Corrosion of Hot-dip Aluminized 9Cr-1Mo Steel in N$_2$/0.1%H$_2$S Gas

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Abstract: ASTM P91 steel (viz. 9Cr-1Mo steel) was hot-dip aluminized to form a ~70 µm thick coating, and was then corroded in N$_2$/0.1%H$_2$S gas for 50 h at 800 and 900 ºC, to study the effect of aluminizing on the corrosion resistance of P91 steel in highly corrosive H$_2$S environments. Before corrosion, the aluminized coating consisted of an Al-rich topcoat, an Al$_{13}$Fe$_4$ upper layer, and an Al$_5$Fe$_2$ lower layer from the surface. During corrosion, Al, oxygen, and sulfur diffused inwardly, while substrate elements diffused outwardly. Impurity oxygen in the gas reacted preferentially with Al to form α-Al$_2$O$_3$ at the surface, which increased the corrosion resistance significantly. Bare P91 steel corroded quickly, to form bi-layered, fragile, nonprotective FeS scales. The coating transformed into either a (Al$_{13}$Fe$_4$, Al$_5$Fe$_2$)-mixed layer, AlFe layer, AlFe$_3$ layer, and α-Fe(Al) layer when corroded at 800 ºC/50 h, or into a AlFe$_3$ layer and α-Fe(Al) layer when corroded at 900 ºC/50 h. Interdiffusion that occurred during corrosion increased the total coating thickness, and transformed (high Al)-Fe phases to (low Al)-Fe phases. The corrosion accompanied the formation of voids and microcracks in the coating.

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1. INTRODUCTION

Ferritic 9Cr-1Mo steels (ASTM P91) are used in heat exchangers, boilers, and pipes because of their high strength and thermal conductivity, low thermal expansion coefficients, and resistance to creep, thermal fatigue, and oxidation. They form outer Fe-rich oxides such as Fe$_2$O$_3$ and Fe$_3$O$_4$, and inner Cr-rich oxides such as FeCr$_2$O$_4$ or (Fe,Cr)$_3$O$_4$ during high-temperature oxidation in air [1], steam [2], and ultra-supercritical power plant [3]. Although they form protective Cr-rich oxide scales during high-temperature oxidation [4], they become less protective in sulfur-containing environments because sulfides are generally highly nonstoichiometric and have lower melting points than their corresponding oxides [5,6]. Sulfur is usually present in fossil fuels, fluxes, or chemical feedstock. In reducing atmospheres, it exists in the gas stream as H$_2$S(g), which limits operating temperature and efficiency during processing in oil refineries, petrochemical units, coal gasification, natural gas reforming, and energy generation in thermal power plants [7-10]. H$_2$S dissociates into sulfur and hydrogen. Hydrogen atoms dissolve to cause embrittlement, ingress into the scale and metals interstitially, generate lattice point defects and hydrogen clusters, resulting in a significant increase in the corrosion of metals [11].

When corroded in H$_2$/H$_2$S gas at 575-650 ºC, 9Cr-1Mo steel formed (FeS, FeCr$_2$S$_4$)-sulfide scales which tended to crack and spall during cooling [12]. In N$_2$/H$_2$S gas at 600-700 ºC, it corroded fast and almost linearly, forming outer FeS scales and inner (FeS, FeCr$_2$O$_4$)-mixed scales [13]. Particularly, Fe$_{1-x}$S grows fast due to its nonstoichiometry (x=0-0.2), and makes the scales highly fragile, non-adherent, and nonprotective [14].

This study aimed to investigate the microstructure and corrosion behavior of hot-dip aluminized 9Cr-1Mo steel in a highly corrosive H$_2$S environment. Aluminizing is widely used on metals in order to protect alloys from oxidation/corrosion [15]. Hot-dip aluminizing of steels leads to the formation of an Al-rich topcoat and the Al-Fe intermetallic...
layer consisting of Fe$_2$Al$_3$ and FeAl$_3$ [16]. In this study, the corrosion behavior of hot-dip aluminized 9Cr-1Mo steel in N$_2$/H$_2$S gas was investigated at 800-900 °C, because the industrially important H$_2$S gas is particularly destructive at high temperatures. Nitrogen was employed as the balance gas in order to simulate coal gasification systems [8]. This study will be a useful contribution to the development of corrosion-resistant coatings for iron-base alloys.

