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Microstructure and elevated-temperature erosion-oxidation behaviour of aluminized 9Cr-1Mo Steel

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Abstract: Degradation of materials by a combination of erosive wear and atmospheric oxidation at elevated temper-atures constitutes a problem in some power generation processes, such as fluidized-bed combustion. In this work, 9Cr-1Mo steel, a common tube material in combustion chambers, is coated by a pack cemen-tation method from an Alcontaining pack in order to improve the resistance to erosion-oxidation at elevated temperatures. The resulting coating is studied in terms of microstructure and microhardness and tested for its resistance against impacts by sand particles in air at temperatures of 550-700 °C under several conditions, with thickness changes and appearance of the exposed surfaces being studied. The coating was found to contain several phases and layers, the outermost of which was essentially Al-rich and contained e.g., small AlN precipitates. The microhardness values for such coating ranged from 950 to 1100 HV_{20g} . The coating provided the substrate with increased protection particularly against normal particle impacts, as manifested by smaller thickness losses for coated specimens as compared to uncoated counterparts. However, much of the coating was lost under all test conditions, despite the fact that parti-cle debris formed a homogeneous layer on the surface. These results are described and discussed in this paper.

Keywords: Coating, Steel, Pack cementation, Erosion-oxidation, Microhardness

1. Introduction

Ferritic-martensitic steels are used in heat exchanger tubes in power generation, because of their relatively low cost, high thermal conductivity and low coefficient of thermal expansion as com-pared to those of austenitic steels, as well as reasonably good mechanical properties and weldability [1]. Although many of these advantageous properties follow relatively low alloving levels, for example, only up to about 13% in Cr content (depends also on the other alloying elements used in the steel [2]), the limited alloying also has some adverse effects: oxidation resistance [3] of ferriticmartensitic steels is their weak point. This is because Cr alloying level is, under some conditions, too low to lead to the formation of a continuous scale of Cr₂O₃ on the steel surfaces at elevated temperatures. Therefore, in aggressive environments, particularly in those involving a combination of erosion and oxidation, i.e., removal of some of the formed oxide scales by impacts by erodent particles, these steels may be prone to rapid degradation. Unfortunately, such aggressive conditions are often encountered in power generation plants, especially in fluidized-bed combustion that has grown in popularity during the last decades, due to improved thermal efficiency, remarkably low adverse emissions and a wider range of fuels that can be burned compared to other existing

combustion techniques [4]. On this basis, the application of coatings on ferritic-martensitic steels, to provide oxidation and erosion-oxidation resistance while preserving the physical and mechanical properties of the steel, is considered an attractive choice.

Diffusion aluminizing is a promising approach of improving the elevated-temperature oxidation and corrosion resistance of alloys by enrichment of the surface with aluminium at elevated temperatures. Aluminium is a scale-forming element, i.e., it easily reacts with the surrounding atmosphere to form a scale of aluminium oxide, Al₂O₃, on the surface [5–7] or e.g., possible cracks that exist in the coating [8]. The formed scale typically shows high thermodynamic stability, low vapour pressure and low concentration of structural defects, resulting in low ionic migration rates [5]. Therefore, the scale practically forms a barrier between the material and the surrounding environment. The application temperatures of aluminium diffusion coatings on ferritic-martensitic steels are typically at maximum 700 °C, in order not to influence the microstructure of the steel. In this study a unique coating procedure was employed: the used temperature was slightly higher than normally in pack-aluminizing, 715 °C, to facilitate thicker coat-ings, and the powder pack contained a boron source in addition to

Table 1 Test conditions.

Variable	Test condition
Atmosphere	Air
Temperature	550, 600, 650 and 700 °C
Time	50 h
Erodent	Angular silica sand, the hardness of which was 7 in Mohs scale
Mean particle size	200 µm
Erodent speed	7.0 to $9.2 \mathrm{m s^{-1}}$
Impingement angle	30°, 90°

aluminium source, to reduce the aluminium activity of the pack and to examine the co-deposition of boron, which is dependent on e.g., temperature and pack composition, such as the used activator [9–11]. The formed coating is characterized in terms of microstructure and erosion-oxidation behaviour at elevated temperatures, the latter of which is compared to that of corresponding uncoated steel. Hence, this paper aims at providing such fundamental understanding on the development and the properties of the aluminized coatings which is essential if these coatings are pursued to be used e.g., on heat exchanger tubes in future power plants.

