Gas Permeation through Oxide Scale Formed at Low Oxygen Potentials

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The severe carburization and decarburization at lower oxygen potentials and internal sulfidation in SO_2 suggest strongly the presence of physical defects, such as micropores and fissures, allowing the passage of gaseous species in the scale, because the solid state diffusion rate of carbon and sulfur in oxide is very low. In the present work sulfur decoration method was applied to detect such defects. Fe-Cr alloys were oxidized at 1173 K in impure Ar, H_2 - H_2O or O_2 . At the end of oxidation run they were sulfidized in H_2S for about 60 s at the same temperature. Presence of physical defects in the scale at low oxygen potential was clearly shown by penetration of sulfur into the scale. Such defects allow oxidant gas penetration to the scale/alloy interface and consequently accelerate the oxidation rate, especially the oxidation of Fe-10 Cr and -15 Cr alloys in Ar.

1. Introduction

In atmospheres with low oxygen potentials, such as He atmosphere in High Temperature Gas-cooled Reactor, carburization or decarburization of materials, which deteriorates mechanical properties of the materials¹⁾, takes place depending on a carbon potential even though an oxide scale covers the alloy surface^{2),3)}. It is, therefore, considered that an oxide scale formed in atmospheres with low oxygen potentials is not sufficiently compact to prevent CO and CO_2 gas permeation. In fact when some steels were oxidized firstly in normal CO_2 and subsequently in CO_2 containing CO_2^{18} or C^{14}O_2 , O^{18} was detected in the inner oxide layer adjacent to the metal substrate and C^{14} in the near interfacial region between the metal and the oxide^{4)~7)}. In addition, when Co, after covered with an apparently compact and adherent scale by oxidation in impure Ar, was exposed to Ar-2% SO_2 , sulfide was observed at the oxide scale/metal interface⁸⁾. On the Ni-25 Cr and Co-25 Cr alloys also were produced sulfide nodules by exposure to H_2 - H_2O - H_2S atmosphere after pre-oxidation in H_2 - H_2O atmosphere⁹⁾. These results suggest very strongly that an oxide scale formed in atmospheres with low oxygen potentials, such as CO_2 , impure Ar and H_2 - H_2O , contains

physical defects such as pores or fissures through which gaseous species can pass inward or outward.

The object of this work is to investigate the oxidation behavior of Fe-Cr alloys in atmospheres with low oxygen potentials and to confirm that physical defects can be produced at low oxygen potentials more extensively than at high oxygen potentials by using sulfur decoration method^{10),11)}.

2. Experimental

2.1 Specimen Preparation

Electrolytic Fe and Cr were weighed and arc-melted. The alloys were hot- and cold-rolled, annealed in a stream of Ar-1% H_2 at 1,373 K for 7.2 ks and cut into coupons about $10 \times 10 \times 1$ mm. Their compositions are given in Table 1. The coupons were polished through 3/0 grit emery paper, washed with alcohol and distilled water, and dried rapidly.

2.2 Oxidation

Specimens, drilled, weighed and hung with a quartz bar on a boat, were inserted into a furnace heated at 1,173 K and oxidized for 90~720 ks in a stream of Ar (residual oxygen partial pressure $p_{\text{O}_2} \sim 10$ Pa), H_2 - H_2O ($p_{\text{O}_2} \sim 2 \times 10^{-17}$ Pa) and O_2 under atmospheric pressure. The flow rate was about 3 cm^3/s for Ar and O_2 , and 17 cm^3/s (=1 l/min) for H_2 - H_2O .

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Table 1 Chemical composition of Fe-Cr alloys (mass%).

Alloy	Cr	C	Si	Ni	S	Al	Fe
Fe-10Cr	9.50	0.003	0.003	0.004	0.010	0.005	Bal.
Fe-15Cr	14.65	0.004	0.002	0.005	0.011	0.003	Bal.
Fe-20Cr	19.20	0.005	0.003	0.005	0.010	0.003	Bal.
Fe-30Cr	29.0	0.005	0.003	0.005	0.013	0.003	Bal.

Fig. 1 Mass gain of Fe-Cr alloys oxidized at 1,173 K.

○: in O₂●: in Ar ($p_{O_2} \sim 10$ Pa)△: in H₂-H₂O ($p_{O_2} \sim 2 \times 10^{-17}$ Pa)

2.3 Sulfur Decoration

At the end of oxidation run, the oxidant gas was replaced by Ar without removing the specimens in the furnace. Then H₂S gas was passed through the reaction tube for 30~60 s. If there are physical defects, such as pores or fissures, in the oxide scale, H₂S gas will penetrate through the defects into the scale/metal interface and sulfides will be formed along the defects and at the metal surface.

The specimens were then mounted in resin and the sulfur distribution was examined by EPMA on a polished section.

3. Results

3.1 Mass Gain

Mass gains of Fe-Cr alloys oxidized at 1,173 K in various atmospheres are shown in Fig. 1. The mass gain was large in Ar, especially for lower Cr alloys. This suggests that the scale formed in Ar is not compact and not adherent to the alloy substrate. The mass gain in O₂ is smaller than those in other gases. The mass gain of Fe-10 Cr alloy was very small in H₂-H₂O. This is because only Cr can be oxidized in this atmosphere and

Fig. 2 Fe-10 Cr oxidized in Ar ($p_{O_2} \sim 10$ Pa) at 1,173 K for 270 ks.

the rate of Cr supply from the bulk to the surface is very low in this alloy. The slow rate of Cr supply is attributed to the low concentration of Cr and the slow diffusion rate of Cr in this alloy which has the fcc structure at 1,173 K.

