

Oxidation of Alumina-Forming Alloys with Small Amounts of Sulfur and Reactive Elements (Y, Hf) at 1273 K

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The oxidation behavior of Fe-20Cr-4Al alloys with sulfur (185 ppmS) and/or reactive element (10, 300, 800, and 3700 ppmY, 500, 900, 1900, and 4300ppmHf) was studied in a dry air at 1273 K for 1800 and 3600 ks by mass gain measurements, X-ray diffraction (XRD). Spalling of oxide scales on all of the alloys was not recognized after the both of oxidation time. Mass gain decreased for alloys with small additions of reactive element, and then increased with increasing reactive element content. Oxide scales on the 185ppmS and the 500 ppmHf alloys showed wavy morphology. On the other hand, Oxide scales on the other alloys with reactive element changed from small wavy to planar morphology with increasing reactive element after the both of oxidation time. Oxide scales formed on all of the alloys were recognized as mainly α -Al₂O₃. After oxidation for 3600 ks, Y₃Al₅O₁₂ particles were observed for the 800 and the 3700 ppmY alloys, and HfO₂ particles were also detected for the 1900 and the 4300 ppmHf alloys.

Key Words: Oxide adherence, Alumina scale, Sulfur, Yttrium, Hafnium

1. INTRODUCTION

An oxide scale of α -Al₂O₃ 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 α -Al₂O₃ 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 [1-13]. On the other hand, to improve the oxide adherence, many studies have been conducted with regard to the effect of small additions of reactive elements such as rare earths, zirconium and hafnium [14-18]. However, high-temperature oxidation studies of heat-resistant alloys containing controlled levels of both sulfur and reactive elements have been scarcely conducted, and the oxidation behavior of such alloys is complicated [11, 13, 19-20]. In the present study, the oxidation behavior of Fe-20Cr-4Al alloys with sulfur (185 ppm) and/or reactive element (Y, Hf) additions was studied in a dry air at 1273K for 1800 and 3600 ks, in order to clarify the relationship between sulfur and yttrium or hafnium.

2. EXPERIMENTAL PROCEDURES

Buttons weighing 50 g were prepared by arc-melting in a water-cooled hearth in an argon atmosphere. The base composition of the alloys was nominally Fe-20Cr-4Al with 185 ppm sulfur. The reactive-element additions to this base composition were: 10, 300, 800, 3700 ppm yttrium, and 500, 900, 1900, 4300 ppm hafnium. The measured sulfur content in the alloys containing 10 ppmY, 300 ppmY, 800 ppmY, 3700 ppmY, 500 ppmHf, 900 ppmHf, 1900 ppmHf and 4300 ppmHf were 151, 80, 40, 159, 138, and 151 ppm, respectively. The buttons were hot- 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 gain 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 the oxide surface and oxide-alloy interface was observed by SEM. The compositions of oxide-alloy interface were examined by EPMA.

3. RESULTS AND DISCUSSION

3.1 Mass gain

Figure 1 shows mass gains of the Fe-20Cr-4Al alloys with sulfur and reactive elements exposed in dry air at 1273 K for 1800 and 3600 ks. Mass gains of the alloys with small amounts of yttrium or hafnium decreased, and then increased with increasing reactive elements. Mass gains of all of the alloys increased with increasing oxidation time, and that of the 900 ppmHf alloy showed the smallest values after the both of oxidation time. Mass gain of the 4300 ppmHf alloy increased markedly in comparison with that of the other alloy.

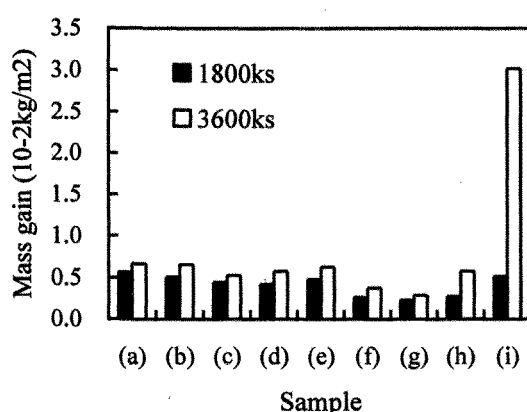


Fig. 1 Mass gain of Fe-20Cr-4Al alloys with small amounts of sulfur and reactive elements (Y, Hf) exposed in a dry air at 1273K for 1800 and 3600ks. (a) 185ppmS; (b) 10ppmY; (c) 300ppmY; (d) 800ppmY; (e) 3700ppmY; (f) 500ppmHf; (g) 900ppmHf; (h) 1900ppmHf; (i) 4300ppmHf.

3.2 Surface appearance and X-ray diffraction

Figure 2 shows the surface appearance of the alloys with sulfur and reactive elements. Oxide scales on all of the alloys showed good adherence, and the color of oxide scales on the alloys tended to change from gray to dark gray increasing with reactive element content after oxidation time of 3600ks.

