1. Introduction

An $\alpha$-Al$_2$O$_3$ scale forms on the alloys when alumina-forming heat-resistant alloys are exposed to high temperatures above 1 273 K in oxidizing atmospheres. The $\alpha$-Al$_2$O$_3$ scale often spalls during cooling after oxidation. Various hypotheses have been offered to explain spalling of the scale, and it has been recently focused on segregation of sulfur and/or chromium-sulfides at the oxide-alloy interface. The present authors studied the oxidation behavior of Fe–20Cr–4Al alloys with small amounts of sulfur (3, 35, 53, 104, and 171 ppm of sulfur) in oxygen up to five cycles at temperatures ranging from 1 273 to 1 673 K. Spalling of the scales on the 3 and 171 ppmS alloys was scarcely observed at any temperature and any cycles of oxidation. However, the scales on the 35 and 53 ppmS alloys spalled massively after cyclic oxidation at 1 473 and 1 573 K. On the other hand, after oxidation at 1 673 K, intensive spalling of scales was observed for the 4, 7, 1 300 and 6 300 ppmS. Spalling of scales on the alloys depends on sulfur content and oxidation temperature. The mass gain of these alloys tended to increase with increasing sulfur content. The scales formed on the alloys were $\alpha$-Al$_2$O$_3$. The scale/alloy interface changed from planar to convoluted morphologies with increasing sulfur content after oxidation at 1 673 K. Sulfur in the alloys with more than 7 ppmS existed all over the matrix as chromium-sulfide particles, and then moved to the oxide-alloy interface during oxidation.

KEY WORDS: stainless steel; superalloy; alumina; sulfur; oxide adherence; oxidation.

2. Experimental

Ingots of Fe–20Cr–4Al alloys with varying levels of sulfur impurity (1, 3, 4, 7, 35, 53, 104, 171, 185, 491, 1 300 and 6 300 ppm) were prepared by arc melting and then, hot-rolled and cold-rolled to a sheet of 0.5 mm thickness. The alloy with 1 ppmS was made by floating zone refining of the alloy with 4 ppmS. Before oxidation, the samples, except for the 1 and 4 ppmS, were cut to dimensions of 20 $\times$ 1 100 $\times$ 0.5 mm$^3$, and the 1 and 4 ppmS were cut to dimensions of 1 mm $\times$ 7–10 mm-diameter discs from rod. The specimens were then annealed in vacuum for 18 ks at 1 473 K and their surfaces were mirror-polished with diamond paste after initial emery-polishing. Each specimen was cleaned ultrasonically in alcohol before being tested. Oxidation tests were conducted in flowing oxygen (100 cc/min) for 18 ks at 1 273, 1 373, 1 473, 1 573 and 1 673 K. The mass change was measured after oxidation, and the appearance of samples was observed. The scale formed on the alloys was identified by X-ray diffraction (XRD). The morphology of the scales on the alloys was observed by scanning electron microscopy (SEM). The compositions of the scale and scale/alloy interface of the alloys were examined by electron probe microanalysis (EPMA).

3. Results and Discussion

3.1. Mass Change

Table 1 shows mass change of Fe–20Cr–4Al alloys with sulfur exposed in oxygen for 18 ks at 1 273, 1 373, 1 473, 1 573 and 1 673 K. The mass change tended to increase...
with increasing sulfur content after oxidation at 1273, 1373, and 1473 K, except for the 4 and 7 ppmS for 1373 K, and the 4, 7, 35, and 54 ppmS for 1473 K. The mass change means the mass gain when the scales on the alloys don’t spall from the alloy surface. The negative values of the mass change suggested that the scales on the alloys spalled massively during cooling. The mass change of the 4, 7, 35, 53, and 104 ppmS at 1573 K, and of the 4, 7, and 6300 ppmS at 1673 K showed small or negative values, and these results suggested that the scales on these alloys also spalled massively during cooling.

