



Rapid oxidation and its effects on mechanical properties of V–Ti–Cr–Si type alloys

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Abstract

A series of V–Ti–Cr–Si type alloys were prepared to develop oxidation-proof vanadium alloys. The alloys of V–4Ti–4Cr–(0–0.5)Si–(0–0.5)Al–(0–0.5)Y were selected for the oxidation experiment. Rapid oxidation experiments in air were carried out at 300°C, 500°C and 700°C for 3.6 ks. After oxidation, measurement of weight gain and Vickers micro hardness test were conducted. The weight gain became appreciable at 700°C oxidation treatment and the more Si, Al and Y added, the larger the weight gain of the specimen was in the present condition. The result of tensile test at room temperature showed that elongation decreased with the oxidation temperature increased. After oxidation at 700°C, each specimen ruptured in elastic deformation region. The specimens were examined by scanning electron microscopy (SEM) in order to characterize the oxide layer and fracture surface. It indicated that there were three distinct regions from the surface of the specimen on the cross-sectional area, which were oxide layer, cleavage fracture zone and ductile rupture zone. The thickness of the oxide layer after 700°C oxidation increased with further addition of Si, Al and Y. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Vanadium alloys with Ti and Cr have been proposed as candidate materials for the first wall/blanket structure in a low-activation fusion reactor. The alloys of V–(4–5)Ti–(4–5)Cr type have been studied as a Ref. [1], because of their low swelling behavior after irradiation [2] and low DBTT [3]. Additions of Ti and Cr improved oxidation resistance of alloys [4–6]. The alloys of V–Ti–Cr–Si type doped with Al and Y have been studied [7,8], and the results showed that good combination of low swelling behavior and enough ductile property after irradiation [9–11]. Additions of Al and Y were expected to contribute to the formation of a protective oxide layer. A major restriction on the use of vanadium alloys at elevated temperatures is the chemical reactivity which induces issues of corrosion, oxidation and embrittlement [12]. In the safety analyses of reactor systems, it is necessary to estimate rapid oxidation due to the leakage of

coolant and the breakaway of vacuum during operation [13–15]. The operating condition for vanadium alloys in fusion applications is regarded as the temperature range around 600°C [16]. So, it is important to investigate the oxidation behavior in this condition. The purpose of this work is to study the oxide formation behavior caused by rapid reaction with air and the effects of oxide layer on mechanical properties of vanadium alloys using small-size tensile specimens.

2. Experimental procedure

A series of V–Ti–Cr–Si type alloys have been prepared for development of oxidation-proof vanadium [17]. Selected vanadium alloys for this study are V–4Ti–4Cr, V–4Ti–4Cr–0.1Si–0.1Al–0.1Y, V–4Ti–4Cr–0.3Si–0.3Al–0.3Y and V–4Ti–4Cr–0.5Si–0.5Al–0.5Y (nominal weight percentages). Chemical compositions of these alloys are shown in Table 1. Buttons of the alloys were arc-melted. The buttons of 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

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1000°C for 3.6 ks, followed by removing the surface layer of about 2 mm in thickness. Sheets of 0.22 mm thick were obtained by cold rolling. Small-size tensile specimens which had a gauge section of $5 \times 1.2 \times 0.22$ mm and weighed about 50 mg were punched out from the sheets. The tensile specimens were annealed at 1100°C for 3.6 ks in a vacuum of 1×10^{-3} Pa. Fully recrystallized microstructure with mean grain size of about 20 μm was obtained.

Oxidation experiments were carried out using an evacuated single ended quartz tube. Four of the tensile specimens were set on a quartz boat and put into the quartz tube. The quartz tube was evacuated by a diffusion pump with a roughing pump. The specimens were heated at elevated temperatures of 300°C, 500°C and 700°C, respectively, and held for 3.6 ks, and then dry air was introduced rapidly into the tube. 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, weight gain of the specimens was measured. Vickers micro hardness tests were carried out with a loading of 1.98 N for 20 s. Tensile tests were conducted at room temperature with a strain rate of $6.67 \times 10^{-4} \text{ s}^{-1}$. The specimens were examined by scanning electron microscopy (SEM) in order to characterize the oxidation layer and the fracture surfaces after tensile tests.

