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by

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CORRELATION OF MICROSTRUCTURE AND TENSILE AND SWELLING BEHAVIOR OF NEUTRON-IRRADIATED VANADIUM ALLOYS *

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The microstructures of V-Ti, V-Cr-Ti, and V-Ti-Si alloys were characterized by transmission electron microscopy (TEM) after neutron irradiation in the Fast Flux Test Facility (FFTF) at 420 and 600°C to fluences up to 114 dpa. Two types of irradiation-induced precipitates were identified, i.e., Ti_2O and $\text{Ti}_5(\text{Si,P})_3$. Blocky $\text{Ti}(\text{O,N,C})$ precipitates, which form by thermal processes during ingot fabrication, also were observed in all unirradiated and irradiated specimens. Irradiation-induced precipitation of spherical (<15 nm in diameter) $\text{Ti}_5(\text{Si,P})_3$ phase was associated with superior resistance to void swelling. In specimens with negligible swelling, $\text{Ti}_5(\text{Si,P})_3$ precipitation was significant. It seems that ductility is significantly reduced when the precipitation of Ti_2O and $\text{Ti}_5(\text{Si,P})_3$ is pronounced. These observations indicate that initial composition; fabrication processes; actual solute compositions of Ti, O, N, C, P, and Si after fabrication; O, N, and C uptake during service; and irradiation-induced precipitation are interrelated and are important factors to consider in developing an optimized alloy.

1. Introduction

The swelling behavior¹⁻⁵ and mechanical properties⁶⁻¹⁰ of vanadium-base alloys (V-Ti, V-Cr, V-Cr-Ti, and V-Ti-Si), irradiated by fast neutrons at 420, 520, and 600°C in the FFTF Materials Open Test Assembly (MOTA) was

reported earlier. Density measurements showed that irradiation-induced swelling of vanadium-based alloys can be effectively inhibited by addition of >5 wt.% Ti in the alloy. For example, swelling of V-base alloys containing >5 wt.% Ti was <1%, in comparison with swelling as high as 3-4% for V, V-14Cr, V-15Cr-1Ti, and V-3Ti-1Si alloys upon irradiation at 420°C up to 114 dpa.¹ The superior resistance to void swelling of several high-Ti alloy specimens was associated in a previous investigation⁵ with irradiation-induced formation of high-density precipitates that are spherical in morphology and approximately <15 nm in diameter. It was suggested in the study that the large interface area between the precipitates and matrix could serve as an effective sink to vacancies, thereby inhibiting void nucleation and growth. However, the very fine spherical precipitates could not be identified in the study.

In a similar effort to provide an understanding of significant ductility degradation of several promising alloys of the V-13.5Cr-5Ti type, Gelles et al.¹¹ investigated microstructural evolution of the alloys following irradiation at 600°C in the FFTF/MOTA. They observed that specimen microstructure was characterized by two types of precipitates that formed in high density, i.e., (1) fine needlelike precipitates approximately <20 nm thick and <200 nm long and (2) spherical precipitates <15 nm in diameter. Based on its morphology, the latter appears to be same type of precipitate as those reported in Ref. 5 and correlated to the superior swelling resistance of some high-Ti alloys. The former type of precipitate was also reported by Loomis and Smith⁷ and by Ohnuki et al.¹² in some high-Ti alloys irradiated at 600°C; however, neither type precipitate could be identified.

Impact tests were also conducted by Cannon et al.¹⁰ on the V-13.5Cr-5Ti alloys, which exhibited significant degradation of ductility in tensile

tests after irradiation at 600°C. The ductile-brittle transition temperature (DBTT) and the temperature of transition from transgranular cleavage to ductile-rupture failure were estimated to be >400°C, indicating a significant degradation of fracture toughness. Hamilton and Loomis⁹ considered hydrogen-induced embrittlement and an unfavorable precipitate development during irradiation as the most likely causes of the ductility and toughness degradation. However, impact behavior was essentially similar after hydrogen removal, indicating that hydrogen-induced embrittlement was not the cause of the degradation.⁹

Thus, it seems evident from these investigations that the swelling and mechanical properties of V-Ti alloys are profoundly influenced by the two types of precipitates, i.e., the very fine spherical type (referred to as Type I in Ref. 5) and the needlelike type (referred to as Type II). The purpose of this investigation is to identify these two types of precipitates and thereby provide insight for development of optimized V-Ti alloy that will exhibit superior mechanical properties and resistance to void swelling.

