is probably due to the presence of impurities in the powders not highlighted with the EDS analyses [38, 39]. Thereafter, the evolution of the transformation of the slurry was characterised by DSC up to 700°C , at which full decomposition of the binder and melting of aluminium are achieved [40].

FIGURE 1. Micrographs of Al micro-particles used in this study (a) and their size distribution (b).

The slurry thermogram shown in Fig. 2. b) reveals four phenomena. The first phenomenon occurs below 100°C and was associated with the free water contained in the slurry [31]. The second event taking place at 100°C is endothermic and was ascribed to the evaporation of water. The third phenomenon appears between 200 and 300°C but is less marked than the previous ones. Rannou et al. ascribed such phenomenon to the PVA, including the free water trapped in the PVA film, its subsequent melting and its final decomposition [31]. A final but important endothermic signal was noticed at $657 \pm 1^\circ\text{C}$ similar to the one of Fig. 2. a) for pure Al.

FIGURE 2. DSC curves upon heating (10°.min^{-1}) under Ar(g) flow of (a) the Al micro-particles and (b) of the Al slurry.

3. 2 – Aluminide coatings

As shown in Fig. 3, the microstructure and the composition of the coatings appeared very homogeneous in the three steels.

FIGURE 3. SEM cross-sections of aluminised (a) IN-800HT, (b) HR3C, (c) P92 steels and their corresponding EDS profiles (d, e and f, respectively).

The coatings can be divided in two major parts: an outer additive layer and an inner interdiffusion layer. The average composition of the additive layer of the IN-800HT substrate was about 35 Fe, 30 Al and 25 Ni (wt%), which corresponds mostly to the B2-(Fe,Ni)Al phase according to the Fe-Ni-Al ternary diagram at 1050°C (Fig. 4. a) [41]. In the HR3C steel, the

additive layer contained more Al (45 wt%) than in the IN-800HT (30 wt%), the Fe content was similar and the Ni content was two times lower (10 and 20 wt% for the coated HR3C and IN-800HT substrates, respectively). Despite these differences, the additive layer of the HR3C also corresponded to the B2 phase, as shown in Fig. 4. a). The XRD analyses carried out on the coated austenitic stainless steels (Fig. 5. a) confirmed this hypothesis with the appearance of the six characteristic peaks of the B2 phase. As shown in Figs. 3. a) and b), the thickness of the additive layer of the coated IN-800HT and HR3C was very similar (about 50 μm). However, the interdiffusion zone of the HR3C specimen appeared 2.5 times thicker than that of IN-800HT. The X-ray maps shown in Figs. 6. a) and b) highlight a homogenous distribution of Al in the entire thickness of the additive layers. Nevertheless, a Cr and Fe depletion was observed close to the interface between the additive and the interdiffusion layers. On the contrary, a Ni enrichment occurred at the same area.

FIGURE 4. (a) Fe-Ni-Al diagram [41] and (b) Fe-Al diagram [42]. Compositions of the additive layer of IN-800HT (yellow circle), HR3C (green circle) and P92 (orange circle).

FIGURE 5. X-ray patterns of the (a) IN-800HT and HR3C austenitic stainless steels and (b) of the P92 ferritic-martensitic steel before and after aluminisation.

FIGURE 6. X-ray maps of the slurry aluminide coatings on (a) IN-800HT, (b) HR3C and (c) P92 steels.

For the P92 ferritic-martensitic steel (Fig. 3. c), the additive layer and the interdiffusion zone appeared thicker compared to the ASS. Indeed, the additive layer was about 60 μm thick while the thickness of the interdiffusion zone was even greater to reach about 70 μm . The additive layer was homogeneous and composed by 50 at% of Al and 45 at% Fe which corresponds to the B2-FeAl phase by comparing with the Fe-Al binary diagram (Fig. 4. b) [42]. The XRD analyses carried out on these samples confirmed the existence of the B2 phase (Fig.5 b). The X-ray maps realized on the aluminised P92 ferritic-martensitic steel (Fig. 5. c) shows a good homogeneity of the Al distribution in the coating and an enrichment of Cr from the additive layer/interdiffusion interface to the rest of the substrate to reach about 10 at% (Fig. 3. c).

