ELSEVIER

Journal of Nuclear Materials 283–287 (2000) 727–730

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Features of radiation damage of vanadium and its alloys at a temperature of 330–340°C

V.A. Kazakov *, Z. Ostrovsky, Yu. Goncharenko, V. Chakin

State Scientific Centre of Russian Federation Research Institute of Atomic Reactors, 433510 Dimitrovgrad-10, Ulyanovsk Region, Russian Federation

Abstract

Microstructural changes of vanadium alloys after irradiation at 340°C to 12 dpa in the BOR-60 reactor in ^{7}Li environment is analyzed. Materials are vanadium and its alloys V–3Ti, V–3Fe, V–6Cr, V–4Cr–4Ti, V–5Cr–10Ti, V–6Cr–1Zr–0.1C. Void formation was observed in the binary alloys V–3Fe, V–3Ti and V–6Cr. It is shown that three–four-fold increase in V–4Cr–4Ti yield stress is produced by the formation of dislocation loops (DLs) and fine radiation-induced precipitates (RIPs) with a density of 1.7×10^{17} cm^{-3}. It is expected that embrittlement of the welds will be worse because density of DLs and RIPs is 1.4–1.6 times higher. Besides, invisible coherent or semi-coherent RIPs are formed in the fusion zone. Elemental maps of the rupture surface of irradiated V–4Cr–4Ti are presented.

1. Introduction

Vanadium alloys are being considered as structural materials for the first wall and blanket of fusion reactors with lithium coolant and breeder. V–Cr–Ti alloys with 3–6% chromium and titanium have some advantages. At present, a period for obtaining the basic experimental results on the alloys behavior at low irradiation temperatures (<430°C) is nearing completion [1–5]. Experiments to be carried out under irradiation at higher temperatures (up to 800°C) for assessment of radiation stability in this operating temperature range are next [6,7].

The objective of the work is to investigate alteration of the microstructure and elemental composition of different vanadium alloys, including V–4Cr–4Ti, after irradiation at 340°C to 12 dpa in the BOR-60 reactor in a ^{7}Li environment. The work is a continuation [8] in which the change in mechanical properties has been analyzed and the type of fracture investigated.

2. Experimental

2.1. Materials, specimens, irradiation conditions

Pure vanadium and six V-base alloys were investigated: V–3.0Ti, V–3.1Fe, V–6.1Cr, V–4.4Cr–3.9Ti, V–5Cr–10Ti, V–5.4Cr–1.1Zr–0.09C wt%, including welds of V–4Cr–4Ti and V–5Cr–10Ti prepared by electron-beam and argon-arc methods. Chemical composition, initial heat treatment and irradiation conditions of the alloys have been presented in previous work [8,9].

TEM-disks of 3 mm diameter × 0.2 mm thick were irradiated in stainless steel subcapsules with lateral holes for free ingress of lithium. The capsules were placed in the top of the Fusion-1 capsule, where the temperature was 340°C and dose 12 dpa.

2.2. Methods

Transmission electron-microscope investigations were performed on a JEM-2000 FX II at an accelerating voltage of 120 kV. Previously, TEM-disks were thinned on a single-jet unit in an electrolyte of 86%CH_3OH–14%H_2SO_4 at room temperature and a current of 120–122 mA.

* Corresponding author. Tel.: +7-842 353 2021; fax: +7-842 353 5648.

E-mail address: fae@omv.niiar.simbirsk.su (V.A. Kazakov).

0022-3115/00/$ - see front matter
PII: S0022-3115(00)00218-X

An ESO-5 Auger-spectrometer was used to map elemental distribution on fracture surfaces of irradiated V–4Cr–4Ti. It has a minimum electron probe diameter of 0.1 μm. The specimens were ruptured at room temperature in air. One fragment was inserted into the Auger-spectrometer and another into a REM-101 scanning electron microscope for fractography. An attempt to map such elements as vanadium, chromium, titanium, carbon and oxygen was made. The size of the investigated area was $\sim 150 \times 150$ μm^2. The scanning of each image was performed for 4 h. The electron beam was slightly defocused to 0.5 μm to increase sensitivity.

