MICROSTRUCTURAL EXAMINATION OF V-(3-6%)Cr-(3-5%)Ti IRRADIATED IN THE ATR-A1 EXPERIMENT - D. S. Gelles (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this effort is to provide understanding of microstructural evolution in irradiated vanadium alloys for first wall applications in a fusion reactor.

SUMMARY

Microstructural examination results are reported for four heats of V-(3-6%)Cr-(3-5%)Ti irradiated in the ATR-A1 experiment to ~4 dpa at ~200 and 300°C to provide an understanding of the microstructural evolution that may be associated with degradation of mechanical properties. Fine precipitates were observed in high density intermixed with small defect clusters for all conditions examined following the irradiation. The irradiation-induced precipitation does not appear to be affected by preirradiation heat treatment or composition.

PROGRESS AND STATUS

Introduction

Vanadium-based alloys are being developed for application as a first wall material for magnetic fusion power system. It has been shown that alloys of composition V-(4-5%)Cr-(4-5%)Ti have very promising physical and mechanical properties.[1] Recent attention in this alloy class has focused on several issues, such as the effect of low-temperature irradiation on fracture toughness, the effect of helium generation, the effect of minor impurities, and heat-to-heat variation in work-hardening behavior at low irradiation temperatures. While other classes of alloys are still considered, the V-(4-5%)Cr-(4-5%)Ti alloys are being optimized to suppress their susceptibility to loss of work-hardening capability following irradiation at low temperatures by consideration of minor changes in major alloying levels. Susceptibility of the alloy class to this process under fusion-relevant conditions is considered to be a major factor in governing the minimum operating temperature of magnetic fusion devices.

Recent irradiation experiments at <430°C have shown that the loss of work-hardening capability and uniform elongation of V-4Cr-4Ti vary from heat to heat.[2] The present effort is a continuation of the effort to provide an understanding of the microstructural evolution in these alloys under irradiation with an expansion of the composition range to V-(3-6%)Cr-(3-5%)Ti by examination of specimens irradiated at low temperatures in the recent ATR-A1 experiment along with corresponding mechanical properties specimens.[3,4]

Experimental Procedure

Specimens in the form of microscopy disks 3 mm in diameter were included in the ATR-A1 test. Companion miniature tensile specimens were also irradiated providing the opportunity for comparison with shear punch and tensile response[4] at a later date. Twelve specimen conditions were selected for examination comprising four heats of material irradiated side-by-side at two

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irradiation temperatures with corresponding unirradiated control specimens. The compositions of the heats are given in Table 1[5,6] and the specimen conditions examined are shown in Table 2. Compositions covered the range V-(3-6%)Cr-(3-5%)Ti based on the availability of two heats recently prepared by ORNL.[3] All were heat treated at 1000°C for 1 or 2 h under vacuum ($<10^{-7}$ torr) at ANL. Specimens were irradiated in ATR-A1 Subcapsules AS5 and AS11.[6] Temperatures and fluences have been estimated for these subcapsules as 284-300°C to 4.1 dpa and 223-234°C to 3.5 dpa, respectively,[5] but will be referred to as 300 and 200°C to 4 dpa in subsequent text. Specimen preparation and examination involved standard procedures. All images were computer processed and printed from scanned negative information.

Table 1. Compositions of heats examined

Heat #	Nominal Composition, wt%	Minor Impurities [appm]				
		O	N	C	Si	Other
832665, BL-71	V-3.8Cr-3.9Ti	310	85	80	783	220 Fe, 190 Al
T87, BL-72	V-5.0Cr-5.0Ti	380	90	110	550	
T91	V-2.84Cr-3.02Ti	230	62	120	940	130 Fe, 200 Al
T92	V-5.97Cr-2.94Ti	280	95	105	950	165 Fe, 255 Al