Despite of a good homogeneity in terms of microstructure, compositions and thicknesses of the coatings, some cracks were detected on austenitic stainless steels. As reported by our group, [27, 29] the number of cracks in aluminised HR3C was a little bit greater than in the IN-800HT case due to the most important stiffness of the former [43]. Previous works have linked these cracks to the mismatch between the thermal expansion coefficients of the different metallurgical phases [28, 44, 45, 46]. Other authors have reported this phenomenon with tensile stress from the substrate occurring upon heating [47].

3. 3 – Metallurgical evolutions induced by the aluminisation process

As shown in Figs. 7. a) and a'), the thermal treatment seemed to reduce the grain size of IN-800HT. Indeed the average grain size of the uncoated and the aluminised substrates were, respectively, $219.5 \pm 39.2 \mu\text{m}$ and $134.2 \pm 11.7 \mu\text{m}$ (Table 2). For the HR3C substrate, it appeared that the grain size had slightly increased after aluminising while different carbides were also observed. Some square-like precipitates were found in the bulk of IN-800HT and were associated with TiC [48]. Moreover, some Cr carbides were detected in both steels as well as Nb-rich carbonitrides [13] and also M_{23}C_6 which are typical of the ASS after annealing at high temperatures [9, 13]. These precipitates were mainly located within the matrix (grains) of the untreated ASS but appeared with a round shape at the grain boundaries and with a cuboidal morphology within the grains after aluminisation [49] as shown in Fig. 7. a') and b').

FIGURE 7. Optical micrographs of uncoated (a) IN-800HT (*Kalling n°2*), (b) HR3C (*Kalling n°2*), (c) P92 (*Nital 5%*) and aluminised (a') IN-800HT (*10% vol H₂SO₄*), (b') HR3C (*Kalling n°2*), (c') P92 (*Nital 5%*).

TABLE 2. Grain sizes of the uncoated and aluminised substrates studied in this work.

IN-800HT austenitic stainless steel		HR3C austenitic stainless steel		P92 ferritic-martensitic steel	
<i>Uncoated</i>	<i>Aluminised</i>	<i>Uncoated</i>	<i>Aluminised</i>	<i>Uncoated</i>	<i>Aluminised</i>
219.5 ± 39.2 μm	134.2 ± 11.7 μm	78.8 ± 11.8 μm	93.5 ± 17.2 μm	4.8 ± 2.3 μm	51.8 ± 8.2 μm

By referring to the Schaeffler diagram [50] shown in Fig. 8 the structure of the HR3C evolved with the aluminising step at high temperature while that of IN-800HT remained unchanged. The change in HR3C could be related to the greater Al and Cr contents underneath the interface between the substrate and the coating that provokes an evolution from 100% austenite to 95% austenite + 5% ferrite. However, the XRD diffractogram obtained on this sample let not appear any ferrite phase probably because of insufficient penetration of the X-rays to this interface. Therefore, the presence of the other minor phases besides austenite cannot be excluded.

FIGURE 8. Schaeffler diagram [50]. Structures of uncoated/aluminised IN-800HT (red points) and HR3C (blue points).

For the P92 substrate, the untreated material (Fig. 7. c) exhibited a tempered martensitic structure, as reported by Bates et al. for Grade 91 ferritic-martensitic alloy [20]. $M_{23}C_6$ carbides characteristic of this type of alloy [51] were found in the P92 substrate as shown in Fig. 7. c). By referring to the CCT diagram for the P92 substrate (Fig. 9), it appeared that the structure of the steel was converted to austenite after the aluminisation carried out in this study. The annealing step also resulted in a 10-fold increase of grain size.

FIGURE 9. CCT diagram for P92 ferritic-martensitic steel [51].