2. Experimental

2.1. Materials

Composition of the 9Cr-1Mo steel P91, supplied by Vallourec and Mannessmann Tubes Corporation and used as a substrate material in this work, was 9 wt.% Cr, 0.93 wt.% Mo, 0.55 wt.% Mn, 0.4 wt.% Si, 0.36 wt.% Ni, 0.22 wt.% V, 0.093 wt.% C, 0.07 wt.% Nb, 0.056 wt.% N, 0.006 wt.% Al and Fe (balance). The steel had been, first, normalized at 1070 °C for 2 h, followed by rapid cooling and, second, tempered at 750 °C for 2 h, giving a final microstructure of tempered martensite and $Cr_{23}C_6$ and Cr_2C precipitates [12,13]. Specimens of the size of 35 mm by 7mm by 4.5 mm were cut from the supplied steel tubes, with length of the specimen being parallel to the longitudinal direction of tube. The specimens were prepared for aluminizing by grinding to 120 grit finish followed by ultrasonic cleaning in acetone and ethanol.

Aluminizing was carried out in a single-step pack-cementation method. The specimens were placed in an alumina crucible, surrounded by a powder mixture of a source supplier (17%), containing 1/3 pure Al and 2/3 B₄C, an activator (NH₄Cl, 2%) and an inert filler (Al₂O₃, 81%). The crucible, covered by an alumina lid, was held in a furnace at 715 °C for 6 h in argon gas atmosphere. After the treatment, the pack was cooled to room temperature and the specimens were removed and cleaned.

2.2. Methods

Microstructure of the aluminized specimens was characterized by scanning electron microscopy (SEM), using a Philips XL-30 microscope equipped with an EDAX DX4 energy-dispersive spectrometer (EDS). An Anton Paar μ -Indenter 5 microhardness meter attached to SEM was used for determination of the microhardness profile across the coating thickness. The microhardness measurements were performed at room temperature by using a load of 20 g. More detailed microstructural examinations were performed using a field-emission (FE-) SEM Zeiss ULTRAplus equipped with an INCAx-act EDS detector. Phase structure of the coated specimens was examined by X-ray diffraction (XRD) technique, using a Philips PW 3710 X-ray diffractometer (XRD) and CuK_{α} radiation.

Isothermal elevated-temperature erosion-oxidation tests were carried out in a whirling arm fluidized-bed rig (Fig. 1) under conditions summarized in Table 1. The rig consists of a fluidized bed with 40 vol.% particles, a heating system and a specimen-holder assembly. The heating system has three independent heating zones which maintain the air entering the bed of particles, the bed itself and the specimen all at the same temperature. During operation, air is pumped through the heated spiral flow tube, enabling it to attain the necessary acceleration in addition to the set temperature before entering the bed. The specimens are fastened in two holders that are located at each end of the specimen arm and fixed at desired impact angles with respect to the bed of particles. The specimen arm is rotated through the fluidized particle bed by a drive motor, the rotational speed of which is adjusted to a desired value using a speed counter. The adjustment of the rotational speed enables constant linear speeds between the specimens and the particles to be obtained. Hence, in this study, the specimens move with respect to the bed of particles: the arm is designed to allow the attached specimens to impact the bed of particles at a constant angle, to be completely immersed in the bed at the lowest point and then to move through the space above the bed. Each location of the specimens travels a different distance during one rotation of the arm, giving a particular linear speed between the specimen at each location and the bed particles. During the tests, the back side and the edges of each specimen were protected by the holder, exposing only the front surface to the impacting particles.

The extent of damage during the erosion-oxidation tests was determined by measuring the thickness of the specimens before and after each test, using a digital point micrometer with an accuracy of 0.001 mm. The measurements were performed at twelve locations along the specimen length, with each location representing a particular linear speed between the specimen and the erodent particles, at five points across the specimen at each location. Ten measurements were taken at each point and the mean thickness change for each linear speed was then calculated from the average values at each location. The surfaces and some of the cross sections of specimens from erosion-oxidation tests were examined with a Philips XL-30 SEM and the attached EDS.

3. Results

3.1. Coating microstructure

SEM examination on the surface of aluminized coating revealed a wavy surface contour with evident hills and valleys (Fig. 2a), although there were also more uniform areas. Some cracks were evident on the coating surface (Fig. 2b), consistent with literature [8]. When studied in cross section, several phases were detected in the coating (Fig. 3). The outermost coating layer comprised of the major aluminium-rich phase (Fig. 3a and b, Table 2) and of two embedded phases: a chromium-rich phase, seen light in SEM BSE images (Fig. 3a and d), and a precipitate phase that appeared dark in SEM BSE examination (Fig. 3c and d). EDS analyses of the dark precipitates by FE-SEM indicated them to contain much nitrogen and less iron and chromium as compared to the other coating phases (Table 2), suggesting they might be AIN. The dark precipitate phase was concentrated on the inner half of the coating, i.e., closer to the substrate, whereas the lighter phase embedded in the coating matrix was relatively evenly distributed throughout the coating thickness. Underneath the outermost coating layer, an inter-metallic layer was detected, with decreased aluminium and increased iron content as compared to the outermost layer. In the substrate, aluminium- and nitrogen-rich, needle-like precipitates were detected down to the depth of about 30 µm below the original surface (indicated by an arrow in Fig. 3a). Also these were probably AlN, consistent with the results by Agüero et al. [18].