2. EXPERIMENT DETAILS

A P91 steel plate with a nominal composition of Fe-9Cr-1Mo-0.45Mn-0.4Si-0.2V-0.08Nb-0.1C (wt%) was ground to a 1000 grit SiC finish, immersed in a 10 vol% HCl solution to remove surface oxides, subjected to a liquid flux treatment with Keller’s reagent and the steel matrix with Villella’s reagent, together examined by etching the aluminized coating with Keller’s solid flux (KCl+NaCl+AlF$_3$ and dipped in Al($\text{Fe}_2$O$_3$)$_3$) for 5 min at 800 °C, on top of which a 1000 grit SiC finish, immersed in a 10 vol% HCl solution was formed by interdiffusion between the Al($\text{Fe}_2$O$_3$)$_3$ layer containing a small amount of Al($\text{Fe}_2$O$_3$)$_3$-rich topcoat transformed to Al($\text{Fe}_2$O$_3$)$_3$ below the Al-rich topcoat (Fig. 1(c)). Further surface grinding revealed Al($\text{Fe}_2$O$_3$)$_3$ only (Fig. 1(d)). The Powder Diffraction File (PDF) numbers of phases in the Al-Fe binary phase diagram are as follows. Al (85-1327), Al$_3$Fe$_4$ (29-0042), Al$_2$Fe$_7$ (47-1435), AlFe (33-0020), AlFe$_5$ (50-0955), and α-Fe (06-0696).

According to the concentration gradients of Al and Fe created during hot dipping, an Al-rich topcoat containing a small amount of Al$_3$Fe$_4$ and Al$_2$Fe$_7$ precipitates, an upper Al$_3$Fe$_4$ layer containing a small amount of Al$_2$Fe$_7$ precipitates, and a lower Al$_2$Fe$_7$ layer were formed on the surface (Fig. 1(e)). This phase distribution is also recognizable in the Al map shown in Fig. 1(f). The Al$_3$Fe$_4$ layer was thick and somewhat columnar, because orthorhombic Al$_3$Fe$_4$ has 30% vacancies along the c-axis, through which the interdiffusion of Al and Fe occurred fast [17,18] (Fig. 1(e)). Dissolution of the alloying elements such as Cr, Mo, and Mn in the Al$_2$Fe$_7$ layer flattened the coating/substrate interface and narrowed the Al$_3$Fe$_4$ layer (Figs. 1(a, f)). It is noted that, in the case of low-alloyed carbon steels, the coating/substrate interface exhibited a finger- or tongue-like morphology that was oriented along the c-axis of Al$_3$Fe$_4$ layer, and the Al$_2$Fe$_7$ layer was typically thick [19-21].

Aluminized 9Cr-1Mo steel was corroded at 800 °C for 50 h, and XRD’ed while successively grinding the coating surface. In Fig. 2(a), the Al$_3$Fe$_4$ and Al$_2$Fe$_7$ peaks are strong, while the α-Al$_2$O$_3$ peaks are weak. This implies that the Al-rich topcoat transformed to Al$_3$Fe$_4$ and Al$_2$Fe$_7$ through the interdiffusion of Al and Fe, and was also partially oxidized to α-Al$_2$O$_3$ at the surface. Moving deeper in the coating, the concentration of Al decreased, while that of Fe increased. Hence, strong Al$_3$Fe$_4$ and weak AlFe peaks came out after the first grinding (Fig. 2(b)). Only AlFe peaks came out after the second grinding (Fig. 2(c)). Strong AlFe$_5$ peaks came out after the third grinding in addition to the α-Fe substrate peak (Fig. 2(d)). In brief, the XRD results indicated the formation of (α-Al$_2$O$_3$ surface scale)/(Al$_3$Fe$_4$, Al$_2$Fe$_7$)-mixed layer)/ (AlFe$_5$ layer)/(AlFe$_3$ layer) on the α-Fe substrate. This is explained further in Fig. 3.

