High-temperature Oxidation of Hot-dip Aluminized 2.25Cr-1Mo Steel

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Abstract: When 2.25Cr-1Mo steel was hot-dip aluminized, a coating consisting of (Al-rich topcoat)/(Al₁₃Fe₄ layer)/(Al₅Fe₂ layer) formed. With increment of oxidation temperature, the transform of Al→Al₁₃Fe₄→Al₅Fe₂→AlFe→AlFe₃→α-Fe(Al)→α-Fe occurred through interdiffusion between the coating and the substrate as follows. The oxidation at 700 °C changed the coating to (α-Al₂O₃ scale)/(α-Al₂O₃, Al₁₃Fe₄, Al₅Fe₂)-mixed layer)/(Al₅Fe₂ layer)/(AlFe layer)/(AlFe₃ layer)/(α-Fe(Al) layer). The oxidation at 800 °C changed the coating to (α-Al₂O₃ scale)/((α-Al₂O₃, Al₅Fe₂)-mixed layer)/(Al₅Fe₂ layer)/(AlFe layer)/(AlFe₃ layer)/(α-Fe(Al) layer). The oxidation at 900 °C changed the coating to (α-Al₂O₃ scale)/((α-Al₂O₃, AlFe)-mixed layer)/(AlFe layer)/(AlFe₃ layer)/(α-Fe(Al) layer). The oxidation at 1000 °C changed the coating to ((α-Al₂O₃, Fe₂O₃)-mixed layer)/(AlFe₃ layer)/(α-Fe(Al) layer).

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1. INTRODUCTION

Developing cost-effective surface modification techniques with enhanced oxidation resistance without sacrificing mechanical properties is attracting enormous interest in power generation, petrochemical, and automotive industries. Hot-dip aluminizing is a popular, highly efficient, easily reproducible, and cost-effective technique that can be applied on substrates of arbitrary configuration [1]. It provides superior high-temperature oxidation resistance by forming highly protective α-Al₂O₃ surface scale in oxidative environments [2]. Interdiffusion between Al atoms from the molten Al bath and Fe atoms from the steel substrate forms a highly adherent coating consisting of Al-rich topcoat and the intermetallic layer consisting of outer minor Al₁₃Fe₄ layer and inner major Al₅Fe₂ layer [3-5]. Hot-dip aluminizing has been applied on Fe-Cr steels such as 2.25Cr-1Mo steel (ASTM P22) [5], 5.2Cr-1.2Mo-0.9V steel (AISI H13) [6], 9Cr-1.4W steel (CLAM)

[7], 9Cr-1Mo steel (P91) [8-10], 12Cr steel [11], and stainless steels [12]. In case of 2.25Cr-1Mo steel that was hot-dip aluminized in pure Al molten bath at 700 °C for 3 min, a pure Al topcoat having needle-like, scattered FeAl₃ islands, an outer minor FeAl₃ layer dissolved with 0.5 at%Cr, and an inner major Fe₂Al₅ layer dissolved with 0.8 at%Cr formed [5]. Chromium in steels retarded the interdiffusion between steels and aluminum, resulting in decrement of the intermetallic layer thickness and flattening of the intermetallic layer/steel interface [5]. However, little information is available in literature concerning the oxidation behavior of hot-dip aluminized 2.25Cr-1Mo steels, although such information is of crucial importance for high-temperature applications. Thickness, morphology, and composition of coating layers are affected by compositions of the molten Al bath and substrate, hot-dipping parameters, and heat-treatment conditions including oxidation. Therefore, the objective of this study was to investigate microstructural transition of hot-dip aluminized 2.25Cr-1Mo steel during oxidation at 700-1000 °C for 20 h utilizing various analytical equipments.

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Fig. 1. Hot-dip aluminized P22 steel. (a) EPMA back-scattered electron (BSE) cross-sectional image (unetched), (b) XRD pattern of coating (as-hot-dipped condition), (c) XRD pattern after grinding off the coating surface, (d) EBSD phase map, (e) EPMA maps of (a).