3. Results

3.1. Microstructure

The microstructure of the alloys is shown in Fig. 1. There were dislocation loops (DLs) in the pure vanadium only, which interacted with each other forming the dislocation network.

Void formation along with DLs and radiation-induced precipitates (RIPs) were observed in three alloys: V–3Ti, V–3Fe and V–6Cr. Voids were distributed extremely irregularly in V–3Ti (Fig. 1(a)). As a result, swelling was low ($< 0.1\%$). There were rather small initial precipitates from 15 to 45 nm. There were fine RIPs with a high density and slightly elongated ($\leqslant 5 \times 2$ nm) after irradiation (Fig. 1(b)). The mean size and density of voids in V–3Fe were larger, swelling reached 4.9%. There were depleted zones near the grain boundaries about 40 nm wide (Fig. 1(c)). Grain boundaries were enriched with iron.

The finest voids, 1–6 nm in size and high density, were observed in V–6Cr (Fig. 1(d)). There were streaks in the ⟨0 0 2⟩ direction on the microdiffraction patterns, which were evidence of the presence of coherent or semi-coherent angular RIPs. The addition of 1% Zr and 0.1% C to the alloy resulted in the full suppression of void formation under irradiation.

The mean size of the particles in the initial state is about 500 nm in V–5Cr–10Ti (Fig. 1(e)). The titanium content in them fluctuates from 48 to 75 at.%. They contain about 2% Cr. The size of the initial particles in the V–4Cr–4Ti alloy is smaller, 150–200 nm (Fig. 1(g)). In addition, there is high density of RIPs in the alloy (Fig. 1(f)). The RIP density in the alloy welds, in both the electron-beam and argon-arc welding, is appreciably higher in comparison to the base metal. The precipitation morphology is close to round or slightly elongated (Fig. 1(h)).

In the analysis of radiation strengthening $\Delta\sigma$ and the radiation defect characteristics (Table 1), it should be born in mind that tensile specimens were displaced in the central part of the Fusion-1 capsule; and therefore, their temperature was slightly lower than the TEM-disks (330°C). However, the radiation damage dose was significantly higher (18–19 dpa). Sometimes, some uncertainty appeared in the determination of sizes and density of DLs and RIPs when they were hardly distinguishable from each other because of superposition of deformation contrasts.

3.2. Elemental maps

We were not able to obtain intergranular fracture of irradiated V–4Cr–4Ti alloy. It is necessary for examination of segregated phenomena on grain boundaries. Investigation of transgranular fracture surfaces was not too interesting. Distribution of vanadium, chromium,

