

Corrosion of Fe-15Ce alloy in three mixed-gas atmospheres^①

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[Abstract] The corrosion behavior of Fe-15Ce alloy was studied at 700 °C in H₂-CO₂, H₂-H₂S and H₂-H₂S-CO₂ mixtures. Internal oxidation occurs on the Fe-15Ce alloy corroded in H₂-CO₂ mixtures. The complex scales are formed during the corrosion of the alloy in H₂-H₂S and H₂-H₂S-CO₂ mixtures. No exclusive Ce scales can be founded in any case. This is because of the limited solubility of Ce in the base metal and the presence of intermetallic compounds in the alloy. The corrosion rate of the alloy at 700 °C in H₂-H₂S-CO₂ is lower than that in H₂-H₂S, and it is the lowest in H₂-CO₂.

[Key words] Fe-15Ce alloy; mixed-gas; corrosion

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1 INTRODUCTION

Metallic materials for high-temperature applications exposed in sulfur and oxygen atmospheres, such as those prevailing in the gas coolers of coal gasification plants^[1~3], will face bad corrosion. The corrosion resistance of common base metals, such as Fe, Co and Ni, may be significantly improved by the addition of refractory metals such as Mo and Nb^[4~7]. However, the corrosion rates of binary Fe, Co and Ni-base alloys containing Mo or Nb to 35% ~ 40% are still too high for practical applications^[4~7]. In view of Ce sulfides such as CeS and Ce₂S₃ are much stabler than Fe sulfides and have quite high melting points^[8]. So the corrosion of Fe-15Ce alloys in H₂-CO₂, H₂-H₂S and H₂-H₂S-CO₂ mixtures at 700 °C will be studied to improve the corrosion resistance of base metal Fe.

2 EXPERIMENTAL

A Fe-Ce alloy with a nominal Ce content of 15% (Fe-15Ce) has been prepared by arc-melting mixtures of appropriate amounts of the two pure metals (99.99%) under Ti-gettered argon atmosphere. The Fe-15Ce alloy is a two-phase mixture of pure Fe (α phase) with the intermetallic compound Fe₁₇Ce₂ (β phase, Fig. 1). Samples with a surface area of about 2.5 cm² were obtained by cutting the original ingots by means of a diamond-wheel saw, ground down to 600 grit emery paper, washed in water, alcohol and acetone and dried immediately before use. Corrosion kinetic measurements were carried out by means of a

Cahn microbalance mod 2000. The corrosive environments were H₂-CO₂, H₂-H₂S and H₂-H₂S-CO₂ mixtures controlled by calibrated electronic mass-flow controllers (Union Carbide). H₂-CO₂ mixtures produced an oxygen pressure of 10⁻²¹ MPa, H₂-H₂S mixtures produced a sulfur pressure of 10⁻⁹ MPa, H₂-H₂S-CO₂ mixtures produced an oxygen pressure of 10⁻²¹ MPa and a sulfur pressure of 10⁻⁹ MPa at 700 °C. At the same time the balance can be protected by a counter flow of nitrogen.

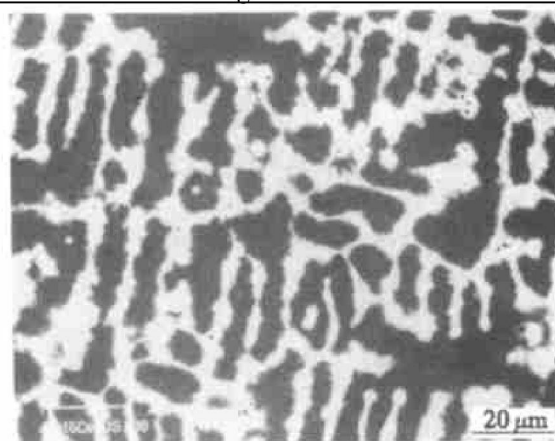


Fig. 1 Microstructure of Fe-15Ce
Dark phase—Fe (α); Light phase—Fe₁₇Ce₂ (β)

Corroded samples were examined by means of X-ray diffraction (XRD), optical microscopy (OM) and electron scanning microscopy (SEM) for phase identification and structural analysis.

