

## Oxidation of Alumina-Forming Alloys with Small Amounts of Sulfur at 1273 K

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High-temperature oxidation behavior of Fe-20Cr-4Al alloys with small amounts of sulfur (2 ~ 1300 ppmS) was studied in a dry air at 1273 K for 1800 and 3600 ks by mass-change measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron probe microanalysis (EPMA). Oxide scales on the 7 ppmS alloy spalled from the entire surface after oxidation for 1800 and 3600 ks. On the other hand, oxide scales on the other alloys showed good oxide adherence after any oxidation time. Mass gains of the alloys, except the 7 ppmS alloy, tended to increase with increasing sulfur content after oxidation for 1800 and 3600 ks. Oxide scales formed on all of the alloys with sulfur were  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. After oxidation for 1800 ks, oxide scales on the alloys with sulfur changed from planar to wavy morphology with increasing sulfur content. Cross-section of the oxide scales formed on the alloys with sulfur also changed from planar to wavy morphology with increasing sulfur content after oxidation for 3600 ks. Before oxidation, sulfur in the alloys more than 40 ppmS existed all over the matrix as chromium-sulfide particles, and then moved to the oxide/alloy interface during oxidation.

Keywords: Oxide adherence, Alumina scale, Sulfur, Heat-resistant alloy, Chromium sulfide

### 1. INTRODUCTION

An oxide scale of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> forms on the alloys when alumina-forming heat-resistant alloys are exposed to high temperatures of more than 1273 K in an oxidizing atmosphere. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale often spalls during cooling after oxidation. Various hypotheses have been offered to explain spalling of oxide scale, and it has been recently focused on segregation of sulfur at the oxide-alloy interface [1-14]. 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 1273 to 1673 K [12]. Spalling of oxide scales on the 3 and 171 ppmS alloys was scarcely observed at any temperature and any cycles of oxidation. However, oxide scales on the 35 and 53 ppmS alloys spalled massively after cyclic oxidation at 1473 and 1573 K. This result suggested that spalling of oxide scales on the alloys depends on sulfur contents and temperature and cycles of oxidation.

In this present study, the oxidation behavior of Fe-20Cr-4Al alloys with small amounts of sulfur was studied in a dry air (100cc/min) for 1800 and 3600 ks at 1273K, in order to better understand the oxide adherence at the oxide-alloy interface.

### 2. EXPERIMENTAL PROCEDURES

Ingots of Fe-20Cr-4Al alloys with varying levels of sulfur impurity (2, 7, 40, 185, 491, and 1300 ppm) were prepared by arc melting, and then hot-rolled and cold-rolled to a sheet of 0.5 mm thickness. The specimens were then annealed in a vacuum for 18 ks at 1473 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 a flowing dry air (100 cc/min) for 1800 and 3600 ks at 1273 K. The mass change was measured after oxidation, and the appearance of samples was also observed. The oxide formed on the alloys was identified by XRD. The morphology of oxide scales on the alloys was observed by SEM. The compositions of the oxide and oxide-alloy interface of the alloys were examined by EPMA.

### 3. RESULTS AND DISCUSSION

#### 3.1 Mass change

Fig. 1 shows mass changes of the Fe-20Cr-4Al alloys with sulfur at 1273 K for 1800 and 3600 ks. Mass changes of the alloys, except the 7 ppmS alloy, increased with increasing sulfur and oxidation temperature [14].

