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Effects of small amount of additional elements on control of interstitial impurities and mechanical properties of V–4Cr–4Ti–Si–Al–Y alloys

Toshinori Chuto [a,*], Manabu Satou [b], Akira Hasegawa [b], Katsunori Abe [b], Takeo Muroga [c], Norikazu Yamamoto [a]

[a] *National Institute for Materials Science, 1-2-1, Sengen, Ibaraki, Tsukuba 305-0047, Japan*
[b] *Department of Quantum Science and Energy Engineering, Graduate School of Engineering, Tohoku University, 01 Aramaki-aza-Aoba, Aoba-ku, Sendai 980-8579, Japan*
[c] *National Institute for Fusion Science, Oroshi-cho, Gifu, Toki 509-5292, Japan*

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Abstract

In order to improve the mechanical properties of low activation vanadium alloys for fusion structural applications, effects of small addition of Si, Al and Y on the control of interstitial impurities (O, C and N) during the fabrication process were examined for several V–4Cr–4Ti–Si–Al–Y alloys produced by the levitation melting method. Charpy impact tests and tensile tests were carried out for five kinds of V–4Cr–4Ti–Si–Al–Y alloys using miniaturized specimens for the purpose of evaluating the effects of these elements on mechanical properties. Oxygen concentration decreased almost linearly with increasing loss of yttrium during melting. This oxygen reduction with yttrium loss during the melting process may have been achieved by two types of mechanisms, they are, (i) suppression of oxygen penetration into the molten materials from the environment and (ii) getting of oxygen from the matrix by forming Y_2O_3, which floats to the surface during the melting. There was no effect of Si and Al addition to control the concentration of interstitial impurities. V–4Cr–4Ti–0.1Si–0.1Al–0.1Y alloy showed the best impact properties out of the alloys investigated. Upper-shelf energy of the alloys decreased with increasing yttrium content. High number density of coarse inclusions containing yttrium could cause the degradation of impact properties, though they hardly affect tensile properties of the alloys. Even at higher yttrium contents, V–4Cr–4Ti–Y alloys without addition of Si and Al showed relatively high upper-shelf energy.

1. Introduction

Vanadium-base alloys such as V–4Cr–4Ti have been identified as attractive high-performance structural materials for first-wall and blanket components in fusion power systems due to their favorable mechanical, physical and nuclear properties. Though considerable progress has been made on development of vanadium alloys for fusion applications, there still remain several critical issues for engineering use of the alloys [1]. Against low-temperature irradiation embrittlement, that is one of the most important issues determining low-temperature performance limit, addition of minor elements such as Si, Al and Y to reduce interstitial impurity levels is considered to be effective [2–5]. Interstitial impurities such as oxygen, nitrogen and carbon could affect various properties of vanadium alloys by means of

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[*] Corresponding author. Tel./fax: +81-29 859 2014.
E-mail address: chuto.toshinori@nims.go.jp (T. Chuto).

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solid solution condition, formation of precipitates and binding with irradiation defects. From this viewpoint, high-purity V–4Cr–4Ti reference alloy, which is so-called NIFS-HEAT, was fabricated by purification of starting materials and control of impurity pick-up during melting and working processes [6,7].

The V–Cr–Ti type alloys modified by adding a small amount of minor elements, such as Si, Al and Y, have been developed as radiation-resistant and oxidation-resistant candidates for fusion applications [2–5,8–11]. Some of the alloys showed not only good resistance to radiation damage at elevated temperatures, but also relatively good tensile properties even after low-temperature irradiation. It is considered that improvement of the low-temperature irradiation performance of the V–Cr–Ti alloys by minor element addition is due to the reduction of oxygen by slag-off of yttrium oxide during the melting process, and the effects of these minor elements to scavenge interstitial impurities. Systematic investigation on effects of Si, Al and Y on various properties of V–Cr–Ti–Si–Al–Y alloys is necessary to determine the optimum composition of the alloys. Recently, fabrication of high-purity kg-scale ingots of V–4Cr–4Ti–Si–Al–Y alloys was demonstrated using a levitation melting method, and the fabrication made it possible to investigate various properties of the alloys systematically [5,12]. In this paper, effects of Si, Al and Y on the reduction of interstitial impurities, Charpy impact properties and tensile properties of V–4Cr–4Ti–Si–Al–Y type alloys were examined.