Results from XRD measurements (Fig. 4) disclosed the presence of the Al_5Fe_2 , AlFe, AlCr₂ and AlN phases. Many of the peaks related



Fig. 1. Schematic diagram of the fluidized-bed rig. (a) Side view. (b) Front view.

to the four detected phases overlapped, but in all cases, there was at least one clear peak that is characteristic of each phase. In addition, in each case, all major peaks appeared in the XRD spectrum. High intensities of the peaks related to the Al₅Fe₂ phase indicated it to be the major coating phase, consistent with SEM studies and EDS analyses. The AlFe phase, the peaks of which were also detected in the XRD spectrum, relatively well corresponded in composition to the layer detected at the coating-substrate interface in SEM and EDS examinations. The chromium-rich precipitate phase was likely

the AlCr₂ phase (keeping in mind the relatively small size of the precipitates and, hence, the fact that in EDS analyses, some of the information originates from the surrounding matrix phase) and the nitrogen-rich dark precipitates in the surrounded coating matrix were evidently the AlN. Also literature [18–20] supports the existence of these phases in the coating, although earlier, the AlN has been mainly detected in the substrate [18].

In general, thickness of the coating (above the original steel surface) varied in the range from 17 to $81\,\mu m$, with a mean



Fig. 2. SEM images, showing the surface of aluminized specimens. (a) A wavy surface topography. (b) Structure in more detail. In (b), the arrows point out a crack.

value being 51 μ m. However, it is emphasized that such thin coating sections, with coating thickness being less than 40 μ m, or, in the other extreme, very thick areas of coating, above 65 μ m in thickness, were very infrequent and therefore not of great

significance for the behaviour in erosion-oxidation test. Further, microstructural changes within the substrate, i.e., the presence of the AlN precipitates, reached a depth of about 20–30 μ m below the original steel surface (Fig. 3). Fig. 5 shows the results from



Fig. 3. SEM images of cross section of the aluminized specimens. (a), (b) A general view. (c) A more detailed view of the outermost coating layer. (d) FE-SEM image, showing the coating phases in more detail. (e) Elemental maps of the area shown in (a). Different phases are indicated by numbers (1–6) and their compositions are given in Table 1.

Table 2

Composition, in at,%, of various phases present in aluminized specimens and indicated by numbers (1–6) in Fig. 3a–d. The last column shows the phase structure, as deduced from composition and XRD analyses. Also hardness values for the phases are given.

	Al	Fe	Cr	Si	Мо	Ν	Phase	Hardness, HV
1	70.5	27.8	1.7				Al_5Fe_2	950–1100 ^a 800 [14]
								1000 [15]
2	56.2	25.3	16.2	1.5	0.8		AlCr ₂	
3	61.7	22.4	1.3			14.6	AIN	1150-2200 [16]
4	50.0	43.4	5.7	0.5	0.4		AlFe	300-600 [14]
								660 [15]
5	30.8	52.6	6.8	0.7	0.4	8.7	AIN	1150-2200 [16]
6		87.7	10.5	1.1	0.7		Substrate	211 [17]

^a Measured by the authors.



Fig. 4. XRD spectrum for the aluminized specimen. \blacktriangle Denotes the Al₅Fe₂ phase, \triangle denotes the AlFe phase, * denotes the AlCr₂ phase and O denotes the AlN phase.

microhardness measurements at various distances from the coating-substrate interface. Microhardness values for the coating were high, typically in the range from 950 to 1100 HV. These values are similar in magnitude to those that we have measured for the aluminized coatings on the same substrate material, i.e., for the Al₅Fe₂ coating. Hardness values for the various phases and the substrate are given in Table 2. However, here, the AlN precipitates in the coating were much smaller than the indentation following the measurements, indicating that their contribution to the measured microhardness values is negligible. It is, nevertheless, good to bear in mind that metal nitrides are very hard, typically in the range from 1150 to 2200 HV [16]. At the coating-substrate interface, the microhardness values sharply decreased to a value of 520 HV and then, gradually within the AlN precipitate zone, to about 200 HV that was measured for the substrate. Again, the AlN precipitates



Fig. 5. Microhardness values, determined in cross-sectional specimens at various distances from the coating-substrate interface.

were smaller than the indentation left behind by hardness measurements and, hence, considered not to contribute much to the measured values.