3 RESULTS

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3.1 Corrosion kinetics

The kinetic curves for the corrosion of the Fe-15Ce at 700 °C in H_2 -CO₂, H_2 -H₂S and H_2 -H₂S-CO₂ mixtures are shown in Fig. 2. In the three atmospheres, the corrosion kinetic curves of the Fe-15Ce alloy are generally regular, the rates decreasing with time. The oxidation rate of Fe-15Ce in H_2 -CO₂ decreases continuously with time more rapidly than that according to the parabolic rate law, so that the instantaneous parabolic rate constant (iprc) is also decreasing continuously with time. The iprc increases with time and tends to constant after an initial stage in H_2 -H₂S. The iprc also increases continuously with time in H_2 -H₂S-CO₂. Approximate values of the parabolic rate constants are reported in Table 1. The corrosion rate of the Fe-15Ce alloys in H_2 -H₂S-CO₂ mixtures is lower than that in H_2 -H₂S mixtures and is the lowest in H_2 -CO₂ mixtures.

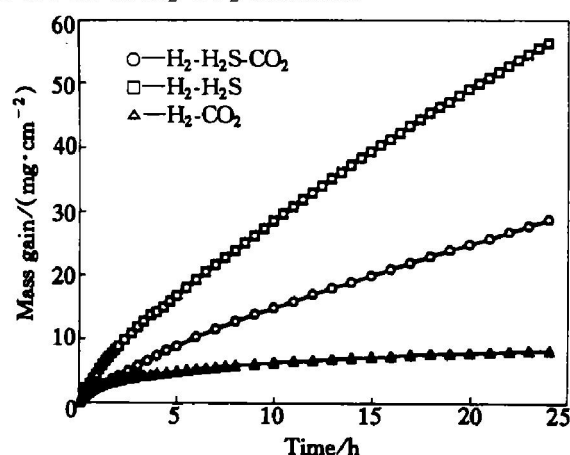


Fig. 2 Kinetics of corrosion of Fe-15Ce in H_2 -CO₂, H_2 -H₂S and H_2 -H₂S-CO₂ mixtures at 700 °C

Table 1 Approximate parabolic rate constants ($g^2 \cdot cm^{-4} \cdot s^{-1}$) for Fe-15Ce corroded in H_2 -CO₂, H_2 -H₂S and H_2 -H₂S-CO₂ mixtures for 24 h at 700 °C

Value	H_2 -CO ₂	H_2 -H ₂ S	H_2 -H ₂ S-CO ₂
Initial values	2.2×10^{-9}	1.6×10^{-8}	1.2×10^{-9}
Final values	2.6×10^{-10}	8.1×10^{-8}	Linear

3.2 Scale microstructure and composition

Scale micrographs of Fe-15Ce alloy samples corroded in H_2 -CO₂, H_2 -H₂S and H_2 -H₂S-CO₂ mixture are shown in Figs. 3, 4 and 5, respectively. Corrosion of Fe-15Ce in H_2 -CO₂ mixture produces a thick layer of internal oxidation, containing a mixture of α -Fe, the double oxide FeCe₂O₄ and CeO₂ (Fig. 3(a)). The size, number, shape and spatial distribution of the dark island phases in Fig. 3(b) correspond closely to those of the particles of α phase in the original alloy. While the islands of β phase transform into a gray mixture zones of Fe with Ce-rich compounds.