Table 2. Conditions of specimens examined by TEM

Specimen ID	Heat #	Heat treatment	Irradiation Temperature	Irradiation Dose
P8	832665, BL-71	1000°C/1h	na	0 dpa
P837			223-234°C	3.5 dpa
P811, P832			284-300°C	4.1 dpa
P7	T87, BL-72	1000°C/1h	na	0 dpa
P706			223-234°C	3.5 dpa
P710			284-300°C	4.1 dpa
P1	T91	1000°C/2h	na	0 dpa
P113			223-234°C	3.5 dpa
P107, P123			284-300°C	4.1 dpa
P2	T92	1000°C/2h	na	0 dpa
P224			223-234°C	3.5 dpa
P215			284-300°C	4.1 dpa

na: not applicable

Results

Pre-irradiation microstructures

The purpose of this work was to provide information on effects of radiation on microstructure in order to provide interpretation of mechanical properties response. As a result, emphasis was placed on examination of irradiated specimens. However, sufficient information was obtained to provide some comparison of the preirradiation microstructures for all four heats. All preirradiation microstructures appeared similarly, consisting, in general, of large equiaxed grains with large Ti,V(O,C,N) precipitate particles non-uniformly distributed. The particles observed were as large as 500 nm in heats 832665 and T87, but were generally 200-300 nm with many smaller particles. However, due to the non-uniform distribution, it is difficult to compare precipitate volume fraction from heat to heat based on electron microscopy. Grain boundaries were often distorted in the vicinity of such particles and many examples could be found where small grains were distributed amongst the larger grains, often where triple points would normally be found. In heats T87 and T92, areas were found where recrystallization had not occurred retaining a relaxed subgrain structure, but the volume fraction is expected to be low. This may be an indication that higher chromium contents discourage recrystallization.

Grain boundaries were often decorated with fine non-equiaxed precipitation on the order of 50 nm, but size and distributions varied from one grain boundary to another. Such precipitation is typically produced during cooling following the 1000°C annealing treatment.[8]

Microstructures following irradiation

The major effects of irradiation both at 200 and at 300°C were development of fine structure and evidence of increased internal strain based on lack of Kikuchi band structure. The fine structure was apparent under strain contrast conditions and can be expected to be the cause of the internal strain. Diffraction patterns showed little detail, but evidence for streaking at approximately $\frac{2}{3}<222>$, found previously,[9] could be identified easily whereas streaking at $\frac{3}{4}<200>$ was very faint and usually impossible to see. Images using $\frac{2}{3}<222>$ were very weak, but the scale of the structure matched that found in matrix dark field images approaching weak beam conditions. Therefore, it is apparent that precipitation due to $\frac{2}{3}<222>$ is responsible for the fine structure and internal strain observed.

Examples

Examples of these microstructures are provided in Figures 1, 2 and 3. Figure 1 shows two low magnification examples for each alloy of interest in the heat treated condition. In all cases, areas were selected to show grain boundary structure. Detailed inspection reveals fine precipitates on grain boundaries, with different size and spacial distributions on neighboring boundaries near triple points. Several examples are included where grain boundaries have been distorted due to associated large precipitate particles. Note that examples of smaller grains at triple points are shown in Figures 1a and 2h, and examples of unrecrystallized grain substructure can be found in Figures 2d and 2g, demonstrating further features of these microstructures prior to irradiation.

Figure 2 provides an example for each of the irradiated conditions at low magnification. The structures appear similar to those found in the unirradiated conditions except that fine precipitates on grain boundaries are no longer visible, and fine structure can be seen within grains. Large precipitate particles, present prior to irradiation, are retained.