2. EXPERIMENT DETAILS

ASTM P22 ferritic steel plate (Fe-2.25Cr-1Mo-0.45Mn-0.3Si-0.12C in wt%) was cut to $80 \times 20 \times 2$ mm³ sized coupons, ground with 1000 grit SiC paper, ultrasonically cleaned in acetone and alcohol, and dipped in the molten Al bath at 800 °C for 5 min, on top of which a solid flux (KCl+ NaCl+AlF₃ in 2:2:1 in ratio) was spread to protect the bath from oxidation. These hot-dip aluminized steel coupons were pulled out, cooled to room temperature in air, cleaned with 5 vol% HNO₃ solution to remove any flux on the surface, and rinsed with water. Oxidation test of hot-dip aluminized steel samples was performed at 700, 800, 900, and 1000 °C for 20 h in air using a furnace. Aluminized/oxidized samples were inspected using an optical microscope (OM), a high power X-ray diffractometer (XRD) with Cu-K α radiation at 40 kV and 100 mA, a field-emission scanning electron

microscope (SEM) equipped with an energy-dispersive spectroscope (EDS), an electron probe microanalyzer (EPMA), and electron backscatter diffraction (EBSD) technique. Cross-sections of the aluminized layer and the steel substrate were examined by etching with the Keller's reagent and Vilella's reagent, respectively. Hereafter, all compositions denoted are atomic percentages (at%) unless otherwise specified.

3. RESULTS AND DISCUSSION

Figure 1 shows EPMA/XRD/EBSD results of hot-dip aluminized P22 steel. Hot-dipping formed ~ 30 μ m-thick topcoat and ~ 35 μ m-thick intermetallic layer on the steel substrate (Fig. 1(a)). Vertical axes of Figs. 1(b) and 1(c) are plotted in logarithmic scale in order to show minor peaks. In Fig. 1(b), strong Al peaks and weak Al₁₃Fe₄ peaks were detected, indicating that a small amount of Al₁₃Fe₄ precipitates was present in

Fig. 2. Hot-dip aluminized P22 steel after oxidation at 700 °C for 20 h. (a) XRD pattern before grinding the surface, (b) XRD pattern after first grinding, (c) XRD pattern after second grinding, (d) EPMA cross-sectional secondary electron (SE) image (unetched), (e) SEM-EDS concentration profiles of spots 1-20 marked in (d), (f) OM image (etched), (g) EPMA maps of (d).

the Al-rich topcoat. When this topcoat was ground off manually using an emery paper, weak Al₅Fe₂ peaks and strong Al₁₃Fe₄ peaks appeared [9] (Fig. 1(c)). Al₁₃Fe₄ and Al₅Fe₂ peaks came from the upper and lower part of the intermetallic layer, respectively (Fig. 1(d)). Al₈Cr₅ that was detected to a small amount in hot-dip aluminized steels containing more than 9 wt%Cr [8,13] was not detected in this study. In Fig. 1(d), Al₁₃Fe₄ precipitates scattered in the Al-rich topcoat [14]. Most grains in the coating were small and equiaxed. Some columnar grains in the lower part of the Al₅Fe₂ layer were aligned along the interdiffusion direction of Al and substrate elements [8,15]. EDS-analyzed compositions (%) were 95.6Al-4.3Fe-0.1Mn for spot ① (viz. Al-rich topcoat), 75.9Al-23.3Fe-0.6Cr-0.2Mn for spot ② (viz. Al₁₃Fe₄ layer), and 69.3Al-

28.1Fe-2.2Cr-0.3Mn-0.1Mo for spot ③ (viz. Al₅Fe₂ layer) (Fig. 1(a)). This indicated that Fe, Cr, Mn, and Mo diffused outwardly toward the surface while Al diffused inwardly across the topcoat according to the concentration gradient. Whitish flakes in the topcoat shown in Fig. 1(a) were Al₁₃Fe₄ islands embedded in Al grains [5] according to Fig. 1(e). The topcoat retained a small amount of dissolved Mn. It was almost free from Cr and Mo (Fig. 1(e)). Maps of Cr and Mo indicated that Cr and Mo dissolved more in the Al₅Fe₂ layer than the Al₁₃Fe₄ layer because the former was closer to the steel substrate than the latter.

