CORROSION OF A Co-15 Ce ALLOY

UNDER 10^{-3} Pa S_2 AT 700 ℃ [①]

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ABSTRACT   The corrosion behaviors of a Co-Ce alloy containing approximately 15% Ce, pure Co and pure Ce have been studied at 700 ℃ in H_2-H_2S mixtures providing a sulfur pressure of 10^{-3} Pa. It is shown that the alloy corroded more slowly than pure cobalt, but more rapidly than pure cerium. The corrosion of the alloy produced duplex scales, containing an outermost layer of pure cobalt sulfide and an inner layer of a cerium sulfide mixed with cobalt sulfide and an innermost layer where cerium sulfide was mixed with cobalt metal. The cobalt sulfide formed a continuous CoS layer on the surface of the alloy, even though at rates reduced with respect to pure cobalt. Thus, a cerium content of 15% was not sufficient to prevent the sulfidation of the base metal. These results were interpreted by taking into account the limited solubility of cerium in the base metal and the presence in the alloy of intermetallic compound rich in cerium.
Key words   Co-Ce alloy   sulfidation   corrosion

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1   INTRODUCTION

Metallic materials for high-temperature applications in atmospheres presenting high partial pressures of sulfur and low partial pressures of oxygen, such as those prevailing in the operation of the gas cooler of coal gasification plants, must have a good resistance to sulfidation. The corrosion resistance to sulfur of common base metals, such as iron, cobalt and nickel may be significantly improved by the addition of refractory metals presenting quite low rates of sulfidation such as Nb and Mo. However, the corrosion rates of binary Fe, Co and Ni alloys containing Nb or Mo are still too high even for refractory metals additions up to 30% ~ 40%[1, 2]. This is mainly due to the formation of double compounds of variable composition between the sulfides of Mo and Nb and those of the base metals, through which the latter can diffuse rather

rapidly, even though significantly more slowly than the corresponding pure sulfides. The present study concerns the sulfidation of a cobalt alloy with cerium, selected in view of the very high thermodynamic stability and high melting points of cerium sulfides[3]. Moreover, the cerium is different from Nb and Mo, it has not double compounds with the base metals[4]. Thus, the addition of cerium could be expected to produce a large reduction in the rate of sulfidation of the Co-Ce alloys with respect to pure cobalt. The sulfidations of pure Ce and pure Co have also been studied for comparison purposes.

2   EXPERIMENTAL

Experimental materials are pure Ce, pure Co and a cobalt-cerium alloy with a nominal cerium content of 15% (Co-15Ce), whose microstructure is shown in Fig. 1. A mixture of ap-

propriate amounts of two pure metals (99. 99%) has been prepared by arc-meltig under an argon atmosphere. The alloy is a two-phase mixture of pure cobalt (α phase, dark) and the intermetallic compound Co_5Ce (β phase, light). It does not show clearly non-homogeneity in composition.

Fig. 1   Microstructure of Co-15 Ce (SEM/ BEI)

Samples with a surface area of about 2. 5 cm^2 were obtained by cutting the original ingot, ground down to 600 grit emery paper, washed in water, alcohol and acetone and dried immediately before use. Corroded samples were examined by means of X-ray diffraction (XRD), optical microscopy (OM), scanning electron microscopy (SEM) and energy-disperse X-ray microanalysis (EDX) for phase identification and structural analysis.

Corrosion experiments were carried out with the help of a Cahn 2000 microbalance mod, equipped with a system to evacuate the reaction chamber and to introduce corrosive mixture, and at the same time the balance was protected with a counterflow of nitrogen. The corrosive atmospheres were obtained by means of adding pure hydrogen to cylinders containing H_2-H_2S mixtures of appropriate and known composition using calibrated mass flow controllers (Union Carbide) and contained 1. 87% H_2S (in volume) to provide 10^{-3}Pa S_2 at 700 ℃.