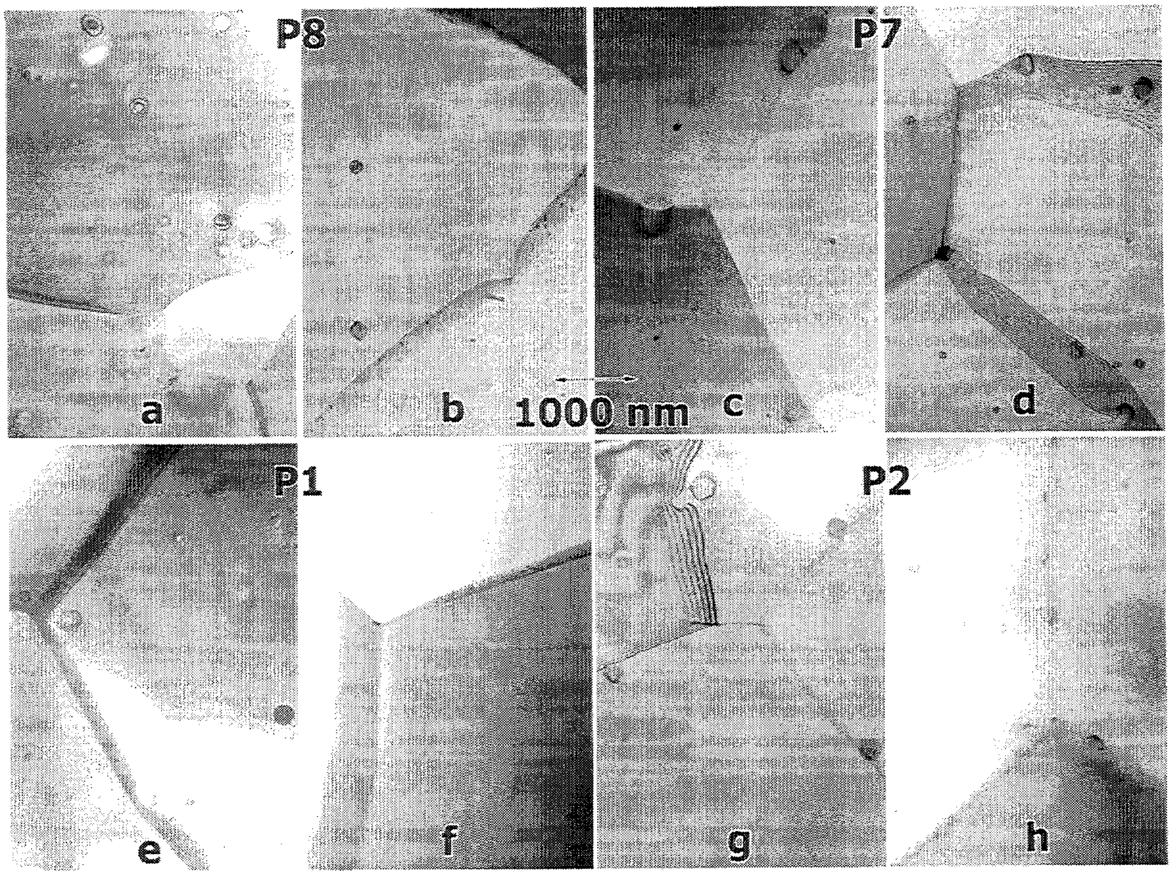

Figure 1. Low magnification examples of microstructures in specimens of V-(3-6%)Cr-(3-5%)Ti prior to irradiation showing the large heat 832665 in a and b, heat T87 in c and d, heat T91 in e and f, and heat T92 in g and h.

Figure 3 was prepared to show features of the fine structure within grains at higher magnification. For each irradiation condition, weak beam dark field images for the same area are shown using $\vec{g}=[01\bar{1}]$ and [200], respectively, for foil conditions near (011) so that the corresponding $\vec{g}$ vectors are orthogonal with <200> horizontal. Where the information was available, the (011) pattern, with 000 on the lower left, has been inset. Also of note is that under the specimen identification code P224 a precipitate dark field image with $\vec{g}= \sim\frac{2}{3}[2\bar{2}\bar{2}]$ has been inset. From this figure, the following can be demonstrated. Diffraction information only indicates the presence of intensity in the vicinity of ⅔<222>; intensity in the vicinity of ~¾<200> is very weak. Precipitate dark field images formed using $\vec{g}$=⅔<222> are very weak but indicate the presence of very small particles. Similar features can be seen in all weak beam images, indicating that the responsible precipitate particles provide strain fields visible under strain contrast conditions (or that matrix [200] and [01$\bar{1}$] reflections superimpose on precipitate reflections.) Comparison of [200] and [011] images consistently shows fine structure in both, but coarser structure as well in the [200] images. Figure 3f in particular can be interpreted to indicate the presence of dislocation loops approximately 20 nm in diameter. Therefore, the dislocation density is likely to be significantly lower than the precipitate particle density.