The hot-dip aluminized P22 steel was oxidized at 700 °C for 20 h and successively ground off from the surface on the emery paper. X-ray analysis results are shown in Figs. 2(a-c). In Fig. 2(a), strong Al₅Fe₂

peaks as well as weak α -Al₂O₃ and Al₁₃Fe₄ peaks were detected at the surface. Such result implied that the Al-rich topcoat transformed to either α -Al₂O₃ or Al₅Fe₂ plus a small amount of Al₁₃Fe₄. Such oxidation and phase transformation would occur fast because the test temperature was above the melting point of Al (660 °C). Below the coating surface, Al₅Fe₂ peaks were mainly detected (Fig. 2(b)). Further grinding revealed strong AlFe and weak Al₅Fe₂ peaks (Fig. 2(c)). These XRD results indicated that the hot-dipped coating transformed to (α -Al₂O₃ scale)/(mostly Al₅Fe₂ plus a small amount of Al₁₃Fe₄)/(Al₅Fe₂ layer)/(AlFe layer) from the surface. Depending on investigators, when hot-dipped (Al₁₃Fe₄ layer)/(Al₅Fe₂ layer) were oxidized at 700-760 °C for 15-30 h, they transformed to (Al₂Fe layer)/(AlFe layer) [7] or (AlFe layer)/(AlFe₃ layer) [16]. Unetched EPMA image (Fig. 2(d)), SEM-EDS analyzed composition profiles (Fig. 2(e)), and etched OM image (Fig. 2(f)) clarified the spots marked in Fig. 2(d) as follows: Spot 1 = (~2 μ m-thick α -Al₂O₃ scale); Spots 2-3 = (~13 μ m-thick, (α -Al₂O₃, Al₅Fe₂)-intermixture having a small amount of Al₁₃Fe₄) (see Fig. 2(a)). Dark spots around spots 2-3 were α -Al₂O₃ particles (Fig. 2(d)). Since spots 2-3 originally belonged to Al-rich topcoat, their Al concentration was high as shown in the Al map of Fig. 2(g). Spots 3-11 = (~80 μ m-thick Al₅Fe₂ layer) (see Fig. 2(b)). Spots 12-13 = (~20 μ m-thick AlFe layer) (see Fig. 2(c)). Spots 14-15 = (~20 μ m-thick AlFe₃ layer). Spots 16-18 = (~30 μ m-thick α -Fe(Al) layer). Spots 19-20 = α -Fe substrate. The α -Fe(Al) phase can form because more than 10% Al dissolves in α -Fe at room temperature according to the Al-Fe phase diagram. Grains in the AlFe layer were columnar while overlying Al₁₃Fe₄ and Al₅Fe₂ grains were fine (Fig. 2(f)). The α -Al₂O₃ scale shown in Fig. 2(d) was loosely adherent and somewhat convoluted owing to its mismatch in thermal expansion coefficients with underlying Al-Fe phases. Thermal expansion coefficient is $8 \times 10^{-6} \text{ K}^{-1}$ for α -Al₂O₃ [17], $18.94 \times 10^{-6} \text{ K}^{-1}$ for Fe₂Al₅, and $19.68 \times 10^{-6} \text{ K}^{-1}$ for FeAl₃ [18]. The coating shown in Fig. 2(d) cracked vertically owing to difference in thermal expansion coefficients [19] and

volume shrinkage arisen owing to transformation of (high Al)-Fe phases to (low Al)-Fe phases during oxidation. Density (g/cm³) is 2.7 for Al, 3.84 for Al₁₃Fe₄, 3.96 for Al₅Fe₂, and 5.666 for AlFe. The brittleness of Al₁₃Fe₄ and Al₅Fe₂ additionally facilitated cracking [6,20,21]. In order to avoid cracks, many attempts have been made as follows. (1) Replace brittle Al₁₃Fe₄ and Al₅Fe₂ with ductile AlFe and AlFe₃ through laser melting [8,22], heat treatment [9,13,16,23], and oxidation [7]. (2) Add Si in the molten Al bath to suppress the growth of Al₅Fe₂ with 30% vacancies along [001] growth direction, leading to reduction of thickness of the intermetallic layer [3,15]. (3) Add alloy elements and second-phase particles to reduce the thickness of the intermetallic layer [6]. (4) Seal cracks by impregnating the coating with H₃PO₄ solution [19]. The unequal inward diffusion of Al and oxygen as well as outward diffusion of substrate elements produced Kirkendall voids at spots 3-15 (Fig. 2(d)). Voids in the Al₅Fe₂ layer were coarser than those in the AlFe or AlFe₃ layer because substrate elements diffused outwardly more in the Al₅Fe₂ layer (Fig. 2(d)). The insufficient adherence of α -Al₂O₃ scale, voids, and cracks led to the formation oxide particles down to spot 15 (see Fig. 2(d) and oxygen map shown in Fig. 2(g)). All Al-Fe phases denoted in Fig. 2(f) were dissolved with substrate alloying elements such as Cr, Mo, and Mn, which diffused outwardly according to concentration gradients (Fig. 2(g)).