2. Experimental procedure

The materials studied were taken from 2.5 kg ingots fabricated by levitation melting. Detailed procedures of the material preparation are described in reference [12]. Table 1 shows chemical compositions of the alloys, where each alloy is designated by an alphabetical symbol for simplification. Concentration of interstitial impurities in raw vanadium is also shown in the table. The alloy (g) of V–4Cr–4Ti without addition of Si, Al and Y was produced as a reference material in order to confirm impurity pick-up during the melting process. In alloys (a)–(e), blocks taken from the middle part of ingots were encapsulated in stainless-steel sheaths, and hot-pressed to about 14 mm in thickness after annealing at 1000 °C for 1.8 ks, followed by removing the surface layer. The blocks were cold-rolled to 2 mm thick plates and partly to 0.25 mm thick sheets. Miniaturized Charpy specimens (1.5CVN), their dimension being 1.5 mm (thickness) × 1.5 mm (width) × 20 mm (length) with a 30° notch angle, 0.3 mm notch depth and 0.08 mm root radius, were machined from the plates. Notch orientation, that is, crack propagation direction, was perpendicular to the rolling direction and into the width of the plates. Miniature size tensile specimens with a gauge section of 5 mm long and 1.2 mm wide were punched out from the sheets. All of the miniaturized specimens were annealed at 1000 °C for 3.6 ks in a vacuum of 1×10^{-3} Pa, wrapped with Ta and Zr foils to obtain a fully re-crystallized condition. The ingots of the alloys (f) and (g) were used to investigate homogeneity of alloying elements, workability in as-melted condition and so on, and residual volume of the alloys was too small to prepare Charpy and tensile specimens.

Charpy impact tests were conducted at temperature from −196 to 0 °C by using an instrumented Charpy machine in the hot cell at the Oarai Branch, Institute for Materials Research, Tohoku University. The test speed was kept at 5 m/s. Tensile tests were carried out using an Instron-type machine at ambient temperature with a strain rate of 6.7×10^{-4} s^{-1}. Fracture surfaces of failed specimens were examined by scanning electron microscopy (SEM) in order to characterize the fracture mode.

3. Results

3.1. Effects of additional elements on impurity control

Oxygen concentration of all the alloys fabricated by the levitation melting is plotted in Fig. 1 as a function of the total amount of additional elements (Si + Al + Y) and the concentration of each element. The oxygen concentration was the result of chemical analysis at the

Table 1
Chemical composition of several vanadium alloys (wt%)

		Cr	Ti	Si	Al	Y	O	N	C	V
(a)	V–4Cr–4Ti–0.1Si–0.1Al–0.1Y	4.31	4.54	0.13	0.13	0.069	0.0112	0.0094	0.0086	Bal.
(b)	V–4Cr–4Ti–0.1Si–0.1Al–0.3Y	4.41	4.81	0.14	0.13	0.25	0.0080	0.0103	0.0064	Bal.
(c)	V–4Cr–4Ti–0.1Si–0.3Y	4.41	4.77	0.14	0.014	0.28	0.0080	0.0100	0.0071	Bal.
(d)	V–4Cr–4Ti–0.3Y	4.38	4.69	0.02	0.014	0.28	0.0067	0.0108	0.0077	Bal.
(e)	V–4Cr–4Ti–0.5Y	3.97	4.49	NA	NA	0.32	0.0054	0.0388	0.0072	Bal.
(f)	V–4Cr–4Ti–0.5Si–0.5Al–0.5Y	4.41	4.75	0.80	0.85	0.50	0.0055	0.0113	0.0071	Bal.
(g)	V–4Cr–4Ti	4.37	4.53	0.02	0.029	<0.01	0.0477	0.0170	0.0064	Bal.
	Raw vanadium						0.0080	0.0093	0.0065	

