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Effects of doping elements on oxidation properties of V–Cr–Ti type alloys in several environments

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Abstract

The alloys examined in this study include V–4Cr–4Ti–0.5Si, V–4Cr–4Ti–0.5Al, V–4Cr–4Ti–0.5Y and V–4Cr–4Ti. Oxidation experiments were conducted in air. After oxidation, tensile tests, hardness measurements and scanning electron microscopy were performed. Surface oxidation layers were identified by X-ray diffraction (XRD) analysis. Based on this study, the alloy doped with Y was excellent in oxidation resistance at 600 and 700 °C. The XRD indicated that V_2O_5 was the primary oxide phase for the alloys tested at 700 °C, except for the V–4Cr–4Ti–0.5Y alloy. The oxide identified at all temperatures in V–4Cr–4Ti–0.5Y alloy was VO_2, that was also observed for the other alloys after testing at 600 °C. It was suggested that the formation of thin and dense VO_2 oxide layers had an important role for superior oxidation properties of the V–4Cr–4Ti–0.5Y alloy. From the results of this study, further optimization of the V–4Cr–4Ti alloy could be possible by controlling the small addition of yttrium.

1. Introduction

The alloys of V–Cr–Ti with and without Si, Al and Y [1] show excellent mechanical properties at high temperature [2–4] and irradiation characteristics [5,6] as low-activation structural materials for nuclear fusion reactors [7,8]. The improvement of the oxidation resistance at high temperature is considered from practical standpoint as one of the important problems [9–11]. In Table 1, the oxidation issues of vanadium alloys for fusion applications are summarized [12–16]. Therefore, it is very important to examine the oxidation behavior (in various atmospheres in high-temperature regions assumed for fusion reactors) of V–4Cr–4Ti and V–4Cr–4Ti–Si–Al–Y alloys regarded as candidates for further development of the practical vanadium alloys. Especially important is to clarify the effect of Si, Al and Y which are the doping elements added to the alloy on the high-temperature oxidation behavior [17–19].

In this study, oxidation experiments were conducted in air at high temperature on the V–4Cr–4Ti type alloys which contained additions of Si, Al and Y. The objectives of this study are to evaluate the oxidation behavior, determine the effect of doping elements of the alloy on the mechanical behavior, and obtain the basic guideline for the development of low-activation oxidation-resistance vanadium alloys for application in fusion reactors.

2. Experimental procedure

The alloys examined in this study included (in wt%) V–4Cr–4Ti–0.5Si, V–4Cr–4Ti–0.5Al, V–4Cr–4Ti–0.5Y and V–4Cr–4Ti. The alloys were prepared at Tohoku University and V–4Cr–4Ti alloy was developed at the National Institute for Fusion Science (NIFS). In order to reduce the contamination of the interstitial impurity elements (such as C, O and N), high purity V and Ti

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Table 1
Oxidation issues of vanadium alloys for fusion applications [12–16]

Exposure environment	Applicable component in a fusion system	Typical service condition
Vacuum	Plasma facing component	$\approx 1 \times 10^{-6}$ Pa [12]
Helium	He-cooled blanket structure	350–650 °C [13]
Lithium	Li-cooled blanket structure with ceramic coating	300–700 °C (for ARIES-RS) [14]
Air	Vacuum component safety under leakage	Operating temperature, ≈600 °C [15]
Water	Component with water cooling	High-temperature pressurized water, 200–300 °C [16]

Table 2
Chemical composition of the vanadium alloys used in the study (in wt%)

	V	Ti	Cr	Si	Al	Y	C	O	N	H
V–4Cr–4Ti	Balance	4.1	4.4	–	–	–	0.0067	0.0181	0.0088	0.0018
V–4Cr–4Ti–0.5Si	Balance	4.01	4.03	0.421	0.02	0.0002	0.0228	0.0161	0.0552	0.0010
V–4Cr–4Ti–0.5Al	Balance	3.85	3.97	0.014	0.44	0.0002	0.0238	0.0140	0.0641	0.0008
V–4Cr–4Ti–0.5Y	Balance	3.95	3.96	0.014	0.02	0.452	0.0230	0.0150	0.0648	0.0012

obtained by electron beam refining were used, and an arc-melting furnace with a contamination reducer was adopted for alloying. The chemical compositions of these alloys are shown in Table 2. Small-size tensile test specimens were punched out from the 0.25 mm thick sheet obtained by cold rolling, and the size of the gauge section was 5×1.2 mm^2. All the specimens were annealed at 1000 °C for 1 h under 1×10^{-3} Pa vacuum to obtain recrystallized microstructures.

