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Fabrication using a levitation melting method of V–4Cr–4Ti–Si–Al–Y alloys and their mechanical properties

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Abstract

Reduction of interstitial impurities such as O and N is a potential method to improve various properties of vanadium alloys. It was shown that addition of Si, Al and Y was useful to reduce the oxygen concentration and to improve post-irradiation ductility at relatively low temperatures for V–Cr–Ti alloys. Several 2.5 kg alloys of V–4Cr–4Ti–Si–Al–Y type were fabricated by using a levitation melting method. Charpy impact test by an instrumented testing machine has been conducted using miniaturized specimens. Tensile tests have been carried out before and after neutron irradiation. The miniaturized specimens were irradiated up to 8×10^{22} n/m^2 ($E > 1$ MeV) at 290 °C in Japan Materials Testing Reactor. By adopting a levitation melting method, high-purity kg-scale ingots of V–4Cr–4Ti–Si–Al–Y alloys with ~80 ppm C, <170 ppm O and ~110 ppm N were obtained. The V–4Cr–4Ti–0.1Si–0.1Al–0.1Y alloy fabricated in this study showed good impact properties compared with a previous laboratory-scale alloy. This alloy showed good tensile properties even after neutron irradiation at 290 °C. Levitation melting can be adopted to produce large ingots of V–Cr–Ti–Si–Al–Y type alloys by controlling the amount of yttrium addition. In this study, the technology for fabrication of high-purity kg-scale ingots of V–4Cr–4Ti–Si–Al–Y alloy has been demonstrated, and has made it possible to investigate systematically various properties of the alloy.

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1. Introduction

Vanadium-based alloys have been considered as attractive structural materials for the first-wall and blanket components of fusion power systems, mainly due to their low induced-radioactivity, favorable mechanical properties at high temperatures and good compatibility with lithium coolant [1]. In the previous experiments on irradiation performance of the alloys, V–4Cr–4Ti has shown good resistance to radiation damage at temperatures raging from 420 to 600 °C [2], and has been identified as a leading candidate alloy. On the other hand, recent irradiation studies of V–4Cr–4Ti reported that irradiation at temperatures below 400 °C produced remarkable changes in its mechanical properties, such as severe irradiation hardening, drops of uniform elongation to less than 1% and large shifts of ductile to brittle transition temperature (DBTT) [3,4]. These changes in mechanical properties can be correlated with the production of a high density of small defect clusters, mainly dislocation loops, or radiation-induced precipitates containing Ti and interstitial impurities, such as C, O and N. Interstitial impurities could affect not only the post-irradiation properties at relatively low temperatures but also the workability and weldability of the alloy [5,6]. Therefore the reduction of these impurities is considered effective to improve several properties of vanadium alloys.

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Alloys of the V–Cr–Ti type modified by adding a small amount of Si, Al and Y have been developed as oxidation-resistant candidates [7–14]. V–(4–5)Cr–(4–5)Ti–Si–Al–Y type alloys containing lower concentrations of interstitial impurities, especially of oxygen, showed good resistance to radiation damage at high temperatures [8]. In addition, the alloys showed relatively good tensile properties even after irradiation at temperatures below 400 °C [12,13]. However, this alloy series was obtained only from laboratory-scale heats, and it is necessary to produce relatively large-scale ingots in order to investigate further properties of the alloys. The purpose of this study is to verify the fabrication procedure to make a high-purity large-heat of V–Cr–Ti–Si–Al–Y type alloys, especially reducing interstitial impurity levels.