Corrosion of Fe-15Ce in H_2 -H₂S mixtures forms

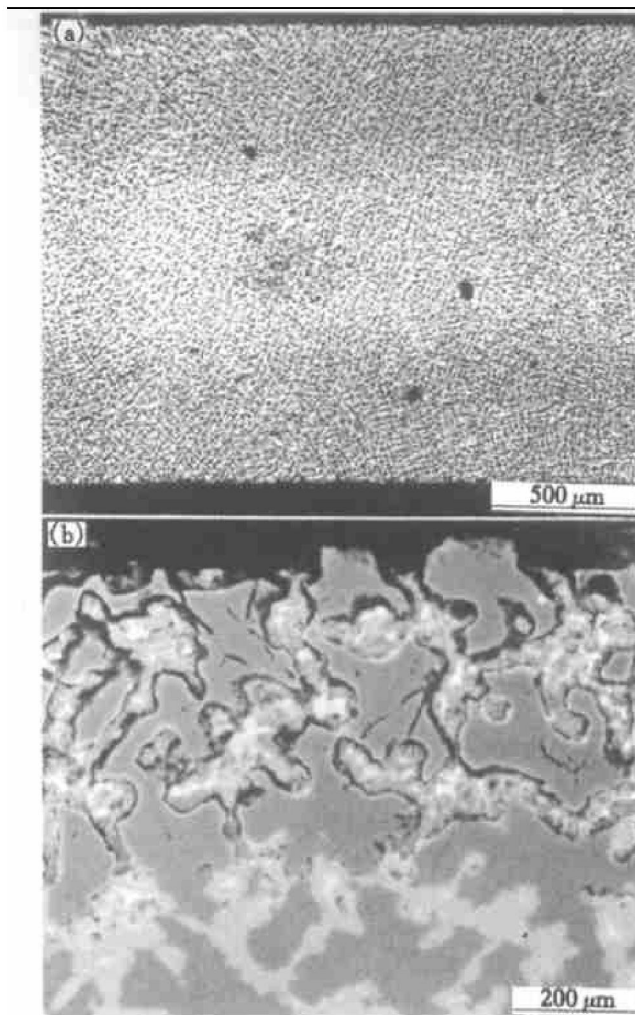


Fig. 3 Cross section micrographs of Fe-15Ce corroded in H_2 -CO₂ mixtures
(a) —General view;
(b) —Enlarged view of sample surface region

complex scales containing an outermost layer of pure FeS followed by an inner region of complex composition containing compounds of both alloy components and then by a region of internal sulfidation of Ce (Fig. 4(a)). The outer FeS layer contains a significant number of large pores, forming a number of sublayers parallel to the alloy surface. The interface between the outer layer and middle mixed zone is very sharp and flat and seems to correspond to the alloy original surface. Middle mixed zone is composed of a mixture of FeS and Ce sulfides, and some FeS has spalled off (black areas). In innermost scale zone EDX analysis shows that sulfur is only present in association with Ce, but not with Fe, so that Fe is effectively present as a metal. Innermost scale zone is an internal sulfidation region of Ce composed of a mixture of Fe and Ce sulfides (Fig. 4(b)).

In H_2 -H₂S-CO₂ mixtures, the Fe-15Ce alloy formed an external scale of pure FeS plus a mixed layer containing compounds of both iron and cerium (Fig. 5). In this mixed scale layer iron was present as FeS or double Fe-Ce oxides. The mixed layer contains