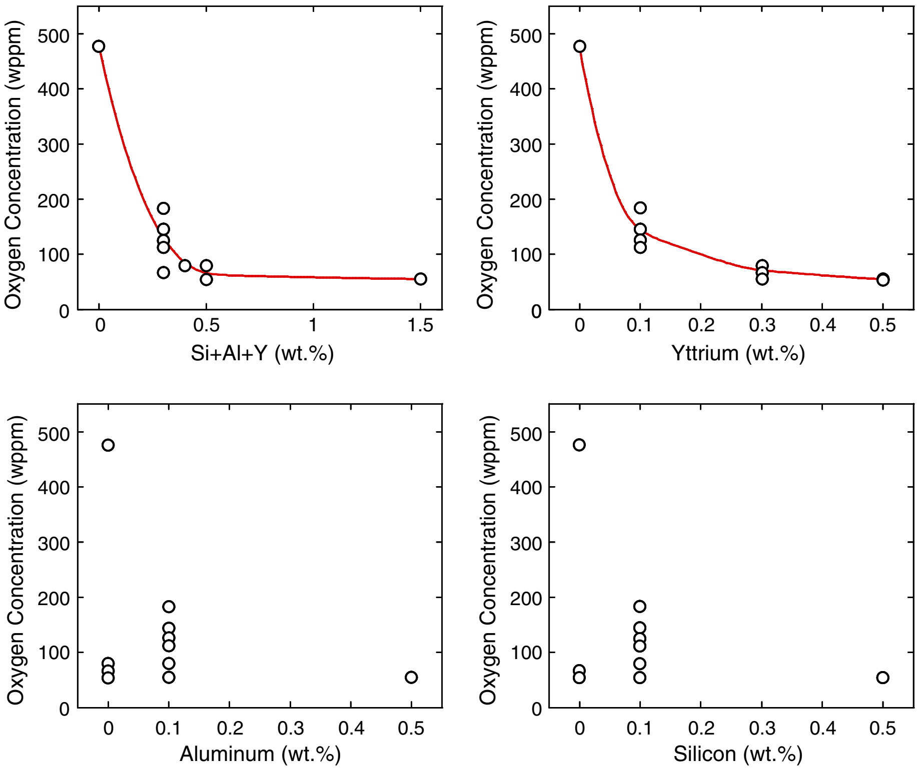

Fig. 1. Dependence of oxygen concentration on the total amount of additional elements (Si + Al + Y) and the addition of each minor element.

inside of each ingot. Therefore, the oxygen concentration in the figure includes oxygen contribution from large inclusions, if these are oxide inclusions. The oxygen concentration decreased with increasing the total amount of additional elements. Oxygen concentration decreased drastically with 0.1 wt% yttrium addition, and slightly decreased with increasing yttrium addition further. On the other hand, no systematic dependence of oxygen concentration on Si and Al addition was observed. There were some ingots with low oxygen concentration without addition of Si and Al. It is considered that addition of Al and Si hardly contributes to the reduction of oxygen during the fabrication processes.

Nitrogen concentration of alloy (b) was almost the same as alloy (a) in spite of the different amount of yttrium addition. In addition, it is obvious by comparing alloy (b), (c) and (d) that nitrogen concentration did not depend on the addition level of Si and Al. Only the alloy (e) showed relatively high concentration of nitrogen. This may have been caused by an exceptional condition such that the substitution of Ar gas in the melting furnace was insufficient. Carbon concentration was almost the same among all materials and hardly increased from the concentration in the raw material. It can be concluded that concentration of nitrogen and carbon is controlled at adequately low levels by using the melting method independent of alloy composition.

3.2. Charpy impact properties

Fig. 2 presents the test temperature dependence of absorbed energy for several V–4Cr–4Ti–Si–Al–Y alloys measured by instrumented Charpy impact test. Absorbed energy, E, in the figure was normalized by size parameter of each specimen using the following equation:

$$E = \frac{E'}{Bb^2},$$

where E' is the raw value of absorbed energy, B and b are the width and the ligament size (= thickness-notch depth) of the specimen, respectively. The alloy designation is the same as in Table 1. Alloy (a) showed the best impact properties among these materials, that is, the highest upper-shelf energy and the lowest ductile–brittle transition temperature (DBTT). The DBTT of the alloy was below −150 °C. Impact properties of the alloys degraded with increasing yttrium addition in spite of the lower oxygen concentration. The alloys with 0.3 or 0.5 wt% yttrium addition showed DBTTs of about

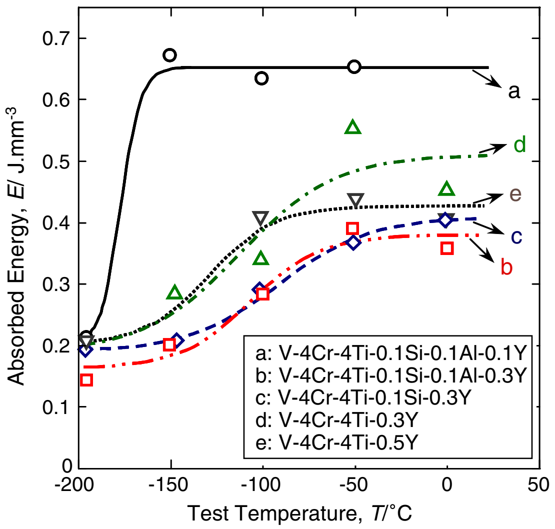

Fig. 2. Charpy impact properties of several V–4Cr–4Ti–Si–Al–Y alloys.