3.2 Sulfur Decoration Results

Figure 2 represents the EPMA results on the Fe-10 Cr alloy oxidized at 1,173 K in a stream of Ar. The considerable penetration of sulfur is observed in the inner layer and along the scale/alloy interface. This means that the oxidant gas penetrated deep into the scale/alloy interface during the oxidation. The large mass gain of the Fe-10 Cr alloy in Ar is reasonably attributed to this extensive gas penetration and to the resulting absence of Cr rich protective oxide layer. In O₂, on the other hand, the gas penetration was more moderate and a Cr rich layer was formed (Fig. 3).

Figures 4 and 5 represent the results on higher Cr alloys. Because the SEM images in these figures do not show ballooning of the scale, compressive growth stress and resultant scale cracking are considered to be of a slight extent at low oxygen potential. However, the S images show local gas penetration through the scale and therefore the

Fig. 3 Fe-10Cr oxidized in O_2 (10^5 Pa) at 1,173 K for 270 ks. The location of the scale/alloy interface is sketched in photos of S as a fine white line.

Fig. 5 Fe-30Cr oxidized in Ar ($p_{O_2} \sim 10$ Pa) at 1,173 K for 270 ks. The uppermost part of the scale was detached from the specimen, as seen in Fig. 4.

Fig. 4 Fe-20Cr oxidized in H_2-H_2O ($p_{O_2} \sim 2 \times 10^{-17}$ Pa) at 1,173 K for 270 ks. Sulfur appears to be distributed in two layers. But the upper layer is the uppermost part of the scale which was detached together with resin from the specimen. One round point on photo b and another point between photos b and c correspond to penetration.

Fig. 6 Fe-15Cr oxidized in Ar ($p_{O_2} \sim 10$ Pa) at 1,173 K for 90 ks.

existence of physical defects in it. Namely, the scale formed at low oxygen potential is not sufficiently protective though cracks are not generated by compressive growth stress. In Figs. 4 and 5, S and Cr are distributed in two layers. This is attributed to the contraction of resin during solidification. This contraction generated very often a crack between the resin and the specimen. When a crack was generated, an uppermost part of the scale stucked firmly in the resin was detached from

the specimen. This detached part corresponds to the upper layer in S and Cr images in Figs. 4 and 5. Only two round points on photos b and c correspond to the penetration.

As reported previously, the crack in the scale was not always observed through the oxidation run in O_2 , because the crack, though produced repeatedly during oxidation, is relatively easily healed in O_2 . Thus it was expected for the oxidation in Ar and also in H_2-H_2O that the healing of physical defects took place, and that the gas penetration occurred intermittently but not continuously. Figures 6 and 7 represent the results of oxidation for 90 ks, and Figure 8 for 720 ks. Contrary to the expectation, the gas penetration

Fig. 7 Fe-20 Cr oxidized in Ar ($p_{O_2} \sim 10$ Pa) at 1,173 K for 90 ks. The uppermost part of the scale was detached from the specimen, as seen in Fig. 4.

Fig. 8. Fe-20 Cr oxidized in Ar ($p_{O_2} \sim 10$ Pa) at 1,173 K for 720 ks. The uppermost part of the scale was detached from the specimen, as seen in Fig. 4.

is always observed irrespective of oxidation time, so the scale formed at low oxygen potential is considered to contain always physical defects.

4. Discussion

As shown in Figs. 2, 4, 5, 6, 7 and 8, physical defects allowing gas penetration exist always in the scale formed at low oxygen potentials. Since the sulfidation time is about 60 s, the observed sulfur penetration is exclusively attributed to gaseous diffusion but not to solid state diffusion. Especially the gas penetration took place very largely in the inner layer of the scale formed on Fe-10 Cr and Fe-15 Cr alloys in Ar (Figs. 2, 6).

This result shows that these inner layers were very porous. Such gas penetration not only causes inward growth of the scale but also accelerates outward growth of outer layer by preventing the formation of a Cr rich protective layer, and resulting naturally in large mass gain of these alloys in Ar (Fig. 1). For higher Cr alloys also the gas penetration must accelerate the oxidation rate.

On the other hand, in O_2 scale cracks are sometimes generated to allow gas penetration but they are more ready to be healed than the physical defects formed at low oxygen potentials. In O_2 even 5- and 10% Cr alloys are able to form a moderately protective oxide layer enriched in Cr.

Although following mechanisms may be cited for the cause of physical defect generation, any of them is not conclusive.

1) Mechanical cracking of scale

Scale cracking due to growth stress is usually an important factor for oxidation resistance. But in this work scale spalling and ballooning were much less extensive than in O_2 , namely the growth stress was low. Therefore, the scale formed in Ar and H_2 - H_2O is considered to crack less readily than that in O_2 .

2) Microchannels remaining at the grain boundary of scale¹²⁾

Microchannels may remain at grain boundaries of growing oxide and serve as a gas penetration path. If it were the case, gas penetration should take place at particular points, where scale morphology and thickness would differ from those at other part. In practice, however, the scale morphology and thickness were similar throughout the scale, when oxidized in Ar and H_2 - H_2O .

3) Dissociation fissure^{13), 14)}

If dissociation fissures were repeatedly opened and closed over the whole scale, gas penetration would be always detected and the scale would have a similar morphology and thickness all over a same specimen. However, it is doubtful that the surface oxide is reduced at the tip of dissociation fissure even in Ar with an oxygen potential of 10 Pa.

Thus conclusive remarks can not be made upon the causes of physical defect generation, but in any way the scale formed at low oxygen potential inherently contains physical defects through which gaseous species can pass.

The characteristics of the oxide scale are summarized as follows:

1) At high oxygen potential the scale is cracked by growth stress but healed readily.

2) At low oxygen potential the scale is not cracked but inherently porous and healed very hardly.

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