ELSEVIER
Journal of Nuclear Materials 258–263 (1998) 1361–1368
journal of nuclear materials

Effect of small additional elements on DBTT of V–4Cr–4Ti irradiated at low temperatures

Tamaki Shibayama [a,*], Ichiro Yamagata [b], Hideo Kayano [a], Chusei Namba [c]

[a] *The Oarai Branch, Institute for Materials Research, Tohoku University, Oarai-machi, Ibaraki 311-13, Japan*
[b] *Power Reactor and Nuclear Fuel Development Corporation, Tokai-mura, Ibaraki 311-13, Japan*
[c] *National Institute of Fusion Science, Toki, Gifu 509-52, Japan*

Abstract

As a part of a program to screen several V–4Cr–4Ti containing Si, Al and Y alloys and optimize the amounts of Si, Al and Y, the Charpy impact test of five kinds of V–4Cr–4Ti–Si–Al–Y alloys by an instrumented Charpy impact testing machine using miniaturized specimens (1.5 mm × 1.5 mm × 20 mm) have been conducted before and after neutron irradiation. Charpy impact specimens were encapsulated in an aluminum vial filled with high purity He and irradiated up to 1.06×10^{19} n/cm^2 ($E > 1$ MeV, 156 h) at low temperatures (about 150°C) in Japan Materials Testing Reactor (JMTR). The ductile brittle transition temperature (DBTT) of each alloy was determined by various methods on absorbed energy, brittle fracture ratio and lateral expansion from a quantitative analysis of fractography for broken specimens after the Charpy impact test. Almost all specimens were embrittled after low temperature irradiation. Decomposition of primary precipitates could result in migration of interstitial elements to irradiation defects and many precipitates are formed under irradiation. Radiation hardening then caused the substantial degradation of its fracture toughness.

1. Introduction

Vanadium alloys have an attractive feature for first-wall and blanket structural materials beyond the DEMO reactor, because of their inherently low irradiation induced activity, high potential for irradiation stability and good compatibility with lithium coolant. Kayano who is one of the authors in this paper has presented a V–Cr–Ti–Si type alloy containing aluminum and yttrium as a part of a newly developed vanadium alloy which has a good resistance to oxidation in fusion environment [1]. In previous experiments, the V–Cr–Ti–Si containing aluminum and yttrium alloy has shown a good resistance to swelling and a good tensile ductility after heavy neutron irradiation at Fast Flux Test Facility/Materials Open Test Assembly (FFTF/MOTA) by Satou et al. [2]. In general, the ductile to brittle transition temperature (DBTT) of body center cubic (bcc) materials may be significantly elevated after neutron irradiation. However V–4Cr–4Ti has a good resistance to irradiation embrittlement and its DBTT is still maintained below liquid nitrogen temperature following 46 dpa irradiation [3].

At the recent IEA workshop which was held at Petten, it was reported that irradiation at low temperatures to less than 1 dpa would cause significant embrittlement and the DBTT was elevated above the room temperature [4]. Alexander also reported low temperature irradiation embrittlement of V–4Cr–4Ti [5].

In this paper, the effects of neutron irradiation at low temperature on the fracture properties of V–4Cr–4Ti–Si, Al, Y alloys have been examined and discussed by means of the small specimen technique. Therefore, their results could provide an understanding of the mechanism on the fracture toughness after irradiation at low temperature and give a solution to improve the toughness of V–4Cr–4Ti–Si, Al, Y.

---

[*] Corresponding author. Present address: Center for Advanced Research of Energy Technology, Hokkaido University, Sapporo 060, Japan. E-mail: shiba@ufml.caret.hokudai.ac.jp.

0022-3115/98/$19.00
PII: S0022-3115(98)00202-5

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

Nominal composition	Heat #	Si	Ti	Cr	Fe Y	Al	C	O	N	H	V
V–4Cr–4Ti (BL47)		0.081	4.3	4.1			0.020	0.035	0.022		Bal.
V–4Cr–4Ti (KINKEN)			3.71	3.72			0.0065	0.016	0.022		Bal.
V–4Cr–4Ti–0.5Si–0.5Al–0.5Y	1–3	0.46	3.99	3.96	0.20	0.49	0.018	0.012	0.011	0.0037	Bal.
V–4Cr–4Ti–0.3Si–0.3Al–0.3Y	3–3	0.34	4.07	3.96	0.10	0.29	0.011	0.025	0.010	0.0037	Bal.
V–4Cr–4Ti–0.1Si–0.1Al–0.1Y	5–3	0.14	4.08	3.96	0.05	0.08	0.011	0.101	0.010	0.0033	Bal.
V–4Cr–4Ti–0.5Si–0.5Y	7–3	0.46	4.04	4.00	0.22	–	0.012	0.019	0.011	0.0034	Bal.
V–4Cr–4Ti–0.1Si–0.1Y	10–3	0.14	4.09	3.92	0.05	–	0.012	0.060	0.009	0.0029	Bal.
V–5Cr–5Ti–Si–Al–Y (KAV6)		0.85	4.79	4.01	0.77	0.95	0.0126	0.014	0.0054		Bal.