3. 4 – Microhardness

Figure 10 summarizes the Vickers microhardness values measured before and after aluminisation. It appeared that the microhardness at the core of the ASS before aluminisation was higher compared to those obtained after aluminisation but the gap was negligible in view of the uncertainties of the measures. Before the annealing step, the microhardness of IN-800HT was 210.8 ± 38.7 HV whereas after aluminisation it was about 169.1 ± 11.7 HV (Fig. 10. a). For the HR3C substrate (Fig. 10. b), the gap between the two values was smaller (252.8 ± 13.4 and 235.8 ± 13.6 HV for, respectively, the uncoated and the aluminised specimens). On the contrary, the difference of Vickers microhardness between the aluminised (401.2 ± 26.3 HV) and the uncoated (217.1 ± 28.4 HV) P92 substrates was quite significant (Fig. 10. c).

The Vickers microhardness of the slurry aluminide coatings on IN-800HT, HR3C and P92 were also evaluated (Figs. 10). For the ASS, it appeared that the additive layers were harder than the interdiffusion zones and than the core of the substrates. In contrast, the opposite occurred in the aluminised P92 since the coating appeared softer than the core of the substrate (Fig. 10. c).

FIGURE 10. Vickers microhardness of uncoated and aluminised (a) IN-800HT, (b) HR3C and (c) P92 substrates.

4. DISCUSSION

4. 1 – Aluminium particles and corresponding slurry characterisation

The DSC analyses carried out with the Al microparticles and the corresponding aluminium slurry allowed to confirm the choice of the thermal treatment conducted in this study. Indeed, with four phenomena taking place below 400°C, the first ramp of the annealing has to be conducted slowly in order to achieve a gradual decomposition of the PVA. Then, a second heating rate up to 650°C followed by a 3h dwell at this intermediate temperature involves the Al melting and the subsequent sintering of the particles. Also, the final dwell of the annealing has to be carried out at higher temperature in order to promote the Al inward and the simultaneous Ni, Fe outward diffusion to create the aluminide coating [23, 32]. The DSC

measurements realized in this study confirm thus previous works realized in our group although the Al particles (supplier and size) were different [25-27, 29].

4.2 – Aluminide coatings

The IN-800HT, HR3C and P92 substrates were aluminised using the slurry analyzed in the first part of this study. The EDS profiles (Figs. 3. a) and b) and the X-ray patterns (Fig. 5. a) show that the additive layers elaborated on IN-800HT and HR3C are mostly composed by the B2-(Fe, Ni)Al phase, which is indicative of inward Al diffusion into the steel matrix and, simultaneously, outward Fe and Ni diffusion. In both cases, the coatings appeared homogeneous in terms of thicknesses and composition. Although the thickness of the additive layers was the same, the interdiffusion zone of the HR3C substrate was thicker than the one on IN-800HT (respectively 49 and 19 μm). Previous works have related this phenomenon to the greater amount of Cr in the HR3C [25-29]. Indeed, during the aluminisation, Cr is incorporated in the Al coating, thus preventing the Al inward diffusion and the outward diffusion of the compounds contained in the substrate [26, 52]. The Al distribution within the additive layers of the ASS appeared homogeneous whereas a Cr and Fe depletion was observed close to the additive/interdiffusion zones interface (Fig.6. a) and b). On the contrary a Ni enrichment was observed in these areas. Cr is known to have a very low solubility in Al-rich and stoichiometric aluminides thus explaining the presence of Cr in the absence of Ni and vice versa [53, 54]. Therefore, a significant increase of the Cr content was observed below the interface between the additive and the interdiffusion layers in both austenitic stainless steels. Moreover, in the HR3C steel, Cr-rich precipitates were highlighted in the interdiffusion zone and again, Cr was detected while Ni was not. Conversely, Ni was detected in the interdiffusion zone in the Cr-poor areas. Carbides were also found within the interdiffusion zone of the IN-800HT substrate. Some elongated precipitates were observed in the HR3C case and were associated to AlN [28, 44, 55, 56].

