1 of 1

INFLUENCE OF TRANSMUTATION ON MICROSTRUCTURE,
DENSITY CHANGE, AND EMBRITTLEMENT OF VANADIUM
AND VANADIUM ALLOYS IRRADIATED IN HFIR

S. Ohnuki^(a)
H. Takahashi^(a)
J. E. Pawel^(c)

K. Shiba^(b)
A. Hishinuma^(b)
F. A. Garner

June 1994

Presented at the
17th International Symposium on Effects
of Radiation on Materials
June 20-23, 1994
Sun Valley, Idaho

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

- (a) Hokkaido University, Sapporo, Japan
(b) Japan Atomic Energy Research Institute, Tokai, Japan
(c) Oak Ridge National Laboratory, Oak Ridge, Tennessee

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

INFLUENCE OF TRANSMUTATION ON MICROSTRUCTURE, DENSITY CHANGE, AND EMBRITTLEMENT OF VANADIUM AND VANADIUM ALLOYS IRRADIATED IN HFIR - S. Ohnuki and H. Takahashi (Hokkaido University, Sapporo, Japan), K. Shiba and A. Hishinuma (Japan Atomic Energy Research Institute, Tokai, Japan), J. Pawel (Oak Ridge National Laboratory, Oak Ridge, TN, USA), and F. A. Garner (Pacific Northwest Laboratory^a)

ABSTRACT

Addition of 1 at.% nickel to vanadium and V-10Ti, followed by irradiation along with the nickel-free metals in HFIR to $2.3 \times 10^{22} \text{ n cm}^{-2}$, $E > 0.1 \text{ MeV}$ (corresponding to 17.7 dpa) at 400°C, has been used to study the influence of helium on microstructural evolution and embrittlement. Approximately 15.3% of the vanadium transmuted to chromium in these alloys. The ~50 appm helium generated from the $^{58}\text{Ni}(n,\gamma)^{59}\text{Ni}(n,\alpha)^{56}\text{Fe}$ sequence was found to exert much less influence than either the nickel directly or the chromium formed by transmutation.

The V-10Ti and V-10Ti-1Ni alloys developed an extreme fragility and broke into smaller pieces in response to minor physical insults during density measurements. A similar behavior was not observed in pure V or V-1Ni. Helium's role in determination of mechanical properties and embrittlement of vanadium alloys in HFIR is overshadowed by the influence of alloying elements such as titanium and chromium. Both elements have been shown to increase the DBTT rather rapidly in the region of 10% (Cr + Ti). Since Cr is produced by transmutation of V, this is a possible mechanism for the embrittlement. Large effects on the DBTT may have also resulted from uncontrolled accumulation of interstitial elements such as C, N, and O during irradiation.

Introduction

Vanadium-base alloys are currently being investigated for potential applications as structural materials in fusion reactors (1-3). As with other alloy systems, however, there is concern that the relatively high levels of helium generated in fusion neutron spectra will strongly influence the microstructural evolution, dimensional stability and especially the mechanical properties. In order to study the potential influence of helium/dpa ratio while irradiating vanadium alloys in reactors whose spectra produce much lower levels of helium, a variety of helium enhancement techniques are being employed. Some involve the use of boron additions to produce helium via the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction (4-6), while others involve the preinjection of ^3He via the "tritium-trick" prior to neutron irradiation (7). The Dynamic Helium Charging Experiment utilizes pre-doping with tritium as well as continuous generation of tritium via transmutation of the ^6Li -enriched lithium coolant surrounding the specimens (8).

Another doping technique explored in the current study involves adding natural nickel to vanadium alloys and irradiating them in a mixed spectrum reactor such as the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. Using this approach, helium is produced via the two-step $^{58}\text{Ni}(n,\gamma)^{59}\text{Ni}(n,\alpha)^{56}\text{Fe}$ sequence (9). To explore the feasibility of this approach, both pure vanadium and V-10Ti (at.%) were irradiated in HFIR, each as two variants, both with and without 1 at.% of natural nickel. As will be seen in the experimental results, however, the potential impact of gaseous transmutant helium was overshadowed by the action of solid transmutant chromium.