The compositions of spots 1, 2, and 3, denoted in Fig. 3(a), were 35.5Al-62.10-0.3Fe-2Si-0.1S, 31.1Al-65.50-1.7Fe-0.1Cr-0.4Mn-1.1Si-0.1S, and 39.7Al-58.60-1.1Fe-0.1Cr-0.4Si-
0.1S (at%), respectively, according to FESEM-EDS analysis (Fig. 3(b)). This implies that spots 1 and 2-3 correspond to the detached and adherent α-Al2O3 scale, respectively. A small amount of substrate elements that diffused outwardly during heating presumably dissolved in the α-Al2O3 scale. The standard Gibbs free energy changes and equilibrium partial pressures for sulfidation/oxidation reaction of Al at 800 °C are as follows [22].

\[
\begin{align*}
2 \text{ Al(s)} + \frac{3}{2} \text{ S}_2(\text{g}) &\rightarrow \text{Al}_2\text{S}_3(\text{s}); \quad \Delta G^\circ = -619.6 \text{ (kJ)}; \quad P_{S_2(\text{eq})} = 7.8 \times 10^{-21} \text{ (atm)} \\
2 \text{ Al(s)} + \frac{3}{2} \text{ O}_2(\text{g}) &\rightarrow \alpha-\text{Al}_2\text{O}_3(\text{s}); \quad \Delta G^\circ = -1337.1 \text{ (kJ)}; \quad P_{O_2(\text{eq})} = 4 \times 10^{-44} \text{ (atm)}
\end{align*}
\]

Since Al2O3 is much more stable than Al2S3, the aluminum at spots 1-3 preferentially reacted with impurity oxygen in N2/0.1%H2S gas, resulting in the formation of protective α-Al2O3 in preference to the less protective Al2S3.

The alumina at spot 1 inevitably spalled for the following reasons. Firstly, growth stress developed due to the dissolution of foreign elements and the phase transformation of Al to α-Al2O3. Particularly, the sulfur incorporation deteriorated the scale adherence [23]. Secondly, thermal stress was generated due to the mismatch in thermal expansion coefficients between spot 1 and spot 2, whose
compositions were different. Thirdly, hydrogen released from
H₂S gas might have dissolved in α-Al₂O₃ and deteriorated the
adherence of α-Al₂O₃ [11]. Spots 4-5 belonged to the
(Al₁₃Fe₄, Al₅Fe₂)-mixed layer (Figs. 2(a-b) and 3(a-b)). Spots
5-8 belonged to the AlFe layer (Figs. 2(c) and 3(a-b)). The
AlFe layer consisted of coarse, columnar grains that aligned
along the interdiffusion direction of the Al and substrate
elements (Figs. 2(b-c) and 3(a-b)). AlFe can dissolve (23.3-
55)% Al, according to the Al-Fe phase diagram. Spots 8-10,
10-12, and 12-13 belonged to the AlFe₃ layer, the Al-
dissolved α-Fe layer, and the α-Fe substrate, respectively
(Figs. 2(d) and 3(a-b)).

Such can also be envisaged in the Al map shown in Fig.
3(c). The detached scale grew through the outward diffusion
of substrate elements, while the inner scale
flow, as well as the phase transformation of low density, high
Al-containing phases to high density, low Al-containing
phases, facilitated the formation of voids at spots 3-10 (Fig.
3(a)). The densities of Al₁₃Fe₄, Al₅Fe₂, AlFe, and AlFe₃ were
3.849, 3.96, 5.67, and 6.57 g·cm⁻³, respectively. The phase
transformation also produced volume shrinkage, developing
microcracks to relieve the stress. Cracks were observed
between spots 3 and 5, as shown in Fig. 3(a).

The generation of voids that can act as stress concentration
sites, the mismatch in thermal expansion coefficients among
the transformed Al-Fe phases, and the dissolution of sulfur
and possibly hydrogen also facilitated the microcracking in
the coating. The detachment of the α-Al₂O₃ surface layer, and
the development of easy-diffusion paths such as voids and
microcracks, resulted in the development of internal oxides in
the coating, as depicted in the oxygen map shown in Fig.
3(c). Like oxygen, sulfur also diffused inwardly through
voids, grain boundaries, and microcracks, but to a lesser
amount because of its very low solubility in most oxides and
metals [24]. This is recognizable from the sulfur map shown
in Fig. 3(c).