3   RESULTS

3. 1   Kinetics

The kinetics curves for the corrosion of Co-15Ce, pure Co and pure Ce at 700 ℃ under 10^{-3} Pa S_2 are shown in Fig. 2. The corrosion rate of the alloy is intermediate between those of pure Co and pure Ce. The instantaneous parabolic rate constant (IPRC) increases continuously with time. The kinetics curve of pure cerium at 700 ℃ is approximately parabolic, with an initial oscillation of the IPRC, which becomes nearly constant after about 6 h. the kinetics curve of pure Cobalt is nearly a straight line.
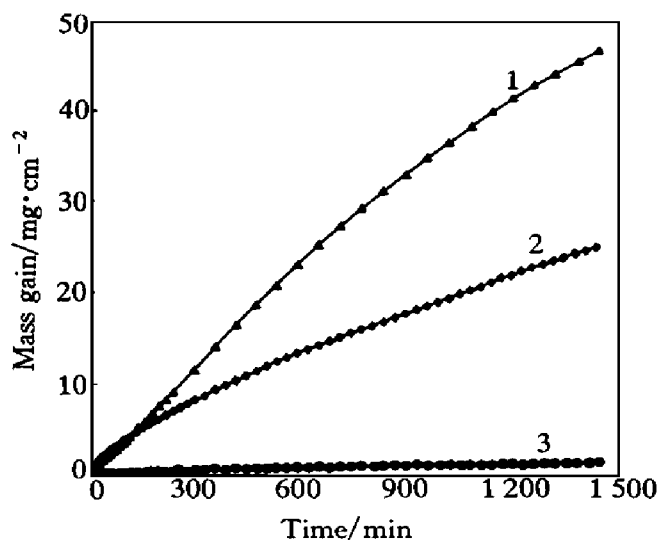

Fig. 2   Corrosion kinetics of the two pure metals and Co-15Ce under 10^{-3}Pa S_2 at 700 ℃.

1 —Pure Co; 2 —Co-15Ce; 3 —Pure Ce

3. 2   Scale microstructure and composition

Cross sections of Co-15Ce corroded at 700 ℃ under 10^{-3} Pa S_2 are shown in Fig. 3. this alloy forms duplex scales containing an outermost layer of pure cobalt sulfide (CoS) followed by an inner region of complex composition in which both alloy components are present. The interface between the two scale layers is very flat and corresponds to the alloy original surface. No cerium is detected in the external CoS scales, so that this element is completely confined in the mixed zone. In corrosion region Ce is present either as a sulfide (mainly Ce_2S_3) or as an oxysulfide ($Ce_2O_2S_2$, Ce_2O_2S), as observed also in the

sulfidation of pure Ce. No depletion of cerium in the alloy is observed beneath this region, in spite of the large difference in the thermodynamic stability of the sulfides of the two alloy components.

When the inner mixed layer is observed at sufficiently large magnifications it appears to be divided into an external and an internal zone. According to the SEM/BEI observations and EDX analyses, the outer zone of the inner mixed scale layer is generally composed of a mixture of large islands of single-phase cobalt sulfide (dark, partly spalled) dispersed in a matrix, which is clearly two-phase and composed of a mixture of cerium sulfide (mostly Ce_2S_3, light phase) and CoS. This matrix contains both cobalt and cerium with an atomic ratio Co/ Ce of around 2/ 1, which is much lower than that in the β phase of the alloy, as a consequence of the loss of cobalt, the external CoS layer is formed. The large particles of cobalt sulfide are generated by the sulfidation of the primary cobalt particles in the alloy and have the same spatial distribution as the islands of α phase in the original alloy. On the contrary, the cerium-rich phase of the alloy transforms into a complex mixture of CoS and CeS_z.

The structure of the innermost zone of the mixed region is different because the α phase remains in the metal state, while the β phase transforms into a very fine mixture of cerium sulfide and cobalt metal, whose particles cannot be resolved even under high magnification. However, EDX point analysis shows that this region contains cerium and sulfur with an atomic ratio of 1/ 1.