2. Materials and Procedures

Procedures for preparation of alloy specimens in this investigation have been described in earlier reports.^{4,5} Chemical composition of as-fabricated alloys are given in Table 1. The alloys were irradiated in the FFTF/MOTA at 420 and 600°C to neutron fluences ($E > 0.1$ MeV) ranging from 3×10^{22} n·cm⁻² (17 dpa) to 1.9×10^{23} n·cm⁻² (114 dpa). The specimens were sealed inside Li⁷-filled TZM/Mo capsules during irradiation to prevent contamination by O, N, and C impurities dissolved in the sodium coolant of the FFTF.

Table 1. Composition of Vanadium Alloys Irradiated in FFTF/MOTA

ANL ID	Nominal Composition (wt.%)	Concentration (wt. ppm)			
		O	N	C	Si
BL-19	V	1101	161	360	----
BL-20	V	570	110	120	325
BL-36	V	810	86	250	<50
BL-51	V	570	49	56	370
BL-35	V-9.5Cr	340	45	120	<50
BL-4	V-10.0Cr	530	76	240	<50
BL-5	V-14.1Cr	330	69	200	<50
BL-50	V-1.0Ti	230	130	235	1050
BL-52	V-3.1Ti	210	310	300	500
BL-11	V-4.9Ti	1820	530	470	220
BL-46	V-4.6Ti	305	53	85	160
BL-34	V-8.6Ti	990	180	420	290
BL-12	V-9.8Ti	1670	390	450	245
BL-13	V-14.4Ti	1580	370	440	205
BL-15	V-17.7Ti	830	160	380	480
BL-16	V-20.4Ti	390	530	210	480
BL-10	V-7.2Cr-14.5Ti	1110	250	400	400
BL-43	V-9.2Cr-4.9Ti	230	31	100	340
BL-21	V-13.7Cr-4.8Ti	340	510	180	1150
BL-22	V-13.4Cr-5.1Ti	300	52	150	56
BL-23	V-12.9Cr-5.9Ti	400	490	280	1230
BL-25	V-14.4Cr-0.3Ti	390	64	120	<50
BL-26	V-14.1Cr-1.0Ti	560	86	140	<50
BL-24	V-13.5Cr-5.2Ti	1190	360	500	390
BL-40	V-10.9Cr-5.0Ti	470	80	90	270
BL-41	V-14.5Cr-5.0Ti	450	120	93	390
BL-43	V-9.2Cr-4.9Ti	230	31	100	340
BL-44	V-9.9Cr-9.2Ti	300	87	150	270
BL-47	V-4.1Cr-4.3Ti	350	220	200	870
BL-49	V-7.9Cr-5.7Ti	400	150	127	360
BL-42	V-3.1Ti-0.5Si	580	190	140	5400
BL-27	V-3.1Ti-0.3Si	210	310	310	2500
BL-45	V-2.5Ti-1.0Si	345	125	90	9900

Irradiated specimens of V-Ti, V-Cr-Ti, and V-Ti-Si alloys were selected and jet-thinned for TEM in a solution of 15% sulfuric acid-72% methanol-13% butyl cellosolve maintained at -5°C. TEM was conducted with a JEOL 100CX-II scanning transmission electron microscope (STEM) operating at 100 keV. Vanadium reflections were used as a standard in each selected-area diffraction (SAD) pattern to calculate reciprocal lattice spacings of the precipitates. In most cases, precipitate reflections were extremely weak and were easy to miss on the screen. It was best to detect the weak precipitate reflections by examining SAD patterns produced with a 22-cm camera length and an attached binocular. Dark-field images were obtained from as many precipitate reflections as possible in each SAD. SADs corresponding to several zone axes were obtained by tilting and transposing the specimen and were indexed to identify the crystallographic structure of the precipitate phase.