Oxidation experiments were conducted in dry air for 1 h at 500, 600, 700 and 750 °C. The weight increase measurements were carried out after oxidation. Tensile tests were conducted at room temperature at a strain rate of 6.7×10^{-4} s^{-1}. Secondary electron microscopy was used to characterize the microstructures of oxidized specimens. The surface oxide layers were identified by X-ray diffraction (XRD) and the effect of the doping elements on the oxidation resistance of the alloy was examined.

3. Results and discussion

Fig. 1 shows the weight increase per surface area of each alloy after oxidation in air for 1 h. None of the alloys showed a significant increase in weight up to 600 °C. The V–4Cr–4Ti alloy showed a substantial weight gain after oxidation at 700 °C whereas V–4Cr–4Ti–0.5Al and V–4Cr–4Ti–0.5Y alloys did not show negligible weight change after oxidation at 700 °C. After oxidation at 750 °C, all the alloys containing dopant elements exhibited substantial weight increase; a similar test could not be conducted on the V–4Cr–4Ti alloy due to melting of the surface oxide (V_2O_5). Among the three alloys, the Y-containing alloy exhibited the maximum weight gain at 750 °C.

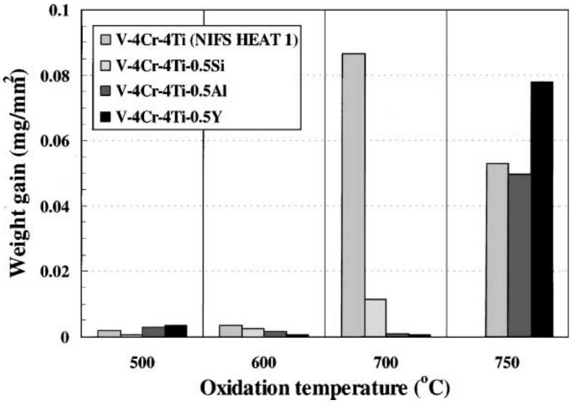

Fig. 1. Weight gain for V–4Cr–4Ti type alloys after oxidation in air for 1 h.

Fig. 2 presents stress–strain curves of the V–4Cr–4Ti and V–4Cr–4Ti–0.5Y alloys, in as-annealed conditions and after oxidation testing at 500, 600, 700 and 750 °C. The tensile elongation of each alloy was reduced with increasing oxidation temperature. The V–4Cr–4Ti alloy specimen oxidized at 700 °C broke with almost no plasticity whereas the V–4Cr–4Ti–0.5Y alloy specimen broke in a similar mode after oxidation at 750 °C.

The results of the fracture surface analysis obtained after the tensile test (see Fig. 3) showed three distinct zones namely, a surface oxidized layer, a cleavage fracture area and ductile rupture zone in both V–4Cr–4Ti and in V–4Cr–4Ti–0.5Y alloys after oxidation at 700 and 750 °C, respectively. The cleavage crack region and surface oxidized layer were related to the embrittlement of the alloy, and they corresponded to the depth of diffusion of oxygen into the alloys.

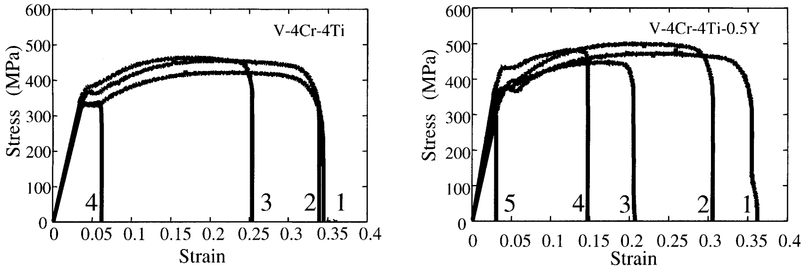

Fig. 2. Stress–strain curve for V–4Cr–4Ti and V–4Cr–4Ti–0.5Y alloys tested at room temperature: (1) as annealed, (2) 500 °C oxidation, (3) 600 °C oxidation, (4) 700 °C oxidation, (5) 750 °C oxidation.