Table I shows X-ray diffraction results for the Fe-20Cr-4Al alloys with sulfur and reactive elements after oxidation at 1273 K for 3600 ks. Oxide scales on all of the alloys were recognized as mainly α -Al₂O₃. Y₃Al₅O₁₂ was detected for the 800 ppmY and 3600 ppmY alloys, and HfO₂ was also detected for the 1900 ppmHf and the 4300 ppmHf alloys. The peak strength of the Y₃Al₅O₁₂ and HfO₂ increased with increasing

reactive element content.

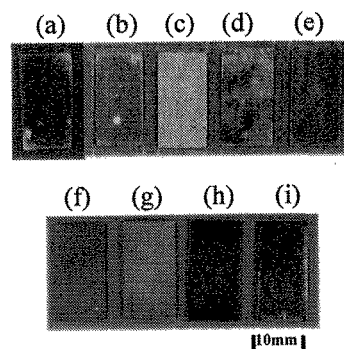


Fig. 2 Surface appearance of Fe-20Cr-4Al alloys with small amounts of sulfur and reactive elements (Y, Hf) exposed in a dry air at 1273K for 3600ks. (a) 185ppmS; (b) 10ppmY; (c) 300ppmY; (d) 800ppmY; (e) 3700ppmY; (f) 500ppmHf; (g) 900ppmHf; (h) 1900ppmHf; (i) 4300ppmHf.

Table I X-ray diffraction analysis of Fe-20Cr-4Al alloys with small amounts of sulfur and reactive elements (Y, Hf) exposed in a dry air at 1273K for 3600ks.

Alloy	Oxides
Fe-20Cr-4Al (185ppmS)	α -Al ₂ O ₃ (m)
Fe-20Cr-4Al (10ppmY)	α -Al ₂ O ₃ (m)
Fe-20Cr-4Al (300ppmY)	α -Al ₂ O ₃ (m)
Fe-20Cr-4Al (800ppmY)	α -Al ₂ O ₃ (m)
	Y ₃ Al ₅ O ₁₂ (vw)
Fe-20Cr-4Al (3700ppmY)	α -Al ₂ O ₃ (m)
	Y ₃ Al ₅ O ₁₂ (w)
Fe-20Cr-4Al (500ppmHf)	α -Al ₂ O ₃ (m)
Fe-20Cr-4Al (900ppmHf)	α -Al ₂ O ₃ (m)
Fe-20Cr-4Al (1900ppmHf)	α -Al ₂ O ₃ (m)
	HfO ₂ (w)
Fe-20Cr-4Al (4300ppmHf)	α -Al ₂ O ₃ (s)
	HfO ₂ (m)

s :strong, m :medium, w :weak, vw :very weak.

3.3 Scanning electron microscopy and electron probe microanalysis

Figure 3 shows typical surface views of the alloys with sulfur and reactive elements exposed in a dry air at 1273K for 3600ks. The oxide surface on the 185ppmS alloy showed markedly wavy morphology, and that on the 10ppmY alloy showed slightly wavy morphology. On the other hand, the oxide morphology of the 300ppmY, the 800ppmY and the 3700ppmY alloys was planar. Small

particles of $0.3 \sim 4.3 \mu\text{m}$ in size on the oxide surfaces of these three alloys with yttrium increased with increasing yttrium content.

The oxide surface on the 500ppmHf alloy showed markedly wavy morphology, and that on the 900ppmHf alloy showed wavy morphology. Many cracks were observed along the center of the ridges of wavy oxide scales. The formation of many cracks may lead to spall oxide scales. On the other hand, the surfaces on the 1900ppmHf and the 4300ppmHf alloys were almost planar. Small particles were also observed on the oxide surfaces of the 1900ppmHf and the 4300ppmHf alloys. These results suggested that the smoothing of the surface oxides was increased by yttrium content more than hafnium. Small particles on the alloys with yttrium and hafnium seemed to be $\text{Y}_3\text{Al}_5\text{O}_{12}$ and HfO_2 , respectively.

