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Corrosion of Fe-2.25%Cr-1%Mo steels at 600-800°C in N₂/H₂O/H₂S atmospheres

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Abstract

Fe-2.25%Cr-1%Mo alloys were corroded at 600, 700 and 800 °C for up to 70 h in 1 atm of N₂/H₂O/H₂S-mixed gases. The base metal sulfidized to FeS. This at the outer scale formed by the outwardly diffusing Fe ions, whereas that at the inner scale formed by the inwardly diffusing sulfur ions. Some of FeS at the inner scale further reacted with Cr₂S₃ to the FeCr₂S₄ spinel. The alloying elements of Cr and Mo sulfidized by the inwardly diffusing sulfur ions at the inner scale. Although FeCr₂S₄ can suppress sulfidation to a certain extent, the alloys corroded fast, owing to the formation of the nonstoichiometric FeS.

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1. Introduction

In many branches of modern technology, such as high-temperature gas turbines, petrochemical units and coal gasification systems, sulfidation can occur. Generally, the sulfidation rates are 10-100 times faster than the oxidation rates because sulfides have much larger defect concentrations, and have lower melting points than the corresponding oxides [1,2].
Conventional oxidation-resistant alloys experience serious corrosion in S-containing atmospheres, due to the formation of non-protective sulfide scales where ionic diffusion is fast [3,4]. In this study, the ferritic Fe-2.25Cr-1Mo alloys (in wt.%) were corroded between 600 and 800 °C in N₂/H₂O/H₂S-mixed gases in order to understand their corrosion characteristics, because such gases were usually present in the synthetic, coal and combustion gases. Fe-2.25Cr-1Mo is the ASTM grade T22 steel. It has been utilized in oil refining, carbochemistry, coal gasification and energy generation in power plants, where high-temperature strength and corrosion resistance, creep resistance, fatigue life and good thermal conductivity are required. However, little is reported about its corrosion behavior in N₂/H₂O/H₂S gases at high temperatures. H₂S dissociates into sulfur and hydrogen ions. Hydrogen atoms ingress into the steels interstitially, form hydrogen clusters, and cause hydrogen embrittlement. Water vapor accelerates corrosion [5,6]. The corrosion of steels in the multicomponent gas containing H₂O and H₂S is therefore quite serious, very complex, and still not satisfactorily understood.

2. Experimental procedures

Fe-2.25Cr-1Mo sheets were cut into a size of 2x10x15 mm³, ground up to a 1000-grit finish with SiC paper, ultrasonically cleaned in acetone, and corroded at 600, 700 and 800 °C for up to 70 h using an apparatus shown in Fig. 1. Each test coupon was suspended by a Pt wire inside a quartz reaction tube at the hot zone of an electrical furnace. An atmospheric gas mixture that consisted of 0.9448 atm of N₂, 0.031 atm of H₂O, and 0.0242 atm of H₂S was achieved by bubbling the N₂ gas through the water bath kept at 25 °C, while flowing the H₂S gas into the reaction tube. The employed N₂ gas was 99.999% pure, and H₂S gas was 99.5% pure. The corroded test coupons were characterized by a scanning electron microscope (SEM), an X-ray diffractometer (XRD) with Cu-Kα radiation, and an electron probe microanalyzer (EPMA).

![Fig. 1. Corrosion testing apparatus.](image-url)
3. Results and discussion

The corrosion kinetics of Fe-2.25Cr-1Mo alloys in N2/H2O/H2S gases at 600-800 °C are shown in Fig. 2. Weight gains displayed are the sum of weight gain due to scaling and weight loss due to scale spallation. Large weight gains were recorded, indicating vastly fast corrosion kinetics. Local cracking, partial spallation and void formation in the formed sulfide scales were unavoidable, the extent of which varied for each test run. The scale failure became more serious as corrosion progressed. The corrosion seemed to follow the linear rate law, implying poor corrosion resistance. Water vapor accelerates the corrosion rates, decreases the plasticity of oxide scale, and develops voids. It transports in the scale as H2(g) and H2O(g) within voids, cavities, and cracks, and as H atom by dissolving in the lattice and thereby affecting point defect concentration [5,6]. The H2S gas seriously increases the corrosion rates. It reacts with Fe according to the following reactions.

\[ \text{Fe} \rightarrow \text{Fe}^{++} + 2e \]
\[ \text{H}_2\text{S} \rightarrow 2\text{H}^+ + \text{S}^- \]

The net reaction is Fe+H2S → FeS+2H.

FeS has a very high concentration of cation vacancies so that it grows rapidly by the outward diffusion of Fe++ ions, which forms voids at the scale-metal interface [1,7].

