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Oxidation and hardness profile of V–Ti–Cr–Si–Al–Y alloys

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Abstract

Several alloys of composition V–4Ti–4Cr–(0–0.5)Si–(0–0.5)Al–(0–0.5)Y were selected for oxidation in air. In addition a V–4Ti–4Cr–0.5Si–0.5Al–0.5Y alloy was pre-implanted with helium to study the effect of helium on oxidation behavior. Rapid oxidation experiments in air were conducted on tensile specimens and disc bend specimens at 300°C, 500°C, 600°C and 700°C for 1 h. After oxidation, tensile specimens were mounted in cross-section, and micro-indentation hardness tests were conducted. The depths of increased hardness obtained by indentation tests and the thickness of cleavage fracture zones measured by using scanning electron microscopy (SEM) micrographs were similar. The hardness profile of the cross-section in the depth direction corresponded to a model of oxygen diffusion in vanadium. Three-point bend tests were conducted on helium-implanted and air- exposed disc specimens. The bending stress of the specimen with 700 appm helium was larger than that with 70 appm helium.

1. Introduction

Because of their demonstrated resistance to degradation by neutron irradiation, such as swelling [1], ductile–brittle transition temperature [2] and other mechanical properties [3–5], alloys of V–(4–5)Ti–(4–5)Cr type doped with Si, Al and Y have been considered as candidate structural materials for fusion reactor applications [6,7]. However, there are additional issues regarding the use of vanadium alloys at elevated temperatures. One of these issues relates to the chemical reactivity of the alloys, such as corrosion, oxidation and embrittlement [8]. From a practical point of view, it is necessary to estimate the effects of oxidation on the vanadium alloys due to the leakage of coolant (e.g., water) or the break of vacuum during operation [9–11] in the temperature range around 600°C [12]. Helium generation by nuclear reaction in a fusion reactor is also expected to have an influence on oxidation behavior. That is, not only helium embrittlement at elevated temperatures caused by helium segregation at grain boundaries [13], but also the effects of helium on corrosion and oxidation behavior may be of concern. The objectives of this study are to evaluate the oxidation behavior of the alloys in terms of oxygen diffusion into the alloy matrix and the effect of helium on the oxidation behavior of the alloys.

2. Experimental procedure

A series of V–Ti–Cr–Si–Al–Y type alloys have been prepared as a part of the effort on the development of vanadium base alloys [14]. For this study, selected vanadium alloys included V–4Ti–4Cr, V–4Ti–4Cr–0.1 Si–0.1Al–0.1Y, V–4Ti–4Cr–0.3Si–0.3Al–0.3Y and V–4 Ti–4Cr–0.5Si–0.5Al–0.5Y (nominal weight percentages). Actual compositions of these alloys are shown in Table 1. Buttons of the alloys were arc-melted. The buttons, about 130 g in weight, were encapsulated in a box made of stainless steel, and hot pressed to about 5 mm in thickness after annealing at 1000°C for 1 h, followed by removing up to 2 mm of surface layer. Sheets of 0.25 mm thick were then obtained by cold rolling. Small-size tensile specimens, which had a gauge section of $5 \times 1.2 \times 0.25\ mm^3$ and weighted about 50 mg,

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Table 1
Chemical compositions of the vanadium alloys examined (wt%)

	Heat#	V	Ti	Cr	Si	Al	Y	C	O	N	H
V–4Ti–4Cr	KAV9611	Bal.	4.04	3.95	–	–	–	0.0224	0.115	0.012	–
V–4Ti–4Cr–0.1Si–0.1Al–0.1Y	KAV9605	Bal.	4.08	3.96	0.14	0.08	0.05	0.0165	0.071	0.012	0.0033
V–4Ti–4Cr–0.3Si–0.3Al–0.3Y	KAV9603	Bal.	4.07	3.96	0.34	0.29	0.10	0.0142	0.034	0.013	0.0038
V–4Ti–4Cr–0.5Si–0.5Al–0.5Y	KAV9601	Bal.	3.99	3.96	0.46	0.49	0.20	0.0173	0.029	0.013	0.0037

and 3 mm-diameter discs were punched out from the sheets. The tensile specimens and the discs were annealed at 1100°C for 1 h in a vacuum of 1×10^{-3} Pa. A fully recrystallized microstructure with a mean grain size of about 20 μm was obtained.