3.2. Wastage by erosion-oxidation

Figs. 6–9 show thickness changes for aluminized and, for comparison, uncoated specimens after erosion-oxidation tests at 550, 600, 650 and 700 °C under particle impacts at the angles of 30 and 90° as a function of particle impact speed. At 550 °C, under particle impacts at 30°, the mean thickness losses for aluminized specimens were in the range from 40 to 60 μ m at all speeds, with no clear dependence of the magnitude of losses on particle speed being detected (Fig. 6a). For comparison, thickness losses for uncoated specimens evidently increased with increase in speed, reaching a loss of about 70 μ m at the highest speeds. At 550 °C, at an angle of 90°, the mean thickness losses for aluminized specimens were



Fig. 6. Mean thickness changes for the specimens exposed at $550 \degree C$ under particle impacts at two impact angles. (a) $30\degree$. (b) $90\degree$.



Fig. 7. Mean thickness changes for the specimens exposed at $600 \degree C$ under particle impacts at two impact angles. (a) $30\degree$. (b) $90\degree$.

about 20 μ m at all speeds, while those for uncoated specimens increased almost linearly with increase in speed, up to about 70 μ m at the highest speed (Fig. 6b).

At 600 °C, at an angle of 30°, the mean thickness losses rang-ing from 20 to 35 μ m were recorded for aluminized specimens independently of particle travel speed (Fig. 7a). Again, the corresponding losses for uncoated specimens increased with increase in particle speed, giving the maximum loss of 135 μ m at the high-est speed. Under 90° impacts, the thickness losses for aluminized specimens were the highest among recorded in this study, varying typically in the range from 50 to 85 μ m (Fig. 7b). Although the magnitude of losses slightly increased with increase in speed from 7 to 8.8 m s⁻¹, further increases in speed introduced signifi-cant decrease in thickness losses. In the case of uncoated specimens, a linear increase in the magnitude of thickness losses with increase in particle speed was apparent, again, with the maximum loss being about 85 μ m.

At 650 °C, the behaviour for both types of specimens, coated and uncoated, was independent of impact angle, with lower thickness losses being obtained for coated specimens (Fig. 8a and b). In the case of aluminized specimens, the mean thickness losses under par-ticle impacts at both 30 and 90° were in the range from 25 to 35 μ m at all speeds, i.e., independent of particle impact speed. In contrast, in the case of uncoated specimens, the thickness losses increased steadily with increase in particle speed, up to a loss of 115 μ m at the maximum speed, at both angles.

At 700 °C, at an angle of 30°, the mean thickness losses for aluminized specimens varied from about 20–40 μ m in magnitude at all speeds and were evidently much greater than those for uncoated specimens that varied in the range from 0 to 10 μ m in magnitude at all speeds (Fig. 9a). At an angle of 90°, conversely, the mean



Fig. 8. Mean thickness changes for the specimens exposed at $650 \degree C$ under particle impacts at two impact angles. (a) $30\degree$. (b) $90\degree$.

thickness losses for aluminized specimens were only from 20 to $35 \,\mu$ m in magnitude, irrespective of particle speed, whereas the corresponding losses for uncoated specimens essentially increased with increase in speed, yielding the maximum loss of about 120 μ m at the highest speed (Fig. 9b).

3.3. Exposed specimens

SEM examination on exposed surfaces revealed that the sand particle debris was deposited on the surfaces, forming a homogeneous and an almost continuous layer (Figs. 10-11), instead of a heterogeneous composite coating together with the exposed alloy and the oxide scale on it, more typically encountered during combined erosion-oxidation. However, SEM studies showed that there were slight differences in the continuity of the particle debris layer between test conditions, especially between particle travel speeds and impact angles. At the lowest speeds, the particle debris layer was evidently less continuous than at the highest speeds, with areas of a bare aluminized coating (without deposited sand particle debris) being occasionally detected at the lowest speeds but much less frequently and at much smaller size than at the highest speeds. Furthermore, typically, at an angle of 30°, the surfaces were smooth and the uncovered areas of the coating contained some wear scars (Figs. 10a and 11a) as a result of a cutting type of wear. At an angle of 90°, in contrast, the surfaces were more irregular, with cracking of both the aluminized coating and, particularly, the sand debris layer, being evident (Figs. 10c,d and 11c). No appar-ent trend between nature of the exposed surfaces and temperature was detected. It is, further, emphasized that since erosion evidently played a key role in behaviour of the surfaces, no indications of oxi-dation could be detected. Therefore, the primary damage mode of



Fig. 9. Mean thickness changes for the specimens exposed at 700 $^{\circ}$ C under particle impacts at two impact angles. (a) 30 $^{\circ}$. (b) 90 $^{\circ}$.

the coating was clearly erosion. It is emphasized that the results clearly indicate that the homogeneous debris layer formed on the specimen surfaces protected the specimens from further particle impacts. This indicates that the aluminized layer had some special characteristics that favoured the formation such sand debris layer, the topic which is discussed in Section 4.