2. Experimental procedure

Five kinds of materials provided in this study were taken from 300 g laboratory heat produced by Daido Bunseki Research Co. Ltd. (DBR). Table 1 shows the detailed chemical composition of each alloy. Each material contains Si, Y and Al from 0.1 to 0.5 wt% respectively, otherwise two materials do not contain Al. Al is one of the harmful elements for low activation, therefore if Al may be found to be less contributed to oxidation resistance, Al could be excluded in the next heat which is currently being investigated. These plates were supplied in the form of 30 mm (width) × 3 mm (thickness) × 100 mm (length) after hot forging of cladding stainless steel something like Japanese bento box and hot rolling prior to machining from DBR. Finally cold rolling was done up to 40% in our laboratory.

Miniature size Charpy specimens which are so-called JP-CVN-1, their dimensions being 1.5 mm × 1.5 mm × 20 mm with a 30° notch angle, 0.3 mm notch depth and a 0.08 mm root radius were chosen in this paper. The notch was machined to orient for crack growth perpendicular to the rolling direction and parallel to the transverse direction. All materials had been annealed at 1000°C for 1 h in which heat up ratio was 500°C/h in a vacuum less than 1×10^{-7} Torr after machining to miniature size Charpy specimens. TEM specimens were also provided to punch out from the cold rolled sheet. These specimens were annealed at the same condition as that of miniature Charpy specimens.

These specimens were irradiated up to 1.06×10^{19} n/cm^2 ($E > 1$ MeV, 156 h) by using a hydraulic irradiation capsule in the Japan Materials Testing Reactor (JMTR) in the Oarai establishment of Japan Atomic Energy Research Institute (JAERI). The hydraulic irradiation capsule was specially designed for this experiment to reach low temperatures below 100°C during irradiation. All specimens were in contact with both the inner and outer capsules designed for transferring gamma heat through thermal contact. The capsule consisted of an outer capsule and an inner capsule which were made from Al alloy. The hydraulic capsule does not have an instrumented temperature measurement system during irradiation, however its average temperature could be kept below 150°C according to the results of the thermal diffusion calculation by JAERI [6].

Charpy impact tests were conducted by using an instrumented Charpy impact machine in a hot cell at the Oarai Branch, Institute for Materials Research, Tohoku University. A strain rate was kept in 5 m/s through testing. DBTT was determined by lateral expansion, absorbed energy and brittle fracture ratio separately.

Vickers hardness test was also conducted at room temperature with a 200 g load on the side surface of the miniature Charpy specimen which was far from a deformed region after impact testing and the measurements were done at least at 10 points on both the side surfaces on each specimen.

3. Results and discussion

The chemical composition of each V–4Cr–4Ti–Si, Al, Y alloy is shown in Table 1. The chemical composition of O, C and N on each V–4Cr–4Ti–Si, Al, Y alloy in this study almost reached the specific level proposed by the US fusion program [7]. However the oxygen level is increased instead of decreasing the amount of small additional elements. It is suggested that the resistance to oxidation depends on the amount of small additional elements. In general the ductility of vanadium alloy is decreased with increasing additional elements. Therefore it is a key issue to define the specific amounts of small additional elements on the development of an oxidation resistance vanadium alloy. Fig. 1 shows the optical metallographs of grain structure on each V–4Cr–4Ti–Si, Al, Y alloy as-rolled and after annealing at 1000°C for 1 h. All micrographs were taken from TEM specimens, however they appear the same as the micrograph taken from the side surface of the miniature Charpy specimen. No inclusions and subgrain structure were visible in Fig. 1. The grain size of each specimen after annealing at 1000°C for 1 h is less than 40 μm. The ASTM number of each alloy existed from 6.5 to 7.0. Further the grain size of V–4Cr–4Ti–Si, Al, Y alloys is slightly smaller than that of non-Al containing alloys. However it looks that the grain size of their alloys would not depend on the amount of small additional elements in this study.