3. Results

Primary Thermal Precipitation - Ti(O,N,C) Phase

All of the specimens of unirradiated or irradiated V-Ti, V-Cr-Ti, and V-Ti-Si alloys contained relatively large, blocky precipitates 100-1500 nm in diameter. Analyses of dark-field images and SAD patterns showed that these precipitates are of *fcc* structure with a lattice constant of approximately 0.42 nm. An example of an indexed SAD is shown in Fig. 1. The diffraction characteristics were consistent with the structure of TiO or TiN (both *fcc*, NaCl-type structure). Lattice constants of TiO and TiN have been reported as 0.418 to 0.424 nm and 0.422 to 0.425 nm, respectively, in the literature (see Table 2). TiC is also isostructural with TiO and TiN, with a similar

lattice constant of 0.431 to 0.433 nm. Therefore, it appears that O, N, and C can dissolve in the structure simultaneously.

Examination of several TEM specimens from various alloys indicated a wide range of sizes and volume fractions, and a somewhat different morphology of the Ti(O,N,C) phase. In general, heats containing high oxygen (e.g., BL-12, O 1670 wt. ppm; BL-24, 1190 wt. ppm; and BL-34, 990 wt. ppm) developed more of this type of precipitate. This is shown in Fig. 2, which shows bright- or dark-field images of the phase obtained from eight alloys. On this basis, it is believed that O is the primary impurity dissolved in the phase. In a previous investigation, impurity composition of the same phase was analyzed by electron energy loss spectroscopy (EELS) on unirradiated specimens containing relatively low O and relatively high N.¹³ The results indicated that N and C were primary impurities and that O was a secondary impurity. However, as pointed out by the authors, O quantification by EELS is very difficult in the presence of V and Ti because of the overlapping K and L edges. Thus, it is believed that the phase is a Ti(O,N,C)-type precipitate with a different degree of impurity composition in each heat of the alloy. However, O seems to be the major impurity that promotes the precipitation by a thermally driven process during fabrication. Ti(O,N,C) precipitates were not observed in V or V-Cr alloys. All of the Type-A, -III, and -V precipitates reported in Ref. 5, Type-III reported in Ref. 6, and the "blocky" precipitates reported in Ref. 11 are Ti(O,N,C) phase, which formed primarily by a thermal process. No evidence of precipitation of the higher-oxide TiO₂ was observed.

Secondary Thermal Precipitation - TiP Phase

In some high-Ti alloys (e.g., BL-15, 20.3 wt.% Ti), minor precipitates were observed. This type of precipitate was usually observed on or near

Fig. 1. Example of indexed SAD pattern (A) showing thermal precipitation of Ti(O,N,C) in V-3.1Ti-0.3Si (BL-27) irradiated at 420°C to 114 dpa. Dark-field morphology produced from the $\langle 111 \rangle_{\text{Ti(O,N,C)}}$ reflection in (A) is shown in (B) in reverse contrast. Subscripts V and B in (A) denote vanadium and Ti(O,N,C), respectively.

Fig. 2. Bright- or dark-field morphologies of Ti(O,N,C) observed in (A) BL-24, irradiated at 600°C to 17 dpa; (B) BL-34, unirradiated; (C) BL-12, unirradiated; (D) BL-15, irradiated at 420°C to 46 dpa; (E) BL-10, unirradiated; (F) BL-16, irradiated at 420°C to 114 dpa; (G) BL-27, unirradiated; and (H) BL-42, unirradiated.

Table 2. Summary of Crystal Structures and Lattice Constants of Ti Compounds Reported in Literature