Cross-sectional study on exposed specimens (Fig. 12) disclosed that the homogeneous layer on the specimen surfaces primarily contained debris of the sand particles but also some remnants of the coating. Such layer was detected all over the exposed surfaces, with the thickness being typically of the order of some micrometres. In all cases, some of the outermost Al-rich coating layer was retained under the sand particle debris layer although it was relatively thin, even less than a micrometer in thickness, particularly at the lowest temperatures. Furthermore, cross-sectional study revealed that various coating layers and their interfaces were not as evident as before the tests, indicating that some diffusion might have taken place. It is also worth mentioning that after the tests at the lowest temperatures, composition of the retained coating corresponded to the Al₅Fe₂ phase, whereas after the tests at the highest temperature, it corresponded essentially to the FeAl phase. The AlN precipitates were evident in the substrate in all cases.

4. Discussion

4.1. Deposited coating

In this study, aluminizing of 9Cr-1Mo steel in a single-step pack cementation process at 715 °C gave a coating with the total thickness (including the zone of microstructural changes, i.e. the AlN precipitates within the substrate) in the range from 35 to 110 μ m.

Nevertheless, as mentioned earlier, the coating thickness showed typically much less scatter, being in most cases in the range from 60 to 85 μ m (including the zone of microstructural changes in the sub-strate). Therefore, the overall coating thickness was slightly higher than previously reported for aluminium diffusion coatings [11], consistent with a slightly higher deposition temperature. The for-mation of Al-Fe intermetallic phases in the coating, namely the Al₅Fe₂ and AlFe phases, is in agreement with previous studies on the aluminized ferritic-martensitic steels [11,21,22]. Similarly, the formation of AlCr₂ precipitates in the coating has been reported earlier [19,20]; it is due to a relatively low solubility of Cr into the Al₅Fe₂ phase, only a few percent [23]. The presence of the AlN in the coating, which has not been reported before, may be explained by three issues. First, a high driving force, i.e., a large negative Gibbs free energy of formation ($\Delta G_{f}^{\circ} = -287.0 \text{ kJ mol}^{-1}$) for the AlN phase [24], which facilitates its formation where both aluminum and nitrogen (from the substrate) are available. Second, the lower alu-minium activity in the pack as compared to many other cases may introduce outward diffusion of the substrate elements together with inward diffusion of Al (typical of high activity pack process), therefore introducing AlN also in the coating. The relative intensi-ties of inward and outward diffusion flows may explain why the AIN precipitates are primarily located on the inner half of the coating,

i.e., areas closer to the substrate with nitrogen available. Third, the activator of the pack, NH₄Cl, may also introduce inward diffusion of nitrogen in the coatings. Why AlN has not been earlier systematically reported in aluminized coatings may be explained by slightly lower deposition temperatures of such diffusion coatings, typically not higher than 650 °C, and a higher aluminium activity of the used powder mixtures, favouring primarily inward aluminium diffusion, as compared to our aluminized coatings.

The absence of boron in the coating may be explained in terms of thermodynamics and kinetics. When boron has successfully been co-deposited with aluminum at 715 °C, it has occurred in a pack containing fluorine as a halide component in the activator [9,11], probably due to a higher partial pressure of boron fluorides as compared to corresponding chlorides at these temperatures [9]. Co-deposition of boron with aluminium has also been reported when the powder mixture has contained two activators, NH₄Cl and KBF₄ [9]. When using merely an NH₄Cl activator, co-deposition of alu-minum and boron has only taken place at such high temperatures as 950 °C [10]. Although we wanted to lower the aluminium activity of the powder mixture by the use of boron, successful co-deposition of these two elements might require even higher temperatures than 715 °C.