The hot-dip aluminized P22 steel that oxidized at 800 °C for 20 h was successively grinded off from the surface. X-ray results are shown in Figs. 3(a-d). Strong Al₅Fe₂ peaks and weak α -Al₂O₃ peaks were detected at the surface (Fig. 3(a)). In this figure, weak Al₁₃Fe₄ peaks detected in Fig. 2(a) were absent owing to the enhanced interdiffusion at 800 °C. Since the formed α -Al₂O₃ scale was thin and loosely adherent, α -Al₂O₃ peaks were weak in Fig. 3(a). Strong Al₅Fe₂, AlFe, and AlFe₃ peaks were detected in Figs. 3(b), (c), and (d), respectively. Such XRD results indicated the formation of α -Al₂O₃/Al₅Fe₂/AlFe/AlFe₃ layers from the surface. The coating was

Fig. 3. Hot-dip aluminized P22 steel after oxidation at 800 °C for 20 h. (a) XRD pattern before grinding, (b) XRD pattern after first grinding, (c) XRD pattern after second grinding, (d) XRD pattern after third grinding, (e) EPMA cross-sectional SE image (unetched), (f) SEM-EDS concentration profiles of spots 1-15 shown in (e), (g) OM image (etched), (h) EPMA maps of (e).

analyzed in more detail as follows using EPMA/EDS/OM. In Figs. 3(e-f), spot 1 corresponded to the loosely adherent $\alpha\text{-Al}_2\text{O}_3$ layer. Spot 2 corresponded to $\alpha\text{-Al}_2\text{O}_3$ particles in the Al_5Fe_2 layer. $\alpha\text{-Al}_2\text{O}_3$ that grew extremely slowly came out as dark spots in Figs. 3(e) and 3(g). Spots 3-4 corresponded to the Al_5Fe_2 layer consisting of fine grains (Figs. 3(b, e-g)). Spots 4-7 corresponded to the AlFe layer consisting of columnar grains whose growth was dominated by the outward transport of Fe and inward migration of Al (Figs. 3(c, e-g)). Figures 3(d) and 3(e-g) indicated that spots 8-11 corresponded to the AlFe_3 layer. This layer was hardly etched because of dissolved Cr (Figs. 3(f) and (h)). Spots 12-14 and 15-16 corresponded to the $\alpha\text{-Fe(Al)}$ layer and the $\alpha\text{-Fe}$ substrate, respectively (Figs. 3(e-h)). Grains of $\alpha\text{-Fe(Al)}$ which were coarser than those of $\alpha\text{-Fe}$ were dissolved with Cr (Figs. 3(f) and (h)). The Al concentration in the $\alpha\text{-Fe(Al)}$ layer

decreased from 1.4% at spot 12 to 0.4% at spot 14 (Fig. 3(f)) while the $\alpha\text{-Fe}$ substrate was virtually Al-free. Vertical cracks, which developed owing to phase transformation of Al-Fe phases and mismatch in thermal expansion coefficients among Al-Fe phases, propagated down to the AlFe layer with columnar grains (Figs. 3(e) and 3(g)). Oxygen diffused inwardly during oxidation. Its concentration decreased from 8% at spot 2 to 3% at spot 16 (Fig. 3(f)). Internal $\alpha\text{-Al}_2\text{O}_3$ particles, voids, and cracks came out dark in Fig. 3(e). The closer to the surface, the bigger voids became because substrate elements diffused out more. Oxides also became bigger because more oxygen and Al were available. The distribution of oxides and elements of concern is displayed in Fig. 3(h). Results obtained from Fig. 3 may be summarized as follows. Oxidation led to the formation of $\sim 2\text{ }\mu\text{m}$ -thick $\alpha\text{-Al}_2\text{O}_3$ surface scale, $15\text{ }\mu\text{m}$ -thick $(\text{Al}_5\text{Fe}_2 + \alpha\text{-Al}_2\text{O}_3)$ -mixed

Fig. 4. Uncoated P22 steel after oxidation at 800 °C for 20 h. (a) cross-sectional EPMA SE image (unetched), (b) EPMA mappings of (a), (c) XRD pattern taken from the surface.

layer, (20-30) μm -thick Al_5Fe_2 layer, (40-50) μm -thick AlFe layer, (40-50) μm -thick AlFe_3 layer, and (35-50) μm -thick $\alpha\text{-Fe(Al)}$ layer on the $\alpha\text{-Fe}$ substrate.