Compound	Crystal Structure	Lattice Constants (in Å)
TiC TiC ₂	fcc, NaCl-type cubic	a = 4.313 to 4.330 a = 3.13
Ti ₂ H, TiH, TiH ₂ TiH ₂	fcc, CaF ₂ -type tetragonal	a = 4.440 a = 4.42 to 4.45, c = 4.18 to 4.35
Ti ₃ N, ε-phase Ti ₂ N TiN	tetragonal tetragonal fcc, NaCl-type	a = 4.92 to 4.94, c = 5.16 a = 4.941, c = 3.037 a = 4.22 to 4.25
Ti ₃ O Ti ₂ O	hcp, ordered Ti ₂ O hcp	a = 5.141, c = 9.533 a = 2.959, c = 4.683
Ti ₃ O ₂ , δ-phase	tetragonal	a = 3.20, c = 5.12 or a = 5.344, c = 6.658
TiO TiO ₂ , rutile TiO ₂ , anatase TiO ₂ , brookite Ti ₂ O ₃	hcp fcc, NaCl-type tetragonal tetragonal orthorhombic rhombohedral hcp	a = 4.991, c = 2.879 a = 4.182 to 4.243 a = 4.954, c = 2.958 a = 3.777, c = 9.501 a = 9.25, b = 5.45, c = 5.15 a = 5.433, α = 56°34' a = 5.149, c = 13.642
Ti ₃ O ₅ Ti ₅ O ₉ Ti ₆ O ₁₁ Ti ₇ O ₁₃ Ti ₈ O ₁₅ Ti ₉ O ₁₇	monoclinic triclinic triclinic triclinic triclinic triclinic	a = 9.75, b = 3.80, c = 9.44 a = 3.75, b = 9.48, c = 9.73
Ti ₃ P Ti ₅ P ₃ TiP	tetragonal hcp, Mn ₅ Si ₃ -type hcp	a = 9.956, c = 4.988 a = 7.234, c = 5.090 a = 3.487 to 3.513 c = 11.65 to 11.75
TiP ₂	orthorhombic, PbCl ₂ -type	a = 6.18, b = 8.25, c = 3.34
Ti ₃ Si Ti ₅ Si ₃ TiSi ₂	tetragonal hcp, Mn ₅ Si ₃ -type orthorhombic, C54-type orthorhombic, ZrSi ₂ -type	a = 10.39, c = 5.17 a = 7.463, c = 5.165 a = 8.25, b = 4.78, c = 8.54 a = 3.62, b = 13.76, c = 3.60
TiS ₃ TiS ₂ Ti ₂ S ₃ Ti ₃ S ₄ Ti ₄ S ₅ TiS Ti ₆ S	monoclinic hcp, CdI ₂ -type hcp, WC-type hcp monoclinic hcp hcp, NiAs-type hcp	a = 4.973, b = 3.433, c = 8.714, β = 97.74° a = 3.408 to 3.413 c = 5.691 to 5.701 a = 3.295, c = 3.190 a = 3.422 to 3.442, c = 11.442 to 11.430 a = 5.98, b = 3.44, c = 10.14, β = 95°40' a = 3.424, c = 26.493 a = 3.299, c = 6.380 a = 2.966, c = 14.495

Fig. 2. Continued.

grain boundaries and was referred to as Type IV in Ref. 5. An example of an indexed SAD pattern and dark-field morphology of this type of precipitate is shown in Fig. 3. The phase was identified as TiP, an *hcp* structure with lattice constants $a = 0.3487$ to 0.3513 nm and $c = 1.165$ to 1.175 nm (Table 2). It seems that P atoms segregate thermally to grain boundaries during fabrication of ingots and that phosphides are formed preferentially on or near grain boundaries. Minor precipitates of $\text{Ti}_{1.7}\text{P}$, TiC, and a number of types of sulfides were also reported in unirradiated alloys in a previous investigation.¹³

Irradiation-Induced Precipitation - Ti_2O Phase

The short needlelike precipitates (<20 nm in diameter and <200 nm in length), previously referred to as Type II in Refs. 5 and 6, were observed primarily in specimens of V-Ti (e.g., V-10Ti and V-20Ti) and V-Cr-Ti (e.g., V-15Cr-5Ti) containing high Ti after irradiation at 600°C. In a similar specimen irradiated at 420°C, precipitation of this type was negligible. Analyses of SAD and dark-field images showed that the precipitates are Ti_2O phase, an *hcp* structure with lattice constants $a = 0.2959$ nm and $c = 0.4683$ nm. No other phase listed in Table 2 was compatible with the observed diffraction characteristics. Examples of indexed SAD and dark-field images, shown in Fig. 4, were obtained from a specimen of V-20Ti (BL-15) irradiated to 84 dpa at 600°C. In the SAD of Fig. 4A, reflections from two grains of V matrix and Ti_2O are visible, as are reflections from the thermally formed precipitates of $\text{Ti}(\text{O},\text{N},\text{C})$ and TiP. In the SAD, $[110]_{\text{Ti}_2\text{O}}$ (d-spacing= 0.149 nm) is nearly parallel to $[002]_{\text{V}}$ (d-spacing= 0.151 nm). The dark-field images produced from $\langle 002 \rangle_{\text{V}}$ reciprocal lattice rods and reported in Ref. 11 probably correspond to those from $\langle 110 \rangle_{\text{Ti}_2\text{O}}$. In Fig. 4B, needlelike Ti_2O precipitates are relatively denuded near a grain boundary where a

Fig. 3. Example of indexed SAD pattern (A) showing thermal precipitation of TiP on and near grain boundary in V-17.7Ti (BL-15) irradiated at 600°C to 84 dpa. Dark-field morphology produced from the $\langle 104 \rangle_{TiP}$ reflection in (A) is shown in (B) in reverse contrast. Subscripts V and P in (A) denote vanadium and TiP, respectively.