Overall, the microstructure and the composition of the two coatings on the ASS are very close to those obtained on AISI 304 steel by chemical vapour deposition (CVD) in fluidised bed reactors [33, 57]. However, the thermal treatments carried out (Ar (g)) in this work were shorter because of the combustion synthesis occurring between Al and the substrate, thus forming an aluminide, as described by Montero et al. [21] and Galetz and collab. [23]. Indeed, the melting

of at least one of two components (Al in this case) is a crucial step because it is the beginning of the intermetallics formation [23, 58]. Previous studies have shown the high exothermic reaction occurring between Fe and Al in argon below the melting temperature of Al (i.e. 660°C) [21, 59]. Therefore, the intermediate step of the aluminisation is set at 650°C, as also performed in [25-27]. A 3h dwell at this temperature was sufficient because of the fast Al enrichment and the simultaneous Fe and Ni dissolution [23]. Such dissolution brings about the formation of the continuous diffusion layer shown in Figs. 3. a) and b). The cracks detected in the additive layers of the austenitic stainless steels were attributed to the difference existing between the different metallurgical phases. Indeed, when a gradient of thermal expansion coefficient exists between the coating and the substrate, the force generated can physically break the system [60]. However, these cracks do not propagate into the substrate, thus not jeopardizing the protection of the latter.

The aluminium diffusion coating elaborated on the ferritic-martensitic P92 steel was thicker than those obtained in the austenitic stainless steels. Nevertheless, the additive layer was also mostly composed by the B2-FeAl phase as highlighted by the EDS profiles (Fig. 3. c) and the X-ray patterns (Fig. 5. b). Needle-like precipitates were observed in the interdiffusion zone of the coated P92 and were attributed to AlN [20, 28, 45]. As reported by Agüero et al. [61, 62], these precipitates are due to the N content in the substrate (0.046 wt%). Porosities were also detected at the coating/substrate interface and could be attributed to a Kirkendall effect due to the formation of chromium aluminides impeding locally further Al inward diffusion [54, 63]. Otherwise, Al was detected in the substrate until about 200 μm from the coating surface to the substrate because the diffusion through a ferritic structure is relative fast [53, 64]. No cracks were detected in the coated P92 because the gap between the substrate and the B2-FeAl phase is not probably significant enough.

4. 3 – Metallurgical evolutions induced by the aluminisation process

A decrease of the grain size of the IN-800HT was noticed after aluminisation ($219.5 \pm 39.2 \mu\text{m}$ and $134.2 \pm 11.7 \mu\text{m}$, respectively for the uncoated and the aluminised substrate). In the HR3C case the evolution was less marked and the grain size was almost comparable. For the two austenitic stainless steels, the morphology observed after the thermal treatment (Figs. 7. a') and b') is typical of an austenitic structure [65]. Some square-like precipitates were found in the

bulk of IN-800HT and the EDS analyses carried out let appeared high Ti and C contents and can be thus associated with TiC [45]. Moreover, some Cr carbides were detected and have been reported to confer high temperature strength to this alloy [11]. Segregation of $M_{23}C_6$ at the grain boundaries of the two steels was highlighted and is typical of the ASS after annealing at high temperatures [9, 13]. Before aluminisation, these precipitates were revealed in the matrix.

By correlating EDS analyses and the Schaeffler diagram, it appeared that the composition underneath the interdiffusion zone/substrate interface did not evolve in the IN-800HT case. On the contrary, an evolution from the austenitic domain to 95% austenite + 5% ferrite was noticed in HR3C. Al and Cr are ferrite stabilizers and could thus result in a 5-10% ferrite transformation in the substrate. Aluminisation through the ferritic phase is known to occur more readily than through the austenitic phase [53, 64]. However, Cr is also a diffusion barrier for Al as Cr_xAl_y intermetallic compounds block the inward Al diffusion [29]. Therefore, the greater Cr content in the interdiffusion zone blocked Al inward diffusion and the additive layer became thus more Al-rich in HR3C than in IN-800HT. Conversely, Fe diffused outwardly through the aluminide layers to stabilise at about 35 at% of the B2-FeAl phase according to the Al-Fe phase diagram of Fig. 4. b). Nevertheless, the compositions at the core of the IN800HT and the HR3C substrates are similar to those retrieved by EDS before aluminisation. It appears that the overall thickness of the Al-modified zone is negligible compared to the entire thickness of the system (coatings + substrates: about 2 mm). Therefore, the cracks may appear because of the greater stiffness of the intermetallic compounds (in particular in the diffusion layer) than that of the substrate.