2. Experimental procedure

In order to obtain relatively large-scale ingots of high-purity alloys, a cold crucible levitation furnace installed at Daido Steel Co. Ltd., was adopted for this study. This furnace is a high-frequency induction furnace and used industrially as a melting furnace for Ti casting production [15]. The furnace has several advantages for titanium melting such as negligible contamination, flexibility for material shape and relatively large pool volume. These advantages are considered available also for melting of vanadium alloys. In this study, as a first step to produce large-scale ingots, several 2.5 kg alloys of V–4Cr–4Ti with or without additions of Si, Al and Y were fabricated. Based on tensile properties after neutron irradiation below 400 °C, the goal of interstitial impurity levels was set below 150 wt ppm for oxygen and below 100 wt ppm for nitrogen and carbon. In order to avoid contamination by gaseous impurities from the atmosphere, melting was carried out in flowing industrial grade Ar gas containing 0.62 ppm O_2 and 0.59 ppm N_2 by volume. High-purity V chips (C: 65, O: 80, N: 93 wt ppm, 20–30 mm) were melted for 10 min, then alloying elements were added to the molten vanadium in the sequence $Si \rightarrow Al \rightarrow Cr \rightarrow Ti \rightarrow Y$ every 2 min. Because segregation of Si and Al to the upper region of the ingot (which may be gravity segregation) occurred when alloying elements were added in order of melting point, the above alloying method was used in order to improve homogeneity of the alloying elements.

Selected ingots were cut into three parts, segment (A), (B) and (C). The chemical composition was analyzed at the upper, middle and lower regions in segment (A). In order to evaluate homogeneity of alloying elements in the ingots, energy dispersive X-ray spectroscopic analysis (EDS) was carried out in segment (B) using a scanning electron microscope (SEM). From the middle part of segment (B), blocks in the form of about 30 mm (length) × 20 mm (width) × 10 mm (thickness) were cut and cold rolled to 0.25 mm thick sheets. Miniaturized tensile specimens with a gauge section of 5 mm long and 1.2 mm wide were punched out from the sheets. Plates of 4 mm in thickness were cut from segment (C) and cold rolled to about 2 mm in thickness. Miniaturized Charpy impact specimens (1.5CVN), their dimensions being $1.5 \times 1.5 \times 19$ mm with a 30° notch angle, 0.3 mm notch depth and 0.08 mm root radius, were machined from the plates.

Based on the homogeneity investigation, blocks of 70 mm in diameter and 30 mm in thickness were cut from the center of the residual ingots. The blocks were encapsulated in a box made of stainless steel, and hot pressed to about 14 mm in thickness after annealing at 1000 °C for 1.8 ks, followed by removing the surface layer. Consequently the blocks were about 10 mm in thickness. The blocks were cold rolled to 2 mm in thickness, and 1.5CVN specimens 20 mm long instead of 19 mm were machined from the resulting plates. The chemical composition of these ingots was analyzed using a part of the 2 mm thick plates. All of the miniaturized specimens were annealed at 1000 °C for 3.6 ks in a vacuum of 1×10^{-3} Pa for recrystallization.

The specimens obtained by cold rolling were neutron-irradiated in the Japan Materials Testing Reactor (JMTR) in the Oarai establishment of Japan Atomic Energy Research Institute (JAERI). Irradiation was carried out at 290 °C up to 8×10^{22} n/m^2 ($E > 1$ MeV).

Charpy impact tests were carried out at temperatures from −196 to 0 °C using an instrumented machine in a hot cell at the Oarai Branch, Institute for Materials Research, Tohoku University. The test speed was kept at 5 m/s throughout testing. Tensile tests were carried out using an Instron-type machine in a vacuum of 1×10^{-3} Pa at a strain rate of 6.7×10^{-4} s^{-1}. Test temperatures were ambient temperature and the irradiation temperature. After these tests, the fracture surface of specimens was examined by SEM in order to characterize the fracture mode.

