Influence of Si or Ti Addition to Fe-23Cr-5Al Alloy on Protectiveness of Preformed Al₂O₃ Scale against Sulfidation*

By Shigeji Taniguchi** and Toshio Shibata**

An Fe-23Cr-5Al alloy and that containing Si or Ti in 0.2 mass% were oxidized to form α-Al₂O₃ scales in a flow of pure O₂ at 1300 K for specified periods up to 400 ks and subsequently sulfidized at 1200 K in an H₂-10% H₂S atmosphere without intermittent cooling. The protectiveness of the scale was evaluated by the protection time after which a remarkable mass gain takes place owing to the rapid growth of sulfides. In general, the protection time increases as the scale thickens. The addition of Si, however, decreases the protection time, which does not vary much with the scale thickness. Contrary to this, the addition of Ti increases the protection time. These results were explained in terms of the structural soundness of the scales.

(Received February 10, 1988)

Keywords: Al₂O₃ scale, protectiveness, iron-chromium-aluminum alloy, sulfidation, H₂-H₂S, silicon addition, titanium addition.

I. Introduction

There has been increasing interest in the development of alloys which can stand atmospheres richer in sulfur than in oxygen in relation to new energy sources and systems such as coal conversion systems(1). The possibility of using a preformed oxide scale as an effective barrier in such an environment was studied(2)-(5).

The present authors and an associate also studied(5) the protectiveness of Al₂O₃ scales formed on an Fe-10 mass% Al alloy against sulfidation at 1200 K in a mixture of H₂-10% H₂S. It was found that the addition of a small amount of Hf to the alloy increases the protectiveness remarkably by forming structurally more sound scales.

Though there are a few studies dealing with the effectiveness of the Al₂O₃ scales formed on Fe-Cr-Al alloys, the number of those dealing with the influence of reactive additional elements is quite limited.

The present paper, comprising a series of such studies, describes the influence of a small addition of Si or Ti to an Fe-Cr-Al alloy on the protectiveness of the Al₂O₃ scales formed on it. The experimental results were explained mainly from a morphological viewpoint. It was revealed that the addition of Ti improves the protectiveness very much whereas that of Si has an adverse effect.

II. Experimental Procedures

As the experimental procedures of the present study were almost the same as those described in the previous paper(5), the main points are given below briefly.

The specimen alloys 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. They were cut into rectangular coupons of various sizes. All the specimens were mechanically polished to a mirror finish and washed ultrasonically in acetone and in alcohol immediately before a test. The chemical composition of the specimen alloys is shown in Table 1.

The specimen was oxidized at 1300 K in a flow of purified oxygen for 100, 200, or 400 ks. Then, the reaction tube was flashed with Ar gas and the specimen temperature was slowly lowered to 1200 K in about 7.2 ks. A gas mix-
Influence of Si or Ti Addition to Fe-23Cr-5Al on Protectiveness of Al₂O₃ Scale against Sulfidation

The gas pressure was the atmospheric pressure throughout the experiment.

The mass gain during the sulfidation was continuously recorded by using a thermobalance, the outline of which was also shown in the previous paper(5). The reaction products, oxides and sulfides, were examined by X-ray diffractometry (XRD), optical microscopy (OM), scanning electron-microscopy (SEM), and X-ray microanalysis (EPMA) equipped with an energy dispersive unit (EDX).

III. Results

1. Kinetics

In the following figures, Alloys 1 to 3 are expressed as FeCrAl, FeCrAl-Si and FeCrAl-Ti respectively for convenience.

Figure 1 shows the mean scale thickness vs preoxidation time curves of the all alloys. The curve of Alloy 1 is approximately parabolic, while those of Alloys 2 and 3 are nearly straight. The scale on Alloy 2 grows much faster than that on Alloy 1. However, the scale on Alloy 3 is somewhat thinner than that on Alloy 1 for short oxidation periods, though similar thicknesses were obtained for the both alloys after the oxidation for 400 ks.

The mass gain per unit specimen area (ΔM·A⁻¹) during the sulfidation after the preoxidation for a specified period is shown in Figs. 2 to 4 for Alloys 1 to 3 respectively. Two or three runs were carried out under the same conditions to understand the reproducibility of the sulfidation kinetics. The reproducibility was usually not so good as shown in these figures, however general characteristics of sulfidation can be understood. There is a protection time after which a remarkable mass gain takes place by the rapid growth of sulfides and the sulfidation rate keeps increasing.

The protection time as a measure of the protectiveness is summarized in Fig. 5. The protection time of Alloys 1 and 3 increases as the preoxidation time increases. Contrary to this, the protection time of Alloy 2 does not vary so much with the preoxidation time and is shorter than those of the other alloys except for the specimens preoxidized for 100 ks.

As the additional elements changed the growth rate of oxide scale, the mean protection time is plotted against the mean scale thickness.
It is concluded from this figure that the addition of Si to the Fe–Cr–Al alloy is detrimental while the addition of Ti is very effective, because the former decreases the protection time but the latter increases it.