Experimental Details

One each of V, V-1Ni, V-10Ti, V-10Ti-1Ni (nominal compositions, all in at.%) specimens were irradiated side-by-side in a HFIR target position at a temperature of 400°C to $2.3 \times 10^{22} \text{ n cm}^{-2}$ ($E > 0.1 \text{ MeV}$) and $8.8 \times 10^{22} \text{ n cm}^{-2}$ (total) corresponding to 17.6 dpa in this spectrum calculated for austenitic stainless steel using the standard NRT

model (10)]. The measured compositions are presented in Table 1. The specimens were irradiated in helium-filled stainless steel subcapsules in the form of 0.25 mm thick x 3.0 mm diameter microscopy disks. The residual radioactivity after two year's decay was ~10 mR/hr at contact for specimens without nickel and ~150 mR/hr for nickel-containing specimens. The calculated helium level for the nickel-containing specimens is ~50 appm; only 0.5 appm or less was calculated for the nickel-free specimens.

Following post-irradiation removal from the subcapsules, the density of the irradiated specimens was measured at Oak Ridge National Laboratory using an immersion density technique shown to be accurate to $\pm 0.1\%$ change in density (11). The density of unirradiated specimens was measured at Pacific Northwest Laboratory using a similar technique.

During the density measurement process, the V-10Ti and V-10Ti-1Ni specimens each broke in a very brittle manner after the second of two density measurements was completed. The physical insult causing this breakage was considered to be minimal, however, since no other specimens have broken during similar handling. The procedure causing the breakage involved pneumatically transporting the specimen through a rubber tube dropping it into a wire mesh basket. Since such extreme embrittlement was unanticipated, repeat measurements were not performed on the V and V-1Ni specimens in order to preclude the possibility of further breakage.

The broken specimens were examined in a JSM 840 scanning electron microscope while the unbroken specimens were thinned for microscopy and examined in a JEOL 2000 FX electron microscope. Energy-dispersive x-ray (EDX) analysis was performed in each instrument to assess transmutation-induced changes in composition. Significant formation of chromium via transmutation of vanadium is expected during irradiation in HFIR. The thinning process and subsequent microscopy involve some stresses being placed on the specimens but fragility was not observed during thinning or examination of the V and V-1Ni specimens.

Results

The density change data are shown in Table 2. The changes in density are relatively small in V and V-1Ni, but significant decreases in density occurred in both V-10Ti and V-10Ti-1Ni; nickel additions appeared to decrease the change somewhat. Density changes are anticipated to result from both void swelling and transmutation-induced changes in lattice parameter.

Figure 1 shows the broken specimens of both V-10Ti and V-10Ti-1Ni. Figure 2 shows typical fracture surfaces observed on two of the three major pieces of the V-10Ti specimen. The fracture surface is dominated primarily by transgranular cleavage facets and secondarily by grain boundary separation. With the exception of a few small precipitates on the grain boundary, there were no resolvable features on the facets or grain boundaries that would indicate the presence of voids or bubbles. Figure 3 shows similar micrographs for the V-10Ti-1Ni specimen. Once again there appeared to be no boundary or facet features that would provide evidence of cavities.

Figure 4 shows a comparison of the microstructure observed in pure V and V-1Ni. Each contained comparable densities ($\sim 5 \times 10^{16} \text{cm}^{-3}$) of small ($\leq 5 \text{ nm}$) cavities. There appeared to be no refinement of the cavity structure due to helium generation from the nickel. The two specimens developed very different surfaces during electropolishing, however. While the V-1Ni specimen had a very smooth surface, the pure V specimen developed a very irregular surface, indicative of selective electropolishing. The regions protruding above the average surface plane appear to be related to be regions of higher chromium level.

As shown in Table 3, the bulk level of transmutant chromium determined by broad-beam electron scans in the JSM 840 of the surfaces of V, V-10Ti and V-10Ti-1Ni show that $15.35 \pm 0.35\%$ of the original vanadium having transmuted to chromium. Thin foil analyses of V and V-1Ni in the JEOL 2000 yielded comparable but somewhat more

variable measurements of 16.0 and 14.0%, respectively. These results are in excellent agreement with the predictions of Greenwood and Garner (12), who predicted 19.3% at 22 dpa. When interpolated, this yields a predicted value of 15.5% at 17.7 dpa, compared to the measured mean of 15.3%.

Typical EDX spectra from the scanning electron microscope are shown in Figure 5, and clearly show the significant amount of chromium formed. Figure 6 shows that chromium tends to segregate at grain boundaries in the absence of nickel, but not to segregate in nickel's presence. Nickel tends to segregate at grain boundaries, however.