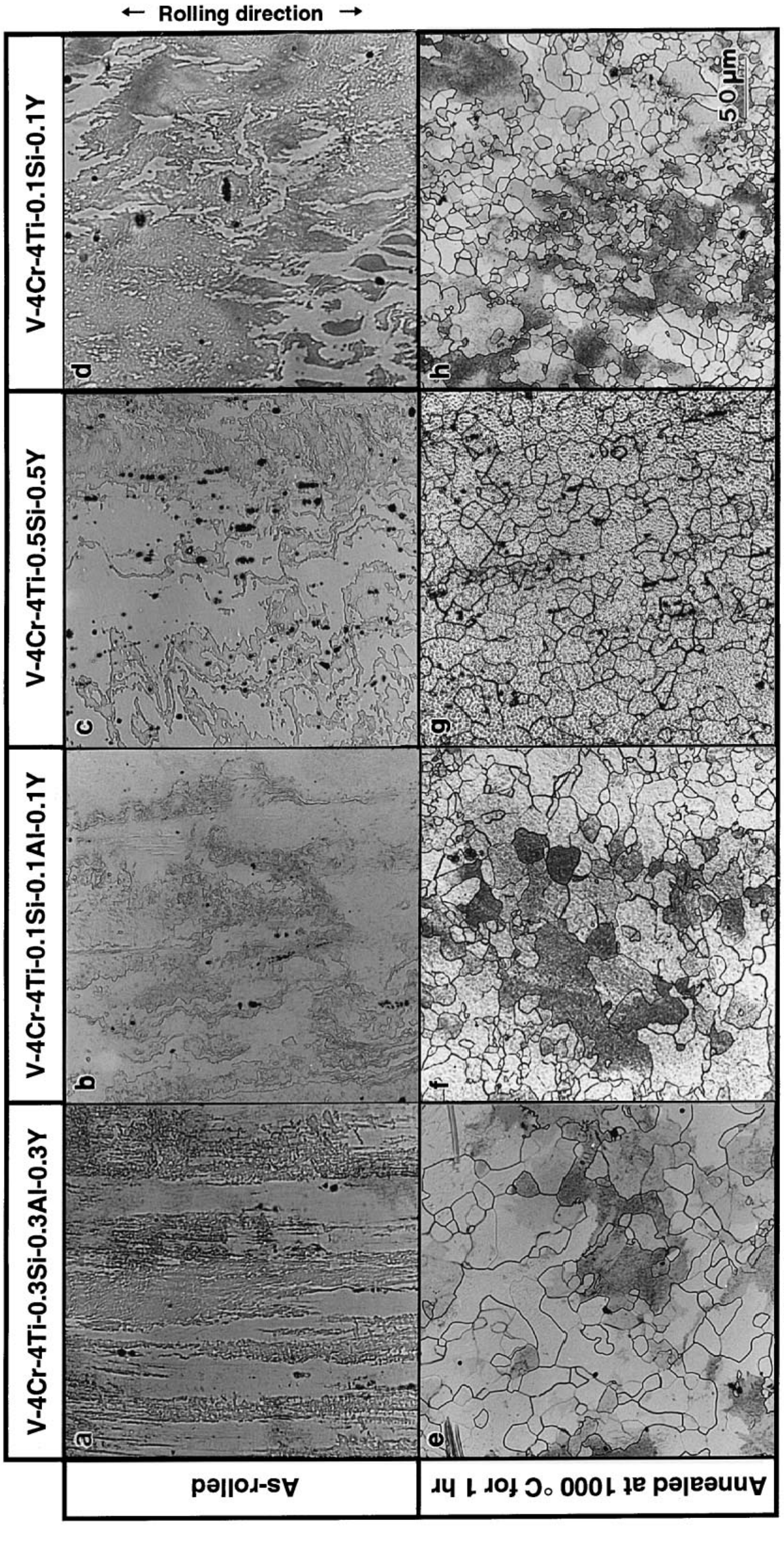

Fig. 1. Optical metallographs of grain structure on several V–4Cr–4Ti–Si–Al–Y alloys as-rolled state, (a)–(d), and after annealing at 1000°C for 1 h (e)–(h).

Fig. 2 shows the TEM micrographs of V–4Cr–4Ti–Si, Al, Y alloys after annealing at 1000°C for 1 h. In general Ti(O, C, N) type precipitates are recognized in extruded, rolled and annealed plates of V–4Cr–4Ti for US reference alloy [7]. However Ti (O, C, N) were not characterized in these alloys except V–4Cr–4Ti–0.1Si–0.1Al–0.1Y. The visible precipitates were spherical in shape, and less than 100 nm in diameter and these precipitates were found to be Ti_5Si_3 by the analytical TEM. The precipitates were uniformly distributed within the grain, however no precipitates are visible on the grain boundary. The precipitate density depended on the amount of small additional elements. Few small precipitates were found on the fracture surface after impact testing. These precipitates were defined to be Al_2O_3, sulfide or unidentified complex precipitates which consisted of Al, Si, S, P and Y were also found.