For the P92 substrate, the microstructure evolved in a larger extent during the aluminisation. Indeed, the initial tempered martensitic structure related by Bates et al. [20] converted to austenite one considering the CCT curves of Fig. 9. In order to recover the initial microstructure of this steel, after a rapid quench in air a subsequent annealing shall be performed at 760°C for 1 hour [66]. Nevertheless, the aluminisation realized in this study was done in a tubular furnace which is not able to cool down quickly. With our thermal treatment, the initial tempered martensitic structure converted –at least partly- to austenite when the samples were heated at 1050°C for 1 hour. Moreover, Wawszczak et al. [66] showed that the microstructure of a ferritic-martensitic steel (compositions close to those obtained for P92) does not change significantly after annealing at temperature below 400°C. In this range of temperatures, the Al coating cannot be formed. The increase of the temperature allows the Al melting and, therefore the wet of the substrate allowing the start of the combustion synthesis process [21] which will

enable the Fe enrichment of the coating. By increasing the temperature up to 1050°C, the intermetallic phases created during the heating ramp become homogeneous to form and to maintain the B2-FeAl phase. Moreover, the relatively slow cooling rate to room temperature results in the precipitation of $M_{23}C_6$ carbides that could have been partly dissolved and the martensitic microstructure recovered upon tempering at 760°C [51]. In contrast, quenching from the high coating temperature (1000 or 1050°C) may introduce mechanical failure of the coating through the ductile-to-brittle transition temperature (DBTT) [67]. The thermal treatment carried out in this study had an other consequence corresponding to the increase of the grain size. Indeed, it appeared that the grains were about 10 times bigger compared to those of the uncoated P92 samples. These observations are in agreement with the findings of Ellis et al. who have reported that the austenite grain size evolves as a function of the austenitization temperature; the higher the austenitization temperature and the bigger the grain size [67]. Such increase of the grain size during the heating of ferritic-martensitic has been also reported by Klueh and Shingledecker [68].

4. 4 – Microhardness

Generally speaking and within uncertainty of the measurements, the slurry aluminising process studied here seemed to soften slightly the matrix of the austenitic stainless steels. Nevertheless, a decrease in term of microhardness has also observed in [33] after a heat treatment due to the dissolution of carbides shown when comparing the microstructures of Fogs 7a) and 7b) (uncoated) with 7a') and 7b') (aluminised). For the P92 substrate, the evolution of the microhardness was non-negligible. Indeed, after aluminisation, the ferritic-martensitic steel appeared two times harder and a significant evolution of microstructure from a martensitic to an austenitic+carbides. As shown in Fig. 9 [51] and as reported by Hahn et al. [69], the P92 substrate should have been cooled sufficiently fast after the austenitization (1050°C) and subsequently tempered. The significant change of the microstructure of the P92 material before and after the aluminisation explain the more pronounced microhardness evolution compared to the ASS.

The changes in composition and in microstructure also affected the Vickers microhardness of the slurry aluminide coatings elaborated on IN-800HT, HR3C and P92 (Fig. 10). For the ASS, it appeared that the additive layers were harder compared to the corresponding interdiffusion zone and substrate. The same trend has been reported for another austenitic steel (AISI 304)

which was previously aluminised by CVD-FBR where comparable values of about 350 HV were reported [33]. Moreover, the additive layer of IN-800HT was harder (700 HV) than that of HR3C (480HV). By comparing these results with the EDS profiles shown in Figs. 3, it appeared that the Ni content in the additive layer was higher for the IN-800HT (24 at%) compared to the one noticed in the HR3C case (10 at%). It is known that nickel accelerates the precipitation by diminishing the solubility of carbon [70] allowing an increase in term of microhardness [13, 71]. In both cases, the microhardness noticed in the IDZ was smaller compared to those obtained in the additive layer, probably due to a Ni content decrease. The absence of Ni in the aluminide coating of P92 can thus also explain why the coating is much softer than that of the ASS substrates and of the P92 steel.