−100 °C. The upper-shelf energy of alloys (b) and (c) was slightly lower than that of alloys (d) and (e) which do not contain Si and Al. These elements may have detrimental effects on impact properties of the alloys.

Fig. 3 shows typical fracture surfaces of the alloys after impact testing at about −50 °C. The alloy designation is the same as in Fig. 2. According to the temperature range showing the upper-shelf in Fig. 2, all samples failed in a fully ductile manner. Coarse inclusions were observed on the fracture surfaces of the alloys doped with 0.3 or 0.5 wt% Y. Number density of the inclusions tended to increase with increasing the yttrium addition. Similar inclusions were observed in the as-melted ingots of the same alloys, and yttrium was detected in the inclusions by energy dispersive X-ray spectroscopic analysis [12]. Degradation of the impact properties of the alloys is mainly due to these coarse inclusions containing yttrium.

3.3. Tensile properties

Tensile properties, that are yield stress, tensile strength, uniform elongation and total elongation, at ambient temperature are compared in Fig. 4. There is a certain difference in the yield stress and the tensile strength, whereas the elongation scarcely changes among the alloys. Difference in the yield stress is explained in terms of difference in composition of alloying elements and concentration of interstitial impurities.

Similar to the case of the impact specimens, coarse inclusions were observed in the alloys containing higher amount of yttrium as shown in Fig. 5. However, these inclusions seem to have no influence on the tensile properties. Reduction in area of the alloys (b)–(e) was slightly lower than that of the alloy (a). Tensile properties shown in Fig. 4 and reduction in area of the alloys are summarized in Table 2. Though difference in the reduction in area between the alloys was small, dependence of reduction in area on alloy composition was compatible to that of the upper-shelf energy in Charpy impact testing.

4. Discussion

4.1. Mechanism of oxygen reduction by yttrium

Oxygen concentration in the alloys is re-plotted in Fig. 6 as a function of the amount of reduced yttrium. Yttrium reduction as abscissa in the figure was calculated by subtracting the total content of yttrium

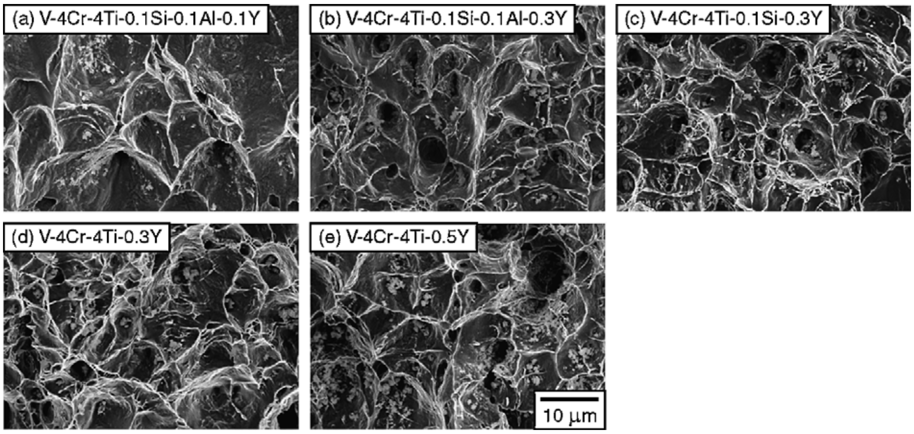

Fig. 3. Scanning electron micrographs of typical fracture surfaces after impact testing at −50 °C.