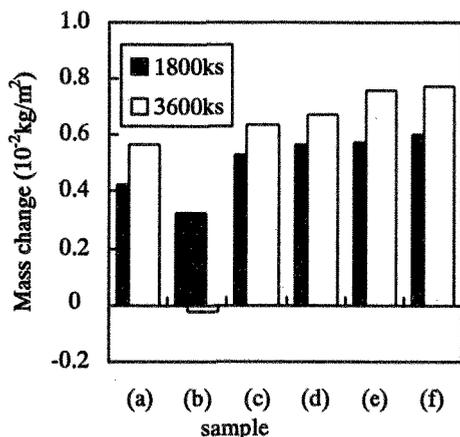


Fig.1 Mass change of Fe-20Cr-4Al alloys with small amounts of sulfur exposed at 1273 K for 1800 and 3600 ks in a dry air. (a) 2 ppmS; (b) 7 ppmS; (c) 40 ppmS; (d) 185 ppmS; (e) 491 ppmS; (f) 1300 ppmS.

On the other hand, mass changes of the 7 ppmS alloy decreased in comparison with those of the other alloys because of spalling of oxide scales on the alloy after oxidation for 1800 and 3600 ks.

### 3.2 Surface appearance and X-ray diffraction

Fig. 2 shows the surface appearance of the alloys with sulfur. After oxidation at 1273 K for 1800 and 3600 ks, oxide scales on all of the alloys, except the 7 ppmS alloy, showed good adherence, and the color of oxide scales on the alloys changed from gray to dark gray with increasing sulfur content. Oxide scales on the 7 ppmS alloy spalled markedly increasing with oxidation time. This result was in good agreement with data of Fig. 1.

Table I shows X-ray diffraction results for the Fe-20Cr-4Al alloys with sulfur after oxidation at 1273 K for 3600 ks. Oxide scales on all of the alloys were recognized as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The very weak peak strength

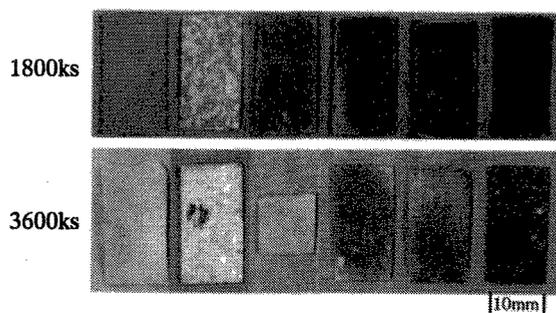


Fig.2 Surface appearance of Fe-20Cr-4Al alloys with small amounts of sulfur exposed at 1273 K for 1800 and 3600 ks in a dry air. (a) 2 ppmS; (b) 7 ppmS; (c) 40 ppmS; (d) 185 ppmS; (e) 491 ppmS; (f) 1300 ppmS.

Table I X-ray diffraction analysis of Fe-20Cr-4Al alloys with small amounts of sulfur exposed at 1273 K for 3600 ks in a dry air.

Alloy	Oxide
Fe-20Cr-4Al (2 ppmS)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (m)
Fe-20Cr-4Al (7 ppmS)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (vw)
Fe-20Cr-4Al (40 ppmS)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (m)
Fe-20Cr-4Al (185 ppmS)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (m)
Fe-20Cr-4Al (491 ppmS)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (m)
Fe-20Cr-4Al (1300 ppmS)	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (m)

vw:very weak. m:medium.

of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> for the 7 ppmS alloy depended on spalling of oxide scales on the alloy.

### 3.3 Scanning electron microscopy and electron probe microanalysis

Figs. 3 and 4 show typical surface views of the alloys with sulfur exposed in a dry air for 1800 and 3600ks, respectively. The surfaces of the 2 ppmS alloy showed almost planar morphology after the both of oxidation time. On the other hand, the surface of the other alloys changed from small wavy to large wavy increasing with sulfur content and oxidation time.