3. Results and discussion

3.1. Chemical compositions

The chemical compositions at the middle part of each V–4Cr–4Ti–Si–Al–Y alloy are shown in Table 1. In the table each alloy is designated by an alphabetical symbol for simplification. The chemical composition of alloy (b), (d), (e) and (f) was analyzed after hot pressing and cold rolling to 2 mm thick plates. Interstitial impurity levels in the starting vanadium are also shown in the table. The interstitial impurity levels in the alloys almost reached the goal for this study, that is, <150 wppm O,

Table 1
Chemical composition of vanadium alloys (wt%)

	Alloy	Heal#	V	Cr	Ti	Si	Al	Y	C	O	N
a	V–4Cr–4Ti–0.1Si–0.1Al–0.1Y	000117	Balance	4.63	4.84	0.14	0.17	0.02	0.0070	0.0167	0.0102
b	V–4Cr–4Ti–0.1Si–0.1Al–0.1Y	11005K	Balance	4.31	4.54	0.13	0.13	0.07	0.0086	0.0112	0.0094
c	V–4Cr–4Ti–0.1Si–0.1Al–0.3Y	123059-4	Balance	4.38	4.75	0.14	0.14	0.24	0.0062	0.0051	0.0176
d	V–4Cr–4Ti–0.1Si–0.1Al–0.3Y	11002K	Balance	4.41	4.81	0.14	0.13	0.25	0.0064	0.0080	0.0103
e	V–4Cr–4Ti–0.1Si–0.3Y	11003K	Balance	4.41	4.77	0.14	0.014	0.28	0.0071	0.0080	0.0100
f	V–4Cr–4Ti–0.3Y	11004K	Balance	4.38	4.69	0.02	0.014	0.28	0.0077	0.0067	0.0108
g	V–4Cr–4Ti–0.5Si–0.5Al–0.5Y	991111	Balance	4.41	4.75	0.80	0.86	0.34	0.0072	0.0055	0.0113
	Raw vanadium								0.0065	0.0080	0.0093

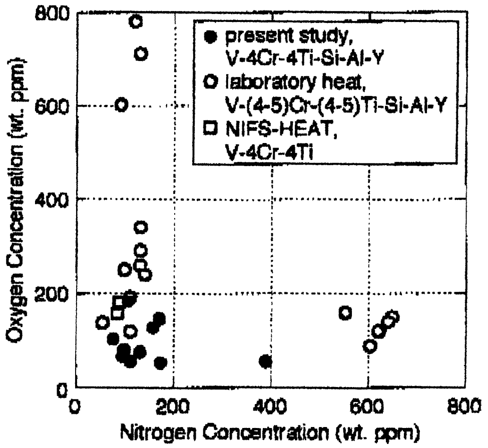

Fig. 1. Interstitial impurity level of the ingots produced in the present study in comparison with previous heats of V–4Cr–4Ti–Si–Al–Y alloys produced by laboratory-scale melting and the large ingots of high-purity V–4Cr–4Ti alloy (NIFS–HEAT).

<100 wppm N and <100 wppm C. Oxygen concentration decreased with increasing yttrium addition. It is believed that this reduction of oxygen was caused by slag off of yttrium oxide during the melting process, similar to the laboratory-scale arc melting [10]. Therefore, the yttrium contents were slightly lower than the nominal amounts. Concentrations of O and N in the ingots fabricated in this study are summarized in Fig. 1 in comparison with those in the previous laboratory-scale heat of V–4Cr–4Ti–Si–Al–Y type alloys and the large ingots of high-purity V–4Cr–4Ti reference alloy (NIFS–HEAT). The nitrogen and oxygen levels in the ingots fabricated in this study are comparable to and almost half or one third of, respectively, those in the laboratory-scale heat and NIFS–HEAT.

Fig. 2 shows the macrostructure at the center of V–4Cr–4Ti–0.1Si–0.1Al–0.1Y (a) alloy and the composition distribution of each alloying elements along the vertical (Z) axis analyzed by EDS. The content of alloying elements was almost constant over a wide region in the ingots, except for the bottom part. The bottom of the ingots formed a skull, as shown in macrostructure, and was scarcely alloyed in the melting process. Because of that, the alloy content were somewhat higher than the intended composition, except for yttrium. Alloys with the intended composition can be obtained by controlling the addition of alloying elements and considering the formation of a skull.