EPMA/XRD results shown in Fig. 4 were obtained from bare P22 steel which was oxidized under the same condition outlined in Fig. 3. Without hot-dipping, $\sim 190 \mu\text{m}$ -thick, porous, nonadherent outer oxide scale, and $\sim 190 \mu\text{m}$ -thick, somewhat dense, and loosely adherent inner oxide scale formed (Fig. 4(a)). Oxygen migrated easily across the outer scale to form the inner scale (Fig. 4(b)). The outer scale grew primarily by outward diffusion of Fe and Mn, while the inner scale grew primarily by inward diffusion of oxygen (Fig. 4(b)). The partial spallation of outer and inner oxide scales yielded a strong $\alpha\text{-Fe}$ peak besides strong Fe_2O_3 peaks and a weak Fe_3O_4 peak in Fig. 4(c). SEM-EDS analysis indicated that the composition of the outer and inner scale was 59O-0.95Mn-40.05Fe

and 56O-0.7Cr-0.3Mn-43Fe (%), respectively, suggesting that the outer and inner scale primarily consisted of Fe_2O_3 and Fe_3O_4 , respectively. Comparison between Fig. 3 and Fig. 4 clearly indicated that hot-dipping significantly improved oxidation resistance.

When hot-dip aluminized P22 steel was oxidized at 900 °C for 20 h, the $\alpha\text{-Al}_2\text{O}_3$ surface scale formed on the coating that consisted of the AlFe outer layer and the AlFe_3 inner layer [6] as shown in Figs. 5(a-c). In the etched OM image shown in Fig. 5(d), $\alpha\text{-Al}_2\text{O}_3$ scale consisting of fine grains, AlFe layer consisting of short columnar grains, and AlFe_3 layer consisting of coarse columnar grains were seen from the surface. In iron aluminides, Al diffusion is always slightly faster than Fe diffusion [24] and Fe diffuses faster in AlFe_3 than FeAl [25]. Hence, AlFe_3 grains can grow coarser and more columnar than AlFe grains as shown in Fig. 5(d). A scratch marker is shown in Fig. 5(d). It was engraved using a knife at the coating surface prior to oxidation. It was covered with a thin $\alpha\text{-Al}_2\text{O}_3$ surface scale, indicating that outward transport of substrate elements did not occur significantly. Unetched EPMA image, EDS-analyzed concentration profiles, and EPMA maps are shown in Figs. 5(e), 5(f), and 5(g), respectively. Phase transformation of Al (Fig. 1(d); density, $\rho = 2.7 \text{ g/cm}^3$) through $\text{Al}_{13}\text{Fe}_4$ (Fig. 2(e); $\rho = 3.84 \text{ g/cm}^3$) and Al_5Fe_2 (Fig. 3(f); $\rho = 3.96 \text{ g/cm}^3$) to AlFe (Fig. 5(f); $\rho = 5.666 \text{ g/cm}^3$) induced volume shrinkage, which generated cracks along columnar AlFe grain boundaries (Fig. 5(e)). Cracks in the AlFe layer stopped propagating in front of more ductile AlFe_3 layer. Although AlFe was softer and less brittle than $\text{Al}_{13}\text{Fe}_4$ and Al_5Fe_2 [6,20,21], it still suffered from cracking as shown in Fig. 5(e) because oxygen dissolution and void formation during oxidation assisted cracking, in addition to phase transformation and mismatch in thermal expansion coefficients among Al-Fe phases. Since oxygen diffused easily through cracks, oxide particles formed down to the AlFe/ AlFe_3 interface (see oxygen map in Fig. 5(g)). From spot 2 to spot 20, the concentration of inwardly diffusing oxygen gradually decreased from 3.2% to 1% while Cr content gradually increased

Fig. 5. Hot-dip aluminized P22 steel after oxidation at 900 °C for 20 h. (a) XRD pattern before grinding, (b) XRD pattern after first grinding, (c) XRD pattern after second grinding, (d) OM image (etched), (e) EPMA cross-sectional SE image (unetched), (f) SEM-EDS concentration profiles of spots 1-20 shown in (e), (g) EPMA maps of (d).