4.2. Erosion-oxidation behaviour

The erosion behaviour of materials can be roughly divided into ductile and brittle, depending on the relative magnitude of wastage experienced at shallow and steep impact angles. Ductile materials typically undergo high material losses at shallow impact angles and relatively much lower losses at steep impact angles, while brittle materials experience relatively lower wear losses at shallow impact angles and the maximum wear at steep angles [16]. In the case of homogeneous bulk materials in an inert environment such division may be simple, but in the case of heterogeneous structures, like the aluminized specimens included in this study, and the fact that the tests were conducted under an oxidizing atmosphere, the particle interactions with the specimen may be far more complex. Here, the results from the erosionoxidation tests clearly show that neither the aluminized nor the uncoated specimens follow a purely ductile or brittle erosion behaviour at all temperatures. Instead, in many cases, the relative material losses at the angles of 30° and 90° were almost equal. For aluminized specimens, the mean thickness losses were in most cases in the range from 20 to 40 μ m independent



Fig. 10. SEM images and EDS analyses of surface of the specimens exposed at 550 °C under several conditions. (a) 30°, 7 m s⁻¹. (b) 30°, 9 m s⁻¹. (c) 90°, 7 m s⁻¹. (d) 90°, 9 m s⁻¹. (e) EDS spectrum corresponding to area 1, indicated in (a). (f) EDS spectrum corresponding to area 2, indicated in (a).

of impact angle of the particles, which indicates that some of the coating is retained on the steel surface after the tests. Naturally, the retained areas of the coating are those closer to the substrate, i.e., where the AlN precipitates are concentrated. Only in some cases, i.e., at 550 °C under particle impacts at 30° and at 600 °C under particle impacts at 90° were the mean thickness losses for aluminized specimens outside the indicated wastage range. For uncoated specimens, the behaviour was far less consistent and the weight losses were systematically much higher than for aluminized specimens, except for at 700 °C at the angle of 30°. Therefore, the coating clearly provided the substrate steel protection under most test conditions.

It is generally accepted that there exists a correlation between the wastage by erosion and the speed of impacting particles, with the faster-moving particles introducing more material losses [16]. In the case of aluminized specimens, thickness losses were almost constant or increased only slightly up to a certain speed, typi-cally 8.6 or 8.8 m s⁻¹, above which the thickness losses typically decreased. It is known that the higher the particle impact speed, the higher the amount of particles that become embedded or deposited on the target material surface [17]. Indeed, here, SEM studies of the exposed specimens revealed a homogeneous layer of sand particle debris on the surfaces, with the layer being the more continuous the higher the used particle impact speed, clearly due to more of the impacting particles being attached to the layer. As the layer of sand particle debris becomes continuous enough, such as at the speeds of 8.6 or 8.8 m s⁻¹, it evidently starts to provide the specimens



Fig. 11. SEM images of surface of the specimens exposed at 700 °C under several conditions. (a) 30°, 7 m s⁻¹. (b) 30°, 9 m s⁻¹. (c) 90°, 7 m s⁻¹. (d) 90°, 9 m s⁻¹.

protection against further particle impacts, therefore leading to smaller thickness losses than at the lower speeds with more discontinuous particle debris layer. In previous studies on aluminium based diffusion coatings, deposition of sand residues on the specimen surfaces has been observed during the tests [20,25-28], consistently with studies on uncoated steels [29-33] and other uncoated alloys [34], but very seldom such deposition has protected the target material against further particle impacts. Only in the cases where the erodent particles have been reported to contain soft constituents, such as Ca, S and K, formation of a homogeneous and protective layer of particle debris has been detected [35,36], with calcium compounds acting as a cement that binds the bed material ingredients together on the metal surface [37]. In some cases, a critical ratio of 1.2 of the hardness values of the erodent particles to the target material has been identified as a prerequi-site for wear [16]. As it is known that most nitrides are harder than quartz (silica) [16], it is possible that the AlN precipitates in the inner areas of the coating might have contributed to the formation of the continuous layer of sand particle debris on the specimen sur-faces. The fact that the formation of such sand debris layer has not been reported before in the connection of aluminium based dif-fusion coatings (without the reported AIN precipitates!) supports such view.