Fig. 4. Example of indexed SAD pattern (A) showing irradiation-induced precipitation of Ti_2O in V-17.7Ti (BL-15) irradiated at 600°C to 84 dpa. Dark-field morphology produced from the $\langle 111 \rangle_{Ti_2O}$ reflection in (A) is shown in (B) in reverse contrast. Subscripts V, B, O, and P in (A) denote vanadium, Ti(O,N,C), Ti_2O , and TiP, respectively.

number of large TiP precipitates are located. Apparently, Ti solutes near the grain boundary had been "used up" to form the TiP precipitates during fabrication; as a consequence, sufficient Ti atoms were not available to permit Ti₂O precipitation during irradiation.

Irradiation-Induced Precipitation - Ti₅(Si,P)₃ Phase

Both V-18Ti (BL-15) and V-20Ti (BL-16) specimens irradiated at 420°C to 46 and 114 dpa, respectively, were characterized by profuse precipitation of a very fine (3-15 nm) spherical phase. This phase was also observed in high density in V-20Ti (BL-16) specimens after irradiation at 600°C to 17 dpa. However, the precipitates were not observed in V-3Ti-0.3Si (BL-27) after irradiation at 420°C to 114 dpa despite the high-Si content. The fine spherical precipitates were referred to as Type I in previous reports.^{5,6} From bright-field imaging alone, it was difficult to either observe the precipitates or discern them from "black-dot" defects, which are of similar size and exhibit similar contrast. Therefore, it was necessary to search for and identify precipitate reflections in SAD patterns and to obtain dark-field images to determine the precipitate size and distribution.

Figure 5 shows examples of an indexed SAD pattern and dark-field images obtained from V-20Ti alloys irradiated at 420°C. The SAD pattern, obtained from the bright-field of Fig. 5A [from a specimen of BL-15 (V-17.7Ti, Si 480 wt. ppm)] after irradiation at 420°C to 46 dpa, contains five rows of very weak reflections of the Type I precipitates that are parallel to the row of [110] of vanadium matrix (see indexed pattern, Fig. 5C). The two outermost rows of the weak precipitate reflections (Fig. 5C) are not visible in the printed SAD pattern (Fig. 5B), but could be identified from the original negative and in the slightly tilted SAD pattern. The patterns of the

• $\text{Ti}_5(\text{Si,P})_3$, SUBSCRIPT-S
 ⊙ VANADIUM, SUBSCRIPT-V

Fig. 5. Bright-field image (A), SAD pattern (B) and indexed pattern of (B) (C) showing irradiation-induced precipitation of $\text{Ti}_5(\text{Si,P})_3$ in V-17.7Ti (BL-15) irradiated at 420°C to 46 dpa. Dark-field morphology produced from the $\langle 1\bar{3}\bar{1} \rangle_{\text{Ti}_5(\text{Si,P})_3}$ reflection in (C) is shown in (D). Subscripts V and S in (C) denote vanadium and $\text{Ti}_5(\text{Si,P})_3$, respectively. A few voids are denoted with arrows in (D).

precipitate reflections could be indexed on the basis of the Ti_5Si_3 phase, an *hcp* Mn_5Si_3 -type structure with lattice constants $a = 0.7463$ nm and $c = 0.5165$ nm (Table 2). A total of five zone axes were obtained and could be indexed consistently on the base of Ti_5Si_3 . No other Ti-base phases listed in Table 2 were compatible with the diffraction characteristics of this type of precipitate. Ti_5P_3 is also isostructural with Ti_5Si_3 , with similar lattice constants of $a = 0.7234$ nm and $c = 0.5090$ nm (Table 2). Therefore, it is expected that P atoms replace some Si atoms in the precipitate. In Fig. 5C, $\langle 01\bar{1} \rangle_V$ (d-spacing = 0.2150 nm) is parallel to $\langle 300 \rangle_{\text{Ti}_5(\text{Si,P})_3}$ (d-spacing = 0.2154 nm). Figure 5D shows a dark-field image produced from $\langle 1\bar{3}\bar{1} \rangle_{\text{Ti}_5(\text{Si,P})_3}$ reflection in Fig. 5C. In this figure, a small number of voids in dark contrast, denoted with arrows, and a large number of the $\text{Ti}_5(\text{Si,P})_3$ precipitates in white contrast are visible. An example of similar dark-field images is also shown in Fig. 6, which was obtained from a BL-16 (V-20.4Ti, Si 480 wt. ppm) specimen irradiated at 420°C to 114 dpa.