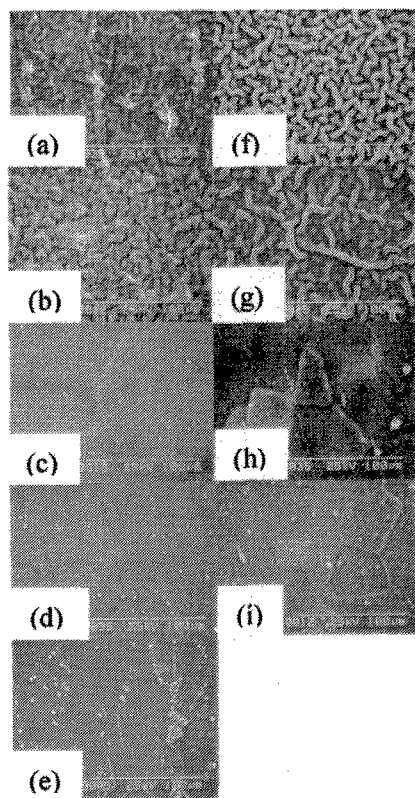


Fig. 3 Scanning electron micrographs of oxide on Fe-20Cr-4Al alloys with small amounts of sulfur and reactive elements (Y, Hf) exposed in a dry air at 1273K for 3600ks. (a) 185ppmS; (b) 10ppmY; (c) 300ppmY; (d) 800ppmY; (e) 3700ppmY; (f) 500ppmHf; (g) 900ppmHf; (h) 1900ppmHf; (i) 4300ppmHf.

Figure 4 shows cross-section of the scales

formed on all of the alloys after oxidation at 1273 K for 3600 ks. The oxide-alloy interface of the 185 ppmS and the 10 ppmY alloys showed wavy morphology. The oxide surfaces of the 300ppmY, the 800ppmY and the 3700ppmY alloys were planar, however, oxide scales on the 800 ppmY and the 3700 ppmY alloys protruded into the substrate along alloy grain boundaries of the oxide-alloy interface.

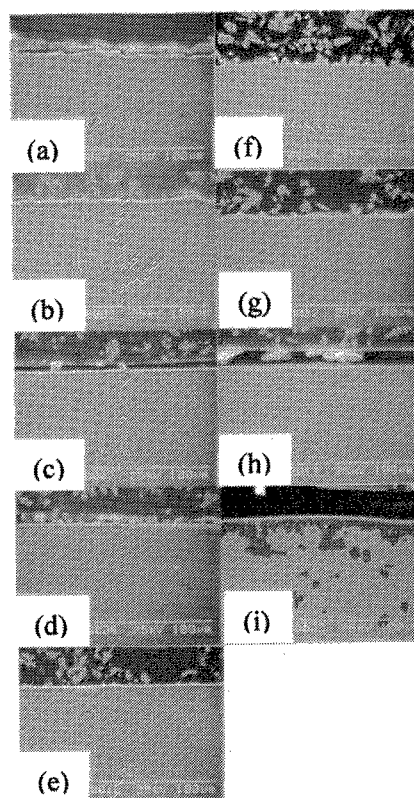


Fig. 4 Microstructure of cross-section of oxide on Fe-20Cr-4Al alloys with small amounts of sulfur and reactive elements (Y, Hf) exposed in a dry air at 1273K for 3600ks. (a) 185ppmS; (b) 10ppmY; (c) 300ppmY; (d) 800ppmY; (e) 3700ppmY; (f) 500ppmHf; (g) 900ppmHf; (h) 1900ppmHf; (i) 4300ppmHf.

The oxide scales on the 185 ppmS, the 10 ppmY, the 300 ppmY, the 800 ppmY and the 3700 ppmY alloys showed good adherence. On the other hand, oxide scales on the 500 ppmHf and the 900 ppmHf were not recognized because of spalling during polishing. The oxide scales on the two alloys did not showed good adherence. This result was presumed from surface morphology of oxide scales on the alloys shown in Fig. 3. The oxide surface of the 1900 ppmHf and 4300 ppmHf alloys showed

planar, and the oxide scales on the both of the alloys protruded into the substrate at many regions, and showed good adherence. The marked protrusion of the 4300 ppmHf suggested that mass gain of the alloy increased considerably as shown in Fig. 1. As mentioned above, sulfur contents in the 10 ppmY, 300 ppmY, 3700 ppmY, 500 ppmHf, 1900 ppmHf and 4300 ppmHf alloys were 151, 80, 40, 159, 138 and 151 ppm, respectively. This result suggests that the effect of yttrium addition is to remove sulfur impurity.

In this respect, yttrium is more effective than hafnium addition. In order to greater clarify oxide adherence on the alloys, it will be important to study the behavior of sulfur, reactive element sulfides, reactive element oxides and reaction between α -Al₂O₃ and reactive element oxides at high temperatures.

4. CONCLUSIONS

The oxidation behavior of Fe-20Cr-4Al alloys with sulfur (185 ppmS) and/or reactive elements (Y, Hf) has been in a dry air at 1273 K for 1800 and 3600 ks; the following results were obtained:

1. Spalling of oxide scales on all of the alloys was not recognized after the both of oxidation time.
2. Mass gain decreased for the alloys with proper additions of reactive elements.
3. Oxide scales on the alloys with reactive elements changed from wavy to planar morphology with increasing reactive elements.
4. Yttrium was more effective than hafnium addition for oxide adherence.

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