5. CONCLUSIONS

Slurry aluminide coatings were elaborated on IN-800HT and HR3C austenitic stainless steels and on P92 ferritic-martensitic steel. All the coatings were composed by an outer layer corresponding to the protective B2-(Fe,Ni)Al and B2-FeAl phase, for, respectively, the ASS and the ferritic-martensitic steel, and an inner interdiffusion layer. The thermal treatments of the three substrates were carried out in Ar and allowed the Al melting involving the combustion synthesis with the substrate. Thereby, the simultaneous Al inward diffusion in the steel matrix and the outward Fe (and Ni for the ASS) occurred forming a continuous and consistent diffusion layer mostly composed by B2.

The aluminisation of the ASS did not significantly change the grain size and the microhardness of the substrate whereas the thermal treatment had a non-negligible impact on the microstructure of the ferritic-martensitic substrate. Indeed, the initial tempered martensitic structure have been converted to austenite + carbides due to the absence of a final quench in air until 760°C. Thus, the grain size appeared 10 times larger after the aluminisation process. The coated P92 specimens also assumed a large increase in term of microhardness because of the precipitation of $M_{23}C_6$ carbides along the grain boundaries during the annealing step.

6. REFERENCES

1. L. Zhao, H. Jing, L. Xu, J. An, G. Xiao, *Materials and Design* **34** (2012) 566
2. S. Khayatzadeh, D. W. J. Tanner, C. E. Truman, P. E. J. Flewitt, D. J. Smith, *Engineering Fracture Mechanics* **75** (2017) 57
3. B. He, L. Tian, J. Chen, X. Wang, *Engineering Fracture Mechanics* **171** (2017) 64

4. K. Nicol, Status of advanced ultra-supercritical pulverized coal technology, *IEA Clean Coal Centre*, ISBN 978-92-9029-549-5 (2013)
5. B. Wang, Z.-D. Liu, S.-C. Cheng, C.-M. Liu, J.-Z. Wang, *Journal of Iron and Steel Research, International* **21(8)** (2014) 765
6. J. Cao, Y. Gong, Z.-G. Yang, *Materials Science and Engineering A* **528** (2011) 6103
7. V. Sklenicka, K. Kucharova, M. Svoboda, L. Kloc, J. Bursik, A. Kroupa, *Materials Characterization* **51** (2003) 35
8. V. Sklenicka, K. Kucharova, M. Kvapilova, M. Svoboda, P. Kral, J. Dvorak, *Materials Characterization* **128** (2017) 238
9. S. Vujic, R. Sandström, C. Sommitsch, *Materials at High Temperatures* **32** (2015) 607
10. L. Y. Xu, P. Zhu, H. Y. Jing, K. Guo, S. X. Zhong, Y. D. Dan, *Engineering Failure Analysis* **31** (2013) 375
11. A. Akhiani, M. Nezakat, J. A. Szpunar, *Materials Science Engineering: A* **614** (2014) 250
12. M. Fulger, M. Mihalache, D. Ohai, S. Fulger, S. C. Valeca, *Journal of Nuclear Materials* **415** (2011) 147
13. Z. Zhang, Z. Hu, H. Tu, S. Schmauder, G. Wu, *Materials Science and Engineering A* **681** (2017) 74
14. S. Khayatzadeh, D. W. J. Tanner, C. E. Truman, P. E. J. Flewitt, D. J. Smith, *Engineering Fracture Mechanics* **75** (2017) 57
15. L. Zhao, H. Jing, L. Xu, J. An, G. Xiao, *Materials and Design* **34** (2012) 566
16. T. Sakthivel, M. Vasudevan, K. Lahan, P. Parameswaran, K.S. Chandravathi, S. Panneer Selvi, V. Maduraimuthu, M.D. Mathew, *Materials Science and Engineering A* **591** (2014) 111
17. N. Saini, C. Pandey, M. M. Mahapatra, *Materials Science and Engineering A* **668** (2017) 250
18. Z. D. Xiang, S. R. Rose, P. K. Datta, *Intermetallics* **17(6)** (2009) 387
19. E.J. Opila, N.S. Jacobson, D.L. Myers, E.H. Copland, *JOM* **58**, 22 (2006)
20. B. L. Bates, Y. Zhang, S. Dryepondt, B. A. Pint, *Surface and Coatings Technology* **240** (2014) 32
21. X. Montero, I. Demler, V. Kuznetsov, M. C. Galetz, *Surface and Coatings Technology* **309** (2017) 179
22. A. Agüero, J. C. del Hoyo, J. Garcia de Blas, M. Garcia, M. Gutierrez, L. Madueno, S. Ulargui, *Surface and Coatings Technology* **213** (2012) 229