Figure 4 shows an unetched image of the corroded sample.
The etched image was shown in Fig. 3(a). In Fig. 4, a scratch
was engraved in the surface prior to corrosion in order to
locate the original sample surface. No significant outward
diffusion of substrate elements was found to have occurred,
although the outward diffusion was confirmed from the
formation of internal voids as shown in Fig. 3(a). The voids
appeared smaller down in the coating. Cracks propagated
across the (Al₁₃Fe₄, Al₅Fe₂)-mixed layer and AlFe layer (Fig.
4). Among Al-Fe intermetallics, Al₁₃Fe₄ and Al₅Fe₂ are
brittle, AlFe is ductile, and AlFe₃ is the most ductile [25].

The α-Al₂O₃ surface scale was partially detached, below
which the adherent α-Al₂O₃ layer existed (Fig. 4).

In order to evaluate the effect of aluminizing on corrosion
resistance, bare 9Cr-1Mo steel was corroded under the
corrosion condition given in Figs. 3-4. Prior to corrosion,
inert Pd powder (< 1 μmΦ) was sprayed onto the sample
surface for the marker test. The outer and inner scale was
about 75-200 and 50 μm thick, respectively, between which
agglomerated Pd powder existed (Fig. 5(a)).

Hence, it can be seen that the outer scale grew by the
outward diffusion of substrate elements, while the inner scale
grew by the inward diffusion of oxygen and sulfur (Fig. 5(b)). The XRD analysis indicated that both the outer and inner scales primarily consisted of FeS (Figs. 5(c-d)). FeS, whose defect structure is \( \text{Fe}_{1-x} \), grows quickly by the outward diffusion of Fe\(^{2+} \) ions [14]. The poor corrosion resistance of the bare 9Cr-1Mo steel was attributed to the formation of nonprotective FeS according to the reaction:
\[
\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2.
\]
Hydrogen evolution, excessive thickening of the FeS scale, and mismatch in thermal expansion coefficients between the outer and inner scale made the outer
The outer FeS scale was coarse and fragile yielding inter- and trans-granular cracking, while the inner FeS scale was fine and adherent (Fig. 5(e)). Small amounts of Cr, Mo, Mn, Si, and V diffused outwardly to dissolve in the outer FeS grains (Fig. 5(b)). The consumption of sulfur in the outer FeS scale decreased the sulfur potential and thereby increased the oxygen potential in the inner scale (Fig. 5(b)). However, the amount of oxygen in N$_2$/0.1%H$_2$S gas was at the impurity level, so the inner scale primarily consisted of FeS (Fig. 5(d)). In contrast, aluminized 9Cr-1Mo steel displayed good corrosion resistance by forming highly protective, stable α-Al$_2$O$_3$ through the reaction of Al with impurity oxygen in N$_2$/0.1%H$_2$S gas, as outlined in Figs. 2-4.

Figure 6 shows XRD/SEM/EDS/EPMA results for the 9Cr-1Mo steel after corrosion at 900 °C for 50 h. Figure 6(a) indicates the formation of α-Al$_2$O$_3$, Fe$_2$O$_3$, and FeAl$_2$O$_4$ around the AlFe$_3$ coating. This suggests that aluminum in the original Al-rich topcoat oxidized to α-Al$_2$O$_3$. At the same time, iron that diffused outward across the original Al-rich topcoat according to the concentration gradient oxidized to Fe$_2$O$_3$, and some of Fe$_2$O$_3$ was further transformed to the more stable FeAl$_2$O$_4$ spinel. When the surface was ground off, α-Fe newly came out besides α-Al$_2$O$_3$, Fe$_2$O$_3$, and AlFe$_3$ (Fig. 6(b)). This indicates the presence of α-Fe underneath the AlFe$_3$ coating containing some oxides. The above oxides and coating phases are illustrated in Fig. 6(c).