4   DISCUSSION

A schematic isothermal phase diagram of the Co-rich corner of the ternary Co-Ce-S system is shown in Fig. 4, in which only the pure sulfides CoS and Ce_2S_3 have been taken into account. The partial pressure of sulfur in the gas is denoted as P_g, while those corresponding to the α-CoS-Ce_2S_3, Co-CoS, α-β-Ce_2S_3 and β-γ-Ce_2S_3 are denoted as p_1, p_2, p_3 and p_4, respectively. In view of the large difference between the stability of the sulfides of the two metals, it is assumed that the alloy composition for the simultaneous equilibrium with the two sulfides is in the stability field of the α phase. According to this diagram and the absence of cerium depletion in the alloy observed experimentally, it is concluded that the diffusion path in Fig. 4 corresponds
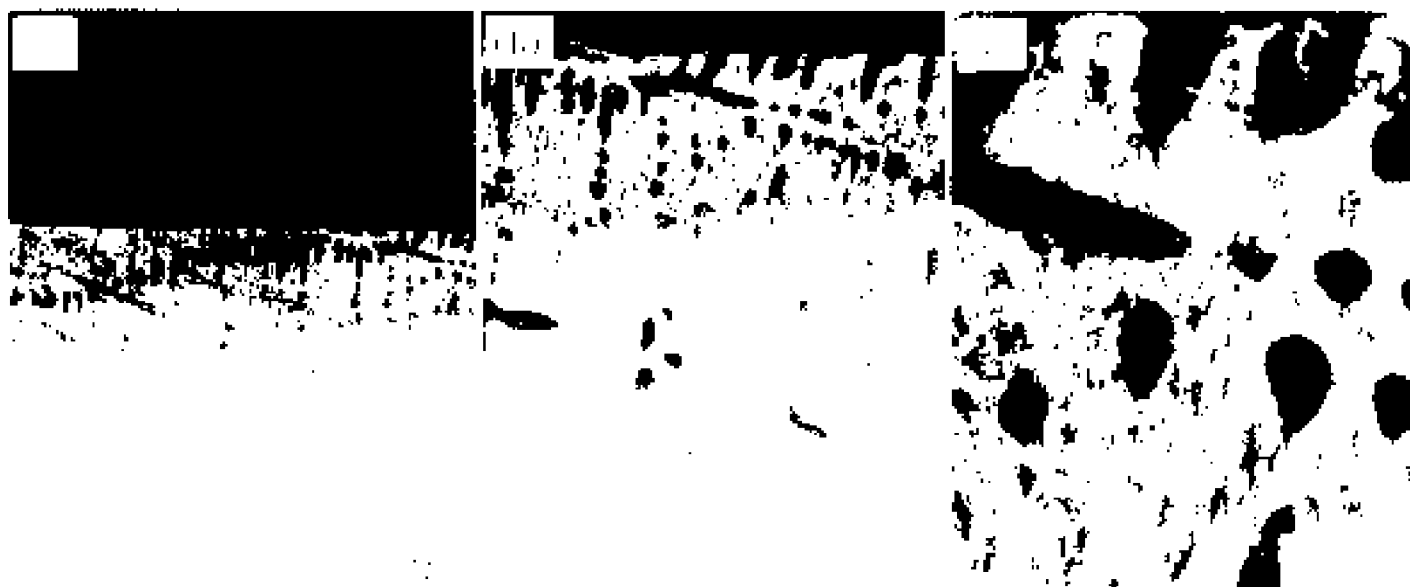

Fig. 3   Cross sections (SEM/ BEI) of Co-15Ce corroded under 10^{-3}Pa S_2 at 700 ℃
(a) —General view; (b) —Expanded view of intermediate and inner scale layers;
(c) —Expanded view of intermediate scale layer

simply to a vertical straight line, as expected for two-phase alloys with a negligible diffusion of the metal components in the metal substrate[5]. In view of this, the innermost corrosion-affected alloy region is expected to contain a mixture of cerium sulfide with cobalt metal. In the outward direction this should be followed by a second region where also cobalt is transformed into its sulfide. This analysis is essentially correct in predicting the actual structure of the scales growing on the present alloys during sulfidation. However, the details of the microstructure of the inner mixed region are complex and strictly related to the microstructure of the original alloys, and particularly to the presence of more than one phase. In fact, the α phase is directly converted in-situ into the corresponding sulfide, even though part of cobalt is able to diffuse outwards to form the external CoS layer. On the contrary, the cerium-rich phase transforms either into a mixture of CeS_z and CoS, part of which is again used to support the growth of the outermost cobalt sulfide layer.
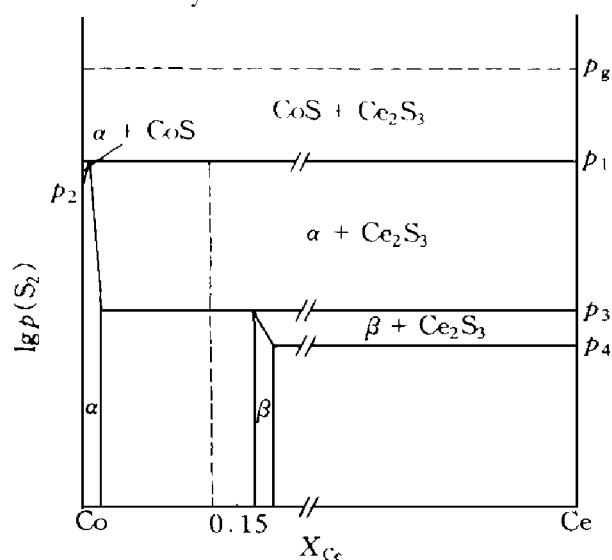