23. M. C. Galetz, X. Montero, M. Mollard, M. Günthner, F. Pedraza, M. Schütze, *Intermetallics* **44** (2014) 8
24. X. Montero, M. Galetz, M. Schütze, *JOM* **67**(1) (2015) 77
25. F. Pedraza, M. Proy, C. Boulesteix, P. Krukovskyi, M. Metel, *Materials and Corrosion* **67** (2016) 1059
26. C. Boulesteix, F. Pedraza, M. Proy, I. Lasanta, T. de Miguel, A. Illana, F. J. Perez, *Oxidation of Metals* **87** (2017) 469
27. F. Pedraza, C. Boulesteix, M. Proy, I. Lasanta, T. de Miguel, A. Illana, F. J. Pérez, *Oxidation of Metals* **87** (2017) 443
28. A. Agüero, R. Muelas, M. Gutiérrez, R. Van Vulpen, S. Osgerby, J. P. Banks, *Surface and Coatings Technology* **201**(14) (2007) 6253
29. C. Boulesteix, B. Grégoire, F. Pedraza, *Surface & Coatings Technology* **326** (2017) 224
30. C. Boulesteix, F. Pedraza, *Surface & Coatings Technology* **327** (2017) 9
31. B. Rannou, F. Velasco, S. Guzman, V. Kolarik, F. Pedraza, *Materials Chemistry and Physics* **134** (2012) 360
32. M. Mollard, F. Pedraza, B. Bouchaud, X. Montero M. C. Galetz, M. Schütze, *Surface and Coatings Technology* **270** (2015) 102
33. F. J. Pérez, F. Pedraza, M. P. Hierro, P. Y. Hou, *Surface and Coatings Technology* **133-134** (2000) 338
34. A. A. Fasching, G. R. Edwards, S. A. David, *Scripta Metallurgica et Materialia* **30**(8) (1994) 1003
35. M. Mollard, PhD thesis “Elaboration de systèmes barrière thermique par barbotine. Comportement du nickel et de ses superalliages revêtus en oxidation cyclique à haute température”, University of La Rochelle (2012) (in French)
36. B. Rannou, PhD thesis “Slurry coatings from aluminium microparticles on Ni-based superalloys for high temperature oxidation protection”, University of La Rochelle (2012) (in English)
37. H. Okamoto, *Journal of Phase Equilibria and Diffusion* **29** (2008) 112
38. D. Webster, *Journal de Physique* **48**(C3) (1987) 685
39. Physical Metallurgy and Processes, Handbook of Aluminum, Volume 1, edited by G. E. Totten, D. Scott MacKenzie, New York (2003) 37
40. X. Montero, M. C. Galetz, M. Schütze, *Surface and Coatings Technology* **206**(7) (2011) 1586
41. L. Eleno, K. Frisk, A. Schneider, *Intermetallics* **14** (2006) 1276