Fig. 3 shows the typical load–deflection curve at various temperatures (a) prior to irradiation and (b) following irradiation. The significant degradation of deflection following irradiation is visible in Fig. 3 (b) and the uniform elongation of each alloy prior to irradiation is one-half that prior to irradiation. The yield strength of each alloy following irradiation at room temperature is much higher than that prior to irradiation [8]. Fig. 4 shows the Vickers micro-hardness of each alloy at room temperature. The irradiation response of Vickers micro-hardness on these alloys is quite similar to the response of yield strength. Furthermore the hardening behavior of each alloy depends on the amount of small additional elements. The hardness of Al addition alloy tended to be higher than the one of non-Al addition. At the IEA workshop, similar irradiation response of V–4Cr–4Ti from 90°C to 290°C was presented [4]. Irradiation hardening at low temperatures could also occur in this study. It is suggested that Al addition would not be possible to control the irradiation hardening at lower temperature. Al is also a harmful element for reduced activation, however Al contributes to oxidation. Therefore it is necessary to provide the exact activation data of Al depending neutron energy to define the specific level for maintaining a good resistance to oxidation, a good resistance to low temperature irradiation hardening and reduced activation.

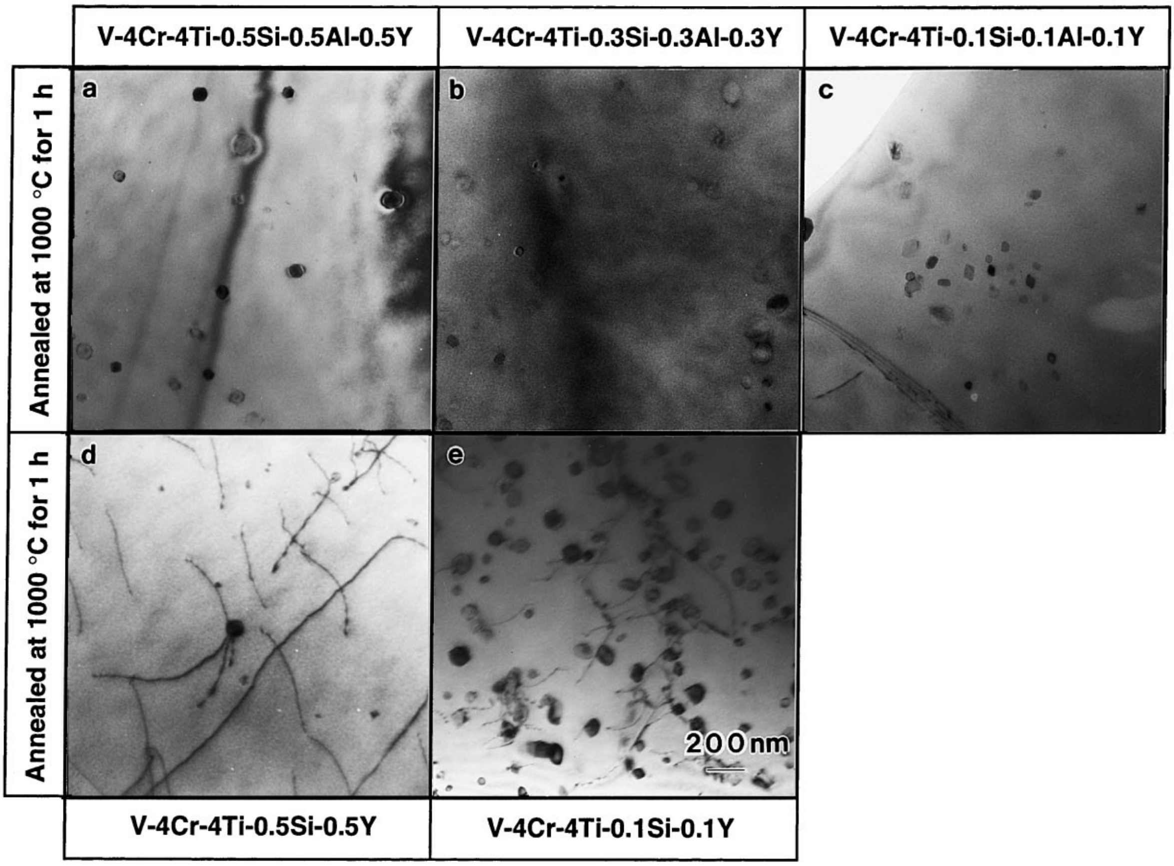

Fig. 2. Typical TEM micrographs of several V–4Cr–4Ti–Si–Al–Y alloys after annealing at 1000°C for 1 h.