In Fig. 7, an indexed SAD pattern and dark-field image obtained from BL-24 (V-13.5Cr-5.2Ti, Si 390 wt. ppm) after irradiation at 600°C to 17 dpa, and similar to those of Fig. 5, are shown. In Fig. 7A, $\langle 1\bar{3}0 \rangle_{\text{Ti}_5(\text{Si,P})_3}$ (d-spacing = 0.244 nm) is nearly parallel to $\langle \bar{1}10 \rangle_V$ (d-spacing = 0.215 nm). The precipitate size shown in Fig. 7B seems to be somewhat larger than that of Figs. 5D or 6 (i.e., 15 vs. 10 nm), probably reflecting the influence of the higher irradiation temperature (i.e., 600 vs. 420°C).

4. Discussion

Precipitation Characteristics

The results of TEM characterization of thermally formed precipitates [namely, $\text{Ti}(\text{O,N,C})$ and TiP] are generally consistent with those observed in

Fig. 6. Reverse-contrast dark-field image of $\text{Ti}_5(\text{Si,P})_3$ precipitates observed in V-20.4Ti (BL-16) irradiated at 420°C to 114 dpa.

Fig. 7. Example of indexed SAD pattern (A) showing irradiation-induced precipitation of $\text{Ti}_5(\text{Si,P})_3$ in V-13.5Cr-5.2Ti (BL-24) irradiated at 600°C to 17 dpa. Dark-field morphology produced from the $\langle 320 \rangle_{\text{Ti}_5(\text{Si,P})_3}$ reflection in (A) is shown in (B) in reverse contrast. Subscripts V and S in (A) denote vanadium and $\text{Ti}_5(\text{Si,P})_3$, respectively.

unirradiated alloys,¹³ except that O is believed to be the major impurity that influences precipitation of the Ti(O,N,C) phase. An important observation is that O, N, P, and probably C and S as well,¹³ dissolve in ingots and tie up Ti solutes via precipitate formation during fabrication. In some cases, this can lead to significant depletion of Ti solutes in the vanadium matrix, thereby reducing the effective Ti content in the matrix below the level that inhibits void swelling. There is no evidence, however, that Si contributes to thermal precipitation.

Fine precipitates of Ti₂O and Ti₅(Si,P)₃ were observed in alloys only after some irradiation treatment. Therefore, both of the precipitates were concluded to be irradiation-induced. Evidently, solute atoms that control the irradiation-induced precipitation are free O, Si, Ti, and probably P that remain dissolved in the matrix after fabrication.

The morphology of the Ti₂O precipitates formed by neutron irradiation at 600°C in the present study is similar to that of Ti₃O precipitates that were observed in a V-14.1 at.%Cr-6.6 at.%Ti specimen irradiated by V⁺⁺ ions at 677°C.¹⁴ The Ti₂O and Ti₃O phases are isostructural and identical in atomic arrangement, except that O vacancies in the latter are distributed orderly in a superstructure of the former.¹⁵ Superlattice reflections characteristic of the O vacancy ordering were not observed in the present analysis of Ti₂O, indicating a salient feature of ion and neutron irradiation, or the effect of irradiation temperature, or both.

The needle- or plateletlike precipitates reported in Refs. 11 and 12 were observed in specimens known to have experienced temperature excursions of 156 to 206°C above the nominal irradiation temperature of 600°C for 50 min. Therefore, some ambiguity remains as to the exact temperature of the irradiation-induced precipitation in those specimens,

and care must be exercised in interpreting the significant ductility and fracture-toughness degradation observed in these specimens. In contrast, the specimen in Fig. 4, in which Ti_2O precipitates were identified, did not undergo such a temperature excursion. Despite the uncertainty of the exact irradiation temperature, it was evident that Ti_2O precipitation was pronounced at $>600^\circ\text{C}$ but negligible at 420°C . Beside the irradiation temperature and availability of Ti solutes in matrix, the availability of O solutes is evidently an important factor that will influence Ti_2O precipitation.