It is emphasized that the formation of sand particle debris layer on the surfaces of aluminized specimens probably introduced an overall erosion-oxidation behaviour that was quite different from that of aluminized specimens reported in literature. This difference may be due to the specific powder composition, i.e., somewhat higher deposition temperature, 715 °C, the lower aluminium activity of the pack, or both. Further, the aluminized specimens of this study did not clearly obey ductile or brittle erosion behaviour, with some thickness changes being detected both at 30° and 90°, whereas aluminized specimens in previous studies have been shown to undergo essentially brittle erosion behaviour [20,28,38], with only very small damage at a shallow impact angle but significant wear at a normal impact angle. Hence, the aluminized specimens obtained from our pack find their superiority over previously studied aluminized specimens particularly under normal particle impacts, where the particle debris layer is evidently formed. SEM studies, anyway, indicated that oxidation did not play a significant role in the erosion behaviour of our aluminized spec-imens, since the oxide scales, if present, were very thin and did not provide protection against particle impacts. Indeed, where the oxide scales were formed, these were fast removed by erosion. Hence, it was primarily erosion that played a role in behaviour of the coating. Another feature that has typically been detected for aluminized steel specimens is that they experience less damage at higher test temperatures, due to increases in ductility and oxida-tion rate with increase in temperature. Here, thickness losses were virtually independent of test temperature, apparently due to the greater contribution of the sand debris layer than of the under-lying coating to the particle impacts. However, as temperature increases, also the inward diffusion of aluminum increases, leading to phases with reduced aluminum content as compared to origi-nal coating composition. This is demonstrated by the results from cross-sectional studies, particularly the existence of the AlFe phase below the sand particle debris layer at the highest test temperature.

4.3. Future challenges

Although the aluminized specimens, in most cases, underwent much smaller thickness losses than the corresponding uncoated specimens, it is clear that much of the coating was lost during the erosion-oxidation tests. Therefore, it is a future challenge to have



Fig. 12. SEM images and EDS analyses of cross sections of exposed specimens. (a) $550 \degree C$, $30\degree$, $8 m s^{-1}$. (b) $550 \degree C$, $90\degree$, $8 m s^{-1}$. (c) EDS spectrum corresponding to area 1, indicated in (b). (d) EDS spectrum corresponding to area 2, indicated in (b). (e) $700\degree C$, $30\degree$, $8 m s^{-1}$. (f) EDS spectrum corresponding to area 3, indicated in (e).

more of the original coating retained on the specimen surfaces after the tests. This may be achieved by several ways. First, thickness of the coating may be increased, either by using longer deposition time or higher deposition temperature. Probably, modification of deposition conditions, such as pack composition, may also facilitate thicker coatings. Second, the coatings with more uniform distribution of the hard precipitates may be aimed at. The results of this study indicated that the AIN precipitates may play a key role with respect to resistance against particle impacts. These precipitates are concentrated only on the inner areas of the coating and only these areas are retained on the surfaces after the test. If hard precipitates, such as AIN, were distributed more uniformly throughout the coating thickness, it would probably result in more of the coating being retained on the surfaces after the test and, hence, improve performance of the coating.

5. Conclusions

Within the framework of enhancing the performance of relatively cheap tube steels by the application of coating, this study demonstrates the improvement in erosion-oxidation behaviour at elevated temperatures by aluminizing. Aluminizing was carried out by a pack cementation method and resulted in a coating that contained several phases and layers, the outermost of which was enriched in aluminium, included small precipitates of aluminium nitrides, AlN, and was characterized by the microhardness values in the range from 950 to $1100 \, \text{HV}_{20g}$. Such coating provided the substrate with protection against erosion-oxidation particularly at relatively high speeds, typically above 8.8 m s⁻¹, and under normal particle impacts (550, 650 and 700 °C) plus occasionally under particle impacts at a shallow angle (600 and 650 °C), by formation of a homogeneous and a protective layer of erodent debris on the aluminized surfaces. Indeed, one of the unique aspects of this work has been to demonstrate that the Al₅Fe₂ phase based diffusion coatings, which typically show ductile erosion behaviour, may also provide protection against particle impacts at a normal impact angle. The greatest challenges, however, remain the relative thinness of the coatings for applications involving both wear and corrosion at elevated temperatures plus more homogeneous distribution of hard precipitates, such as AlN, in the coating.

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References

- R. Viswanathan, W.T. Bakker, Materials for boilers in ultra supercritical power plants, in: Proceedings of International Joint Power Generation Conference, Miami Beach, Florida, USA, 2000.
- [2] H.K.D.H. Bhadeshia, R.W.K. Honeycombe, Steels, Microstructure and Properties, third ed., Butterworth-Heinemann, Oxford, UK, 2006.
- [3] A. Shibli, F. Starr, International Journal of Pressure Vessels and Piping 84 (2007) 114–122.
- [4] B.L. Eyre, Progress in Materials Science 42 (1997) 23-37.
- [5] M. Schütze, Protective Oxide Scales and their Breakdown, first ed., John Wiley & Sons, Chichester, UK, 1997.
- [6] G. Wahl, Thin Solid Films 107 (1983) 417-426.
- [7] R. Mevrel, Materials Science and Engineering A 120 (1989) 13-24.
- [8] V. Rohr, Developpement de Revetements Pour Les Aciers D'Echangeurs Thermiques Et Amelioration De Leur Resistance A La Corrosion En Environnement Simulant Les Fumees De Combustion De Carbon. PhD Thesis, L'Institut National Polytechnique de Toulouse, France, 2005.
- [9] S.A. Tsipas, H. Omar, F.J. Perez, D.N. Tsipas, Surface and Coatings Technology 202 (2008) 3263–3271.
- [10] N.E. Maragoudakis, G. Stergioudis, H. Omar, H. Paulidou, D.N. Tsipas, Materials Letters 53 (2002) 406–410.