3.2. Surface Appearance and X-ray Diffraction

Figure 1 shows the surface appearance of alloys with sulfur exposed in oxygen for 18 ks at 1273, 1373, 1473, 1573, and 1673 K. After oxidation at 1273 and 1373 K, spalling of scales was not recognized, except for the 4 and 7 ppmS at 1373 K. After oxidation at 1473, 1573, and 1673 K, scales on the 4, 7, 35, and 54 ppmS at 1473 K, and those on the 4, 7, 35, and 104 ppmS at 1573 K, and then those on the 4, 7, 35, and 6300 ppmS at 1673 K, spalled from almost the entire surface. These results showed a good agreement with the mass change shown in Table 1. Table 2 shows surface features of the scales on the alloys with sulfur exposed in oxygen for 18 ks at 1273, 1373, 1473, 1573, and 1673 K. It is suggested that spalling of the scales depends on sulfur content and oxidation temperature.

After oxidation at any temperature, the scales on all the alloys were recognized as α-Al2O3 by XRD.

3.3. Scanning Electron Microscopy and Electron Probe Microanalysis

Figure 2 shows typical surface views of several alloys with sulfur after oxidation at 1273 and 1673 K. After oxidation at 1273 K, the scale surface of the 1 ppmS was planar, and the alloy surface was covered with fine and granular particles of less than 0.2 μm in size. On the other hand, the scale surface of the 4 ppmS is slightly wavy, and the alloy surface was covered with small granular particles of less than 0.4 μm in size. The scale surface of the 7 ppmS has a wavy shape of about 0.2 μm in width, and then intervals of amplitude in each rod-shaped oxide increased with increasing sulfur content. The interval of amplitude of the 6300 ppmS was about 20 μm as shown in Fig. 2(d).

According to a recent study of 18O tracer, it was demonstrated that oxidation of Al2O3-forming alloy occ-
curred predominantly by inward diffusion of oxygen, with some outward diffusion of aluminum. This suggested that the wavy morphology on the alloy with more than 4 ppmS results from the formation of scale within the existing scale layer by reaction between oxygen diffusing inward down the oxide grain boundaries and aluminum diffusing outward through the bulk oxide.20) On the other hand, Pint et al.21) have found that segregation of yttrium and zirconium at the Al2O3 grain boundaries blocks diffusion of cations and then alters the oxidation mechanism for oxidation of Al2O3-forming alloys with yttrium and zirconium. That is to say, α-Al2O3-forming alloys with reactive elements show planar morphologies by blocking outward diffusion of aluminum.20–22) In this study, the scale surface on the 1 ppmS alloy was planar, suggesting that oxidation of the alloy also take place only at the scale/alloy interface.

After oxidation at 1 673 K, surface morphology of all the alloys was almost the same, and was coarsened reticular as shown in Fig. 2. This result suggested that the wavy scale surface (scale formed on the 4, 7, and 6 300 ppmS after oxidation at 1 273 K as shown in Fig. 2) grows laterally, and then changes to planar because of higher plasticity of alloy and/or scale with increasing oxidation temperature. The reticular structure at the oxygen interface coarsens with increasing oxidation temperature as a result of grain growth in the scale.23)

Figure 3 shows scale surface and spalled area of the 7 ppmS oxidized at 1 373 K. In Fig. 3(a), many cracks were observed along the rod-shaped scale. The formation of many cracks may be attributed to compressive stress induced by different thermal expansion coefficients of oxide and alloy during cooling, and growth stresses. In Fig. 3(b), crater was recognized along the alloy grain boundaries.

Figure 4 shows (a) scale surface, (b) rear of scale and (c) alloy surface of the 53 ppmS exposed in oxygen for 18 ks at 1 473 K. The scale surface showed a convoluted morphology. Worm-like cavities were observed at the rear of the scale, and many craters were also recognized at the alloy surface. These results suggested that the worm-like cavities are formed at the rear of rod-shaped scale, and many craters on the alloy surface may be attributed to the formation of cavities.