In contrast to the strong influence of irradiation temperature on the precipitation of Ti_2O , precipitation of $\text{Ti}_5(\text{Si,P})_3$ does not seem to be sensitive to irradiation between 420 and 600°C . Precipitation of the phase appears to be more sensitive to availability of Ti, Si, and probably P solutes in the matrix. Absence of $\text{Ti}_5(\text{Si,P})_3$ precipitates in the Si-rich BL-27 (V-3.1Ti-0.3Si) specimens, irradiated at 420°C to 114 dpa, is most likely due to matrix depletion of Ti solutes by thermal precipitation of $\text{Ti}(\text{O,N,C})$.

Correlation with Swelling Behavior

Void swelling and density change were relatively significant in BL-27 (e.g., 3% after irradiation at 420°C to 77 dpa) compared to those of high-Ti alloys (e.g., $<0.8\%$ for BL-15 and BL-16) irradiated under similar conditions.⁴ An example of significant void swelling in a specimen of BL-27, which contained negligible $\text{Ti}_5(\text{Si,P})_3$ precipitates, is shown in Fig. 8. If sufficient Ti (e.g., >7 wt.%) were added and O, N, and C contents were minimized in the alloy, a significant amount of $\text{Ti}_5(\text{Si,P})_3$ precipitate would form; as a result, void swelling would be negligible for a similar irradiation condition.

Even if Ti content is sufficiently high (i.e., >5 wt.%), precipitation of $\text{Ti}_5(\text{Si,P})_3$ is expected to be negligible, and hence, swelling is expected to be

Fig. 8. Examples of significant void swelling observed in (A) V-3Ti-0.3Si (BL-27) and (B) V (BL-20) in absence of fine precipitates after irradiation at 420°C to 114 dpa.

significant if Si content is very low in the specimen. An example of this effect appears to have been manifested in the swelling of four alloys of V-13.5Cr-5Ti type, i.e., BL-21 (1150 wt. ppm Si), BL-23 (1230 Si), BL-24 (390 Si), and BL-22 (56 Si).¹¹ Swelling of BL-22 containing very low Si was significantly higher than swelling of the other alloys containing relatively high Si after irradiation at 420, 520, and 600°C up to 31 dpa, i.e., 1.56 to 2.39 vs. 0.0 to 1.4%.

Copious amounts of $\text{Ti}_5(\text{Si,P})_3$ were observed in BL-15 irradiated at 420°C to 46 dpa (Fig. 5D), BL-16 irradiated at 420°C to 114 dpa (Fig. 6), and BL-24 irradiated at 600°C to 17 dpa (Fig. 7B). Void swelling in these specimens was negligible and the average density change was relatively small, i.e., 0.5, 0.4, and 0.14%, respectively.⁴ Thus, it seems that void swelling, and to a large extent density change, can be correlated with the number density of the $\text{Ti}_5(\text{Si,P})_3$ precipitate. That is, the higher the precipitate density, the lower the void swelling. This could be attributed to the large interface area generated between the matrix and high-density precipitates of $\text{Ti}_5(\text{Si,P})_3$, which acts as an efficient sink for vacancies and thereby inhibits nucleation and growth of voids. According to this model, the kinetics of void formation would be strongly influenced by the rates of vacancy formation, vacancy diffusion, and $\text{Ti}_5(\text{Si,P})_3$ precipitation. Apparently, the rate of $\text{Ti}_5(\text{Si,P})_3$ precipitation, e.g., at 420°C irradiation, would be slower than the rate of vacancy formation and may require some incubation time. In this situation, void swelling may be significant at an earlier stage, but diminishes at a later stage as a large number of $\text{Ti}_5(\text{Si,P})_3$ precipitates form, resulting in a threshold fluence at which swelling reaches a maximum and subsequently decreases.⁴