3. Results and discussion

Fig. 1 shows weight gain (Fig. 1(a)) and Vickers micro hardness increase (Fig. 1(b)) of each alloy after oxidation. Each datum of the weight gain is an average value of two specimens. While oxidation at 300°C and 500°C induces small weight gain for each alloy, weight gain after oxidation at 700°C is extremely large. The more Si, Al and Y added, the larger the weight gain of the specimen is in this condition. Increases in hardness of the alloys after oxidation at 300°C are very small. After 500°C oxidation, the increases in Vickers hardness number are about 60 for four of the alloys. Large increases in hardness are observed in oxidation at 700°C. The hardening of V-4Ti-4Cr is about 320 in hardness number. The datum shown in Fig. 1(b) for 700°C is only that of V-4Ti-4Cr. The surface of the specimens con-

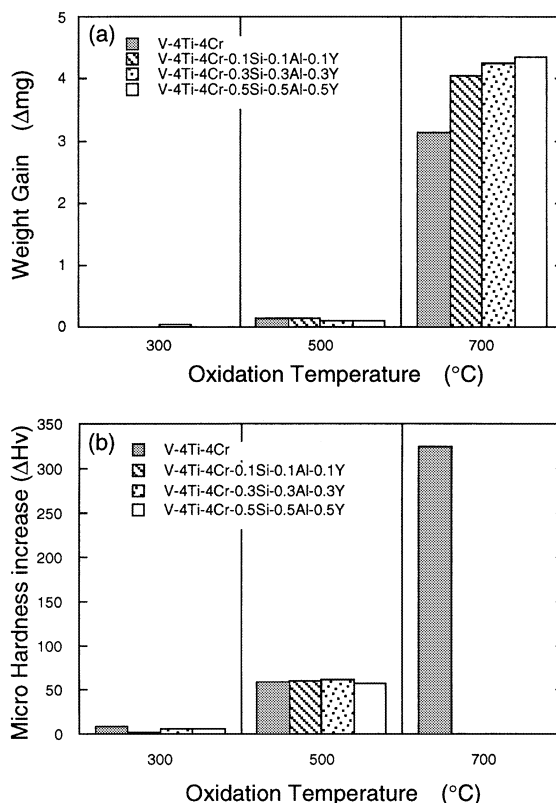


Fig. 1. Weight gain and Vickers micro hardness increase for V-4Ti-4Cr-Si, Al, Y alloys after oxidation. (a) Weight gain, (b) Vickers micro hardness increase.

taining Si, Al and Y were so rough and probably so hard after oxidation that no indentation traces could not be found out.

Fig. 2 shows stress-strain curves for each alloy tested at room temperature. Total elongation of all of the alloys decreases by oxidation, except for V-4Ti-4Cr-0.1Si-0.1Al-0.1Y alloy tested after oxidation at 300°C. The alloys show ductile behavior after oxidation at 300°C and 500°C. All of the alloys are broken at elastic deformation region after oxidation at 700°C. Yield stress of the alloys of V-4Ti-4Cr and V-4Ti-4Cr-0.5Si-0.5Al-0.5Y, increases with increasing oxidation temperatures. These hardening are caused by oxidation. In case of V-4Ti-4Cr-0.1Si-0.1Al-0.1Y alloy and V-4Ti-4Cr-0.3Si-0.3Al-0.3Y alloy, increase in yield stress does

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

Alloys	Heat#	V	Ti	Cr	Si	Al	Y	C	O	N	H
V-4Ti-4Cr-0.5Si-0.5Al-0.5Y	KAV9601	Bal.	3.99	3.96	0.46	0.49	0.2	0.0173	0.029	0.013	0.0037
V-4Ti-4Cr-0.3Si-0.3Al-0.3Y	KAV9603	Bal.	4.07	3.96	0.34	0.29	0.1	0.0142	0.034	0.013	0.0038
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	KAV9611	Bal.	4.04	3.95	-	-	-	0.0224	0.115	0.012	