2. Metallography and microanalysis

The oxide scales formed on the all alloys were identified mainly as $\alpha$-Al$_2$O$_3$ by the XRD. Typical surface features of the scales formed on Alloys 1 to 3 are shown in Fig. 7(a), (b) and (c), respectively. The scales formed on Alloys 1 and 2 are wavy, however those formed on Alloy 3 are almost flat. The degree of waviness is larger for Alloy 2 than for Alloy 1.

Alloy 1 is ductile enough to follow the development of the wavy scale to some extent as shown in Fig. 8(a). 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. The scales on Alloy 2 are separated over wider areas and the substrate
surfaces under the fractured scales are covered with new scales as shown in Fig. 8(b). However, these scales become defective soon. The scales formed on Alloy 3, shown in Fig. 8(c), are almost flat, very adherent to the substrate and seem to be almost free of defects, making a good contrast with those formed on the other alloys.

Figure 9(a), (b) and (c) show outer surfaces and fractured edges of the scales, and the substrate surfaces of Alloys 1 to 3 respectively which were oxidized for 200 ks and subsequently sulfidized for 10 ks, Though these conditions correspond to the protection period, sulfides already started to grow having particular shapes; filamentary, blade-like and nodular. Sulfide nodules were observed on the substrate surface under the separated scales for Alloys 1 and 2. An example of such sulfide nodule is shown in Fig. 9(b). This indicates that these separated scales are permeable to the sulfidizing gas. On the other hand, filamentary and blade-like sulfides in Fig. 9 seem to grow on or from the area near the scale surface.

After the protection time the scales were spalled over relatively wide areas and agglomerates of sulfides of various shapes develop. Agglomerates of platelet sulfides are seen in Fig. 10 and massive sulfides are also seen in Fig. 10(b) and (c). These agglomerates and massive sulfides are loosely packed and hence cannot be protective. It was also found that these sulfides grow preferentially on the scales covering the specimen edges and corners as shown in Fig. 11. This is considered to be due to the geometrical conditions under which the scales grow outward and become defective because of oxide growth stresses. It should be noted that the sulfides grow also on the scales covering the flat area for Alloy 2.

The analysis with XRD and EDX showed that the sulfides consist mainly of Fe$_{1-x}$S and Cr$_2$S$_3$. Further, the EDX analysis showed that the sulfides grown on the scales of all the alloys do not contain Al. Typical values obtained are; Fe:31, Cr:10 and S:59 in at% for the sulfide shown in Fig. 10 (a). Contrary to this, the sulfide nodules on the substrate shown in Fig. 9(b), and the sulfides formed by the sulfidation of Alloy 1 for 2 ks without preoxidation contained Al in 4.2 and 16.8 at% respectively.

IV. Discussion

It is an ultimate prerequisite to minimize or eliminate mechanical defects, which admit a sulfidizing gas into the substrate, for an Al$_2$O$_3$ scale to be an effective barrier. However, Al$_2$O$_3$ scales formed on Fe–Cr–Al alloys at high temperatures were reported$^{[6][7]}$ to be wavy or convoluted and usually associated with mechanical defects. Similar phenomena were observed in the present study for Alloys 1 and 2 (cf. Figs. 7 and 8). The mechanism of formation of the wavy scale was explained$^{[6]}$ in terms of the formation of new oxides within the existing oxide layer by reactions between oxygen and aluminum. The oxygen diffuses inward.
down the oxide grain boundaries and aluminum diffuses outward through the bulk oxide. Such reaction processes result in large compressive stresses\(^\text{(8)-(10)}\) in the oxide scale and hence lead to its outward growth.

This view is supported by a study of Skeldon et al.\(^\text{(11)}\) who used an oxygen isotope as a tracer to understand the mechanism of growth of wavy \(\text{Cr}_2\text{O}_3\) scales on pure Cr in pure oxygen.

It was found that Alloys 1 and 2 are ductile enough to follow the wavy scales to some extent. The partial separation, however, takes place when the scales deform largely (cf. Fig. 8) leading eventually to the fracture of the scales during the sulfidation.

The observation that the protection time of Alloy 2 is relatively short and does not vary much with the scale thickness is therefore attributable to the defective scales resulted from the addition of Si at any thickness of interest. In other words, the addition of Si cannot suppress the oxide growth stresses. The almost linear oxidation kinetics is also attributable to the deformed scales.

Contrary to this, the addition of Ti increased the protection time greatly (cf. Fig. 6). This can be explained by the almost flat scale which looked very sound (cf. Fig. 8).

As the examinations with OM, SEM, and EPMA showed no particular enrichments of Si or Ti in the scale or in the substrate near the scale/alloy interface, these elements are thought to be partly in solution and partly incorporated in the \(\text{Al}_2\text{O}_3\) scale in the form of simple oxides or complex oxides finely and uniformly dispersed.