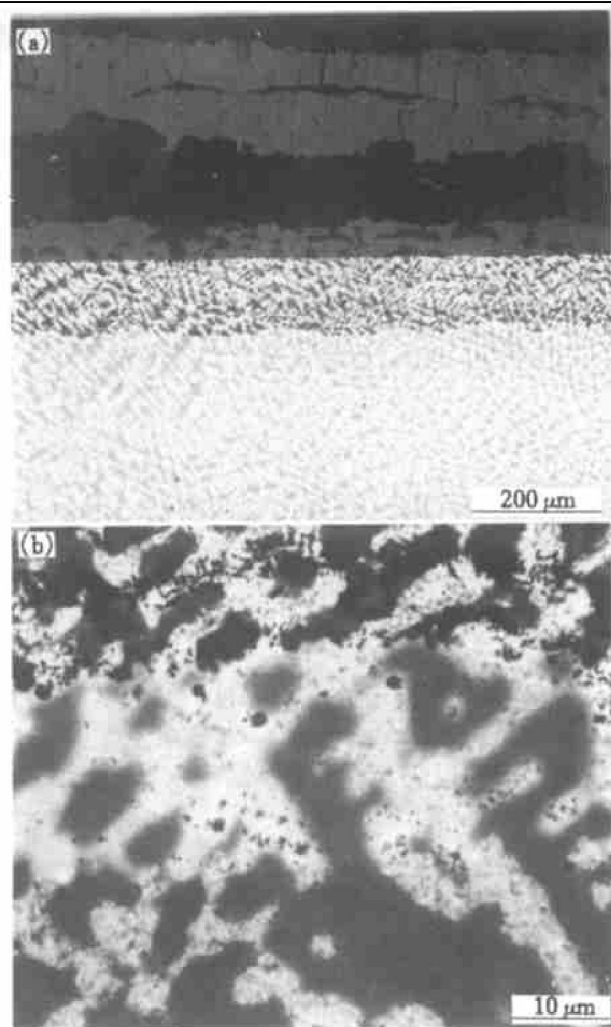


Fig. 4 Cross section micrographs of Fe-15Ce corroded in H_2 - H_2S mixtures

(a) —General view; (b) —Enlarged view of inner scale region

large islands of FeS corresponding to the α phase particles in the original alloy, some of which has partly spalled off (black areas). While the rest of the scale is apparently composed of a fine mixture of two kinds of regions: the lightest particles are composed of nearly pure cerium oxide, while the middle gray regions contain a mixture of different phases, including FeS plus cerium compounds. Moreover, the corroded samples always contain an innermost region of internal attack of cerium: the external zone of this region contains a mixture of sulfur and oxygen, while the inner zone contains only oxygen. The distribution of the cerium compounds in both the mixed region and in the zone of internal oxidation corresponds closely to that of the cerium-rich phases in the original alloy.

4 DISCUSSION

The oxygen pressure in H_2 - CO_2 mixture is in the field of stability of Fe_3O_4 , Fe-15Ce alloy would form an external layer of Fe oxide, which however is not observed. On the contrary, the oxygen pressures used are always much higher than that for Ce and Ce oxide

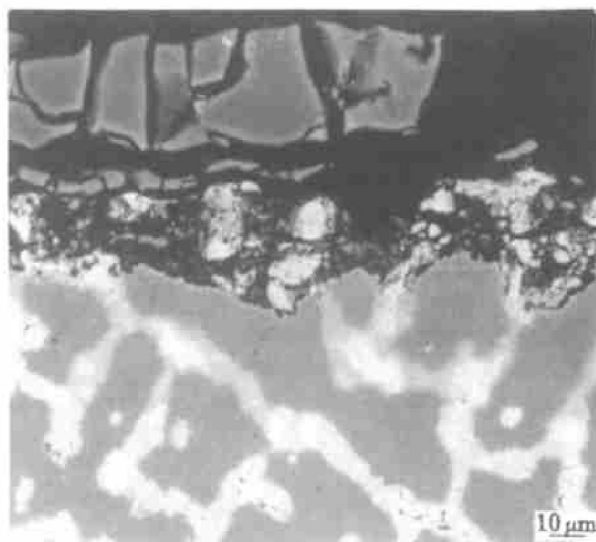


Fig. 5 Cross section micrographs of Fe-15Ce corroded in H_2 - H_2S - CO_2 mixtures

equilibrium, so that Ce would be oxidized either internally or externally to the alloy. In the present alloy, the internal oxidation of Ce occurred due to the low solubility of cerium in iron and the presence of intermediate phases in the alloy. The microstructure of the corrosion-affected region is closely related to that of the original alloy. It means α phase remain in metal state, while the β phase will transform into a very fine mixture of Fe and Ce oxides, and the mixture will correspond closely to that of the β phase in the original alloy.

The partial pressure of sulfur in H_2 - H_2S mixture is high enough to form Fe sulfide and Ce sulfide. So corrosion of Fe-15Ce in the mixture formed complex scales. In the innermost corrosion-affected region of the alloy, the partial pressure of sulfur is low, this implies that the innermost corrosion-affected alloy region should contain a mixture of Ce sulfide with metal Fe. Moving outwards from the innermost corrosion-affected region of the alloy, the partial pressure of sulfur in this region gradually becomes high where Fe is also transformed into its sulfide to form a mixed region. The microstructure of the mixed region is quite complex and strictly related to that of the original alloy. In fact in this region the α phase is directly converted into the corresponding sulfide, even though a part of Fe originally present in this zone has been diffused outwards to form the external FeS layer. The Ce-rich phase transform into a mixture of Ce sulfide with FeS. In outermost layer the partial pressure of sulfur is the highest, it should contain the compounds of both metals but only FeS. The presence of the outermost layer of pure FeS is due to kinetic reason, due to the much faster growth rate of FeS with respect to Ce sulfides, due to the fact that FeS grows by means of outward Fe diffusion.