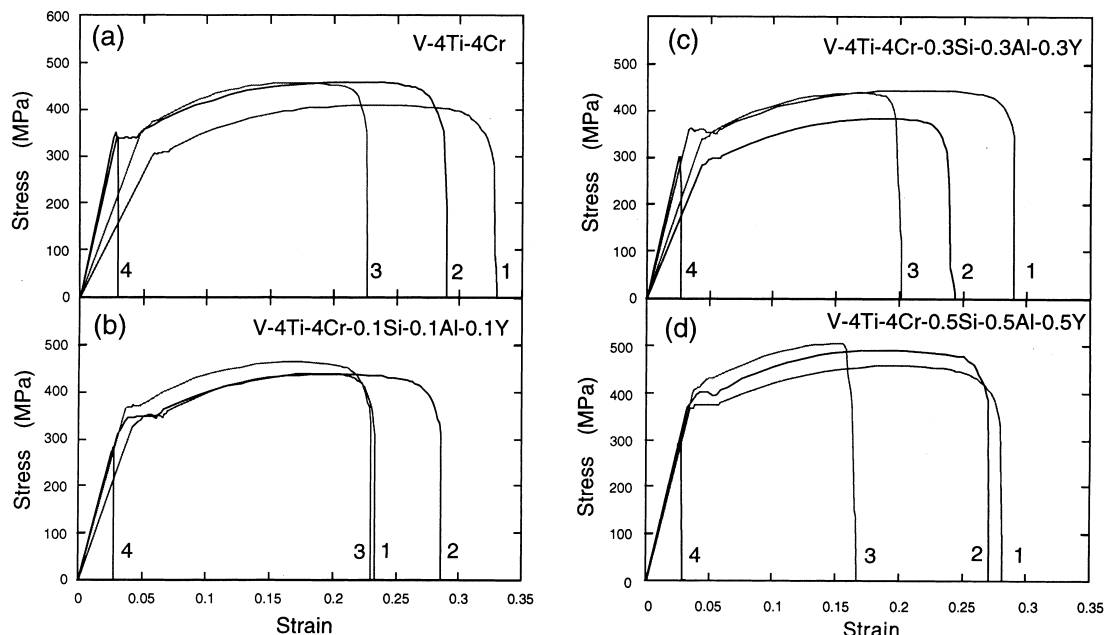


Fig. 2. Stress–strain curves for each alloy tested at room temperature. (1) As annealed, (2) 300°C oxidation, (3) 500°C oxidation, (4) 700°C oxidation.

not show a simple trend. It is considered that the oxidation layer became thick during high temperature oxidation so that plastic deformation region became small. Therefore, effective cross section of the ductile part of specimens was varied with the oxidation conditions.

Total elongation of the alloys is summarized in Fig. 3. Moderate effects on elongation are observed in the specimens after 500°C oxidation. Drastic reductions in the elongation of all the alloys are observed after 700°C oxidation.

Fig. 4 shows scanning electron micrographs of fracture surfaces after tensile tests of V–4Ti–4Cr–0.5Si–0.5Al–0.5Y alloys after oxidation at 500°C and 700°C for 3.6 ks and as annealed. Large reductions in area and

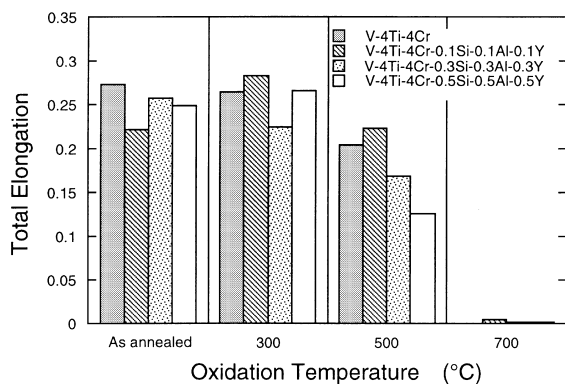


Fig. 3. Total elongation of V–Ti–Cr–Si type alloys after oxidation.

ductile fracture mode are observed in the specimens as annealed and after oxidation at 500°C. In the specimen oxidized at 500°C, oxidation layer is observed. This layer have been broken with the plastic deformation of the specimen. In the specimen oxidized at 700°C for 3.6 ks, reduction in area is small and it is possible to discriminate clearly between oxide layer, cleavage fracture region and ductile rupture region. The cleavage fracture mode may be due to oxygen which diffused into the specimen during oxidation experiment. From the results of the SEM observation, mechanical properties and morphology of oxide layer are very different between those after 500°C and after 700°C oxidation.