Fig. 4　Schematic isothermal phase diagram of ternary Co-Ce-S system

At the interface of the alloy, cerium from the β phase is transformed into sulfide, yielding a two-phase mixture of cobalt metal plus CeS_z. Since the particles of the two phases are produced by a rather fast solid-state reaction, their size is very small, so that usually they cannot be resolved. When the local sulfur pressure rises up to the Co/CoS equilibrium value and above,

cobalt is transformed into CoS. The sulfidation of cerium at the interface of the alloy does not involve any cerium depletion in the metal substrate, only a penetration of sulfur through the cobalt matrix. This process is probably assisted by the large volume increase associated with the sulfidation of cerium, which may produce large concentrations of dislocations, acting as preferential penetration paths for sulfur[6]. Moreover, a preferential penetration of sulfur may also occur along the cobalt/CeS_z interface, as the internal oxidation of M-Nb alloys[7].

The formation of the outermost layer of pure CoS is only due to kinetic reasons, and more precisely to the much faster growth rate of CoS with respect to CeS_z, as well as to the fact that the growth of cobalt sulfides occurs by means of outward cation diffusion[3]. Thus the presence of CeS_z in the mixed region should reduce the rate of sulfidation of the alloy with respect to that of pure cobalt by reducing the cross-section area available for the outward cobalt transport. Theoretically, the presence of sufficient concentrations of cerium in the alloy could block the sulfidation of cobalt completely. The first of the two main factors, which may be responsible for the absence of this effect, is the rapid outward diffusion of cobalt through a continuous network of cobalt sulfide, at variance with cerium, which thus remains confined in the inner region. The second is related directly to the very low solubility of cerium in cobalt and to the corresponding two-phase nature of the present alloy. In fact, the transition from the internal to the external oxidation of the most-reactive component in the corrosion of binary two-phase A-B alloys is more difficult than for solid-solution alloys under the same values of all the relevant parameters, requiring higher B contents[8]. Moreover, the critical B content for this transition in two-phase alloys is also a function of the solubility of B in A and tends to increase as this solubility value decreases[8]. A similar situation also applies to the transition from the formation of mixed external AO+ BO scales to the exclusive external growth of BO[9]. Therefore, the relatively low cerium content of Co-15Ce is only

able to reduce the rate of sulfidation of this alloy with respect to that of pure cobalt, but not to prevent completely the corrosion of the base metal.

The absence of outward diffusion of cerium is not only connected with its very low sulfidation rate, and slow transport through the cerium sulfide, but also with the very low solubility and diffusivity of cerium in cobalt sulfides. A similar behavior has already been observed in the sulfidation of cobalt alloys containing refractory metals such as niobium or molybdenum[2]. Thus, cerium remains in the metal consumption region and marks approximately the original location of the alloy surface.

The presence of some cerium oxysulfide in samples of pure cerium and of the alloy corroded in H_2-H_2S mixtures, that must be due to the existence of traces of impurities of oxygen-bearing compounds in the gas mixtures used.

5 CONCLUSIONS

The sulfidation of a cobalt alloy containing approximately 15% cerium showed a significant decrease in the rate of corrosion with respect to pure cobalt under 10^{-3}Pa S_2 at 700 ℃, however, the sulfidation of cobalt was not completely prevented and the corrosion rates of the alloy were too high for practical applications. The scales were duplex and contained an outermost layer of pure cobalt sulfide, an inner layer of a cerium sulfide mixed with cobalt sulfide and an innermost layer where cerium sulfide is mixed with cobalt metal. No cerium depletion was observed in the alloy beneath the scale, as a consequence of the very low solubility of cerium in cobalt. The scale structures observed are in agreement with the thermodynamic predictions based on the different stability of the cobalt and cerium sulfides. The microstructure of the inner scale region was closely related to that of the original alloy and in particular to the spatial distribution of the two metal phases as a consequence of the very low solubility of cerium in cobalt and of the two-phase nature of the alloy.

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