from 0.6% to 2.7% (Fig. 5(f)). Aluminum diffused inwardly and all substrate elements diffused outwardly according to concentration gradients (Fig. 5(g)). Unequal mass flow was responsible for the formation of Kirkendall voids, particularly in the AlFe layer (Fig. 5(e)). The $\alpha\text{-Al}_2\text{O}_3$ scale was $\sim 25\ \mu\text{m}$ -thick. It was convoluted to relieve the residual stress accumulated during oxidation (Fig. 5(e)). It was dissolved with 4.4% Fe according to the EDS analysis (spot 1 in Fig. 5(f)). This would favor alumina growth and stress accumulation [26]. Dark dots scattered inside spots 1-3 (width = $\sim 45\ \mu\text{m}$) were $\alpha\text{-Al}_2\text{O}_3$ particles embedded in the AlFe layer (Fig. 5(e)). The AlFe layer (spots 2-8) was $\sim 120\ \mu\text{m}$ -thick. It had voids and vertical cracks (Figs. 5(e-f)). The ductile AlFe_3 layer (spots 8-14) and $\alpha\text{-Fe(Al)}$ layer (spots 15-18) were ~ 160 and $\sim 45\ \mu\text{m}$ -thick, respectively (Figs. 5(e-f)). Spots 19-20 belonged

to $\alpha\text{-Fe}$ substrate (Figs. 5(e-f)). Average compositions of AlFe layer, AlFe_3 layer, and $\alpha\text{-Fe(Al)}$ layer were 49.7Al-46.3Fe-0.9Cr-0.4Mn-2.7O, 18.4Al-76.3Fe-1.6Cr-0.7Mn-0.2V-2.8O, and 0.9Al-93.3Fe-2.2Cr-0.7Mn-0.2V-2.7O, respectively, according to SEM-EDS analysis. Such results were attributed to interdiffusion of Al, substrate elements, and oxygen during oxidation.

Figure 6 shows XRD/EPMA/EDS/OM results of hot-dip aluminized P22 steel after oxidation at 1000 °C for 20 h. Strong $\alpha\text{-Al}_2\text{O}_3$ and AlFe_3 peaks and weak Fe_2O_3 peaks were detected in Fig. 6(a). However, only strong $\alpha\text{-Fe(Al)}$ peaks were detected in Fig. 6(b). Such results indicated the formation of $\alpha\text{-Al}_2\text{O}_3$ -rich scale containing a small amount of Fe_2O_3 on the coating that primarily consisted of the AlFe_3 outer layer and the $\alpha\text{-Fe(Al)}$ inner layer. In Figs. 6(c-d), spot 1 corresponded to $\alpha\text{-Al}_2\text{O}_3$ surface scale. Spot 2

Fig. 6. Hot-dip aluminized P22 steel after oxidation at 1000 °C for 20 h. (a) XRD pattern before grinding, (b) XRD pattern after grinding, (c) EPMA cross-sectional SE image (unetched), (d) SEM-EDS concentration profiles of spots 1-19 shown in (c), (e) OM image (etched), (f) EPMA maps of (e).

corresponded to $\alpha\text{-Al}_2\text{O}_3$ -rich scale containing a small amount of Fe_2O_3 which was not identified in Fig. 5(a) due to its small amount. Spots 3-4 corresponded to the AlFe_3 layer. The composition of spot 3 was 22.5Al-73.3Fe-1Cr-0.6Mn-0.2V-2.4O (%), implying the dissolution of oxygen and some substrate elements. Spots 4-15 corresponded to the $\alpha\text{-Fe(Al)}$ layer whose average composition was 84.4Fe-9.5Al-2.2Cr-0.6Mn-0.3Si-0.2V-2.8O (%), implying the dissolution of Al, Cr, Mn, Si, V, and oxygen in the $\alpha\text{-Fe(Al)}$ layer. Spots 15-19 corresponded to the $\alpha\text{-Fe}$ substrate whose average composition was 92.8Fe-0.2Al-3.1Cr-0.5Mn-0.3Si-0.3V-2.8O (%), implying that a small amount of Al and oxygen diffused inwardly into the $\alpha\text{-Fe}$ substrate. Internal oxides and voids in the AlFe_3 layer were coarser than those in the $\alpha\text{-Fe(Al)}$ layer because more oxygen was available. Aluminum in the AlFe_3 layer diffused inwardly to form the thick $\alpha\text{-Fe(Al)}$ layer and outwardly to form the $\alpha\text{-Al}_2\text{O}_3$ surface scale to a meager amount (Figs. 6(c) and (e)). Figure 6(e) indicated that $\alpha\text{-Fe(Al)}$ grains were coarser and more