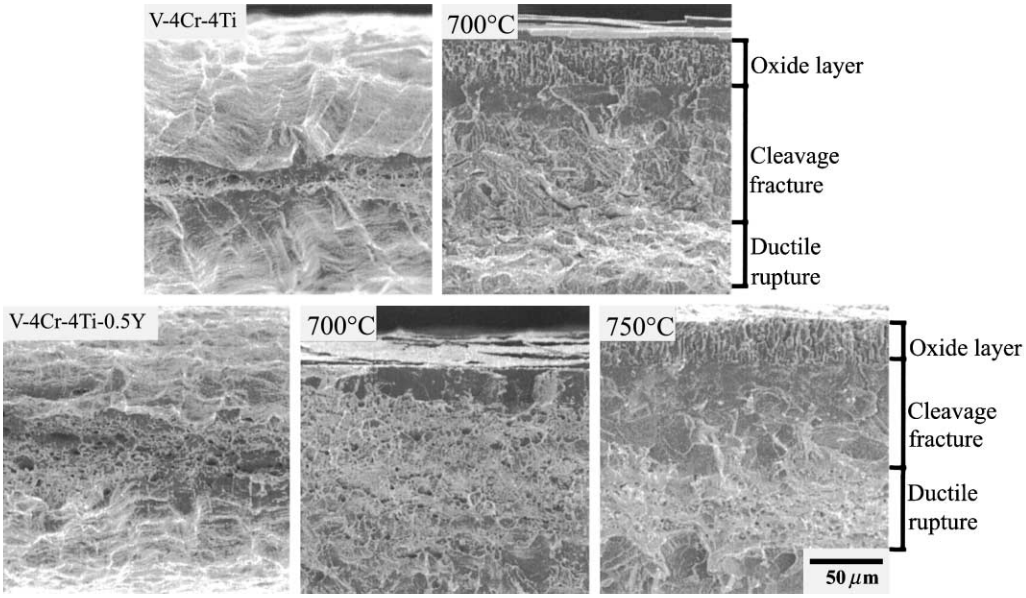

Fig. 3. Scanning electron micrographs of fracture surfaces after tensile test, V–4Cr–4Ti alloy and V–4Cr–4Ti–0.5Y alloy after oxidation at 700 and 750 °C for 1 h, and as annealed.

In V–4Cr–4Ti–0.5Y that was oxidized at 700 °C, the surface oxide layer was thin and dense and the cleavage crack region was thinner than that of other alloys. Therefore, it was considered that the growth of the oxidized layer and the diffusion of oxygen into the alloy were suppressed by the Y addition. Fig. 4 shows the oxide thickness measured in all of the alloys after oxidation at several temperatures. In the V–4Cr–4Ti alloy, a significant growth of the oxide layer was observed at 700 °C. In the V–4Cr–4Ti–0.5Y alloy, the oxide layer did not grow up to 700 °C, while the layer grew at 700 °C and substantially at 750 °C in the V–4Cr–4Ti–0.5Si alloy. The V–4Cr–4Ti–0.5Al alloy showed an intermediate behavior between those of V–4Cr–4Ti–0.5Si and V–4Cr–4Ti–0.5Y alloys.

XRD analysis of the oxide scales on the V–4Cr–4Ti alloy showed predominantly the VO_2 phase after oxidation at 600 °C and the V_2O_5 phase after oxidation at 700 °C. On the contrary, VO_2 was stable in the Y-containing alloy even after oxidation at 700 °C; however, it changed to V_2O_5 after oxidation at 750 °C. The superior oxidation resistance of the Y-containing alloy at 700 °C can be attributed to the formation and slow growth rate of the VO_2 phase, as evidenced by the thinness and denseness of the scale in this alloy. Yttrium plays two roles to impart a slower growth rate in this alloy. The presence of Y in the alloy seems to lower the oxygen partial pressure in the near-surface region of the scale thereby stabilizing the VO_2 phase in the scale, and the Y segregation near the surface suppresses inward diffusion of oxygen into the alloy.