The sulfur pressure in H_2 - H_2S - CO_2 mixtures always falls in the field of stability of FeS, and the oxy-

gen pressure is in the field of stability of Fe_3O_4 . In agreement with this, the corrosion of Fe in the alloy fields FeS or Fe oxides, where mainly FeS as the oxidation of Fe-15Ce alloy in $\text{H}_2\text{-CO}_2$, Fe oxide is not observed. While the corrosion of Ce produces various cerium compounds, including CeO_2 , CeS , Ce_2S_3 and the oxysulfides $\text{Ce}_2\text{O}_2\text{S}$ and $\text{Ce}_4\text{O}_4\text{S}_3$. So the corrosion of Fe-15Ce produces an external FeS layer overlying an inner complex multiphase layer containing a mixture of iron sulfide with various cerium compounds, followed by a region of internal attack of cerium. The microstructure of the region of internal corrosion is strictly related to that of the original alloy. In particular, the islands of α phase in the region of internal attack of cerium keep the same number, shape and spatial distribution as in the original alloy. Conversely, in the region of internal attack, the β phase decomposes into a mixture of α iron and cerium compounds. The main difference of the microstructure of the intermediate scale layer from the internal corrosion zone is that iron is converted into FeS as the interface between the two regions moves inwards with time. The sulfur pressure prevailing at this interface corresponds to that for the Fe/FeS equilibrium. The corresponding oxygen pressure is not well defined thermodynamically, but must be sufficient to oxidize cerium. The overall structure of these scales is very similar to that observed in the sulfidation of the same alloy in $\text{H}_2\text{-H}_2\text{S}$ mixtures, the only difference being the presence of oxygen in the intermediate and innermost scale regions in the present case.

In spite of the large differences between the stability of the sulfides and the oxides of the two metals, a continuous external layer of cerium compounds, which in principle could reduce the rate of iron corrosion quite significantly, is never observed for the Fe-15Ce alloys in above three atmospheres. This is very likely a consequence of the low solubility of cerium in iron and of the presence of intermediate phases in the alloy examined. In fact, the critical concentration of B required to form continuous external BO scales in the oxidation of two-phase binary $\alpha + \beta$ alloys or even of single-phase β alloys under low oxygen pressures is larger than that for solid-solution alloys and increases as the solubility of B in A decreases^[9,10]. In particular, if the solubility of B in α phase becomes too small, the formation of an external layer of pure BO may even be prevented completely^[9,10]. Thus, a cerium content of 15%, corresponding to about 6.9% (mole fraction), is insufficient to avoid the sulfidation or oxidation of iron in the present three mixed atmospheres. The lowest corrosion rate of the Fe-15Ce alloys in $\text{H}_2\text{-CO}_2$ mixtures is related to the absence of Fe oxides or sulfides in the sample corroded. Reactions of metals in mixed sulfidizing-oxidizing environments lead in most cases to the production of scales containing both metal oxides and sulfides. The

rates of these reactions are often significantly higher than those measured in pure oxygen at the same temperature, mainly as a result of the presence of sulfides in the scales. In view of the high stability of metal oxides compared with sulfides, the forming of metal oxides is superior to sulfides. If the gas composition is in the oxide stability field, the sulfide is not stable and is not expected to form at the outer scale surface. The sulfide can still be produced inside the scale. In principle, this process could take place either by solid-state diffusion of sulfur and diffusion along the grain boundaries or by penetration of a gaseous species through discontinuities in the scale, and reaction with the metal within or beneath the scale. However, since the presence of sulfides in the scale generally produces high reaction rates with high metal activities at the outer scale surface, the coupled formation of oxides and sulfides can take place for reasonably long times under conditions of non-equilibrium with the gas. Thus, once initiated, the process tends to become self-sustaining and results in overall rapid metal consumption. The reverse situation is also possible, as the formation of oxide in a mixture with sulfide is observed under condition where the sulfide is stable alone. In any case, it is not deleterious, as it tends to produce a decrease rather than an increase in the rate of metal consumption^[1]. The corrosion of Fe-15Ce alloy in $\text{H}_2\text{-H}_2\text{S-CO}_2$ mixtures is an instance.

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