Fracture surfaces of V–4Ti–4Cr, V–4Ti–4Cr–0.1Si–0.1Al–0.1Y and V–4Ti–4Cr–0.3Si–0.3Al–0.3Y oxidized at 700°C for 3.6 ks are shown in Fig. 5. That of V–4Ti–4Cr–0.5Si–0.5Al–0.5Y oxidized at 700°C is in Fig. 4. Oxide layer, cleavage fracture region and ductile rupture region are clearly discriminated for all of the alloys after 700°C oxidation. The thickness of surface oxide layer increases with increasing concentration of Si, Al and Y in the V–4Ti–4Cr alloys. The oxide layer of V–4Ti–4Cr is about 10 μm in thickness and that of V–4Ti–4Cr–0.5Si–0.5Al–0.5Y is about 35 μm . It is supposed that the reason why the thickness of surface oxide layer increases is due to the lower free energy of aluminum or yttrium oxide formation than that of vanadium oxide.

In Fig. 6, typical rupture surface of the specimen oxidized at 700°C for 3.6 ks is schematically illustrated. The specimen oxidized in this condition can be charac-

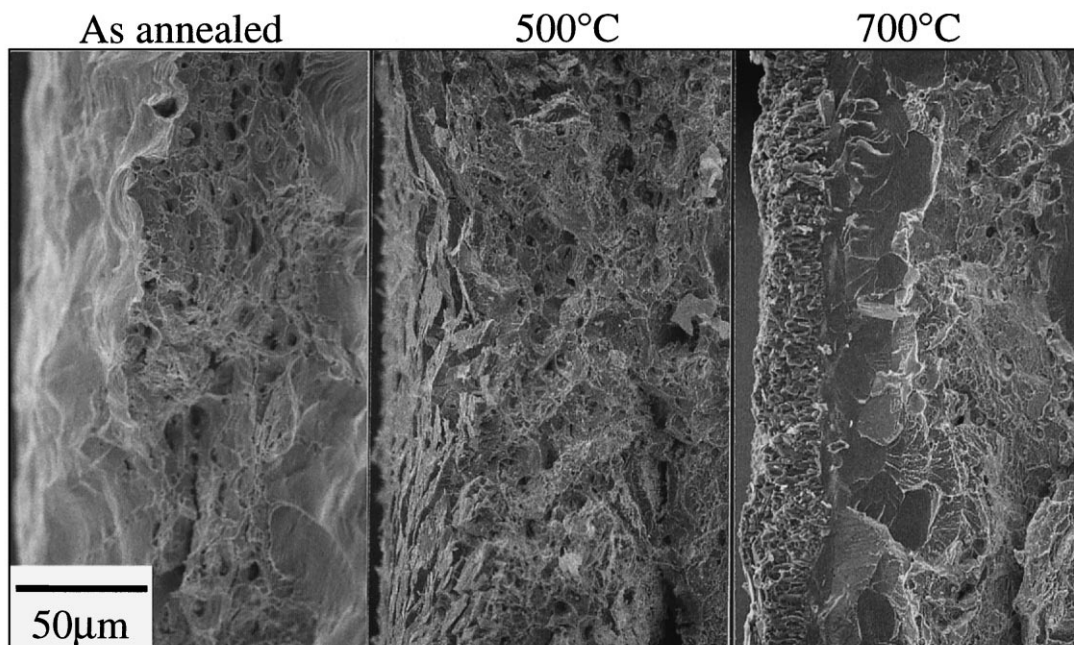


Fig. 4. Scanning electron micrographs of fracture surfaces after tensile tests, V-4Ti-4Cr-0.5Si-0.5Al-0.5Y alloys after oxidation at 500°C and 700°C for 3.6 ks, and as annealed.