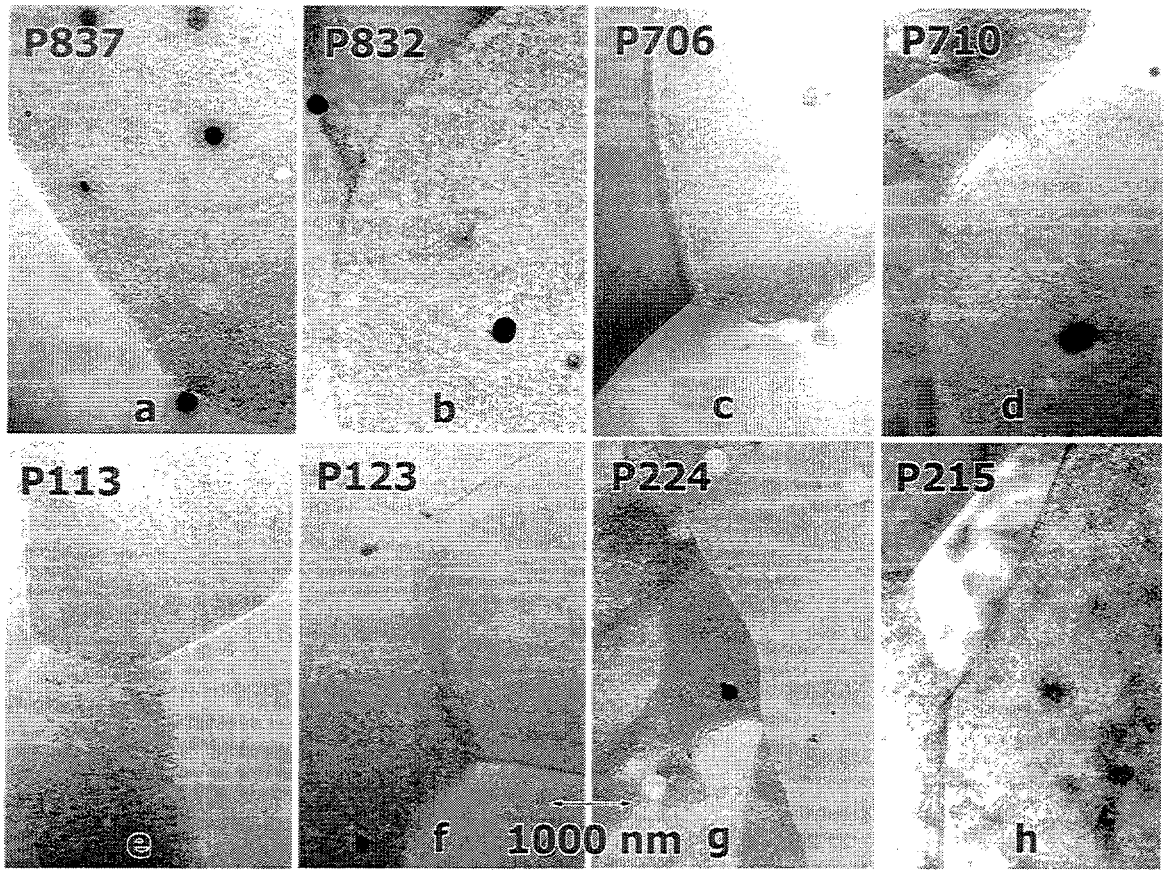

Figure 2. Low magnification examples of irradiated microstructures in specimens of V-(3-6%)Cr-(3-5%)Ti irradiated in the ATR-A1 experiment showing the large heat 832665 at 200 and 300°C in a and b, heat T87 at 200 and 300°C in c and d, heat T91 at 200 and 300°C in e and f, and heat T92 at 200 and 300°C in g and h.

Quantification of precipitation

As all weak beam images presented in Figure 3 were taken with matching stereo pairs, it is possible to quantify the precipitate features in order to estimate the consequences of such features on mechanical properties. Table 3 provides results from measurements of the fine structure observed on <01$\bar{1}$> images, assuming the particles are spherical. Based on examination of stereo information in thin areas, it can be noted that the precipitates are non-uniformly distributed. Precipitation is in patches, with areas of similar size separating the patches. The results in Table 3 indicate that precipitates are between 3 and 4 nm in average diameter at number densities between 1 and 3 $\times 10^{17}$ cm^{-3} corresponding to volume fractions on the order of 0.5%. Surprisingly, the observed response appears to be insensitive to irradiation temperature.

