Influence of Hf Addition to Fe–10 mass% Al Alloy on the Protectiveness of Preformed Al₂O₃ Scale against Sulfidation*

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In order to assess the protectiveness of preformed Al₂O₃ scale in an H₂–10%H₂S atmosphere and the influence of Hf addition on it, Fe–10 mass%Al alloys with or without Hf were oxidized in pure O₂ at 1300 K for specified periods up to 400 ks and subsequently sulfidized at 1200 K without an intermittent cooling. The addition of 0.088 mass%Hf suppresses the formation of wavy scales which are often associated with mechanical defects and improves the mechanical soundness of the scale. As a result of this the protection time also increases. These benefits were considered to be due to the modification of the mode of diffusion through the scale. The complete prevention of sulfidation by the scale was found to be impossible, since sulfides were formed on scales which looked very sound.

(Received June 8, 1987)

Keywords: Al₂O₃ scale, protectiveness, iron–10 mass% aluminum alloy, sulfidation, H₂–10%H₂S, preoxidation, hafnium addition

I. Introduction

The idea of using a preformed oxide scale as a protective barrier to the subsequent corrosion at high temperatures is not new and there have been several studies(1)–(6) on it. If this idea turns out to be practical the oxidation treatment will have a great advantage in that it is usually simpler than other surface treatments. However, further studies are necessary to systematically summarize the fundamental knowledge concerning the subject of interest, and the effectiveness of such a scale should be reasonably evaluated.

An Al₂O₃ scale has a high potential as a protective barrier(3)–(6) provided its structural integrity and thermodynamical stability are well maintained in a given environment. The nature of Al₂O₃ scales formed on Fe–Cr–Al alloys was, however, usually associated with mechanical defects(7)(8). Though the addition of rare earth or reactive elements was reported(7)–(13) to be effective to form adherent and protective scales in oxidizing atmospheres, studies(3)–(6) dealing with the protectiveness of Al₂O₃ scales in a sulfidizing atmosphere are quite limited.

The present study deals with the influence of small additions of Hf to an Fe–Al alloy on the protectiveness of oxide scales preformed on it during the subsequent sulfidation in an H₂–H₂S atmosphere. An Fe–Al alloy was chosen, because it forms scales consisting predominantly of α-Al₂O₃ with a least impurity, Fe, in it.

The protectiveness of the scale is evaluated by the protection time during which the mass gain accompanying the sulfide formation is negligible.

II. Experimental Procedures

1. Specimen alloys

The specimen alloys used in the present study were prepared by vacuum melting of high purity metals in suitable proportions and by hot rolling of the castings to about 1 mm thick sheets. Then, the sheets were cut into rectangular coupons of various sizes.

Specimens of 30 mm × 10 mm × 1 mm were
used for kinetic tests of sulfidation after preoxidation and those of 15 mm × 15 mm × 1 mm were used for oxidation. Specimens of 15 mm × 15 mm × 1 mm or 15 mm × 8 mm × 1 mm were used for X-ray diffractometry, metallography and microanalysis. The chemical compositions of the specimen alloys are shown in Table 1, together with their grain sizes.

All the specimens were polished to a mirror finish with successively finer SiC polishing papers and 0.3 μm alumina polishing powder, and washed ultrasonically in acetone and in alcohol immediately before the test.

The specimen edges and corners were polished to be round, because preliminary tests indicated that sulfides grow preferentially on the scales covering the sharp edges and corners.

2. Experimental apparatus

The apparatus used for measurement of the sulfidation kinetics after preoxidation is shown in Fig. 1. The mass gain of a specimen during sulfidation was detected by the displacement of the target connected to the quartz spring and was continuously recorded with the aid of an optical sensor. The sensitivity of the measuring system was 5 mg.

A horizontal reaction tube made of quartz was also used for studying the oxidation kinetics and for preparing the specimens which were subjected to metallography and other examinations.

3. Procedures

After a prepared specimen was hung from the quartz spring with thin Pt chains and thin quartz hooks, the reaction tube was closed and flashed with Ar gas. Then, the furnace temperature was raised to 1300 K in about 9 ks and oxygen gas was introduced to start the preoxidation. When a specified period passed, the reaction tube was flashed with Ar gas and the temperature was slowly lowered to 1200 K in about 7.2 ks. Then, a gas mixture of H2–10.4%H2S was introduced to start sulfidation. The sulfur partial pressure was 2.7 Pa.

Though the preoxidation temperature is one of the factors to be studied, the temperature of 1300 K was chosen as the preoxidation temperature in the present study to obtain relatively thick scales in reasonably short periods. The sulfidation temperature was decided to be 1200 K in order to avoid the appearance of a liquid phase by the eutectic reaction between Fe and FeS which takes place at 1261 K.

When the horizontal reaction tube was used, the specimen was held in an alumina boat and other procedures were the same as those for the case of the vertical reaction tube.