Discussion

Although nickel was added to enhance the helium production, a significant role of helium on cavity nucleation is not evident in Figure 4. At this point, however, the helium build-up was not very large (~ 50 appm), due to the delay required to form the ^{59}Ni from ^{58}Ni . The small sizes of the cavities are consistent with their invisibility on the fracture surface. Even more important, the extreme fragility seems to be associated with the presence of titanium rather than with the presence of either nickel or helium. At this point, it is tempting also to preclude chromium as a cause of the embrittlement, since within $\sim 10\%$, the chromium levels are all approximately equal in the four alloys. V-Cr binaries (Cr=5.0-14.1%) have been irradiated in the Fast Flux Test Facility (FFTF) to exposure levels ranging from 42 to 77 dpa at temperatures from 400 to 600°C in earlier studies, and did not exhibit such fragility (13,14).

The preferential polishing does appear to be associated with segregation of chromium, but the presence of nickel alters chromium segregation at grain boundaries and presumably at other sinks such as dislocations, thereby also influencing the electropolishing behavior.

While helium derived from nickel appears to play no large or direct role in cavity structure or density change in V and V-1Ni, nickel addition appears to depress swelling somewhat in V-10Ti. The density change values should not be interpreted to result from cavity swelling alone, however, since chromium additions tend to increase the density of vanadium alloys (15). Thus, the swelling of V-10Ti and V-10Ti-1Ni may actually be larger than inferred from the data in Table 2. Swelling appears to have been enhanced in V-10Ti by the transmutation, since only $\leq 1\%$ swelling was observed after irradiation in FFTF at 420°C to exposures of 36-77 dpa (13).

Nickel additions tend to increase the density of vanadium alloys (15) but they also have been shown to exert a strong direct role in alteration of radiation-induced microstructure in electron irradiations (16) and fast reactor irradiations (17), neither of which lead to significant generation of helium.

Loomis and coworkers (18) have shown that the ductile-to-brittle transition temperature (DBTT) of V-Ti binaries increases strongly for titanium concentrations greater than 5% after fast reactor irradiation (no significant transmutation) at 420°C to 34-44 dpa, but increases even more strongly in V-Ti-Cr alloys for increasing chromium levels above 5% Cr. For (Cr+Ti) levels above 9%, the DBTT after irradiation increases 200°C or more, as shown in Figure 7. Since the (Cr+Ti) level of the broken specimens after irradiation is on the order of 25%, the DBTT of these specimens may be 250°C or greater. Note that even before irradiation, the DBTT of such high solute alloys is near room temperature. It is interesting to note that vanadium alloys with high chromium and titanium levels irradiated in FFTF also showed significant embrittlement, but that V-3Ti-1Si resisted embrittlement (19,20).

As shown by Greenwood and Garner (12), however, the transmutation rates experienced by vanadium in HFIR are more than an order of magnitude greater than those expected in fusion neutron spectra or that of liquid metal cooled fission reactors. Mori (21) has calculated that for the International Thermonuclear Experiment Reactor (ITER),

transmutation of vanadium to chromium would be less than 1% per year at any position on the first wall when operating at 2 MW/m^2 . Therefore, the extreme fragility exhibited by V-Ti alloys after irradiation in HFIR may be very atypical of the response that will occur in fusion reactors. Therefore, if fusion-relevant tests are to be successfully conducted in mixed spectrum reactors, the thermal component of the neutron flux must be reduced significantly by shielding the specimens with materials that are strong absorbers of low energy neutrons.

It must also be noted that interstitial impurity elements such as carbon, oxygen, and nitrogen cause embrittlement of vanadium alloys (19). The environmental pick-up of these elements was neither controlled nor measured in this HFIR experiment and thus may be a significant contributing factor to the embrittlement.

This experiment demonstrates once again that the possible influence of solid transmutation must be taken into account when designing and evaluating experiments that will be conducted in neutron spectra which are only surrogates for the spectrum of actual application. A summary of previously cited situations where transmutation was found to be an important concern is presented in other papers (22,23). Also demonstrated in this experiment is the principle that the impact of elemental tailoring of alloys to study the effects of transmutant helium is often overshadowed by the direct action of the tailoring agent itself.

