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The effects of Cr and Al concentrations on the oxidation behavior of oxide dispersion strengthened ferritic alloys

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ABSTRACT

The oxidation of six oxide dispersion strengthened (ODS) ferritic alloys was investigated at 1050 °C in air up to 200 h. Al plays the dominant role in improving the oxidation resistance of the ODS alloys. Cr and Y are of importance in forming the stable Al_2O_3 scale. To produce the dense alumina layer with enhanced adherence to the metal substrate, the concentrations of Al and Cr should be larger than 2 and 14 wt.%, respectively.

1. Introduction

Oxide dispersion strengthened (ODS) alloys have been considered as candidates for turbine blade in space industry and for high temperature units in chemical industry because of their good high temperature strength and resistance to high-temperature oxidation and sulfidation. Oxide dispersions not only enhance the creep strength, but also bring benefit to the oxidation resistance of both Fe and Ni-base ODS alloys [1–5]. Among various oxides, Y_2O_3 is one of the most effective oxides to improve the high temperature performances of Fe/Ni-base alloys and intermetallic compounds [4–7]. Recently, in order to improve the efficiency of energy production, advanced nuclear power plants are designed to operate at higher temperatures under different coolants including sodium, Pb–Bi alloy, He gas and super critical water [8–11]. Since the austenitic steels have a significant problem of high thermal expansion, the ferritic ODS alloys have been recognized as the potential materials for fission and fusion systems [12].

The oxidation behavior of ferritic ODS alloys has been investigated previously. Kaito and coworkers suggested that the 12Cr–ODS alloys had superior high temperature oxidation resistance compared to 17 wt.% Cr ferritic stainless steel due to the effects of Y_2O_3 [13]. It was also reported that the oxidation rate of the 13Cr–ODS alloys at 1000 °C was 200 times higher than that of the 21Cr–ODS alloys, which is known to form a protective chromia scale [14,15]. On the other hand, the Fe–Cr–Al ODS alloys often exhibit good oxidation resistance [16–19]. Previous studies showed that MA956 (4.5 wt.% Al and 20 wt.% Cr), ODM751 (4.5 wt.% Al and 16.5 wt.% Cr) and PM2000 (5.5 wt.% Al and 20 wt.% Cr) formed an external adherent scale of α-Al_2O_3 during the exposure to air at 1100–1200 °C up to 4800 h. Moreover, the oxidation rate of ODM751 was lower than MA956 [20,21]. However, the oxidation behavior of the ODS alloys with the Al concentration lower than 4 wt.% and Cr concentration between 11 and 18 wt.% have not been discussed systematically in the previous studies. Moreover, the synergistic effect of the Al and Cr concentration on the oxidation behavior of ODS alloys need to be investigated further. Therefore, in this work, ODS ferritic alloys with Cr ranging from 11 to 18 wt.% and Al from 0 to 4 wt.% are adopted to examine their oxidation behavior with particular emphasis on the role of the alloying elements.

2. Experimental

The chemical compositions of six ODS alloys referred as S1–S6 are given in Table 1. For comparison, one commercially available Fe–Cr alloy (SUS430) was also tested, whose composition is listed in Table 2. The manufacturing process of the ODS alloys was described elsewhere [22,23]. All the specimens were cut from the extruded rods in the form of square-sheet with the dimension of $7 \times 7 \times 1$ mm^3. The surfaces of the specimens were mechanically abraded with SiC papers up to 1200 grade to remove the preformed oxide layer. Then, the samples were ultrasonically cleaned in acetone for 5 min. Before the oxidation tests, their weights were measured using a balance with a resolution of 0.01 mg.

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Table 1
The compositions of the ferritic ODS alloys (wt.%).

ID	Cr	Al	Ti	Y_2O_3	C	Fe
S1	16	4	0.1	0.35	0.02	Balance
S2	14	4	0.1	0.35	0.02	Balance
S3	18	4	0.1	0.35	0.02	Balance
S4	16	2	0.1	0.35	0.02	Balance
S5	16	0	0.1	0.35	0.02	Balance
S6	11	2	0.1	0.35	0.02	Balance

Table 2
The composition of SUS430 (wt.%).

Cr	Mn	Ni	P	S	Si	C	Fe
16.8	0.94	0.04	0.03	0.02	0.68	0.1	Balance

The oxidation experiments were conducted at 1050 °C in air with each specimen in one alumina crucible. The mass variations were evaluated to determine the oxidation kinetic by weighing the specimens at the intervals of 1, 3, 6, 15, 30, 60, 100, 150 and 200 h. After the oxidation tests, the cross-section samples were prepared using an argon ion beam cross section polisher (JEOL SM-09010) at 6 kV. Then, the surfaces and cross sections of the selected specimens were analyzed by scanning electron microscopy (SEM, JEOL JSM-5800) at 20 kV coupled with electron probe microanalysis (EPMA, JEOL JXA-8100) at 5.77×10^{-8} A and 20 kV to evaluate the thickness, morphology and element distribution of the oxide scales. X-ray diffractometer (XRD, Rigaku D/Max) with monochromatic Co Kα radiation was used to determine the phases of the oxidation products on the surface of these specimens. The scanning rate was 2°/min from 20° to 110°.