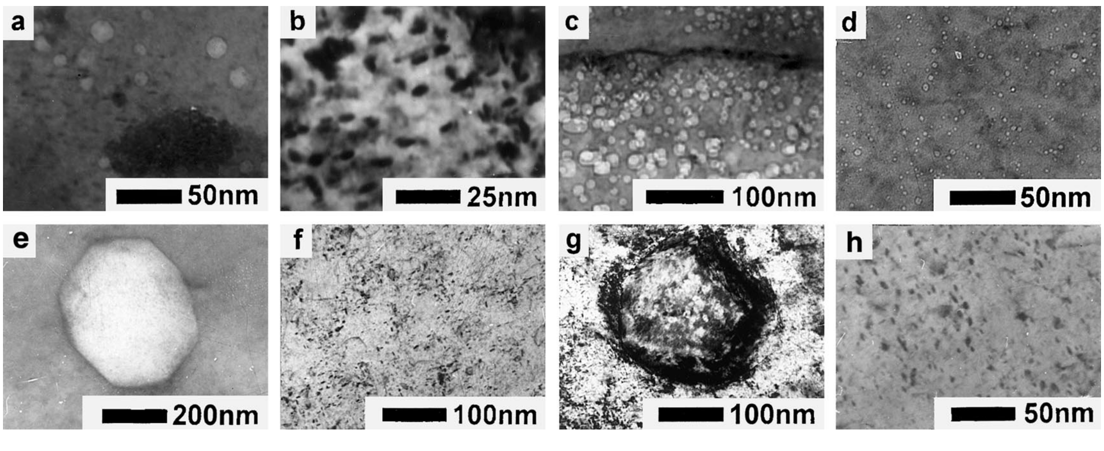

Fig. 1. Microstructure of some vanadium alloys after irradiation in the BOR-60 reactor at a temperature of 340°C to 12 dpa. RIPs – radiation-induced precipitations, AAW – argon-arc welding. (a) V–3Ti, voids; (b) V–3Ti, RIPs; (c) V–3Fe, voids; (d) V–6Cr, voids; (e) V–5Cr–10Ti, precipitations; (f) V–4Cr–4Ti, RIPs; (g) V–4Cr–4Ti, particle; (h) V–4Cr–4Ti, AAW, RIPs.

Table 1
Parameters of radiation damage of vanadium and its alloys after irradiation at 340°C to 12 dpa in the BOR-60 reactor

Alloy	Voids		DLs		RIPs		$\Delta V/V$ (%)	$\Delta\sigma_{350}$ (%)[a]
	d (nm)	N (cm^{-3})	d (nm)	N (cm^{-3})	d (nm)	N (cm^{-3})		
Vanadium	–	–	5–55	2.1×10^{16}	–	–	0	140
V–3Ti	5–18	2.4×10^{14}	?	?	5–10	4.4×10^{16}	<0.1	100
V–3Fe	16	1.5×10^{16}	10–20	4.4×10^{16}	–	–	4.9	100
V–6Cr	1–6	6.0×10^{17}	5–35	5.3×10^{16}	–	–	0.5	80
V–6Cr–1Zr–0.1C	–	–	2.5–45	3.7×10^{16}	–	–	0	220
V–5Cr–10Ti	–	–	5–40	5.0×10^{16}	–	–	0	140
V–4Cr–4Ti	–	–	∼10	1.5×10^{16}	∼5	9.0×10^{16}	0	310
V–5Cr–10Ti. EBW[b]	–	–	5–45	3.0×10^{16}	–	–	0	–
V–4Cr–4Ti. EBW	–	–	∼10	2.7×10^{16}	2.5–5	1.4×10^{17}	0	–
V–4Cr–4Ti. AAW[c]	–	–	10–70	2.7×10^{16}	3–10	1.2×10^{17}	0	–

[a] $\Delta\sigma_{350}$ – difference between yield stress in the irradiated and initial states at $T_{test} = 350$°C related to the initial value.
[b] EBW – electron beam weld.
[c] AAW – argon-arc weld.

titanium, oxygen and carbon through one of the facet surface was more or less uniform.

4. Discussion

Analysis of the radiation damage microstructure of vanadium alloys at 340°C shows the following:

- RIPs make the main contribution to the radiation strengthening of the V–4Cr–4Ti alloy.
- The low susceptibility of V–3Ti, V-3Fe and V–6Cr alloys to RIP formation during irradiation probably leads to the appearance of voids, but the radiation strengthening is 3–4 times smaller in comparison with the V–4Cr–4Ti alloy.
- The density of DLs and RIPs in the welds were 1.4–1.6 times more than in the base metal. Besides, formation of coherent or semi-coherent RIPs takes place in the weld. Therefore, the degree of the weld embrittlement, especially in the fusion zone, should be much more than for the base metal.