4. Metallography and microanalysis

The specimens which were oxidized or successively oxidized and sulfidized under specified conditions were examined by optical mi-

| Table 1 Chemical compositions (mass%) of the specimen alloys and their grain sizes (μm). |
|-----------------------------------|---|---|---|---|
| Fe  | Al  | Hf  | Grain size |
| --- | --- | --- | ---------- |
| Alloy 1 | 89.64 | 9.52 | — | 300 |
| Alloy 2 | 89.55 | 9.64 | 0.088 | 150 |
croscopy (OM), scanning electron-microscopy (SEM) and X-ray microanalysis (EPMA) with a help of an energy dispersive unit (EDX). Scales remaining on the specimens were also examined with X-ray diffractometry.

III. Results

1. Kinetics

In the following figures, Alloys 1 and 2 are expressed as FeAl and FeAl–Hf respectively for convenience. Figure 2 shows the mass gain vs time curves of the both alloys during the preoxidation. The mass gain curve of Alloy 2 is approximately parabolic for, at least, up to 400 ks, whereas that of Alloy 1 shows a breakaway phenomenon after about 200 ks until which the mass gains of the both alloys are quite similar.

Figure 3 shows changes in the mean thickness of scales formed on the both alloys and in the mean width of the internally oxidized zone of Alloy 2 (broken line) with the preoxidation time. The formation of internal oxide particles will be shown later. In the case of Alloy 1 the measurement of the thickness was made for adhesive scales away from the breakaway site. The thickness of the scale on Alloy 1 increases nearly parabolically, whereas that of the scale on Alloy 2 increases with time for up to 200 ks after which it is almost constant though the internally oxidized zone below the scale becomes wider. Therefore, it is concluded that the mass gain of Alloy 2 after 200 ks can be attributed to the formation and growth of the internal oxide particles, while that of Alloy 1 is mainly due to thickening of the scale.

The mass gains during the sulfidation after preoxidation for specified periods are shown in Figs. 4 and 5 for Alloys 1 and 2, respectively. Two or three runs were carried out under the same conditions to understand the reproducibility of the sulfidation kinetics. The reproducibility was generally not so good as shown in the both figures.

In general, there is a protection or incubation time after which an extensive mass gain takes place by the rapid growth of sulfides. The protection time is summarized in Fig. 6. The both alloys show a similar feature such that the protection time increases as the preoxidation time increases. The protection time of Alloy 2 is somewhat larger than that of Alloy 1 for all the preoxidation times tested.

However, a great difference between Alloys
1 and 2 was revealed when the mean protection time is plotted against the mean scale thickness as shown in Fig. 7. It is noteworthy that the protection time of Alloy 2 increases remarkably with an increase in the scale thickness. Contrary to this, the protection time of Alloy 1 increases at a smaller rate.

2. Metallography and microanalysis

Typical features of cross sections of Alloys 1 and 2 after preoxidation are shown in Fig. 8(a) and (b), respectively. Alloy 1 forms wavy or wrinkled scales of an almost uniform thickness except for those at the breakaway
site. The substrate alloy is ductile enough to follow the development of the wavey scales. However, the partial separation of the scale from the substrate occurs at several points, when the deformation of the scale progresses. After this separation the scale becomes prone to fracture because of oxide growth stresses\(^{(15)(16)}\). Once the scale fractures, oxygen gas is admitted to the substrate surface, where rapid oxidation starts. There was no sign of internal oxidation in Alloy 1.

Contrary to Alloy 1, Alloy 2 formed oxide scales, the outer surface of which is almost flat and lustrous though wavy scales is formed exceptionally at very limited places, such as the area on the alloy grain boundaries. The scale on Alloy 2 is very adherent to the substrate. The scale/substrate interface is rugged because of the formation of internal oxide particles some of which are connected to the scale.

Figure 9 is an example of the microanalysis of a cross-section of Alloy 1, showing that the wavy oxide scale is separated from the substrate and that the substrate surface under it is covered with oxides. The results of both X-ray diffractometry and microanalysis showed that the oxide scale formed on Alloy 1 consists of \(\alpha\)-\(\text{Al}_2\text{O}_3\) with a very thin layer of \(\text{FeAl}_2\text{O}_4\) on it. The oxide covering the substrate under the separated scale was found to be mainly \(\alpha\)-\(\text{Al}_2\text{O}_3\).

Figure 10 shows a similar example of Alloy 2. The scale formed on Alloy 2 consists of \(\alpha\)-\(\text{Al}_2\text{O}_3\) with \(\text{HfO}_2\) particles incorporated in it.

Typical surface features of the oxide scales formed on Alloys 1 and 2 are shown in Fig. 11(a) and (b), respectively. It was found for Alloy 1 that wavy scales are preferentially formed on areas of the alloy grain boundaries and scales on other areas are also wavy in a smaller degree. On the other hand, the outer surface of scales on Alloy 2 is generally very flat. It was also found that the grain size of the oxide is reduced greatly by the addition of Hf.