- [11] V. Rohr, M. Schütze, E. Fortuna, D.N. Tsipas, A. Milewska, F.J. Perez, Materials and Corrosion 56 (2005) 874–881.
- [12] S. Saroja, P. Parameswaran, M. Vijayalakshmi, V.S. Raghunathan, Acta Metallurgica et Materialia 43 (1995) 2985–3000.
- [13] K. Kaneko, S. Matsumura, A. Sadakata, K. Fujita, W.-J. Moon, S. Ozaki, N. Nishimura, Y. Tomokiyo, Materials Science and Engineering A 374 (2004) 82–89.
- [14] T. Sasaki, T. Yakou, Journal of Materials Processing Technology 197 (2008) 89–95.
- [15] S. Kobayashi, T. Yakou, Materials Science and Engineering A 338 (2002) 44–53.
 [16] I.M. Hutchings, Tribology, Friction and Wear of Engineering Materials, first ed.,
- Edward Arnold, London, UK, 1992. [17] E. Huttunen-Saarivirta, M. Antonov, R. Veinthal, J. Tuiremo, K. Mäkelä, P. Siitonen, Wear 272 (2011) 159–175.
- [18] A. Agüero, R. Muelas, A. Pastor, S. Osgerby, Surface and Coatings Technology 200 (2005) 1219–1224.
- [19] J. Metsäjoki, E. Huttunen-Saarivirta, T. Lepistö, Journal of Materials Engineering and Performance 20 (2011) 298–305.
- [20] E. Huttunen-Saarivirta, F.H. Stott, V. Rohr, M. Schütze, Corrosion Science 49 (2007) 2844–2865.
- [21] M. Schütze, M. Malessa, V. Rohr, T. Weber, Surface and Coatings Technology 201 (2006) 3872–3879.
- [22] V. Rohr, A. Donchev, M. Schütze, A. Milewska, F.J. Perez, Corrosion Engineering, Science and Technology 40 (2005) 226–232.
- [23] M. Palm, Journal of Alloys and Compounds 252 (1997) 192-200.
- [24] J.A. Dean, Lange's Handbook of Chemistry, 15th ed., McGraw Hill, 1999, Available online at: http://www.knovel.com/web/portal/browse/display?_ EXT_KNOVEL_DISPLAY_bookid=47&VerticalID=0 (viewed 16.02.12).
- [25] E. Huttunen-Saarivirta, S. Kalidakis, F.H. Stott, V. Rohr, M. Schütze, Tribology International 43 (2010) 161–170.
- [26] E. Huttunen-Saarivirta, S. Kalidakis, F.H. Stott, F.J. Perez, T. Lepistö, Wear 267 (2009) 2223–2234.
- [27] E. Huttunen-Saarivirta, F.H. Stott, V. Rohr, M. Schütze, Oxidation of Metals 68 (2007) 2844–2865.
- [28] E. Huttunen-Saarivirta, F.H. Stott, V. Rohr, M. Schütze, Wear 261 (2006) 746-759.
- [29] A.V. Levy, P. Chik, Wear 89 (1983) 151-162.
- [30] A. Levy, Y.-F. Man, Wear 111 (1986) 135–159.
- [31] A. Levy, E. Slamovich, N. Jee, Wear 110 (1986) 117–149.
- [32] B.Q. Wang, G.O. Geng, A.V. Levy, Surface and Coatings Technology 42 (1990) 253-274.
- [33] R. Nordling, A. Nylund, Oxidation of Metals 63 (2005) 87-111.
- [34] C.T. Kang, F.S. Pettit, N. Birks, Metallurgical Transactions A 18 (1987) 1785-1803
- [35] B.A. Lindsay, A.R. Marder, J.J. Lewnard, Wear 188 (1995) 33–39.
- [36] A.V. Levy, B.Q. Wang, G.Q. Geng, Materials Science and Engineering A 121 (1989) 603–609.
- [37] A.V. Levy, Corrosion Science 35 (1993) 1035–1043.
- [38] E. Huttunen-Saarivirta, S. Kalidakis, F.H. Stott, V. Rohr, M. Schütze, Materials and Corrosion 56 (2005) 897–906.