We have not yet determined the RIP's chemical composition. However, we tried to analyze data on chemical composition, size and density of precipitates in V–(3–6)Cr–(3–5)Ti alloys from recent literature during the last 2–3 yr for both the initial and irradiated states. There are FCC-phase precipitates from 100 to 500 nm with a composition of either Ti(OCN) or (TiV)(OCN) in the initial state [10–15]. Sometimes a segregation of N, S,

Table 2
Parameters of the radiation damage microstructure of V–(3–6)Cr–(3–5)Ti alloys in the irradiation temperature range of 110–505°C

T_{irr} (°C)	Parameters			Chemical composition	Additional information	Reference
	Type	d (nm)	N (cm^{-3})			
110	DLs	3	1×10^{17}	–	0.5 dpa HFBR + 0.1% Cr	[18]
275		3.7	1×10^{17}			
200,300	DLs	∼20	≈5×10^{16}	–	4 dpa ATR. Streaks are on 2/3 ⟨2 2 2⟩ only	[15]
	Precipitations	3–4	$(1–3)\times10^{17}$	Ti(OCN)		
315	Clusters	<3	>1.5×10^{17}	Ti enriched	0.5 dpa HFBR + 0.1%Cr	[18]
390		≈5[a]	≈10^{17}[a]	–	0.1 dpa HFBR + 0.02%Cr	
390	Precipitations	3–10	3.5×10^{17}	V(CON)	4 dpa EBR-II. Streaks	[13]
∼400		4–5	$(1.1–4)\times10^{17}$	Ti(OCN) (?)	4.5 dpa EBR-II. Streaks	[14]
415	DL	200	<10^{14}	–	0.5 dpa HFBR + 0.1%Cr Ti, Cr segregates on clusters[b]	[18]
	Clusters	40	∼10^{14}			
430	Precipitations	3–10	3.5×10^{16}	(VTi)(CON)	27 dpa FFTF	[13]
505	DL	500	<10^{13}	–	dpa HFBR + 0.02%Cr Ti segregates on clusters	[18]
	Clusters	42	2.6×10^{15}			

[a] Approximate values because authors of [18] give cluster parameters for 315°C only, but at that they inform that density of ones decreases slowly at irradiation temperature increasing to 390°C.
[b] – Early stage of RIPs formation.

P and C was found on grain boundary [16]. In the weld and heat-affected zone, disks or plate-like precipitates were observed with the next chemical composition: $Ti_{16}(O_3N_3C_2)$, $(V_8Ti_8)(C_3NO_{0.65})$, $Ti_7(O_4N_2C)$ [12,14, 17]. As a whole, results of this work do not contradict these literature data.

As is seen from Table 2, the DLs are present in the temperature range from 110°C to 505°C after irradiation, but their size increases from 3 to 500 nm and their density decreases from 10^{17} to $<10^{13}$ cm^{-3}. The greatest increase in DL size and decrease in density takes place within 300–415°C. If we consider the clusters and RIPs to be the same, but in different stages of evolution, then RIP-phase formation begins at 300°C. All investigators agree that it contains titanium and interstitial impurities, but some consider that it also contains chromium and/or vanadium.

In considering the evolution of RIPs in the range of 300–505°C under irradiation in reactors with different neutron spectra, the following should be noted:

1. A rather sharp increase of RIP size and decrease in density is observed in the temperature range 390–415°C. When the temperature is increased by only 25°C and damage dose is decreased 5 times, the RIP density decreases by three orders of magnitude.
2. The RIP size (40–42 nm) does not change when the irradiation temperature increases from 415°C to 505°C in the HFBR reactor and simultaneously the damage dose decreases from 0.5 to 0.1 dpa. However the density increases by 25 times.
3. The RIP size after irradiation in the fast neutron spectrum of the FFTF reactor at 430°C up to 27 dpa is 3–10 nm, whereas after irradiation in the mixed neutron spectrum of the HFBR reactor to 0.1–0.5 dpa it is 40–42 nm.
4. Similarly, irradiation results from the fast neutron spectrum of the BOR-60 reactor and the mixed neutron spectrum of the HFBR reactor do not agree at a temperature of 315–390°C. An increase in dose of 24–120 times does not result in an increase of RIPs density.

By this means, in the initial state of the microstructure of V–4Cr–4Ti is known to a greater or lesser degree, but after irradiation many of the results need some additional investigation. In this case, it is impossible to accept that all disagreements are related to accumulation of transmutated chromium under irradiation in the mixed neutron spectrum. Transmutation may cause substantial ‘perturbations’ in the processes of microstructure formation and segregation on grain boundaries and interface surfaces during irradiation.