columnar than AlFe_3 grains, suggesting that interdiffusion along the growth direction occurred faster in the $\alpha\text{-Fe(Al)}$ layer than the AlFe_3 layer. Coating phases identified in Fig. 5 (900 °C-oxidation) changed in Fig. 6 (1000 °C-oxidation) as follows: (1) $\alpha\text{-Al}_2\text{O}_3$ -rich surface scale (thickness, $\delta = 25 \mu\text{m}$, fine grains.) $\rightarrow (\alpha\text{-Al}_2\text{O}_3, \text{Fe}_2\text{O}_3)$ -mixed surface scale ($\delta = 45 \mu\text{m}$, fine grains); (2) AlFe layer ($\delta = 120 \mu\text{m}$, short columnar grains) $\rightarrow \text{AlFe}_3$ layer ($\delta = 120 \mu\text{m}$, short columnar grains); and (3) AlFe_3 layer ($\delta = 160 \mu\text{m}$, coarse columnar grains) $\rightarrow \alpha\text{-Fe(Al)}$ layer ($\delta = 450 \mu\text{m}$, coarse columnar grains). EPMA maps shown in Fig. 6(f) also confirmed the dissolution of oxygen and substrate alloying elements such as Cr, Mn, and Mo in the AlFe_3 layer (spot 3-4) and $\alpha\text{-Fe(Al)}$ layer (spots 4-15) besides interdiffusion of O, Al, and substrate elements.

4. CONCLUSIONS

Microstructural change of hot-dip aluminized 2.25Cr-1%Mo steel during oxidation is graphically summarized

Fig. 7. Schematic diagram showing the phase transition and coating thickness variation of hot-dip aluminized P22 steel. (a) before oxidation, and after oxidation for 20 h at (b) 700 °C, (c) 800 °C, (d) 900 °C, and (e) 1000 °C.

in Fig. 7. Hot-dip aluminizing produced (30 μm -thick Al-rich topcoat)/(15 μm -thick $\text{Al}_{13}\text{Fe}_4$ layer)/(20 μm -thick Al_5Fe_2 layer) on the $\alpha\text{-Fe}$ substrate. The Al_5Fe_2 layer partly consisted of columnar grains aligned along the interdiffusion direction of Al and substrate elements while other layers mainly consisted of rather equiaxed grains. Oxidation at 700 °C for 20 h produced (15 μm -thick $\alpha\text{-Al}_2\text{O}_3$ -rich oxide layer)/(80 μm -thick Al_5Fe_2 layer with a small amount of $\text{Al}_{13}\text{Fe}_4$ at its upper part)/(20 μm -thick AlFe layer)/(20 μm -thick AlFe_3 layer)/(30 μm -thick $\alpha\text{-Fe(Al)}$ layer) on the $\alpha\text{-Fe}$ substrate. Here, the AlFe layer consisted of short or underdeveloped columnar grains while other layers consisted of fine grains. Oxidation at 800 °C for 20 h produced (17 μm -thick $\alpha\text{-Al}_2\text{O}_3$ -rich oxide layer)/(25 μm -thick Al_5Fe_2 layer without $\text{Al}_{13}\text{Fe}_4$)/(45 μm -thick AlFe layer)/(45 μm -thick AlFe_3 layer)/(40 μm -thick $\alpha\text{-Fe(Al)}$ layer) on the

$\alpha\text{-Fe}$ substrate. Here, the AlFe layer consisted of short columnar grains while other layers consisted of fine grains. Oxidation at 900 °C for 20 h produced (25 μm -thick $\alpha\text{-Al}_2\text{O}_3$ -rich oxide layer)/(120 μm -thick AlFe layer)/(160 μm -thick AlFe_3 layer)/(45 μm -thick $\alpha\text{-Fe(Al)}$ layer) on the $\alpha\text{-Fe}$ substrate. Here, grains of the AlFe_3 layer were coarser and more columnar than those of the AlFe layer. Oxidation at 1000 °C for 20 h produced (45 μm -thick $\alpha\text{-Al}_2\text{O}_3$ -rich oxide layer)/(120 μm -thick AlFe_3 layer)/(450 μm -thick $\alpha\text{-Fe(Al)}$ layer) on the $\alpha\text{-Fe}$ substrate. The transition of the AlFe layer to the AlFe_3 layer as well as the (AlFe_3 layer)/($\alpha\text{-Fe(Al)}$ layer) to the $\alpha\text{-Fe(Al)}$ layer owing to enhanced interdiffusion of Al and Fe was noticeable when the oxidation temperature was increased from 900 to 1000 °C.