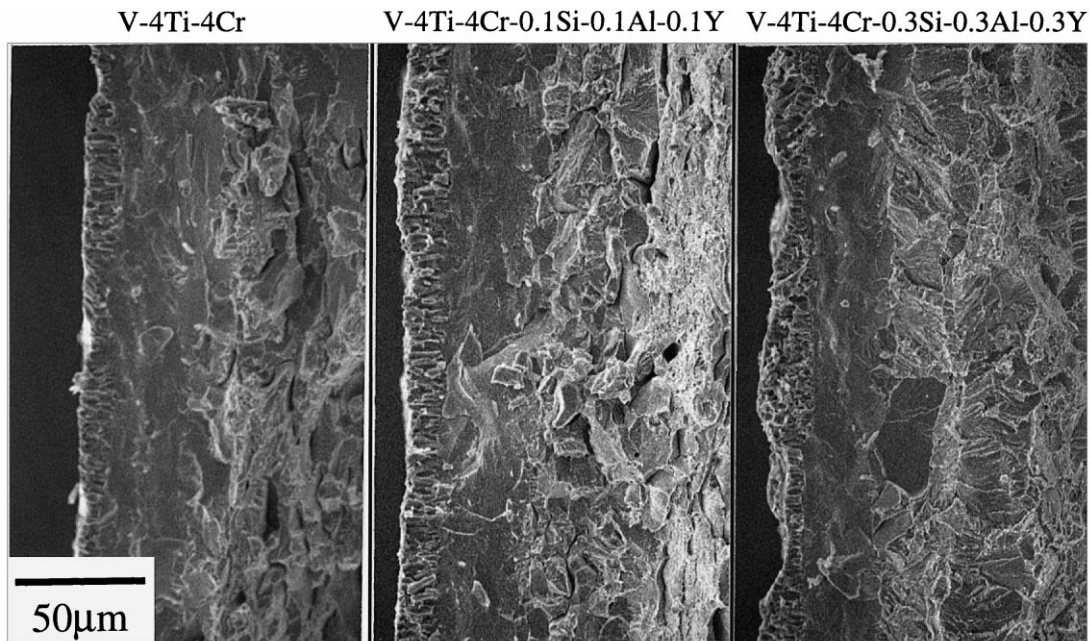


Fig. 5. Fracture surfaces of V-4Ti-4Cr, V-4Ti-4Cr-0.1Si-0.1Al-0.1Y and V-4Ti-4Cr-0.3Si-0.3Al-0.3Y oxidized at 700°C for 3.6 ks.

terized by oxide layer, cleavage fracture zone and ductile rupture zone. It is necessary to estimate the soundness of oxide layer and to examine the influence of Al and Y

addition on the composition and structure of the layer in future. It is planned to examine oxygen distribution in oxide layer, cleavage fracture zone and ductile zone.

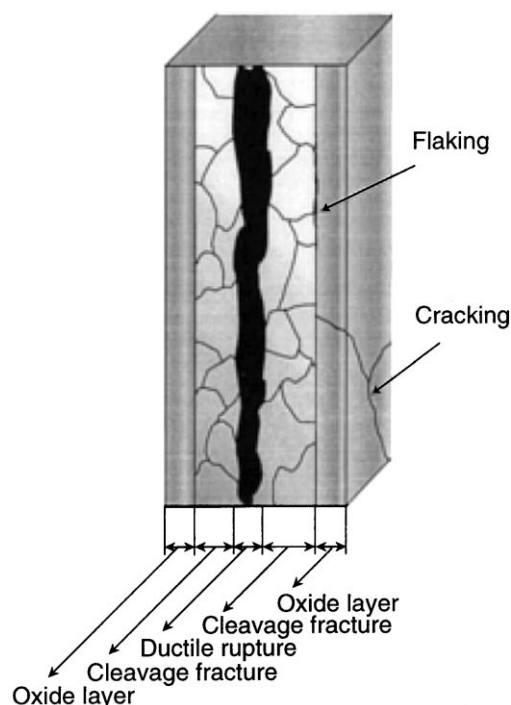


Fig. 6. A schematic illustration of a typical rupture surface of the specimen oxidized at 700°C for 3.6 ks.

4. Summary

Rapid oxidation experiments for the alloys of V–4Ti–4Cr–(0–0.5)Si–(0–0.5)Al–(0–0.5)Y were carried out at 300°C, 500°C and 700°C for 3.6 ks in air.

1. Each alloy had small weight gain after oxidation at 300°C and 500°C. The weight gain was large after 700°C oxidation and the more Si, Al and Y added, the larger the weight gain was in this oxidation condition.
2. The results of tensile test at room temperature showed that elongation decreased with increasing oxidation temperature. After oxidation at 700°C, each specimen ruptured within elastic deformation region.
3. Fracture surfaces of the specimen examined by SEM indicated that it was clearly discriminated between oxide layer, cleavage fracture zone and ductile rupture zone from the surface of specimen. The thickness of the oxide layer increased with further addition of Si, Al and Y. From the practical point of view, it is noted that the total thicknesses of oxide layer and

brittle region of the alloys were limited below 100 μm , which it may be thin enough compared with the thickness of structure materials.

Acknowledgements

This work was partly supported by JUPITER program (Japan–USA Program of Irradiation Test for Fusion Research) and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan. Authors thank Emeritus Professor H. Kayano for encouraging the study and to Mr. C. Akama, machine shop of Tohoku University, for his help with the preparation of the experimental equipment.

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