5. Summary

1. The formation of voids takes place in the binary alloys of V–3Fe, V–3Ti and V–6Cr after irradiation in BOR-60 at 340°C to 12 dpa.
2. A three- to -four-fold increase of yield stress in V–4Cr–4Ti is related to DLs and fine RIP formation with a total density of about 1.7×10^{17} cm^{-3}.
3. The density of DLs and RIPs in V–4Cr–4Ti welds is 1.4–1.6 times higher than in the base metal. The intensive formation of angular coherent or semi-coherent RIPs takes place in the fusion zone.

References

[1] D.J. Alexander, L.L. Snead, S.J. Zinkle, A.N. Gubbi, A.F. Rowcliffe, W.S. Eatherly, E.E. Bloom, in: Effects of Radiation on Materials, 18th International Symposium, ASTM STP, vol. 1325, 1999, p. 1119.

[2] H. Tsai, J. Gazda, M.C. Billone, D.L. Smith. Effects of low-temperature neutron irradiation on mechanical properties of vanadium-base alloys, Report on the fourth workshop on vanadium, Argonne National Laboratory, USA, 21–23 April, 1999.

[3] S.J. Zinkle, H. Matsui, D.L. Smith, A.F. Rowcliffe, E. van Osh, K. Abe, V.A. Kazakov, J. Nucl. Mater. 258–263 (1998) 205.

[4] H.M. Chung, D.L. Smith, J. Nucl. Mater. 258–263 (1998) 1442.

[5] J. Gazda, M. Meshii, H. Tsai, Fusion reactor materials semiannual progress Report DOE/ER-0313/24, 1998, p. 20.

[6] T.S. Bray, H. Tsai, L.J. Nowicki, M.C. Billone, D.L. Smith, W.R. Johnson, P.W. Trester, Tensile and impact properties of V–4Cr–4Ti alloy heats 832665 and 832864, Report on the fourth workshop on vanadium, Argonne National Laboratory, USA, 21–23 April, 1999.

[7] S.J. Zinkle, A.F. Rowcliffe, C.O. Stevens, Fusion reactor materials semiannual progress Report DOE/ER-0313/24, 1998, p. 11.

[8] V.A. Kazakov, V.P. Chakin, Y.D. Goncharenko, J. Nucl. Mater. 258–263 (1998) 1492.

[9] V.A. Kazakov, H.-C. Tsai, V.P. Chakin, F.W. Wiffen, A.F. Rowcliffe, D.L. Smith, A.E. Rusanov, A.A. Teikovtsev, N.V. Markina, L.R. Greenwood, J. Nucl. Mater. 258–263 (1998) 1458.

[10] A.F. Rowcliffe, D.T. Hoelser, Fusion reactor materials semiannual progress Report DOE/ER-0313/25, 1998, p. 42.

[11] D.T. Hoelser, Fusion reactor materials semiannual progress Report DOE/ER-0313/25, 1998, p. 59.

[12] H.M. Chung, J.-H. Park, R.V. Strain, K.H. Leong, D.L. Smith, J. Nucl. Mater. 258–263 (1998) 1451.

[13] H.M. Chung, J. Gazda, D.L. Smith, Fusion reactor materials semiannual progress Report DOE/ER-0313/24, 1998, p. 49.

[14] D.S. Gelles, P.M. Rice, S.J. Zinkle, H.M. Chung, J. Nucl. Mater. 258–263 (1998) 1380.

[15] D.S. Gelles, Fusion reactor materials semiannual progress Report DOE/ER-0313/24, 1998, p. 41.

[16] R.J. Kurtz, M.L. Hamilton, H. Li, J. Nucl. Mater. 258–263 (1998) 1375.

[17] M.L. Grossbeck, J.F. King, D.L. Alexander, P.M. Rice, G.M. Goodwin, J. Nucl. Mater. 258–263 (1998) 1369.

[18] P.M. Rice, S.J. Zinkle, J. Nucl. Mater. 258–263 (1998) 1414.