Fig. 5 shows the spalled region of oxide scale on the 7 ppmS alloy exposed for 3600 ks at 1273 K. Many voids, about 10 ~ 70  $\mu$ m in size, were observed along with alloy grain boundaries and in the grains at the oxide-alloy interface. The void formation may enhance spalling of oxide scale because of a decrease in adherent

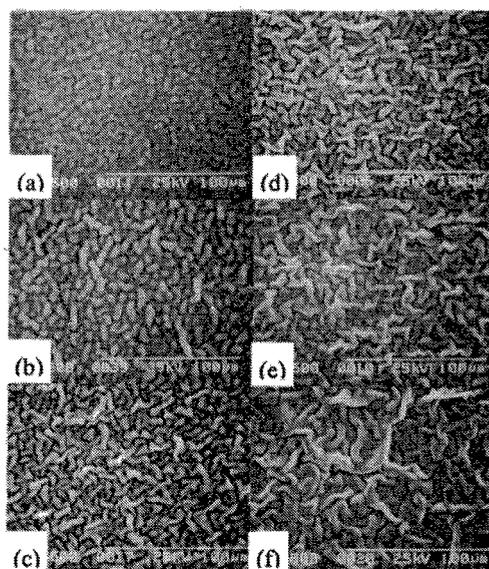


Fig.3 Scanning electron micrographs of oxide on Fe-20Cr-4Al alloys with small amounts of sulfur exposed at 1273 K for 1800 ks in a dry air. (a) 2 ppmS; (b) 7 ppmS; (c) 40 ppmS; (d) 185 ppmS; (e) 491 ppmS; (f) 1300 ppmS.

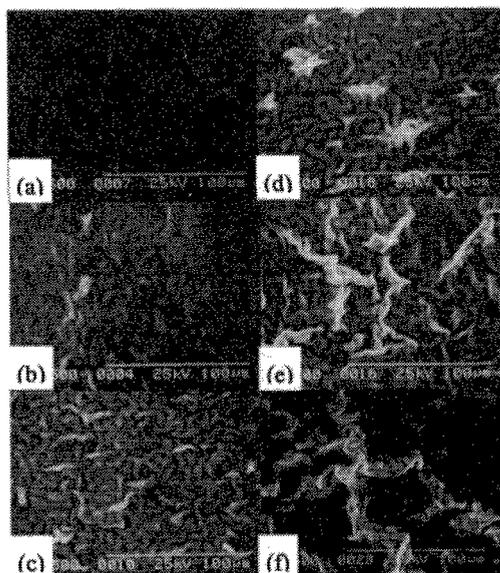


Fig.4 Scanning electron micrographs of oxide on Fe-20Cr-4Al alloys with small amounts of sulfur exposed at 1273 K for 3600 ks in a dry air.

(a) 2 ppmS; (b) 7 ppmS; (c) 40 ppmS; (d) 185 ppmS; (e) 491 ppmS; (f) 1300 ppmS.

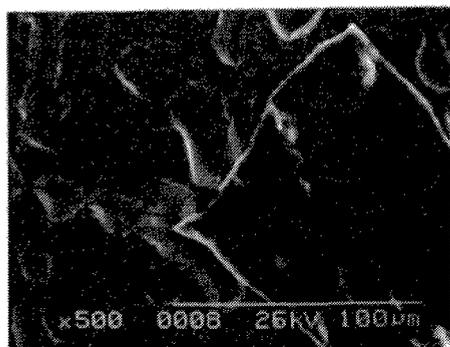


Fig.5 Scanning electron micrographs of spalled area of oxide on the 7 ppmS alloy exposed at 1273 K for 3600 ks in a dry air.

cross-section of the oxide-alloy interface [3, 9, 10, 12, 13].

Fig. 6 shows cross-section of the scales formed on all of the alloys after oxidation at 1273 K for 3600 ks. The oxide scale of the 2 ppmS alloy showed planar morphology, and those of the other alloys, except the 7 ppmS alloy, changed from small wavy to large wavy morphology increasing with sulfur content. On the other hand, some concave curvatures were observed at the oxide-alloy interface of the 7 ppmS alloy. The region of the concave curvatures suggests the void formation.