The formation of the crater, as well as the case of Fig. 3(b), may be one of reasons of spalling of the scales because of reduction of adhesive area of the scale/alloy interface.3,9,10,12,13)

Figure 5 shows scales near triple points of alloy grain boundaries on the 53 ppmS exposed in oxygen for 18 ks at 1 573 K after cooling in (a) air and (b) liquid nitrogen. The surface oxide showed an intensive convoluted morphology. Some cracks were observed along the center of swollen area of the scales as shown in Fig. 5(a). After cooling in liquid nitrogen, spalling of scales was observed near the triple points of alloy grain boundaries because of compressive stresses induced by different thermal expansion coefficients of oxide and alloy, and high cooling rate. This result suggested that spalling of the scale is also influenced by cooling rate.

Figure 6 shows SEM of spalled areas of (a) 7 ppmS, (b) 491 ppmS and (c) 6 300 ppmS exposed in oxygen for 18 ks at 1 673 K. Many cups were observed in the scale/alloy im-
prints left in the alloy in the secondary-electron image. This
implies that the inward grain-boundary diffusion of oxygen
caused preferential growth at oxide grain boundaries, leav-
ing behind the centers of oxide grains. The dimple in the
center of the grain corresponds to a protrusion in the under-
lying alloy.

Figure 7 shows SEM and X-ray images of spalled area
of the 1 300 ppmS after oxidation for 18 ks at 1 473 K.
Chromium-sulfide particles, 1–5 μm in size, were found at
the alloy surface of the scale/alloy interface. The alloy sur-
face showed a convoluted morphology.

Figure 8 shows SEM and X-ray images of spalled area
of the 491 ppmS after oxidation for 18 ks at 1 573 K.
Large crater area, 100×17 μm² in size, was also recognized at the alloy surface. The chromium-sulfide particles of more than
10 μm in size were mainly observed at the edge area of the
crater. Sulfur (chromium sulfide) in the alloy mainly moves
toward the crater area on the alloy surface during oxidation,
and then large chromium-sulfide particles may be formed at
the alloy surface of the scale/alloy interface.

Figure 9 shows SEM and X-ray images of rear of scale
on the 6 300 ppmS after oxidation for 18 ks at 1 673 K.
Large chromium-sulfide area of 27 μm in size, and chromi-
num sulfide particles of 1 μm in size, were observed at the

Fig. 4. SEM micrographs of the scale on Fe–20Cr–4Al alloy
with 53 ppmS exposed in oxygen for 18 ks at 1 473 K. (a)
Outer scale surface, (b) inner scale surface and (c) alloy
surface.

Fig. 5. SEM micrographs of surface of Fe–20Cr–4Al alloy
with 53 ppmS exposed in oxygen for 18 ks at 1 573 K. (a)
Cooled in air and (b) cooled in liquid nitrogen.

Fig. 6. SEM micrographs of spalled areas of Fe–20Cr–4Al al-
loys with sulfur exposed in oxygen for 18 ks at 1 673 K.
(a) 7 ppmS, (b) 491 ppmS and (c) 6 300 ppmS.
scale-side of the scale/alloy interface. The scale-side consists mainly of alumina particles, 4–13 μm in size, and a concave was observed at the center of the alumina grains. As mentioned above, the formation of the concave suggested that the inward grain-boundary diffusion of oxygen causes preferential growth at alumina grain boundaries.12)

Figure 10 shows SEM and X-ray images of spalled area of the 6300 ppmS after oxidation for 18 ks at 1673 K. Comprehensive chromium-sulfide areas were observed at the alloy surface of the scale/alloy interface. Many cups were also observed at the chromium sulfide area. From observation of Figs. 9 and 10, it was suggested that a large number of chromium-sulfides are formed at the scale/alloy interface, and the chromium-sulfides increases at the alloy surface in comparison with the rear of the scales.

Figures 11 and 12 show SEM and X-ray images of cross-sections of the 6300 ppmS after oxidation at 1273 and 1473 K, respectively. Chromium-sulfide particles, 0.2–
2.5 μm in size, were observed along the scale/alloy interface, into the gains, and/or along the alloy grain boundaries after oxidation for 18 ks at 1 273 and 1 473 K. On the other hand, Cr-rich area was recognized along the grain boundaries near the alloy surface after oxidation for 18 ks at 1 273 K as shown in Fig. 11.