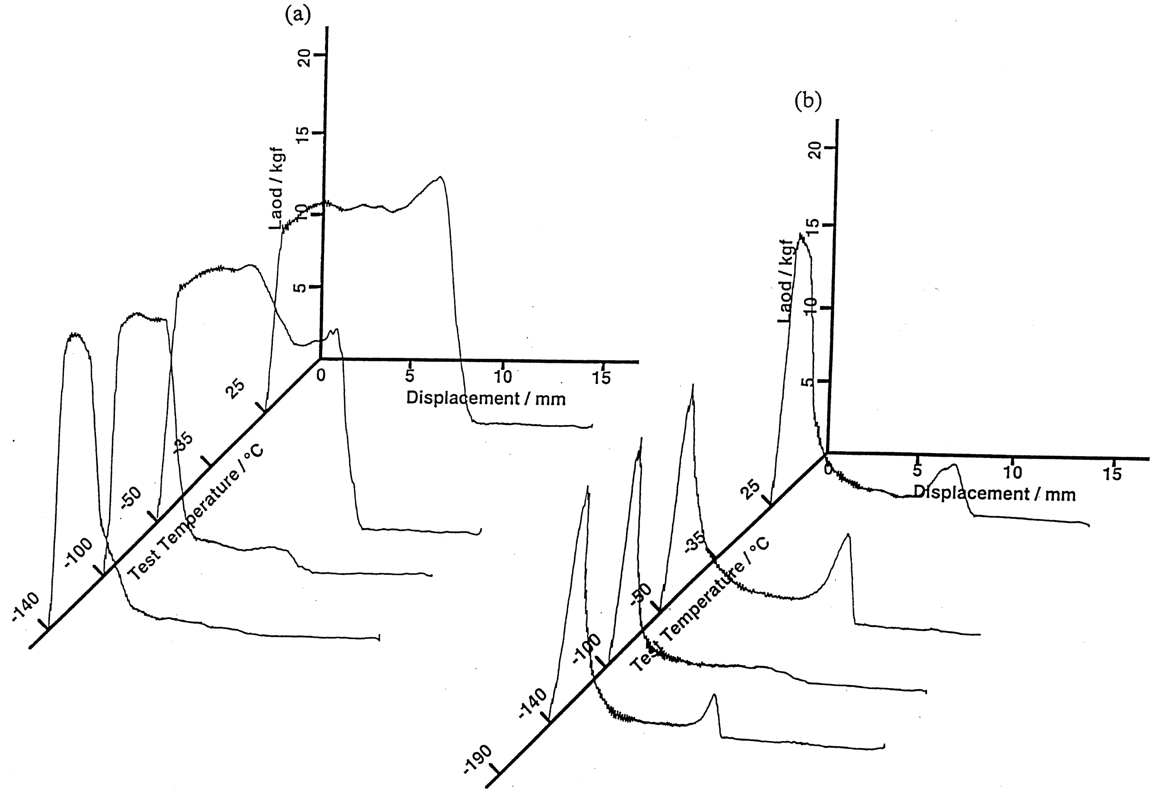

Fig. 3. Typical load–deflection curve at various temperature: (a) prior to irradiation; (b) following irradiation.

The result of Charpy impact testing on V–4Cr–4Ti (KINKEN heat) is shown in Fig. 5. In this study the only control V–4Cr–4Ti alloy had subsize Charpy impact specimens. Size effects is clearly observed in Fig. 5. A DBTT of V–4Cr–4Ti for miniature size specimen could be below −190°C and for its subsize specimen was

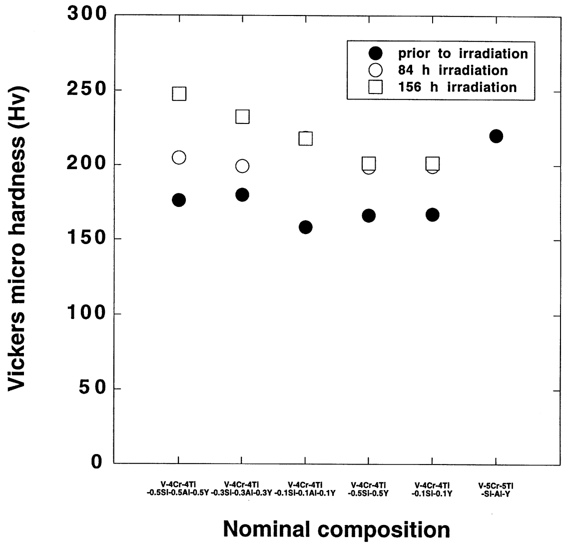

Fig. 4. Vickers micro-hardness of each alloy at room temperature.