Spot 1 in Fig. 6(c) indicates ~5 μm-thick, nonadherent α-
Al₂O₃ scale with a composition of 32.5Al-66.6O-0.1S-0.1Cr-
0.2Mo-0.5Si (%), according to the EDS spot analysis (Fig.
6(d)). The dissolution of foreign elements, including sulfur,
favored spallation of the α-Al₂O₃ surface scale. Spot 2 was
located at the (adherent scale)/(AlFe₃ coating) interface. The
adherent scale was ~10 μm-thick, and mostly consisted of α-
Al₂O₃. Fe₂O₃ and FeAl₂O₄ tended to exist underneath the
adherent or nonadherent α-Al₂O₃–rich surface scale, as can
be noted from the O-Al-Fe maps shown in Fig. 6(e).

Spots 2-5 indicate a ~40 μm-thick AlFe₃ layer containing
some oxides and voids (Fig. 6(c)). Their average composition
was 26.8Al-64.4Fe-2.6O-0.2S-5.2Cr-0.4Mn-0.7Si-
0.1V (%), implying the incorporation of oxygen, sulfur, and
alloying elements in coarse AlFe₃ grains (Figs. 6(c-e)). Spots
5-12 indicate a ~110 μm-thick Fe(Al) layer. Their average
composition was 76Al-11.2Al-8.4Cr-0.5Mo-0.4Mn-0.7Si-
0.1V (%).
0.2V-2.5O-0.1S, indicating that coarse, columnar α-Fe grains were dissolved with a large amount of Al plus a small amount of alloying elements, oxygen, and sulfur (Figs. 6(e-e)). The oxygen map shown in Fig. 6(e) indicates scattered internal oxides at spots 2-5. Dark dots at spots 5-12 were voids that formed primarily due to the Kirkendall effect (Fig. 6(c)). The sulfur map shown in Fig. 6(e) indicates the presence of sulfur sporadically distributed around the surface.

Oxygen and sulfur can ingress rather easily through Kirkendall voids, and imperfect oxide scale. However, the sulfur concentration was less than 1% at spots 1-13, because the solubility of sulfur in most oxides and metals was very low [24] (Fig. 6(d)). The detached scale at spot 1 primarily consisted of fine, round α-Al₂O₃ grains, reflecting the slow growth rate of alumina (Fig. 6(f)). This is also displayed in Fig. 3(d). Despite the detachment and imperfection of the α-Al₂O₃-rich scale, the aluminized coating effectively resisted the harsh H₂S-gas corrosion.

Results obtained from Figs. 2-4 and 6 can be summarized as follows. Corrosion at 800 °C for 50 h produced an α-Al₂O₃ layer with a small amount of Fe₂O₃, an (Al₁₃Fe₄, Al₅Fe₂)-mixed layer, an AlFe layer consisting of columnar grains aligned along the interdiffusion direction, and an α-Fe(Al) layer. Corrosion at 900 °C for 50 h produced the α-Al₂O₃ and AlFe₃ layers with some Fe₂O₃ and FeAl₂O₄, and the α-Fe(Al) layer consisting of fully grown columnar grains. This transformation of the Al-Fe phases in the coating at 800-900 °C originated from the interdiffusion of Al and Fe in the Al/Fe diffusion couple. For example, the interdiffusion coefficient of Fe and Al in the iron aluminate was determined to be 5.93 × 10⁻¹⁶ and 2.92 × 10⁻¹⁴ m²/s at 550 and 640 °C, respectively [26]. Likewise, increasing the corrosion temperature from 800 to 900 °C transformed (high Al)-Fe phases to (low Al)-Fe phases, and drastically broadened the coating, as schematically illustrated in Fig. 7.

4. CONCLUSIONS

ASTM P91 steel was subjected to a hot-dip aluminized coating, which consisted of an Al-rich topcoat with a small amount of Al₁₃Fe₄ and Al₁₅Fe₂ precipitates, an Al₁₃Fe₄ layer having a small amount of Al₁₃Fe₄ precipitates, and an Al₁₅Fe₂ layer with dissolved substrate elements. Aluminizing effectively improved corrosion resistance by forming Al₂O₃-rich surface scales through the preferential reaction of Al with impurity oxygen in corrosive N₂/0.1%H₂S gas. When a bare sample was exposed, a nonprotective, thick, bilayered FeS scale formed. In the aluminized samples, substrate elements diffused outwardly, while Al, sulfur, and oxygen diffused inwardly, which broadened and transformed the Al-Fe phases during corrosion. This was accompanied by the formation of internal oxides, voids, and microcracks in the coating.

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