After surface chemical polishing, helium implantation of some of the disc specimens to two helium levels was carried out using a 3 MeV He ion beam at the Dynamitron accelerator at Tohoku University. The helium-implanted regions were 1 and 3.5 μm in depth from the surface. The total amount of helium-implanted was 70 and 700 appm.

Oxidation experiments were carried out using an evacuated single ended quartz tube. In separate exposures, four of the tensile specimens or 12 of the discs were set on a quartz boat and put into the quartz tube. A diffusion pump with a roughing pump was used to evacuate the quartz tube. The specimens were heated at elevated temperatures of 300°C, 500°C, 600°C and 700°C, using a furnace, and then dry air was introduced rapidly into the tube and held for 1 h. After exposure the specimens were cooled in air from the elevated temperature to ambient temperature. The typical cooling rate from 700°C to 200°C was 100°C/ min.

After oxidation, tensile tests were conducted at room temperature on exposed tensile specimens, and surface microstructures of selected specimens were observed by scanning electron microscopy (SEM). After testing, the tensile specimens were mounted in cross-section and micro- indentation hardness tests were conducted with loads of 5 and 10 g for 5 s. Three-point bend tests were conducted on disc specimens. The bending direction was selected such that the helium pre-implanted surface of each specimen was subjected to a tensile stress during testing. The discs were then examined by SEM to observe fracture morphology.

3. Results and discussion

3.1. Oxidation behavior

Fracture surfaces of tensile test specimens were observed by SEM. After oxidation at 700°C, the observations clearly discriminated between an oxide layer, a cleavage fracture zone and a ductile rupture zone inward from the surface of the specimens [15]. The thickness of the oxide layer and cleavage fracture zone were measured for 700°C exposed alloy, as shown in Fig. 1. The thickness of the surface oxide layer increases with increasing concentration of Si, Al and Y in the alloys. However, the thicknesses of the cleavage fracture zone were almost the same and were somewhat independent of the levels of the additional minor elements. It appears that the addition of Si, Al and Y had an effect on the formation of the oxide layer but did not alter the diffusion of oxygen into the matrix.

On tensile specimen cross-sections, micro hardness measurements were made in the matrix below the oxide scale to investigate the effect of oxygen diffusion on hardness. In Fig. 2, the hardness profiles of each alloy oxidized at 700°C are shown. These hardness tests were conducted with a load of 10 g. Within a zone of 20 μm from surface, the hardness values increased with increasing concentration of Si, Al and Y. Above 50 μm, the increased hardness was caused by oxygen diffusion into the matrix for all the alloys. At a depth of 50μm, it is believed that hardness differences depend on alloy

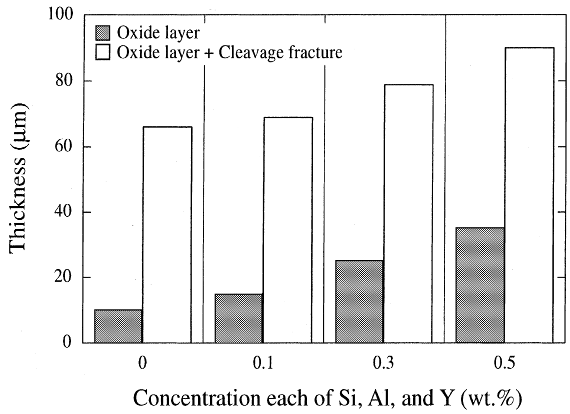

Fig. 1. Thickness of oxide layer and cleavage fracture zone of V–4Ti–4Cr type alloys, after 700°C air exposure and tensile testing at room temperature.