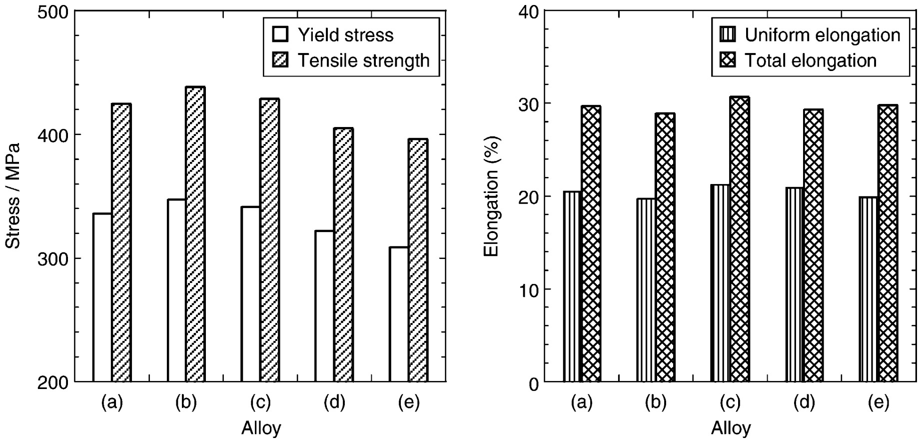

Fig. 4. Comparison of yield stress, tensile strength, uniform elongation and total elongation between five kinds of alloys tensile-tested at ambient temperature; (a) V–4Cr–4Ti–0.1Si–0.1Al–0.1Y, (b) V–4Cr–4Ti–0.1Si–0.1Al–0.3Y, (c) V–4Cr–4Ti–0.1Si–0.3Y, (d) V–4Cr–4Ti–0.3Y, (e) V–4Cr–4Ti–0.5Y.

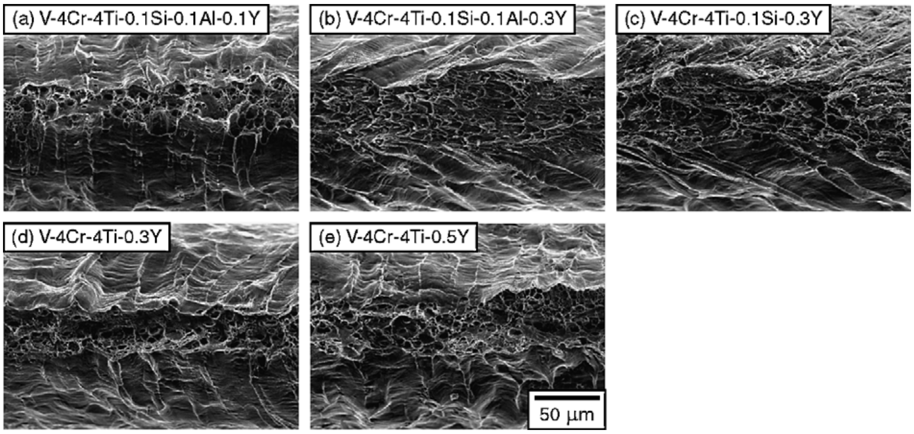

Fig. 5. SEM fractographs of the V–4Cr–4Ti–Si–Al–Y alloys tensile-tested at ambient temperature.

Table 2
Summary of tensile properties of the V–4Cr–4Ti–Si–Al–Y alloys tested at ambient temperature

Alloy composition	Yield stress (MPa)	Tensile strength (MPa)	Uniform elongation (%)	Total elongation (%)	Reduction in area (%)
(a) V–4Cr–4Ti–0.1Si–0.1Al–0.1Y	336	425	19.9	27.8	89.2
(b) V–4Cr–4Ti–0.1Si–0.1Al–0.3Y	347	439	19.7	28.9	82.7
(c) V–4Cr–4Ti–0.1Si–0.3Y	341	429	21.2	30.7	82.6
(d) V–4Cr–4Ti–0.3Y	322	405	20.9	29.3	86.6
(e) V–4Cr–4Ti–0.5Y	309	396	19.9	29.8	85.5

including the large inclusions in each ingot, which was estimated based on the results of chemical analysis at several points in the ingots except for the surface layer, from the amount of doped yttrium. Oxygen concentration showed a tendency to decrease almost linearly with increasing yttrium reduction. It is considered that oxygen was removed as yttrium oxide with a certain composition during the melting process. The yttria, Y_2O_3, is