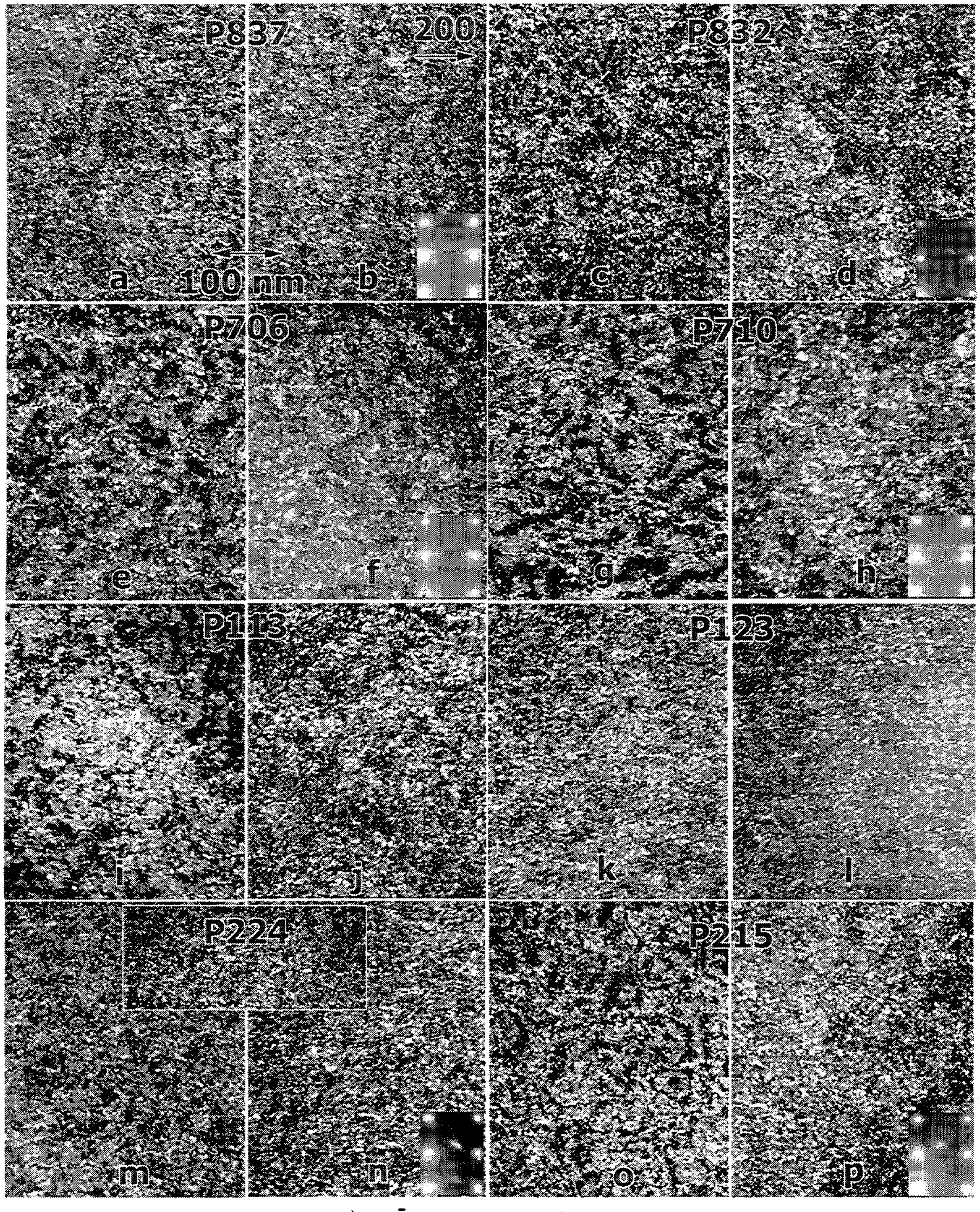

Figure 3. Dark field images using $\vec{g}=[01\bar{1}]$ and [200], respectively, of irradiated microstructures in specimens of V-(3-6%)Cr-(3-5%)Ti from the ATR-A1 experiment showing the large heat 832665 at 200°C in a and b and at 300°C in c and d, heat T87 at 200°C in e and f and 300°C in g and h, heat T91 at 200°C in i and j and at 300°C in k and l, and heat T92 at 200°C in m and n and at 300°C in o and p. Where available, (011) diffraction patterns have been inserted and P224 contains an insert showing precipitate dark field contrast.