Conclusions

The addition of nickel to vanadium and to V-10Ti appears to influence swelling of these alloys when irradiated at $\sim 400^\circ \text{C}$ in HFIR, but its action appears to be related to nickel's direct influence on microstructural evolution, rather than to its role as a source of helium. Helium's role in determination of mechanical properties and embrittlement

of vanadium alloys in HFIR is overshadowed by the influence of alloying elements such as titanium and chromium. Both elements have been shown to increase the DBTT rather rapidly in the region of 10% (Cr + Ti). Since Cr is produced by transmutation of V, this is a possible mechanism for the embrittlement. Large effects on the DBTT may have also resulted from uncontrolled accumulation of interstitial elements, such as C, N, and O during irradiation.

The extreme embrittlement observed in this experiment resulting from chromium formation will not be representative of that expected in fusion neutron spectra, where the V-Cr transmutation rate per dpa will be lower by more than an order of magnitude.

Acknowledgements

Work supported by the Japanese Ministry of Education, Science and Culture, under both the US/Japan Collaboration in Fusion Materials using Fission Reactors and the International Scientific Research Program. The U.S. participation was supported by the U.S. Department of Energy under Contracts DE-AC06-76RLO 1830 and DE-AC05-84OR21 400. The density measurements were performed at ORNL by L. T. Gibson and at PNL by Gary Whiting. The manuscript was prepared by Loree Swegle and Diane Forsyth.

References

1. D. L. Smith, J. Nucl. Mater., 122 & 123 (1984) 51.
2. D. R. Diercks and B. A. Loomis, J. Nucl. Mater., 141-143 (1986) 1117-1124.
3. B. A. Loomis, A. B. Hull and D. L. Smith, J. Nucl. Mater., 179-181 (1991) 148-154.

4. H. Kawanishi, Y. Arai and S. Ishino, J. Nucl. Mater., 191-194 (1992) 933-937.
5. N. Sekimura and F. A. Garner, Fusion Reactor Materials Semiannual Progress Report DOE/ER-03131/13, 1990, pp. 235-237.
6. H. M. Chung, Fusion Reactor Materials Semiannual Progress Report DOE/ER-0313/14, 1993, pp. 299-305.
7. M. Satou, K. Abe and H. Matsui, J. Nucl. Mater., 191-194 (1992) 938-941.
8. D. L. Smith, H. Matsui, L. Greenwood and B. Loomis, J. Nucl. Mater., 155-157 (1988) 1359.
9. C. H. De Raedt, Proc. Conf. on Fast, Thermal and Fusion Reactor Experiments, Amer. Nucl. Soc., La Grange Park (1982), p. 226.
10. J. J. Norgett, J. T. Robinson and I. M. Torrens, Nucl. Eng. Design 33 (1975) 50.
11. H. Kanazawa, T. Sawai and L. J. Turner, Fusion Reactor Materials Semiannual Progress Report DOE/ER-0313/8, 1990, pp. 17-20.
12. L. R. Greenwood and F. A. Garner, "Transmutation of Mo, Re, W, Hf, and V in Various Irradiation Test Facilities and STARFIRE," proceedings ICFRM-6, J. Nucl. Mater., in press.
13. B. A. Loomis, D. L. Smith and F. A. Garner, J. Nucl. Mater., 179-181 (1991) 771.
14. F. A. Garner, D. S. Gelles, H. Takahashi, S. Ohnuki, H. Kinoshita and B. A. Loomis, J. Nucl. Mater., 191-194 (1992) 948-951.

15. F. A. Garner and B. A. Loomis, Fusion Reactor Materials Semiannual Progress Report DOE/ER-0313/16, 1994, in press.
16. D. S. Gelles, S. Ohnuki, H. Takahashi, H. Matsui and Y. Kohno, J. Nucl. Mater., 191-194 (1992) 1336-1341.
17. D. S. Gelles and J. F. Stubbins, proceedings ICFRM-6, J. Nucl. Mater., in press.
18. B. A. Loomis, H. M. Chung, L. J. Nowicki and D. L. Smith, Proceedings of ICFRM-6, J. Nucl. Mater., in press.
19. D. N. Braski, in Influence of Radiation on Material Properties: 13th Intern. Symp. (Part II), ASTM STP 956, F. A. Garner, C. H. Henager, Jr. and N. Igata, Eds., American Soc. of Testing and Materials, Philadelphia, 1987, pp. 271-290.
20. M. L. Grossbeck and J. A. Horak in Influence of Radiation on Material Properties: 13th Intern. Symp. (Part II), ASTM STP 956, F. A. Garner, C. H. Henager, Jr. and N. Igata, Eds., American Soc. of Testing and Materials, Philadelphia 1987, pp. 291-309.
21. M. Mori, ITER/EDA Design Data, JA93-JA0132.
22. F. A. Garner, H. L. Heinisch, R. L. Simons and F. M. Mann, Radiation Effects and Defects in Solids, 113 (1990) 229-255.
23. F. A. Garner and L. R. Greenwood, Mater. Trans., JIM, 34 (1993) 985-998.