Correlation with Mechanical Properties

Significant precipitation of spherical $\text{Ti}_5(\text{Si,P})_3$ and needlelike Ti_2O is believed to be detrimental to material ductility and fracture toughness, as discussed relative to earlier findings.¹¹ The two alloys of V-13.5Cr-5Ti type (i.e., BL-23 and BL-24), in which densities of irradiation-induced precipitates were high (Fig. 7 and Ref. 11), exhibited relatively low ductility after irradiation at 420, 520, and 600°C in comparison with V-7.5Cr-15Ti, V-20Ti, and V-3Ti-0.3Si alloys.⁶ The two alloys and the BL-21 for which fracture toughness was reported to be minimal¹⁰ contained either relatively high O (up to 1190 wt. ppm) or high Si (up to 1230 wt. ppm). Therefore, these three alloys of the V-13.5Cr-5Ti type seem to be conducive to significant precipitation of Ti_2O or $\text{Ti}_5(\text{Si,P})_3$ or both during irradiation; as a consequence, they are susceptible to significant degradation of ductility and fracture toughness. However, it is difficult to determine which type of irradiation-induced precipitation, i.e., Ti_2O or $\text{Ti}_5(\text{Si,P})_3$, is more detrimental to mechanical properties.

The specimens characterized in this study (Figs. 4-7) and in Ref. 11 (Figs. 3-6) still exhibited a significant level of total elongation, i.e., in excess of 10%.⁶ Tensile elongations in most of the V, V-Ti, V-Cr-Ti, and V-Ti-Si alloys measured after irradiation at 420, 520, and 600°C were >9% except in V-13.5Cr-5Ti alloys irradiated at 420°C.⁶ Only in the high-Cr alloys irradiated at the low temperature have total elongations of <5% been measured. This seems to indicate that in addition to the effects of irradiation damage and precipitation of Ti_2O or $\text{Ti}_5(\text{Si,P})_3$, another type of irradiation-induced process may contribute to degradation of mechanical properties of V-Cr-Ti alloys containing Cr>10 wt.% and irradiated at 420°C [e.g., irradiation-induced formation of Cr (precursor of Cr-rich α' phase) or Cr-C clusters (precursor of M_{23}C_6 -type phase)].

5. Conclusions

1. Primary and secondary precipitates that form via thermal processes during fabrication of vanadium-base alloys containing Ti are $\text{Ti}(\text{O},\text{N},\text{C})$ and TiP , respectively. The thermal precipitation influences the solute contents of Ti, O, and P atoms that remain in the matrix, which influence irradiation-induced precipitation during neutron irradiation at 420-600°C.
2. Two types of very fine irradiation-induced precipitates have been identified, i.e., needlelike Ti_2O (<20 nm thick and <200 nm long) and spherical $\text{Ti}_5(\text{Si},\text{P})_3$ (<15 nm in diameter). Precipitation of the latter can be significant at irradiation temperatures of 420 to 600°C, while the former seems to be more pronounced at higher temperatures. Besides the irradiation temperature, the actual concentration of Ti, O, Si, and probably P atoms that are not bound to thermal precipitates seem to be important in the formation of the irradiation-induced precipitates.
3. Significant precipitation of the Ti_2O and the $\text{Ti}_5(\text{Si},\text{P})_3$ phases seems to be a major factor in the degraded ductility and fracture toughness after irradiation. Void swelling and density change seem to be influenced primarily by number density of the fine $\text{Ti}_5(\text{Si},\text{P})_3$ precipitates. A higher number density of the precipitates is conducive to a lower swelling during irradiation. This is believed to be due to the large interface area between the matrix and the high-density precipitates of $\text{Ti}_5(\text{Si},\text{P})_3$, which acts as an efficient sink for vacancies and thereby inhibits nucleation and growth of voids.

4. Minimizing Ti_2O precipitation and optimizing $\text{Ti}_5(\text{Si,P})_3$ precipitation could be important in inhibiting swelling and at the same time ensuring acceptable mechanical properties of vanadium-base alloys containing Ti. This seems to involve controls of not only the relative but also the absolute contents of Ti and Si and the impurity elements O and N, and probably C, P, and S as well. Besides the precipitation of Ti_2O and the $\text{Ti}_5(\text{Si,P})_3$, V-Cr-Ti alloys containing >10 wt.% Cr may be susceptible to an unidentified irradiation-induced process at 420°C, e.g., Cr or Cr-C clustering, which can lead to further degradation of mechanical properties. In this respect, it is desirable to limit Cr content in V-Cr-Ti alloys, e.g., to <6 wt.%.

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