Quadakkers et al. and Khanna et al. studied the high-temperature oxidation of Ni–10Cr–9Al alloys with sulfur (20, 90 and 900 ppm) in air at 1 273 K, and Ni–10Cr–8Al alloys with sulfur (140, 540 and 800 ppm) in air at 1 373 K, respectively, and reported that oxidation rate of these alloys increased with an increase in the sulfur level of the alloy. They suggested that the presence of chromia and nickel oxide along with alumina on the alloys containing sulfur resulted in a higher growth rate. In the present study, it is considered that chromia is formed by initial oxidation of chromium sulfide particles in the alloy surface, therefore, the formation of chromia may relate to an increase of oxidation rate for the alloys containing sulfur.

Figures 13, 14, 15 and 16 show SEM and X-ray images of cross-sections of the 1, 4, 171 and 6 300 ppmS, respectively, after oxidation for 18 ks at 1 673 K. Oxygen/scale and scale/alloy interfaces of the 1 ppmS were almost planar and the both interfaces of the 4 ppmS showed slightly convoluted morphologies, however, the both interfaces of the 171 ppmS showed convoluted morphologies, and chromi-
um-sulfide particles were mainly observed at the scale/alloy interface. On the other hand, the both of oxygen/scale and scale/alloy interfaces of the 6 300 ppmS showed intensively convoluted morphologies. Chromium-sulfide layer was recognized at the scale/alloy interface, and chromium-sulfide particles were observed at the alloy grain boundaries near the alloy surface. From Figs. 13, 14, 15 and 16, the thickness of the 1, 4, 171 and 6 300 ppmS were 7, 8, 10 and 12 μm, respectively. This result also suggested that oxidation rate of the alloys increased with increasing sulfur content after oxidation at 1 673 K.

The scales on the alloys with 1 and 3 ppmS were planar, and they showed good adherence at any oxidation temperature. Intensive spalling of the scales was observed for the 4 and 7 ppmS after oxidation at 1 373 K, for the 4, 7, 35 and 104 ppmS after oxidation at 1 473 K, and for the 4, 7, 350 and 6 300 ppmS after oxidation at 1 673 K. The spalling of the scales is attributed to the convolution, void formation at the scale/alloy interface, and formation of chromium-sulfide layer at the interface.1,3–6,12)

Forest and Davidson6) suggested that the oxide-alloy interface in Fe–Cr–Al alloys containing less than 2 ppm sulfur resisted growth stresses in the oxide and the oxide remained adherent. Furthermore, the alloys containing 4 ppm sulfur caused considerable spalling. Therefore, our results are in good agreement with their study. On the other hand, the scales on the alloys with 35–6 300 ppmS at 1 373 K, with 171–6 300 ppmS at 1 473 K, showed good adherence. The thermal-expansion coefficient of the chromium-sulfide particles may show an intermediate value between those of Fe–Cr–Al and alumina. The formation of fine chromium-sulfide particles at the scale/alloy interface may have help to relieve the stress generated by the differential thermal-expansion coefficients of alumina and the alloy, thereby improving adherence.12) The presence of chromia, which was formed at the initial oxidation of fine chromium-sulfide particles at the alloy surface, may also improve ductility of alumina scales.14,15)

Table 3 shows summary of the features for oxide surface and scale/alloy interface of Fe–20Cr–4Al alloys with sulfur exposed to oxygen for 18 ks at 1 273, 1 373, 1 473, 1 573 and 1 673 K.

4. Conclusions

The oxidation of Fe–20Cr–4Al alloys with 1, 3, 4, 7, 35, 53, 104, 171, 185, 491, 1 300 and 6 300 ppmS has been studied in flowing oxygen for 18 ks at 1 273–1 673 K; the following results were obtained:

(1) The scales on the 4 and 7 ppmS alloys spalled from the entire surface after oxidation for 18 ks at any temperature, except for 1 273 K. On the other hand, the scales on the 1 and 3 ppmS showed good adherence after oxidation at any temperature.

(2) Scale morphology of the alloys changed from planar to convoluted with increasing sulfur content.

(3) Oxidation rate of the alloys tended to increase with increasing sulfur content.