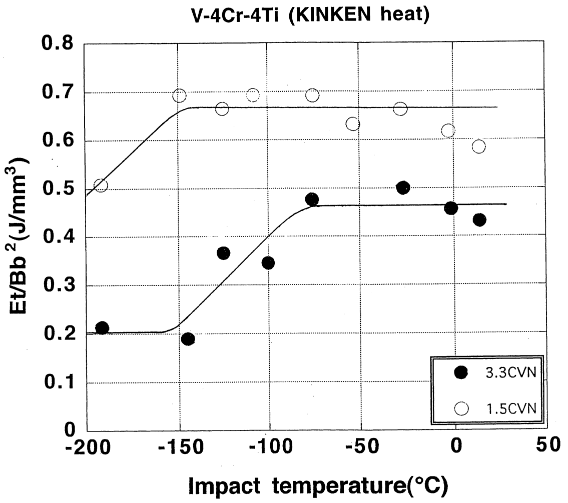

Fig. 5. DBTT on V–4Cr–4Ti (KINKEN heat) following annealed at 1000°C for 1 h.

−110°C. In some cases, a crack perpendicular to the notch was visible and an irregular load peak after maximum load was observed in the load/deflection curve on ductile cleavage fracture specimen. Therefore it would be caused by sub-crack growth after yield point. Therefore the irregular load peak was cut off for evaluating the absorbed energy in this study.

Fig. 6 shows the result of Charpy impact testing on several V–4Cr–4Ti–Si–Al–Y alloys. All miniature specimens have DBTTs below −50°C. However the only miniature specimen of V–4Cr–4Ti has a DBTT below −190°C. Since the DBTT is one of the key issues to decide the candidate material from the various alloys, the DBTTs of these oxidation resistance vanadium alloys should be improved in near future. An increase in the total amount of small additional elements resulted in improved resistance to oxidation and DBTT in alloy with Al. On the other hand, the DBTT of alloys without Al does not depend on the total amount of small additional elements and the DBTT existed almost as same value. The upper shelf energy of all specimens was kept over 0.3 J/mm^3. Only V–4Cr–4Ti–0.3Si–0.3Al–0.3Y has a much higher upper shelf energy than the other alloys and the lower shelf energy was also higher than the other alloys. The results of DBTT on various vanadium alloys prior to irradiation were varied and they depend on Al addition. As a result of unirradiated data, V–4Cr–4Ti–0.3Si–0.3Y–0.3Al alloy is a tentative candidate material in this study.

Fig. 7 shows a comparison of impact properties of unirradiated and irradiated miniature specimens on several V–4Cr–4Ti–Si–Al–Y alloys. Upper shelf energy of each alloy is constant. However lower shelf energy of alloys with Al addition is somewhat lower than that without Al addition. However it is quite clearly observed that all irradiated alloys exhibited the brittle fracture surface after 8.5×10^{18} n/cm^2 (156 h) irradiation. Irradiation for 4.6×10^{18} n/cm^2 (84 h) at low temperatures caused a slight increase of their DBTT and a large degradation of the upper shelf energy for Al addition alloys. Indeed for non-Al addition alloys, the large shift of DBTT was observed with the increasing amount of Al addition. Following irradiation, a yield point was not be observed in Fig. 5 and these alloys fail rapidly prior to yielding. Low temperature radiation hardening of V–4Cr–4Ti–Si–Al–Y alloys could also have occurred in this irradiation. In general radiation hardening at low temperatures (below 250°C) would be common for BCC alloys as in the case of ferritic/martensitic steels. The degradation of fracture toughness would be caused by means of many small defects or fine precipitates. Fig. 8 shows TEM micrograph on V–4Cr–4Ti–0.3Si.–0.3Al–0.3Y irradiated to 8.5×10^{18} n/cm^2 (156 h). Fine radiation defects are clearly observed in Fig. 8 and small arrows indicate something like precipitates existing within the grain. It is suggested that many carbide-like precipitates caused the substantial degradation of fracture toughness after irradiation to 8.5×10^{18} n/cm^2 (156 h) at lower temperature. One possible reason for embrittlement of V–4Cr–04Ti–Si–Al–Y type alloys irradiated at low temperatures is that many vanadium carbide and fine defects clusters formed during irradiation. Primary precipitates may be quite unstable under irradiation and have released their in-