3.2. Impact properties

Fig. 3 shows the results of Charpy impact testing on miniaturized specimens of several V–4Cr–4Ti–Si–Al–Y alloys. The alloy designation is same as in Table 1. The

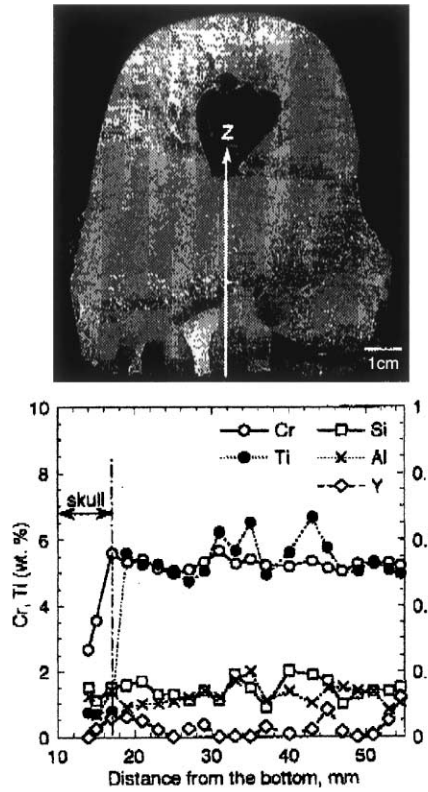

Fig. 2. Macrostructure at the center of V–4Cr–4Ti–0.1Si–0.1Al–0.1Y alloy and distribution of alloying elements along the vertical axis (Z) analyzed by EDS.

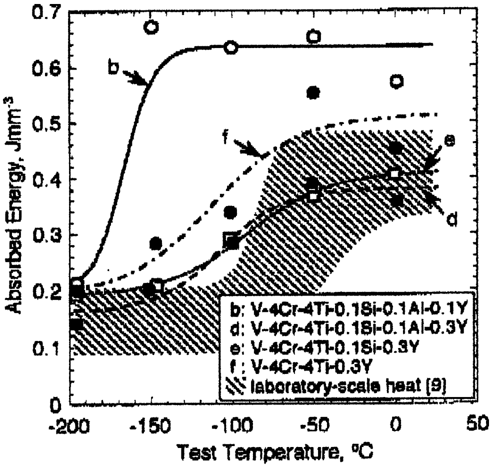

Fig. 3. Charpy impact properties of miniaturized specimens of several V–4Cr–4Ti–Si–Al–Y alloys.

hatched area indicates the results from the previous laboratory-scale heat [9]. Absorbed energy, E, defined as

$$E = E_{\mathrm{exp}}/Bb^2, \tag{1}$$

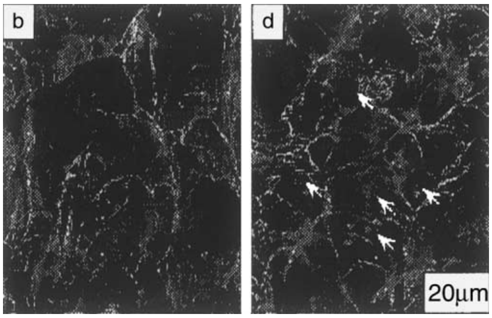

Fig. 4. Scanning electron micrographs of typical fracture surfaces for (b) V–4Cr–4Ti–0.1Si–0.1Al–0.1Y and (d) V–4Cr–4Ti–0.1Si–0.1Al–0.3Y alloys after impact testing at −50 °C.

where $E_{\mathrm{exp.}}$ is the raw value of absorbed energy, B is the width and b is the ligament size of each specimen. Alloy (b) of V–4Cr–4Ti–0.1Si–0.1Al–0.1Y fabricated in this study shows the best impact properties among these materials and has a DBTT below −150 °C. Impact properties of the alloys (d)–(f) with addition of 0.3 wt% Y are similar to those of the laboratory-scale heat and the DBTT of these alloys is about −100 °C in spite of the lowest interstitial impurity levels.