42. ASM Handbook, “Alloy Phase Diagrams” **Vol. 3** (1992) Ohio 2.44
43. R. Viswanathan, *Advanced Materials and Processes* **162** (2004) 73
44. A. Agüero, V. Gonzalez, M. Guttierrez, R. Knödler, R. Muelas, S. Straub, *Materials and Corrosion* **62** (2011) 561
45. A. Agüero, M. Hernandez, A. Santaballa, *Oxidation of Metals* **79** (2013) 601
46. K. Wang, Z. Gui, P. Liu, Y. Wang, Y. Zhang, *Procedia Engineering* **81** (2014) 1713
47. L. Xie, D. Chen, E. H. Jordan, A. Ozturk, F. Wu, X. Ma, B. M. Cetegen, M. Gell, *Surface and Coatings Technology* **201** (2006) 1058
48. L. A. Spyrou, P. I. Sarafoglou, N. Aravas, G. N. Haidemenopoulos, *Engineering Failure Analysis* **45** (2014) 456
49. Y. Zhou, Y. Liu, X. Zhou, C. Liu, J. Yu, Y. Huang, H. Li, W. Li, *Journal of Materials Science and Technology*, DOI: 10.1016/j.jmst.2017.01.025 (2017)
50. D. J. Kotecki, T. A. Siewert, *Welding Research Supplement* (1992) 171
51. B. Hahn, W. Bendick, Vallourec report “Pipe steels for modern high-output power plants” (2015)
52. W. J. Cheng, C. J. Wang, *Applied Surface Science* **277** (2013) 139
53. F. Pedraza, C. Gomez, M. C. Carpintero, M. P. Hierro, F. J. Pérez, *Surface and Coatings Technology* **190** (2005) 223
54. A. J. Rasmussen, A. Agüero, M. Gutierrez, M. J. Ostergard, *Surface and Coatings Technology* **202**(8) (2008) 1479
55. P. Berthod, S. Michon, S. Mathieu, R. Podor, C. Rapin, P. Steinmetz, *Materials Science Forum* **461-464**, 1117 (2004)
56. T. Sourmail, *Materials Science and Technology* **17**, 1 (2001); W.E. White, I. Le May, *Metallography* **5**, 333 (1972)
57. F. J. Pérez, M. P. Hierro, F. Pedraza, M. C. Carpintero, C. Gomez, R. Tarin, *Surface and Coatings Technology* **145**(1-3) (2001) 1
58. J. J. Moore, H. J. Feng, *Progress in Materials Science* **39** (1995) 275
59. H. Gao, Y. He, P. Shen, J. Zou, N. Xu, Y. Jiang, B. Huang, C. T. Liu, *Intermetallics* **17** (2009) 1041
60. K. Nicol, “High temperature steels in pulverised coal technology”. IEA Clean Coal Centre (2014) 40
61. A. Agüero, R. Muelas, A. Pastor, S. Osgerby, *Surface and Coatings Technology* **200** (2005) 1219
62. A. Agüero, R. Muelas, *Materials Science Forum* **461-464** (2004) 957

63. P. Moretto, J. Bressers, D. J. Arrell, *Materials Science and Engineering A* **272** (1999) 310
64. L. Levin, A. Ginzburg, L. Klinger, T. Werber, A. Katsman, P. Schaaf, *Surface and Coatings Technology* **106** (1998) 209
65. R. Dehmlaei, M. Shamanian, A. Kermanpur, *Materials Characterization* **60**(3) (2009) 246
66. R. Wawszczak, A. Baczanski, M. Marciszko, M. Wrobel, T. Czeppe, K. Sztwiertnia, C. Braham, K. Berent, *Materials Characterization* **112** (2016) 238
67. P. J. Ennis, A. Czyrska-Filemonowicz, *Shadana* **28** (2003) 709
68. R. L. Klueh, J. P. Shingledecker, Report: "Investigation of a modified 9Cr-1Mo (P91) (2006)
69. B. Hahn, V. Baumhoff, M. Zschau, "Advanced Heat Resistant Steels for Power Generation" in Book – Institute of Materials **708** (1998) 157
70. M. F. Mc Guire, ASM International, *Stainless Steels for Desing Engineers* (2008) 69
71. R. Dehmlaei, M. Shamanian, A. Kermanpur, *Materials Characterization* **60**(3) (2009) 246