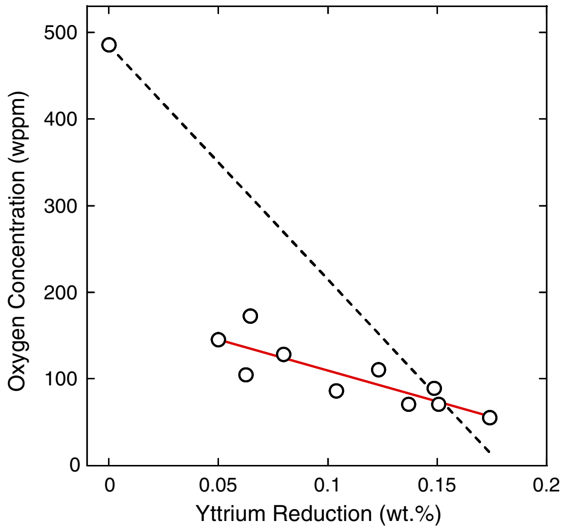

Fig. 6. Correlation between oxygen concentration and amount of reduced yttrium for the V–4Cr–4Ti–Si–Al–Y alloys fabricated by levitation melting.

the most likely oxide from the viewpoint of the free energy of formation. Relation between oxygen concentration (C) and yttrium reduction (ΔC_Y) is expressed as the following equation:

$$C = C_o - \alpha \cdot \Delta C_Y,$$

where C_o is oxygen concentration in molten materials before yttrium addition, α is a ratio of oxygen removal against decrease in yttrium. Dashed line in this figure indicates the relation between oxygen concentration and yttrium reduction calculated in the case where oxygen is removed as Y_2O_3. The values of α of experimental results (solid line) and calculation (dashed line) were 70 and 270 wppm O/0.1 wt% Y, respectively. A value of C_o of the calculation was set at 477, which was oxygen concentration in the V–4Cr–4Ti alloy (g) without addition of yttrium. A value of C_o for experimental results was 180 obtained by extrapolation to zero reduction of yttrium. Both C_o and α of the experimental results are smaller than those in the case of Y_2O_3. From these results, there may be two types of mechanisms of the oxygen reduction by yttrium during the melting process. One is the suppression of oxygen penetration into the molten materials at the surface and the other is the removal of oxygen from the inside by forming Y_2O_3 and floating to the surface. According to Fig. 6, the former effect that resulted in decrease of C_o is considered predominant for the suppression of the oxygen level. It is estimated that about 1/4 of reduced yttrium contributed to the latter effect from comparison of α between experimental results and calculation.

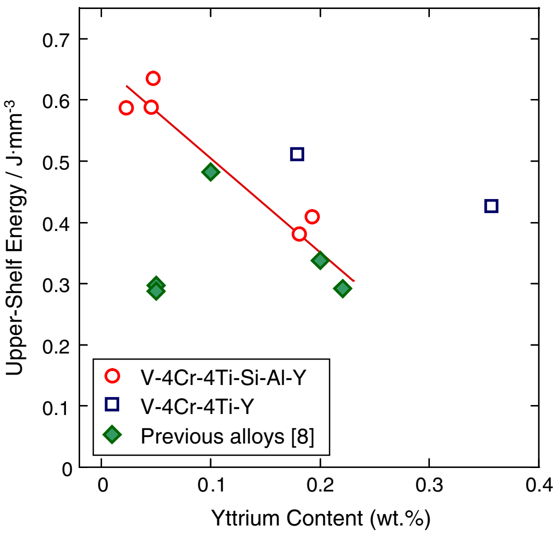

Fig. 7. Correlation between upper-shelf energy and yttrium content for several V–4Cr–4Ti–Si–Al–Y alloys.

4.2. *Influence of additional elements on mechanical properties*

Fig. 7 shows the upper-shelf energy obtained by Charpy impact testing as a function of yttrium content in comparison with previous laboratory-scale heat of V–4Cr–4Ti–Si–Al–Y alloys. Within the temperature range showing dimple fracture surface, absorbed energy can be affected by volume fraction of secondary-phase particles such as inclusions and precipitates, strength of matrix itself and so on. The upper-shelf energy of the V–4Cr–4Ti–Si–Al–Y alloys including the previous alloys decreased linearly with increasing yttrium content. It is considered that main cause of decrease in upper-shelf energy of the alloys is the increase in size and number density of the inclusions containing yttrium. As for the alloys containing more than 0.1 wt% Y, yttrium is in excess even if all the oxygen is presumed to form Y_2O_3. Because the solubility limit of yttrium in vanadium is quite low [13], the excess yttrium, and also Y_2O_3, could precipitate and form the coarse inclusions. Assuming that all the oxygen in solution is converted to Y_2O_3 by yttrium addition, addition of about 0.15 wt% Y is necessary to consume all the oxygen. The amount of excess yttrium increases with yttrium content, whereas the amount of Y_2O_3 is almost constant because of limited concentration of oxygen. Therefore it is important to control the addition of yttrium so as to minimize the excess yttrium. Two alloys of previous heat showed very low upper-shelf energy (~0.3 J/mm) regardless of relatively low yttrium content (~0.05 wt%). These alloys contained high concentration of oxygen, 0.060 and 0.101 wt%, respectively [9], whereas oxygen concentration in the previous alloys with higher amount of yttrium was comparable to the alloy (a) fabricated in the present study. Oxygen in solution can strengthen matrix significantly, and form precipitates and inclusions with alloying elements. All of these may cause decrease in upper-shelf energy.