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REFERENCES

1. M. S. Kwon and C. Y. Kang, *Korean J. Met. Mater.* **54**, 40 (2016).
2. M. A. Abro and D. B. Lee, *Met. Mater. Int.* **23**, 92 (2017).
3. B. Lemmens, H. Springer, I. De Graeve, J. De Strycker, D. Raabe, and K. Verbeken, *Surf. Coat. Technol.* **319**, 104 (2017).
4. A. Van Alboom, B. Lemmens, B. Breithbach, E. De Grave, S. Cottenier, and K. Verbeken, *Surf. Coat. Technol.* **324**, 419 (2017).
5. W. J. Cheng and C. J. Wang, *App. Surf. Sci.* **277**, 139 (2013).
6. Q. Y. Zhang, Y. Zhou, J. Q. Liu, K. M. Chen, J. G. Mo, X. H. Cui, and S. Q. Wang, *Wear* **344**, 22 (2015).
7. J. Chen, X. Li, P. Hua, C. Wang, K. Chen, Y. Wu, and W. Zhou, *Fusion Eng. Des.* **125**, 57 (2017).
8. R. A. Jeshvaghani, M. Emami, O. Shafiee, and H. R. Shahverdi, *Surf. Coat. Technol.* **240**, 365 (2014).
9. Z. Shi, J. Cao, and F. Han, *J. Nucl. Mater.* **447**, 77 (2014).
10. M. A. Abro and D. B. Lee, *Coatings* **7**, 31 (2017).
11. J. H. Kim, S. Y. Kim, and C. Y. Kang, *Surf. Coat. Technol.* **240**, 387 (2014).
12. E. Frutos, P. Adeva, J. L. González-Carrasco, and P. Pérez, *Surf. Coat. Technol.* **236**, 188 (2013).
13. K. Stein-Fechner, J. Konys, and O. Wedemeyer, *J. Nucl. Mater.* **249**, 33 (1997).
14. W. J. Cheng and C. J. Wang, *Surf. Coat. Technol.* **204**, 824 (2009).
15. I. D. Graeve, I. Schoukens, A. Lanzutti, F. Andreatta, A. Alvarez-Pampliega, J. De Strycker, L. Fedrizzi, and H. Terryn, *Corros. Sci.* **76**, 325 (2013).
16. Y. Sun, J. Dong, P. Zhao, and B. Dou, *Surf. Coat. Technol.* **330**, 234 (2017).
17. R. Riedel, *Handbook of Ceramic Hard Materials*, p.986, Wiley-VCH, Germany (2000).
18. Q. Wang, X. S. Leng, T. H. Yang, and J. C. Yan, *Trans. Nonferrous Met. Soc. China* **24**, 279 (2014).
19. C. Boulesteix and F. Pedraza, *Surf. Coat. Technol.* **327**, 9 (2017).
20. M. J. Rathod and M. Kutsuna, *J. Weld.* **83**, 16s (2004).
21. C. G. McKamey, *Physical Metallurgy and Processing of Intermetallic Compounds* (eds. N. S. Stoloff and V. K. Sikka), p.351, Springer, USA (1996).
22. M. Emani, H. R. Shahverdi, S. Hayashi, and M. J. Torkamany, *Metall. Mater. Trans. A* **44**, 3176 (2013).
23. S. Kobayashi and T. Yakou, *Mater. Sci. Eng. A* **338**, 44 (2002).
24. H. Mehrer, *Diffus. Found.* **2**, 1 (2014).
25. H. Mehrer, M. Luckabauer, W. Sprengel, *Defect Diffus. Forum* **333**, 1 (2013).
26. S. Y. Park, D. Y. Seo, S. W. Kim, S. E. Kim, J. K. Hong, and D. B. Lee, *Intermetallics* **74**, 8 (2016).