![Graph showing Weight Gain versus Corrosion Time Curves of Fe-2.25Cr-1Mo alloys at 600, 700 and 800 °C for 70 h in N2/H2O/H2S gases.](image)

Fig. 2. Weight gain versus corrosion time curves of Fe-2.25Cr-1Mo alloys at 600, 700 and 800 °C for 70 h in N2/H2O/H2S gases.

Figure 3 shows the XRD patterns of Fe-2.25Cr-1Mo alloys corroded at 600-800 °C for 40-70 h in N2/H2O/H2S gases. The scale consisted primarily of FeS and FeCr2S4 (Fig. 3(a)). The FeCr2S4 spinel enhances the corrosion resistance, because it reduces the cross-sectional area for diffusion, and diffusion in the spinel was relatively slow. As shown in Figs. 3(b) and (c), the scale consisted primarily of the outer FeS layer and the inner (FeS, FeCr2S4)-mixed layer. In Fig. 3(d), only the outer FeS layer was detected, because the X-ray beam could not penetrate the FeS layer. No corrosion products related with Mo were detected from the XRD analyses, due to their small amount or dissolution in FeS or FeCr2S4.
Fig. 3. XRD patterns of scales formed on Fe-2.25Cr-1Mo after corrosion in N\textsubscript{2}/H\textsubscript{2}O/H\textsubscript{2}S gases. (a) 600 °C/40 h, (b) 600 °C/70 h; outer scale, (c) 600 °C/70 h; inner scale, (d) 800 °C/40 h.

The scale formed after corrosion at 700 °C for 70 h in N\textsubscript{2}/H\textsubscript{2}O/H\textsubscript{2}S gases was analyzed, as shown in Fig. 4. The outer, coarse, faceted FeS grains kept growing outward, as Fe continuously diffused out from the matrix via the pre-formed FeS grains to the outermost surface (Fig. 4(a)). The outer, fast-growing layer was susceptible to cracking and detached off from the inner (FeS, FeCr\textsubscript{2}S\textsubscript{4})-mixed scale, owing to excessive, compressive stress developed in the thick scale (Fig. 4(b)). Cracks propagated inter- and transgranularly, because the formation of FeS from Fe resulted in 261% volume expansion. FeS was fragile, and nonadherent because it grew fast and formed voids at the scale-matrix interface [8]. Cracking and spallation of scales facilitated the ingress of corrosive gases. Hence, Fe-2.25Cr-1Mo alloys corroded almost linearly in Fig. 2.

Fig. 4. SEM analyses of Fe-2.25Cr-1Mo after corrosion at 700 °C for 70 h in N\textsubscript{2}/H\textsubscript{2}O/H\textsubscript{2}S gases. (a) top view of the scale, (b) cross-sectional image.
The scale formed after corrosion at 800 °C for 70 h in N2/H2O/H2S gases was analyzed, as shown in Fig. 5. It cracked and detached. The outer FeS layer had either an equiaxed or columnar structure, and the inner (FeS, FeCr2S4)-mixed layer consisted of fine grains (Fig. 5(a)). Cr, Mo, and oxygen were segregated in the inner scale rather than the outer scale (Fig. 5(b)). The outer scale formed by the outward diffusion of predominantly Fe and a small amount of Cr and Mo, whereas the inner scale formed by the inward diffusion of predominantly sulfur and a small amount of oxygen. The compositional difference between the outer and inner oxide layers seemed to aggravate stresses in the scale, facilitating crack propagation. The FeCr2S4 spinel in the inner scale suppresses the outward diffusion of iron to reduce the growth rate of the outer FeS scale, and inward transport of sulfur by forming a little dense or adherent inner scale. The inner FeS dissociates according to the reaction; FeS=Fe^{2+}+1/2S_2+2e^{-} [9]. This delivers S gas for the inward growth of the innermost layer, and the released iron ions and electrons diffuse to the outer surface to form FeS.

Fig. 5. EPMA analyses of Fe-2.25Cr-1Mo after corrosion at 800 °C for 70 h in N2/H2O/H2S atmosphere. (a) cross-sectional image, (b) line profiles.

4. Conclusions

Fe-2.25Cr-1Mo alloys were corroded at 600, 700 and 800 °C for up to 70 h in N2/H2O/H2S gases under total pressure of 1 atm. Sulfidation occurred almost linearly. The outer scale consisted primarily of FeS that formed by the outward diffusion of iron ions. The inner scale that consisted primarily of FeCr2S4 and FeS formed by the inward diffusion of predominantly sulfur and a small amount of oxygen. The FeCr2S4 spinel could not effectively deter corrosion, because it was intermixed with nonprotective FeS. The outer scale was coarse, the inner scale was fine, and the whole sulfide scale formed was nonadherent, and susceptible to cracking.
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References