The V–4Cr–4Ti–Y type alloys without addition of Si and Al showed relatively high upper-shelf energy even with higher yttrium content. This detrimental effect of Si and Al may arise from solid solution strengthening of matrix. Strengthening by addition of each element was estimated to be 142 MPa/wt% Si and 43 MPa/wt% Al by comparing the tensile properties between alloys (b), (c) and (d). One possible reason for decrease in upper-shelf energy of the V–4Cr–4Ti–Sl–Al–Y alloys at higher yttrium content is the increase in yield stress especially by solid solution strengthening of Si.

4.3. Optimum amount of additional elements

Oxygen concentration in the alloys decreased with increasing the yttrium addition. However, in the alloys of yttrium addition more than 0.3 wt%, excess yttrium formed coarse inclusions that brought about degradation of impact properties. Addition of Si and Al seems to have no effect on reduction of oxygen. Though Si and Al are effective in improvement of the strength, these elements deteriorate impact properties in the case of the alloys containing higher amount of yttrium.

As for the resistance to low-temperature irradiation embrittlement, both V–4Cr–4Ti–0.1Si–0.1Al–0.1Y and V–4Cr–4Ti–0.1Si–0.1Al–0.3Y alloys showed good tensile properties after low-dose and low-temperature irradiation, and are expected to maintain the good properties to higher neutron dose because of their low oxygen levels [5]. From these results, it is proposed that optimum composition of irradiation-resistant candidate is V–4Cr–4Ti–xSi–yAl–0.15Y ($x, y = 0$ or 0.1). In order to determine the addition of Si and Al, that is x and y, effects of each element on low-temperature irradiation performance need to be clarified. And also dependence of oxidation resistance on the amount of Si, Al and Y should also be investigated further.

5. Summary

Effects of minor elements on impurity control and mechanical properties were examined for the V–4Cr–4Ti–Si–Al–Y type alloys fabricated by levitation melting.

Oxygen concentration in the alloys decreased linearly with increasing yttrium loss. There may be two types of mechanism of the reduction of oxygen concentration by yttrium during the melting process. One is suppression of oxygen penetration into the molten materials through the surface and the other is removal of oxygen from the inside by Y_2O_3 forming and floating to the surface. Addition of Si and Al hardly contributes to the reduction of oxygen. Nitrogen and carbon concentration can be controlled to adequately low levels by using this melting method independent of the amount of additional elements.

The V–4Cr–4Ti–0.1Si–0.1Al–0.1Y showed the best impact properties out of the alloys examined and had a DBTT of the temperature <-150 °C. The upper-shelf energy of V–4Cr–4Ti–Si–Al–Y type alloys decreased with increasing the yttrium content. It is considered that the main factor decreasing the upper-shelf energy of the alloys is the increase in size and number density of the inclusions containing yttrium. The V–4Cr–4Ti–Y type alloys without addition of Si and Al showed relatively high upper-shelf energy up to high yttrium content. One possible reason for the decrease in upper-shelf energy by Si and Al addition is the solid solution strengthening of the matrix.

There is some difference in yield stress and tensile strength, whereas elongation scarcely changes among the alloys. Increase in yield stress by addition of Si and Al was estimated to be 142 MPa/wt% Si and 43 MPa/wt% Al. Coarse inclusions were observed on the fracture surface of the alloys doped with 0.3 or 0.5 wt% Y. These inclusions seem to have no influence on tensile properties, though they might cause degradation of impact properties.

It is proposed that V–4Cr–4Ti–(0–0.1)Si–(0–0.1)Al–0.15Y (nominal weight percentage) is the optimum composition as irradiation-resistant candidate at present.

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