Fig. 4 shows typical fracture surfaces of the alloy (b) and (d) tested at −50 °C. Small arrows indicate large inclusions on the surface. Similar inclusions were observed also in the alloys (e) and (f). Large inclusions were observed in the as-melted ingots of the alloys doped with 0.3 or 0.5 wt% Y. Y, Si and Al were detected in the inclusions by EDS analysis. From the viewpoint of the free energy of formation, the major component of the inclusion is considered to be yttrium oxide. Because the large inclusions are formed in the melting process and remain after hot working, it is necessary to control the yttrium addition in order to avoid the formation of the inclusions. For the melting condition in this study, the inclusions in the alloys doped with 0.1% Y had a lower density and a smaller size than those in the others. It is believed that impact property of alloy (b) was improved by reducing interstitial impurity levels and inclusions containing yttrium.

3.3. Tensile properties

Fig. 5 shows typical stress–strain curves of V–4Cr–4Ti–0.1Si–0.1Al–0.1Y (a) alloy before and after neutron irradiation. The solid line indicates the result of the specimens after neutron irradiation at 290 °C and the dashed line indicates that of the unirradiated specimens. Test temperature is noted in parentheses. The increase in yield stress was relatively small (∼100 MPa) and uniform elongation remained about 10%. Because of low interstitial impurity levels, good tensile properties could be retained even after irradiation at 290 °C.

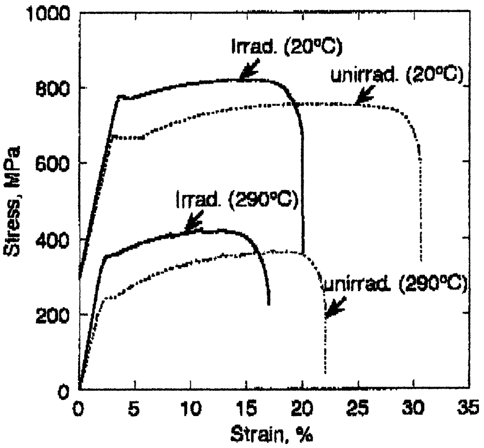

Fig. 5. Typical stress–strain curves of V–4Cr–4Ti–0.1Si–0.1Al–0.1Y alloy before and after neutron irradiation at 290 °C to 8×10^{22} n/m^2. Test temperature is noted in parentheses.

4. Summary

In this study, the technology for fabricating high-purity ingots of V–4Cr–4Ti–Si–Al–Y type alloy has been demonstrated. By adopting a levitation melting method, high-purity ingots could be produced on a scale of 2.5 kg, and that made it possible to investigate systematically various properties of the alloy.

(1) Concentration of interstitial impurities almost reached low levels ($O < 170$, $N \sim 110$, $C \sim 80$ wt ppm). Oxygen concentration decreased with increasing yttrium. Contamination with nitrogen and carbon was small in this melting process. Because deviation from the intended composition was large for alloying elements, further optimization of the melting condition is necessary.
(2) Charpy impact properties of miniaturized specimens were improved by selecting the appropriate composition of yttrium and avoiding the formation of large inclusions mainly made of yttrium oxide. The DBTT of V–4Cr–4Ti–0.1Si–0.1Al–0.1Y was below −150 °C and much lower than that of a previous laboratory-scale heat.
(3) The alloy fabricated in this study showed good tensile properties even after neutron irradiation at 290 °C up to 8×10^{22} n/m^2 ($E > 1$ MeV). Because of the low oxygen concentration, good tensile properties could be retained for this irradiation condition.

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