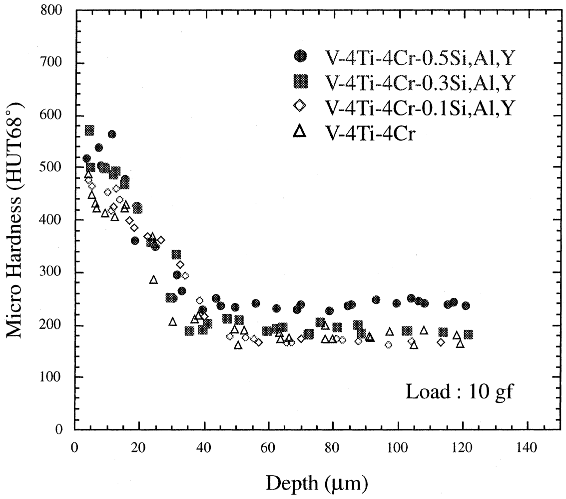

Fig. 2. Hardness profiles on cross-sections of V–4Ti–4Cr type alloy specimens oxidized in air at 700°C.

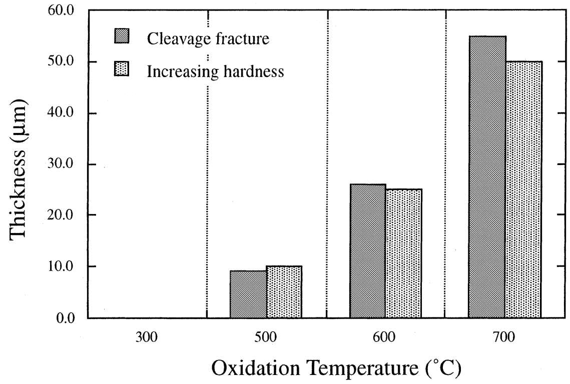

Fig. 4. Comparison between the depth of increased hardness and the thickness of cleavage fracture zone for tensile-tested V–4Ti–4Cr–0.5Si–0.5Al–0.5Y alloy specimens oxidized in air at several temperatures.

composition. Fig. 3 shows the hardness profiles for the V–4Ti–4Cr–0.5Si–0.5Al–0.5Y alloy matrix after exposures at several temperatures. These profiles indicate the dependence on temperature of the oxidation of this alloy. The samples as-annealed and after oxidation at 300°C have almost the same hardness. But after oxidation at temperatures above 500°C, areas of increasing hardness were obtained with increased temperature. The depth of increased hardness increases with increasing exposure temperature. The depth of hardness is about 10 μm at 500°C, about 25 μm at 600°C, and about 50 μm at 700°C. Comparisons of the depth of increased hardness

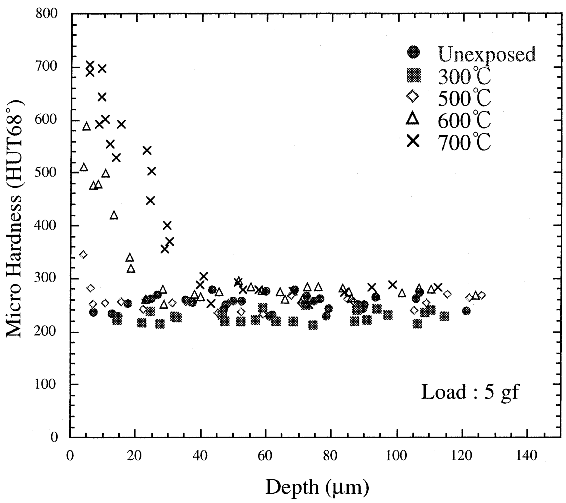

Fig. 3. Hardness profiles on cross-sections of V–4Ti–4Cr–0.5Si–0.5Al–0.5Y alloy specimens exposed in air at several temperatures.

and the cleavage fracture zone thickness measured from SEM micrographs of fractured tensile specimens for each exposure temperature are shown in Fig. 4. These dimensions are nearly the same for each temperature. It is proposed that the depths of increased hardness and the thickness of the cleavage fracture zones are related to oxygen diffusion into the matrix of the vanadium alloys.