3. Results and discussion

3.1. Oxidation kinetics

It is well known that the oxidation kinetics determine the lifetime of the alloys operated at high temperatures, and the low oxidation rate is accomplished through the formation of a protective external oxide scale. In an attempt to analyze the oxidation kinetics, the mass changes of the alloys annealed at 1050 °C in air are drawn as a function of time, shown in Fig. 1. It is found that the slopes of the rapid increasing part in the mass gain curves depend on the alloy composition. The lower the Al concentration in the ODS alloys is, the steeper the mass gain curve becomes. After passing the rapid weight increasing region of about 30 h, the curves of S1–3 become almost parallel, and the same is true for the curves of S4 and S5. However, the slopes of S1–3 are slightly lower than those of S4 and S5. It is also found that after 200 h of oxidation, S1, S2 and S3 with the same Al content of 4 wt.% exhibit quite similar oxidation resistance, with very low mass gain of about 4 g/m^2. This indicates that if the Al content is high enough, the change of Cr (between 14 and 18 wt.%) does not influence the mass gain of the ODS alloys apparently. For the ODS alloys S5, S4 and S1 with the same Cr content of 16 wt.%, after 200 h of oxidation, the oxidation resistance is greatly improved with the increase of Al concentration from 0 to 2 and 4 wt.%, and the mass gain decreases from 8.6 to 7.6 and 4 g/m^2. Compared with S4 (16 wt.% Cr and 2 wt.% Al), S6 (11 wt.% Cr and 2 wt.% Al) shows severe oxidation with mass gains of 95 g/m^2 after 200 h of oxidation, about 10 times higher

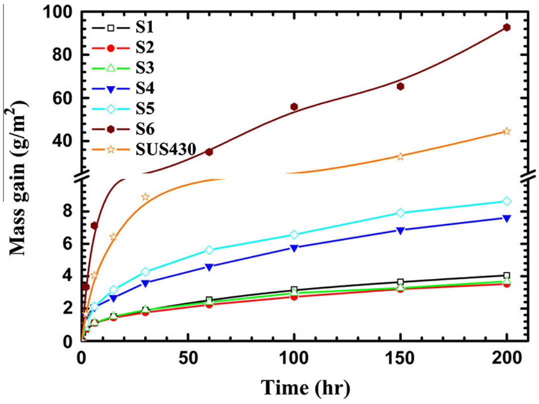

Fig. 1. The mass gain dependence of the time of the samples annealed at 1050 °C in air.

Table 3
The n values of each sample annealed at 1050 °C in air.

Sample ID	n	Error of n
S1	0.382	0.007
S2	0.346	0.009
S3	0.338	0.006
S4	0.384	0.012
S5	0.397	0.013
S6	0.767	0.049
SUS430	0.522	0.078

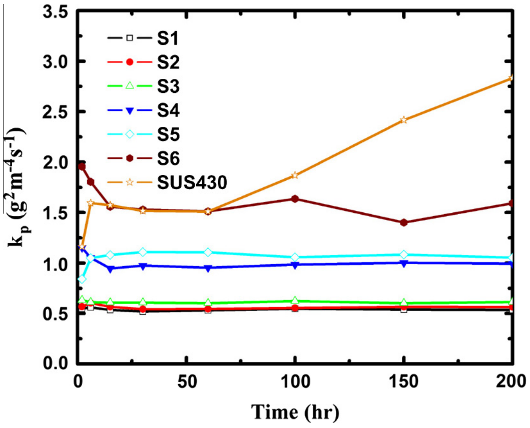

Fig. 2. The variation of k_p versus exposure time for each sample annealed at 1050 °C.

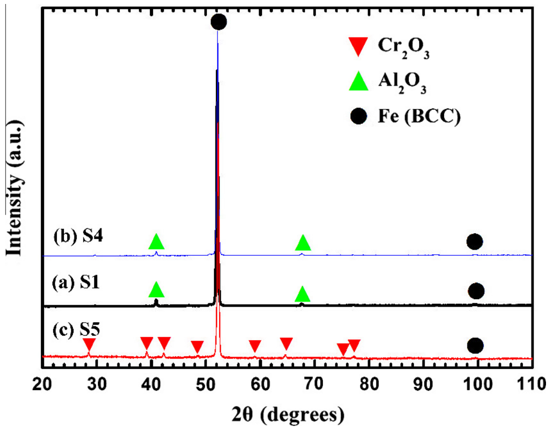

Fig. 3. XRD patterns of S1, S4 and S5 annealed at 1050 °C for 200 h.