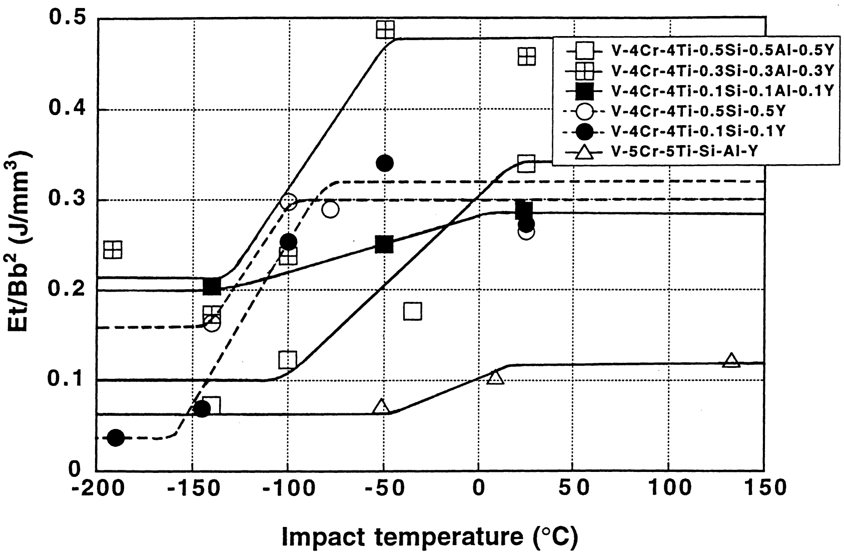

Fig. 6. Impact properties of miniature unirradiated specimens after annealing at 1000°C for 1 h on several V–4Cr–4Ti–Si–Al–Y alloys.

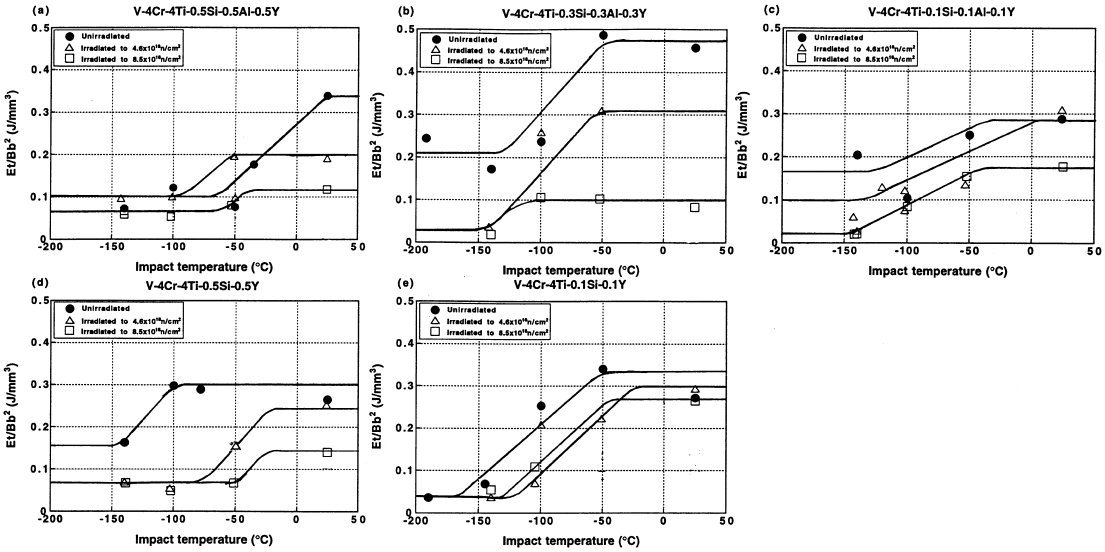

Fig. 7. A comparison of impact properties of unirradiated miniature specimens and irradiated miniature specimens on several V–4Cr–4Ti–Si–Al–Y alloys.