Discussion

The purpose of this work is to provide microstructural information allowing interpretation of test results for mechanical properties measurements including those on miniature tensile specimens and disks tested by shear punch procedures.[3,4] Results are not yet available, but preliminary results[10] indicate that all materials showed large degradation in properties following irradiation.

Based on the present and previous microstructural observations,[9] mechanical property degradation appears to be due to precipitation during irradiation. Unfortunately, the composition of the precipitate has not yet been established, so that it is not yet possible to provide recommendations for composition modifications for improved properties. However, recent results[11,12] indicate that precipitation of interstitial elements with titanium is likely responsible. This discussion is provided as further speculation on the likely causes for the behavior observed.

Table 3. Irradiation induced precipitate size and density as determined from weak beam images

Specimen ID	Conditions: Heat/dose/temp.	Mean diameter (nm)	Number density (10^{17} cm^{-3})	Volume fraction (%)
P837	BL-71/4 dpa/200°C	3.29	3.2	0.6
P832	BL-71/4 dpa/300°C	3.46	2.5	0.6
P706	T87/4 dpa/200°C	3.89	1.6	0.6
P710	T87/4 dpa/300°C	3.64	1.6	0.5
P113	T91/4 dpa/200°C	3.83	1.8	0.6
P123	T91/4 dpa/300°C	3.01	1.1	0.2
P224	T92/4 dpa/200°C	3.89	1.6	0.5
P215	T92/4 dpa/300°C	3.80	2.0	0.7

It is noteworthy that diffraction response for precipitates formed during irradiation is found to vary with irradiation temperature. Following irradiation at 400°C to 4.5 dpa in HFIR, streaks were found both at ¾<200> and ⅔<222>, whereas the present results following irradiation at 200 and 300°C to 4 dpa show streaks only at ⅔<222>. Therefore, two types of precipitation formed at 400°C, but at lower temperatures, one of those precipitates is not found, at least following irradiation to doses on the order of 4 dpa.

The precipitation identified following irradiation in the ATR-A1 experiment at 200 and 300°C is found to consist of particles on the order of 3 nm in diameter at densities in the range 1 to 3 $\times 10^{17}$ cm^{-3} corresponding to volume fractions on the order of 0.5%. As the precipitates are best imaged using strain contrast, it is likely that strain centers of this size and density would have a major effect on hardening and embrittlement. It is not yet understood why precipitation is similar in size following irradiation at both 200 and 300°C. Nor is it understood why number densities are found to vary as a function of composition such that heat 832665 gave higher densities by about a factor of two. Given the very small sizes of the precipitates, perhaps the best explanation lies in experimental uncertainty. Errors on the order of a factor of 2 are not unreasonable with such fine microstructures.

CONCLUSIONS

Eight specimen conditions from the ATR-A1 experiment irradiated at ~200 and 300°C to ~4 dpa, comprising four heats of V-(3-6%)Cr-(3-5%)Ti given similar preirradiation heat treatments and directly corresponding to mechanical properties specimens, have been examined to identify the cause of irradiation hardening. It is found that hardening is due to precipitation of a high density of small particles, but differs from response at 400°C, because one precipitate type dominates at the lower irradiation temperatures. Particle sizes are on the order of 3 nm in diameter at densities in the range 1 to 3 $\times 10^{17}$ cm^{-3} corresponding to volume fractions on the order of 0.5%. The irradiation-induced precipitation appears to be insensitive (to within a factor of ~2) to preirradiation heat treatment and composition.

FUTURE WORK

This work will be continued within the confines of funding and specimen availability.

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