There are two diffusion modes by which the development of the compressive stress can be circumvented;

(A) exclusive inward diffusion of oxygen, and
(B) exclusive outward diffusion of aluminum.

The following interesting points were reported in relation to the effect of Ti incorporated in \(\text{Al}_2\text{O}_3\);

(C) titanium is reported\(^\text{(12)}\) to enter \(\text{Al}_2\text{O}_3\) substitutionally as \(\text{Ti}^{+3}\) and \(\text{Ti}^{+4}\), and
(D) precipitates of \(\text{TiAl}_2\text{O}_5\) at grain boundaries are reported\(^\text{(13)}\) to enhance the oxygen transport.

\(\text{Ti}^{+4}\) will contribute to (A), while (D) contributes to (B). However, it is difficult to suggest any mechanism by which the development of stresses can be suppressed now without further studies. Detailed studies on the microstructures of and diffusion mode through the scales seem to be at least necessary. A similar discussion applies to the influence of Si.

Even during the protection period the permeation of the sulfidizing gas seems to take place through the microcracks and oxide
Influence of Si or Ti Addition to Fe-23Cr-5Al on Protectiveness of $\text{Al}_2\text{O}_3$ Scale against Sulfidation

Fig. 9 SEM micrographs of Alloys 1 (a), 2 (b) and 3 (c) preoxidized for 200 ks and sulfidized for 10 ks; showing fractured edges and outer surfaces of scales containing filamentary or blade-like sulfides, and substrate surfaces associated with nodular sulfides.

Fig. 10 SEM micrographs of Alloys 1 (a), 2 (b) and 3 (c); preoxidized for 100 ks and sulfidized for 100, 150 and 100 ks respectively. All show loosely packed agglomerates of platelet sulfides, and (b) and (c) show massive sulfides also.

Fig. 11 Macroscopic view of (a) Alloy 1 preoxidized for 400 ks and sulfidized for 250 ks, (b) Alloy 2 preoxidized for 100 ks and sulfidized for 65 ks, and (c) Alloy 3 preoxidized for 100 ks and sulfidized for 150 ks, showing preferential growth of sulfides on specimen edges. Specimen size is about 30 mm × 10 mm.
grain boundaries (cf. Fig. 9). The possibility of latter was shown by Yang and Whittle\(^{(14)}\). The mass gain due to the sulfide growth during this period seems to be negligible.

When the sulfur partial pressure at the substrate surface becomes enough high, sulfides nucleate. These sulfides are mainly iron sulfides growing at relatively high rates and hence the consumption of alloy beneath the scale causes its spallation leading to an increase in the sulfidation rate (cf. Figs. 2 to 4). The above processes are considered to be the mechanism by which the protectiveness is lost. A similar mechanism was proposed by Stott et al.\(^{(4)}\)

### V. Conclusions

1. Al\(_2\)O\(_3\) scales formed on the Fe–23Cr–5Al alloy at 1300 K in pure oxygen are protective at 1200 K in H\(_2\)–10% H\(_2\)S for certain periods, after which considerable mass gains take place because of the rapid growth of sulfides.
2. The addition of Si in a small amount to the alloy results in defective scales and hence the protection time is relatively short and does not vary much with the scale thickness.
3. The addition of Ti in a small amount to the alloy results in sound scales and hence increases the protection time considerably.

### REFERENCES

1. "High Temperature Corrosion in Energy Systems" Ed. M. F. Rothman, Metals Society AIME (1985).
2. P. A. Mari, J. M. Chaix and J. P. Larpin: Oxid. Met., 17 (1982), 315.
3. T. Narita, K. Przybylski and W. W. Smeltzer: Oxid. Met., 22 (1984), 181.
4. F. H. Stott, F. M. F. Chong and C. A. Stirling: Proc. 9th ICMC Vol. 2 (1984), 1.
5. S. Taniguchi, T. Shibata and H. Tsuruoka: Trans. Japan Inst. Metals, 28 (1987), 788.
6. F. A. Golightly, F. H. Stott and G. C. Wood: Oxid. Met., 10 (1976), 163.
7. F. H. Stott, G. C. Wood and F. A. Golightly: Corros. Sci., 19 (1979), 869.
8. F. N. Rhines and J. S. Wolf: Met. Trans., 1 (1970), 1701.
9. J. Stringer: Corros. Sci., 10 (1970), 513.
10. S. Taniguchi: Trans. Iron Steel Inst. Japan, 25 (1985), 3.
11. M. Skeldon, J. M. Calvert and D. G. Lees: Oxid. Met., 28 (1987), 109.
12. S. K. Mohapatra and F. A. Kroger: J. Amer. Ceram. Soc., 60 (1977), 381.
13. H. A. Wang and F. A. Kroger: J. Amer. Ceram. Soc., 63 (1980), 613.
14. F. C. Yang and D. P. Whittle: Corros. Sci, 23 (1983), 285.