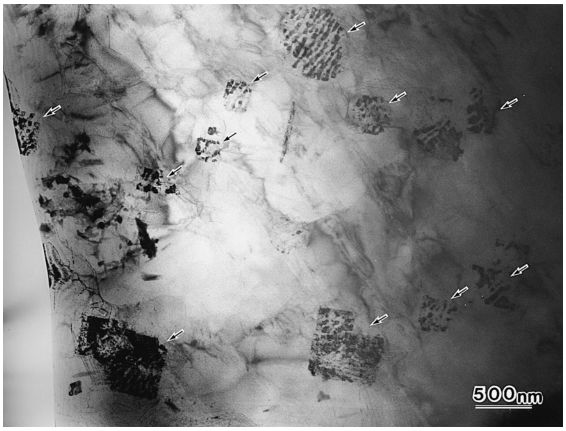

Fig. 8. TEM micrograph on V–4Cr–4Ti–0.3Si.–0.3Al–0.3Y irradiated to 8.5 × 10^{18} n/cm^2 (156 h). The precipitates would be irradiation induced carbide.

terstitial elements by decomposition of primary precipitates. Their interstitial impurities migrate to irradiation defects and many precipitates are formed under irradiation. The hardening could cause the substantial degradation of its fracture toughness. However it was hard to define the precipitates by a conventional microscopy and it seems that irradiation temperatures in this study are somewhat lower than migration temperature of interstitial atoms such as C, O and N in vanadium alloy. Additional work of a nano-probe analysis by something like a field emission transmission electron microscopy is needed to verify the presence of such precipitates. Irradiation temperature cross check with JMTR is also needed.

4. Summary

Effect of small additional elements on DBTT of V–4Cr–4Ti–Si–Al–Y type alloys irradiated up to 1.06×10^{19} n/cm^2 at low temperatures (below 150°C) was discussed. The summary is as follows:

(1) The DBTT of V–4Cr–4Ti–Si–Al–Y type alloys in this study is much lower than the DBTT of V–5Cr–5Ti–Si–Al–Y alloy.

(2) The yield and maximum strength of V–4Cr–4Ti–Si–Al–Y type alloys prior to irradiation do not significantly depend on the total amount of small additional elements. However the increase in the amount of Al addition cause a decrease in its maximum strength. Irradiation response of hardness on V–4Cr–4Ti–Si–Al–Y type alloys is quite similar to impact properties.

(3) The Al addition caused a decrease in DBTT. However the DBTT of Al addition alloys after irradiation for 84 h is lower than that of no Al addition alloys. However more irradiation cause a serious sever degradation of fracture toughness for alloys without Al addition.

(4) Many precipitates are observed within grains after irradiation. It is tentatively proposed that the precipitate could be an irradiation induced carbide. One possible reason for embrittlement of V–4Cr–4Ti–Si–Al–Y type alloys irradiated at low temperatures is that many vanadium carbide and fine defects clusters formed during

irradiation. Primary precipitates may be quite unstable under irradiation and they have released their interstitial elements by decomposition of primary precipitates. Their interstitial impurities migrate to irradiation defects and many precipitates are formed under irradiation. The hardening could cause the substantial degradation of its fracture toughness.

Acknowledgements

The authors gratefully acknowledge the help of Mr. M. Narui and Mr. M. Yamazaki who provided a shipment of miniature specimens from the hot laboratory. This work was been partly supported by the Japan–USA Program of Irradiation Test for Fusion Research (JUPITER) between the US DOE and Monbusho, the Japanese Ministry of Education, Science and Culture.

References

[1] H. Kayano, Sci. Rep. RITU A 40 (1994) 105.

[2] M. Satou, K. Abe, H. Kayano, J. Nucl. Mater. 212–215 (1994) 794.

[3] B.A. Loomis, M. Chung, L.J. Nowicki, D.L. Smith, J. Nucl. Mater. 212–215 (1994) 799.

[4] V.M. Chernov, R.J. Kurtz, in: E.V. Van Osch (Ed.), Proceedings of Second Workshop on Vanadium Alloy Development for Fusion, 20–22 May 1996, ECN Petten, The Netherlands, p. 23.

[5] D.J. Alexander, L.L. Snead, S.J. Zinkle, A.N. Gubbi, A.F. Rowcliffe, E.E. Bloom, Fusion reactor materials, Semiannual Prog. Report DOE/ER-0313/14, Oak Ridge National Laboratory, Oak Ridge, TN, 1996, p. 87.

[6] M. Narui, private communication.

[7] W.R. Johnson, J.P. Smith, R.D. Stambaugh, Fusion reactor materials, Semiannual Prog. Report DOE/ER-0313/19, Oak Ridge National Laboratory, Oak Ridge, TN, 1995, p. 5.

[8] T. Shibayama, I. Yamagata, H. Kayano, to be published.