Table 1. Starting Composition* of Vanadium and Vanadium Alloys in at.%

Alloy	C	O	N	H	Al	Fe	Si	Ni	Ti
V	0.0051	0.0194	0.0083	0.0610	0.034	0.047	0.005	-	-
V-1Ni	-	-	-	-	-	-	-	0.91	-
V-10Ti	-	-	-	-	-	-	-	-	9.5
V-10Ti-1Ni	-	-	-	-	-	-	-	0.88	9.3

* Minor impurities measured only for vanadium.

Table 2. Density changes measured in vanadium and several alloys after irradiation to 17.7 dpa at 400°C in HFIR.

	<u>Unirradiated density,</u> <u>g cm⁻³</u>	<u>Irradiated density,</u> <u>g cm⁻³</u>	<u>Change, %*</u>
V	6.13038	6.1525	0.36
V-1Ni	6.19391	6.1784	-0.25
V-10Ti	5.97293	5.8336 5.8354**	-2.33 -2.30
V-10Ti-1Ni	5.98426	5.8955 5.8926**	-1.48 -1.53

* Change contains contributions from both cavities and transmutation-induced changes in composition. A negative sign implies volumetric swelling.

** Second independent measurement.

Table 3. Compositions of HFIR-irradiated specimens determined by EDX technique.

	V	Cr	Ti	Ni	Method*	%V-Cr
Pure V	84.3	15.7	-	-	SEM/EDS	15.7
Pure V	84.0	16.0	-	-	TEM/ED S	16.0
V-1Ni	80.0	13.9	-	0.9	TEM/ED S	14.0
V-10Ti	77.1	13.6	9.4	-	SEM/EDS	15.0
V-10Ti-1Ni	77.0	13.7	8.7	0.7	SEM/EDS	15.3

* Scanning electron microscope or transmission electron microscope used to perform energy dispersive x-ray spectroscopy.

Fig. 1. Fragments of broken microscopy disks from irradiated V-10Ti (top) and V-10Ti-1Ni (bottom).

Fig. 2. Fracture surfaces of irradiated V-10Ti specimen.

Fig. 3. Fracture surfaces of irradiated V-10Ti-1Ni specimen.

Fig. 4. Comparison of cavity microstructures observed in V and V-1Ni after irradiation. These alloys now contain ~15% chromium.

V : H F I R

V-10Ti : H F I R

Fig. 5. EDS spectra observed in irradiated V and V-10Ti.

Fig. 6. Segregation profiles observed at grain boundaries in V and V-1Ni.

Fig. 7. Dependence of DBTT on solute concentration for V-Cr-Ti alloys irradiated at 420°C in FFTF to 32-44 dpa (18). Closed symbols denote Charpy impact data, open symbols denote TEM impact data.

Figure Captions

Fig. 1. Fragments of broken microscopy disks from irradiated V-10Ti (top) and V-10Ti-1Ni (bottom).

Fig. 2. Fracture surfaces of irradiated V-10Ti specimen.

Fig. 3. Fracture surfaces of irradiated V-10Ti-1Ni specimen.

Fig. 4. Comparison of cavity microstructures observed in V and V-1Ni after irradiation. These alloys now contain ~15% chromium.

Fig. 5. EDX spectra observed in irradiated V and V-10Ti.

Fig. 6. Segregation profiles observed at grain boundaries in V and V-1Ni.

Fig. 7. Dependence of DBTT on solute concentration for V-Cr-Ti alloys irradiated at 420°C in FFTF to 32-44 dpa (18). Closed symbols denote Charpy impact data, open symbols denote TEM impact data.

DATE

FILMED

8/24/94

END