Figure 12 shows the shape, size and distribution of sulfide crystals formed on relatively sound scales of the both alloys, which were preoxidized for 100 ks and subsequently sulfdized for 150 ks. These conditions correspond to the extensive sulfide formation as can be understood from Figs. 4 and 5. In fact, massive mounds of sulfides were formed on specimen edges. Each crystal in Fig. 12 is fundamentally a hexagonal platelet in shape and its distribution is almost uniform. It is noteworthy that the nature of sulfide crystal on Alloy 2 is almost the same as that on Alloy 1 if they are formed on flat or wavy scales.

When hexagonal crystals grow further, they form a mound consisting of loosely packed platelets. In some cases they form para...
layers with an almost constant distance. The top of the mound is usually covered with recrystallized sulfides. Further, relatively large mounds were formed on specimen edges and corners. Most of the mounds were, however, spalled off during handling after the reactions. A good example of such a mound is shown in Fig. 13(a). Even wrinkled scales next to the mound seem to be free of sulfides in Fig. 13(b), indicating that the sulfiding gas is relatively more permeable through the scale covering the edges than that covering the other area. The EDX analysis showed that the sulfids shown in Figs. 12 and 13 are Fe$_{1-x}$S containing a small amount of Al.

IV. Discussion

The experimental results of the present study showed the following interesting points regarding the influence of Hf addition; (1) the formation of wavy scale is much suppressed (cf. Fig. 8) and (2) the protection time is increased (cf. Fig. 6). Therefore, the subsequent discussion is extended mainly to these points.

The formation of wavy scales similar to those shown in Figs. 8(a), 9(a) and 11(a) was observed by Golightly et al.\(^{(7)}\) when they oxidized an Fe–Cr–Al alloy to form an Al$_2$O$_3$ scale. They also suggested that the wavy scale develops by the formation of oxide within the existing oxide layer by reaction between oxygen diffusing inward down the oxide grain boundaries and aluminum diffusing outward through the bulk oxide. Such reaction processes result in large compressive stresses\(^{(15)-(17)}\) in the oxide scale and hence lead to its lateral growth.

A similar mechanism may apply to the present study since the scales formed here are predominantly Al$_2$O$_3$. It was also found that the substrate alloy is ductile enough to follow the development of the wavy scale to some extent. The partial separation, however, takes place when the degree of deformation becomes large. Particularly, this kind of separation was enhanced at the specimen edges and corners because of the geometrical conditions.

The observation that the addition of Hf suppressed the formation of wavy scales can be
explained by the following mechanism. Hf incorporated in the scale changes the mode of diffusion through the scale from the diffusion of both oxygen and aluminum to the predominant diffusion of oxygen toward the scale/alloy interface, where a new oxide is formed with aluminum available there. The formation of internal oxide particles which were observed only in Alloy 2 supports this view. The oxide grain size reduced by the Hf ad-
The addition may also have some contribution to the change in the diffusion mode. However, this view may need a further study.

The protection time can be referred to as the time necessary for the sulfidizing gas to pass through the oxide scale and nucleate sulfides. For almost all the specimens, the sulfide formation started preferentially at the specimen edges and corners (cf. Fig. 13), even though the thickness of scales is not so different whether they are formed on such areas or flat areas. This may indicate that the scales formed on these edges and corners are more defective.

The increase in the protection time which was resulted from the Hf addition is thought to be due to the improvement of the soundness of the scale. Further, the protection time is much larger for Alloy 2 than Alloy 1 when the preoxidation time is more than 200 ks (cf. Fig. 7). During this period the thickness of the scale on Alloy 2 hardly increases, but the protection time increased very much. This is assumed to be due to some structural changes such as recrystallization of the scale caused by an annealing effect at the high temperature.

It was further understood from the experimental results that the complete prevention of sulfidation is impossible in the H$_2$-H$_2$S atmosphere at high temperatures, since the sulfide grows even on the scale which seems to be very sound under the magnification of the SEM (cf. Fig. 12). In this case the diffusion of sulfidizing gas seems to take place through the oxide grain boundaries. Possibility of sulfur diffusion through an oxide was shown by Yang and Whittle(18) for an iron oxide and H$_2$-H$_2$S system.

V. Conclusions

(1) The addition of Hf to an Fe–10 mass%Al alloy changes the shape of the oxide scale from wavy to flat and improves its mechanical soundness.

(2) As a result of the above, the protectiveness of the scale in an H$_2$–10%H$_2$S atmosphere increases.

(3) The complete prevention of sulfidation by the scale is impossible, because sulfides grow on the scale even though it looks very sound.

Fig. 13 SEM micrographs of Alloy 1 preoxidized for 100 ks and subsequently sulfidized for 5 ks; (a) a mound of sulfide formed on the oxide scale covering a specimen edge, and (b) a high magnification of (a) showing the mound consisting of sulfide platelets and wrinkled oxide scales free of sulfides.
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