Fig. 5 shows the relationship between tensile behavior and oxidation morphology of the V–4Cr–4Ti alloy. The morphological structure of the fracture surface obtained after oxidation can be related to the concentration of oxygen that diffused into the alloy during

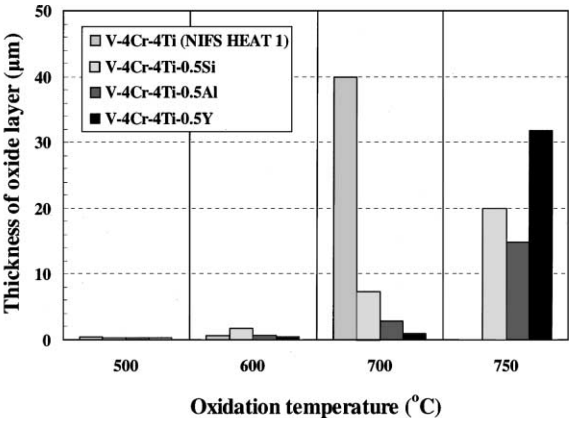

Fig. 4. Thickness of the oxide layer for each alloy oxidized in air for 1 h.

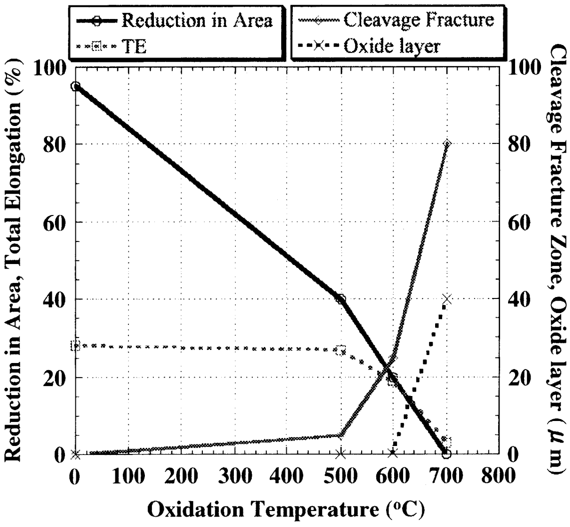

Fig. 5. Tensile properties and oxidation morphology of the V–4Cr–4Ti alloy oxidized in air for 1 h.

oxidation. The fracture surface was composed of an oxide scale, a cleavage fracture zone, and a ductile rupture zone, the thickness of each of which depended on the oxygen concentration. The tensile behavior of the oxidized-material seemed to show the material tensile behavior that stretched the three materials of which characteristics differ, because it has the strength in which this organization respectively differs. The thickness of the brittle zone (comprising of the scale and the cleavage fracture areas) relative to the ductile zone increased with temperature, primarily because of increased diffusion of oxygen and increased oxygen ingress into the alloy. A quantitative assessment of the beneficial effects of dopant elements on oxidation resistance of the alloys and on ductility loss needs further experimental work that involve a range of oxygen partial pressures in the exposure environment and may be longer exposure time.

4. Conclusions

The compatibility of V–4Cr–4Ti, V–4Cr–4Ti–0.5Si, V–4Cr–4Ti–0.5Al, and V–4Cr–4Ti–0.5Y alloys with oxygen was examined in dry air. The results showed improved oxidation resistance for the Y-containing alloy at temperatures up to 700 °C. The implication of this improved resistance is that under accident conditions that involve air ingress at elevated temperatures, the Y-containing alloy may offer adequate resistance when compared with that of the alloy without Y addition. For example, if the alloys were exposed to air at 700 °C for 1 h during an accidental air ingress situation, the depth of the brittle layer in the alloys with and without Y would be 20 and 100 μm, respectively.

Acknowledgements

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