Fig. 7 shows cross-sectional plus corresponding X-ray images of the scales formed on the 491 ppmS alloy after oxidation at 1273 K for 1800 ks. Before oxidation, sulfur in the 491 ppmS existed in the substrate as

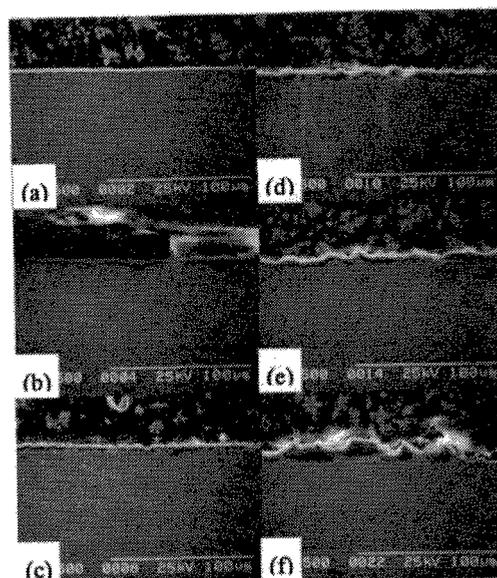


Fig.6 Microstructure of cross-section of Fe-20Cr-4Al alloys with small amounts of sulfur exposed at 1273 K for 3600 ks in a dry air. (a) 2 ppmS; (b) 7 ppmS;

(c) 40 ppmS; (d) 185 ppmS; (e) 491 ppmS; (f) 1300 ppmS.

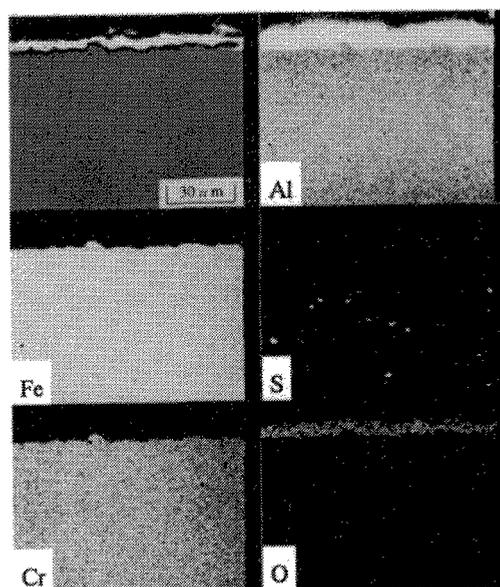


Fig.7 Microstructure and X-ray images of cross-section of the 491 ppmS exposed at 1273 K for 1800 ks in a dry air.

chromium-sulfide particles less than  $2 \mu\text{m}$  in size. After oxidation at 1273 K for 1800 ks, the surface of the alloy was covered with an  $\alpha\text{-Al}_2\text{O}_3$ , and the oxide surface and oxide-alloy interface showed a wavy morphology. Some chromium-sulfide particles, 1-2  $\mu\text{m}$  in size, were observed in the substrate and at the oxide-alloy interface, as shown in Fig. 7. The formation of small chromium-sulfide particles at the

oxide-alloy interface is believed to lead to oxide adherence [12].

#### 4. CONCLUSIONS

The oxidation of Fe-20Cr-4Al alloys with 2, 7, 40, 185, 491, and 1300 ppm of sulfur has been studied in a dry air at 1273 K for 1800 and 3600 ks; the following results were obtained:

1. Oxide scales on the 7 ppmS alloy spalled from the entire surface after oxidation for 1800 and 3600 ks. On the other hand, oxide scales on the other alloys showed good oxide adherence after any oxidation time.
2. Spalling of oxide scales was dependent upon the void formation at the oxide-alloy interface.
3. Mass gains of the alloys, except the 7 ppmS alloy, tended to increase with increasing sulfur content after oxidation for 1800 and 3600 ks.
4. The formation of fine chromium-sulfide particles at the oxide-alloy interface may help to relieve the stress generated by the differential thermal-expansion coefficients of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and the alloys.

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