(4) The formation of fine chromium-sulfide particles at the scale/alloy interface may help to relieve the stress generated by the differential thermal-expansion coefficients of α-Al2O3 and the alloys, however, the formation of chromium-sulfide layer at the scale/alloy interface resulted in massive scale spallation.

Acknowledgements

The authors are indebted to T. Sugawara of IMR, Tohoku University for preparation of alloys. This work was partially supported by the Grant-in-Aid for Scientific Research (C), The Ministry of Education, Science, Sports and Culture, Japan (No. 10650719). A part of this study was carried out under the inter-university cooperative research program of Laboratory for Advanced Materials, Institute for Materials
Table 3. Summary of the features of the scale and scale/alloy interface of Fe–20Cr–4Al alloys with sulfur exposed in oxygen for 18 ks at 1 273, 1 373, 1 473, 1 573 and 1 673 K.

| Alloy (ppm) | 1273 (K) | 1373 (K) | 1473 (K) | 1573 (K) | 1673 (K) |
|-------------|----------|----------|----------|----------|----------|
| 15          | no spalled, planar | no spalled, planar | no spalled, planar | no spalled, planar, reticular | no spalled, planar, coarsened reticular |
| 35          | no spalled, planar | no spalled, planar | no spalled, planar | no spalled, planar, reticular | no spalled, planar, coarsened reticular |
| 45          | fairly spalled, planar | entirely spalled, planar | entirely spalled, planar | entirely spalled, planar, reticular | entirely spalled, planar, coarsened reticular |
| 75          | no spalled, slightly wrinkled | entirely spalled, fine reticular | entirely spalled, fine reticular | entirely spalled, planar, nodule, reticular, voids, coarsened interfacial sulfides | partially spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |
| 35s         | no spalled, slightly wrinkled | no spalled, very wrinkled | entirely spalled, wrinkled, fine reticular, coarsened interfacial sulfides, voids | entirely spalled, planar-nodule, reticular, voids, coarsened interfacial sulfides | slightly spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |
| 55s         | no spalled, slightly wrinkled | no spalled, very wrinkled | partially spalled, wrinkled, fine reticular, coarsened interfacial sulfides, voids | entirely spalled, planar-nodule, reticular, voids, coarsened interfacial sulfides | no spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |
| 104s        | no spalled, slightly wrinkled | no spalled, very wrinkled | no spalled, slightly wrinkled, fine reticular, coarsened interfacial sulfides, bulk sulfides | partially spalled, planar-nodule, reticular, voids, coarsened interfacial sulfides | no spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |
| 171s        | no spalled, slightly wrinkled | no spalled, very wrinkled | no spalled, slightly wrinkled, fine reticular, coarsened interfacial sulfides, bulk sulfides | some spalled, planar-nodule, reticular, voids, coarsened interfacial sulfides | partially spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |
| 185s        | no spalled, slightly wrinkled | no spalled, very wrinkled | no spalled, slightly wrinkled, fine reticular, coarsened interfacial sulfides, bulk sulfides | partially spalled, planar-nodule, reticular, voids, coarsened interfacial sulfides | some spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |
| 491s        | no spalled, slightly wrinkled | no spalled, very wrinkled | no spalled, slightly wrinkled, fine reticular, coarsened interfacial sulfides, bulk sulfides | some spalled, planar-nodule, reticular, voids, coarsened interfacial sulfides, bulk sulfides | some spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |
| 1300s       | no spalled, slightly wrinkled | no spalled, very wrinkled | no spalled, slightly wrinkled, fine reticular, coarsened interfacial sulfides, bulk sulfides | entirely spalled, planar+rods, coarsened reticular, voids, plate-like interfacial sulfides, bulk sulfides | no spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |
| 6300s       | no spalled, slightly wrinkled | no spalled, very wrinkled | no spalled, slightly wrinkled, fine reticular, coarsened interfacial sulfides, bulk sulfides | entirely spalled, planar+rods, coarsened reticular, voids, plate-like interfacial sulfides, bulk sulfides | no spalled, planar+rods, coarsened reticular, voids, coarsened interfacial sulfides |

© 2004 ISIJ