In order to determine if the observed hardness changing is the hardening resulted from oxygen diffusion into the alloy matrices, hardness profiles were compared to oxygen diffusion profiles calculated for vanadium alloys. Since diffusion distances were small, the model of oxygen diffusion in the alloy can be expressed by the following equation:

$$C(x,t) = C_0[1 - \mathrm{erf}(x/2\sqrt{Dt})], \tag{1}$$

where C is the concentration of oxygen in the vanadium, C_0 the initial concentration of oxygen, x the depth, D the oxygen diffusion coefficient, and t is the time. The diffusion coefficient of V–4Ti–4Cr alloy, D (cm^2/s), can be expressed by the following equation [9]:

$$D = 0.04\exp(-130kJ/RT), \tag{2}$$

where R and T are the gas constant and absolute temperature, respectively. The initial oxygen concentration, C_0, was obtained from the V–O phase diagram for each temperature [16]. To obtain the relationship between hardness and matrix oxygen concentration in the exposed alloys, the increase of Vickers hardness at room temperature caused by oxygen addition to vanadium from a previous study [17] was used. The comparisons between hardness increase calculated using this correlation with oxygen diffusion and those measured in this study are shown in Table 2. The comparisons were made for depths of 5 and 20 μm. The calculated values are larger than measured ones at all points. A relationship

Table 2
Comparisons between hardness increase calculated using oxygen diffusion and that measured in this study

Temperature (°C)	Depth (μm)	Calculation	Measurement
500	5	380	100
	20	0	0
600	5	560	350
	20	330	80
700	5	640	450
	20	540	300

between oxygen concentration and hardness for pure vanadium was used in this calculation. Therefore, one of the reasons for the above discrepancy may be due to the affect of other elements (Ti and Cr) or additional minor elements (Si, Al and Y) on hardness increases caused by oxygen diffusion into the matrix.

3.2. The effect of helium pre-implantation

Fig. 5 shows the results of three-point bend tests on discs which were pre-implanted with 70 and 700 appm helium and oxidized at 500°C. For comparison, the results of a bend test on an as- annelated disc are also plotted in this figure. The thicknesses of all the discs were 0.21 mm. The increase of bending yield stress of the oxidized specimen with helium pre-implantation to 700 appm is larger than that of the 70 appm helium-implanted specimen. By comparison with the stress of the as-annealed sample, the difference in stress of the disc pre-implanted with 70 appm helium is small. As far as the increase of stress is concerned, the hardening associated with helium implantation is dominant in this oxidized condition. The fracture surfaces of specimens implanted with 70 and 700 appm helium had almost the same appearance. The surfaces of each specimen had some cracks with cleavage fracture.

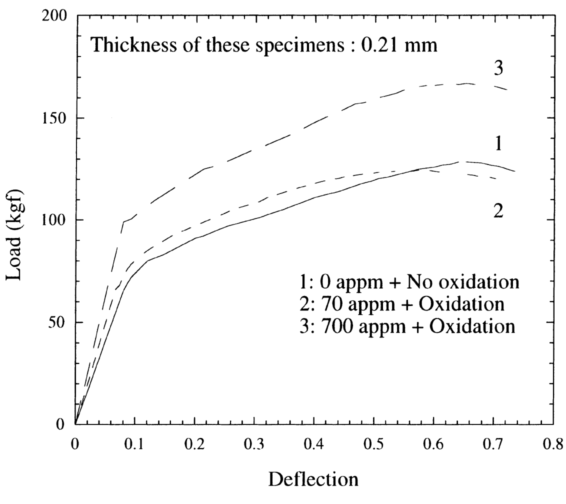

Fig. 5. Load-deflection curves for V–4Ti–4Cr–0.5Si–0.5Al–0.5Y alloy, helium-implanted and oxidized in air at 500°C.

4. Summary

Rapid oxidation studies were conducted at 300°C, 500°C, 600°C and 700°C to evaluate the oxidation behavior and the effect of helium pre-implantation on the oxidation behavior of V–4Ti–4Cr–(0–0.5)Si–(0–0.5)Y alloys. The results obtained are as follows:

- Although the oxide layer depended on additional elements, the thickness of the cleavage fracture zone was relatively independent of the concentrations of Si, Al and Y.
- After micro-indentation tests, the area of increasing hardness and cleavage fracture zone measured by using micrographs of SEM had almost the same thickness.
- The measured hardness profiles approximately corresponded to a model of oxygen diffusion in vanadium alloys after exposure in air.
- The bending stress of a specimen implanted with 700 appm helium was larger than that implanted with 70 appm helium after oxidation at 500°C.

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