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Effect of periodic temperature variations on the microstructure of neutron-irradiated metals

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Abstract

Specimens of pure copper, a high purity austenitic stainless steel, and V–4Cr–4Ti were exposed to eight cycles of either constant temperature or periodic temperature variations during neutron irradiation in the High Flux Isotopes Reactor to a cumulative damage level of 4–5 displacements per atom. Specimens exposed to periodic temperature variations experienced a low temperature (360 °C) during the initial 10% of accrued dose in each of the eight cycles, and a higher temperature (520 °C) during the remaining 90% of accrued dose in each cycle. The microstructures of the irradiated stainless steel and V–4Cr–4Ti were qualitatively similar to companion specimens that were continuously maintained at 520 °C during the entire irradiation. The microstructural observations on pure copper irradiated at a constant temperature of 340 °C in this experiment are also summarized. The main radiation-induced microstructural features consisted of dislocation loops, stacking fault tetrahedra and voids in the stainless steel, Ti-rich precipitates in the V alloy, and voids (along with a low density of stacking fault tetrahedra) in copper.
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1. Introduction

It is well known that the irradiation temperature can have a profound impact on the microstructure that develops in materials [1]. In qualitative terms, nucleation of defect clusters is maximized at lower temperatures whereas growth and coarsening of clusters are maximized at higher temperatures. Modest temperature excursions are expected to be a common occurrence in any commercial nuclear system due to scheduled startup and shutdown events. These varying-temperature excursions allow the possibility of enhanced nucleation and growth of radiation-induced defect clusters compared to a constant-temperature irradiation. Several previous ion irradiation and low-dose neutron irradiation studies [2–10] have found that these temperature excursions may exert a significant influence on the microstructural evolution, particularly if the temperature excursion transcends the recovery stage V temperature regime (which corresponds to thermal dissociation of small vacancy clusters). The recovery stage V occurs at ≃280 °C in austenitic stainless steel [11–13], ≃320 °C in V–4Cr–4Ti [14], and ≃220 °C in copper [15]. Void formation was generally enhanced and loop formation suppressed for the cyclic temperature irradiation [4] or preirradiation at low temperatures [2].

In the present paper, results are presented for V–4Cr–4Ti and stainless steel irradiated with fission neutrons to a dose of 4–5 dpa at 520 °C (constant temperature) vs. 360/520 °C (varying temperature), and for pure copper irradiated at a constant temperature of 340 °C.

2. Experimental procedure

The materials used for this study were 'P7' austenitic stainless steel (Fe–17Cr–16.7Ni–2.5Mo), V–4Cr–4Ti

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(300 ppm O, 100 ppm N, 80 ppm N, Teledyne Wah Chang heat 832 665), and Johnson–Matthey 'Puratronic' 99.999% copper. All of the specimens were irradiated in the annealed condition as 3 mm diameter by 0.5 mm thick transmission electron microscope disks. The annealing conditions were 1050 °C for 0.5 h (stainless steel), 1000 °C for 2 h (V–4Cr–4Ti), and 550 °C for 2 h (Cu). The specimens were irradiated for a total of eight irradiation cycles in the High Flux Isotopes Reactor (HFIR) at ORNL, which resulted in a fast neutron fluence ($E > 0.1$ MeV) of $\simeq 8 \times 10^{21}$ n m^{-2}. This corresponds to a damage level of $\simeq$4 dpa in the stainless steel and vanadium specimens, and $\simeq$5 dpa in copper. Electrical heaters and a mixture of helium and argon gases were used to control the irradiation temperatures. The temperatures were continuously monitored and controlled during the irradiation. The capsule was divided into four independently controlled zones in order to achieve four different irradiation temperature profiles [16]. The temperature profiles for each of the eight HFIR irradiation cycles were as follows: zone A, constant temperature of 340 °C; zone B, constant temperature of 520 °C; zone C, first 10% of dose for each cycle at 360 °C and remaining 90% at 520 °C; zone D, first 10% of dose for each cycle at 225 °C and remaining 90% at 340 °C. Further experimental details are described elsewhere [16]. Following irradiation, the TEM specimens were jet electropolished and examined in a JEOL 2000FX or Philips CM30 electron microscope at Oak Ridge National Laboratory.

3. Results

The dominant microstructural feature in V–4Cr–4Ti irradiated at both a constant temperature of 520 °C and the variable (360/520 °C) condition was a high density of disk-shaped precipitates on 0 0 1 matrix habit planes. Fig. 1 shows an example of the precipitates observed in V–4Cr–4Ti irradiated at a constant temperature of 520 °C. Void or dislocation loop formation was not observed in either specimen. A very low density of network dislocations was observed in both specimens.

The microstructure of V–4Cr–4Ti irradiated at constant (520 °C) vs. varying (360/520 °C) temperature was qualitatively similar. However, as shown in Fig. 2, the varying temperature irradiation produced precipitates of a finer size and higher density compared to the constant temperature irradiation condition. The constant temperature irradiation produced precipitates with a mean diameter of 24 nm and a density of $\simeq 4 \times 10^{21}$ m^{-3}. The varying temperature irradiation produced precipitates with a mean diameter of 11 nm and a density of $\simeq 1.2 \times 10^{22}$ m^{-3}. According to a quantitative parallel electron energy loss spectrometry analysis, the composition of the radiation-produced precipitates was $Ti_x(O,N)_y$, where $x > 90$ at.% and $y < 10$ at.%. There was no evidence for carbon in the radiation-produced precipitates. The crystal structure of the radiation-produced precipitates was determined to be face-centered cubic from a selected area electron diffraction analysis. Comparison of simulated and experimental selected area diffraction patterns of the precipitates and matrix indicates that a Baker–Nutting orientation relationship is obeyed, i.e. $[0\,0\,1]_m \| [0\,1\,1]_p$ and $(2\,0\,0)_m \| (2\,0\,0)_p$, where the subscripts m and p refer to the matrix and precipitate, respectively. Further details regarding the precipitate analysis are given elsewhere [17].

A moderate density of small defect clusters (dislocation loops, stacking fault tetrahedra) and voids were produced in stainless steel during irradiation at either constant (520 °C) or varying (360/520 °C) irradiation conditions. The general microstructural features were qualitatively similar for the two irradiation conditions, although there were some quantitative differences. Fig. 3 compares the general microstructure of stainless steel for

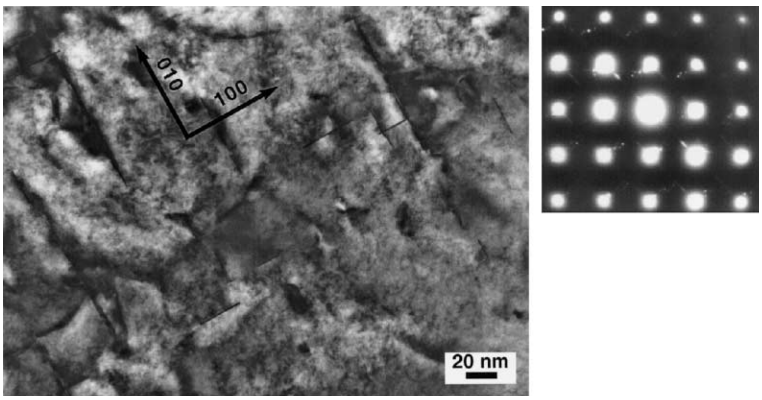

Fig. 1. Precipitates observed on {0 0 1} matrix habit planes in V–4Cr–4Ti irradiated to 4 dpa at 520 °C. Streaks associated with the precipitates are visible in the diffraction pattern.

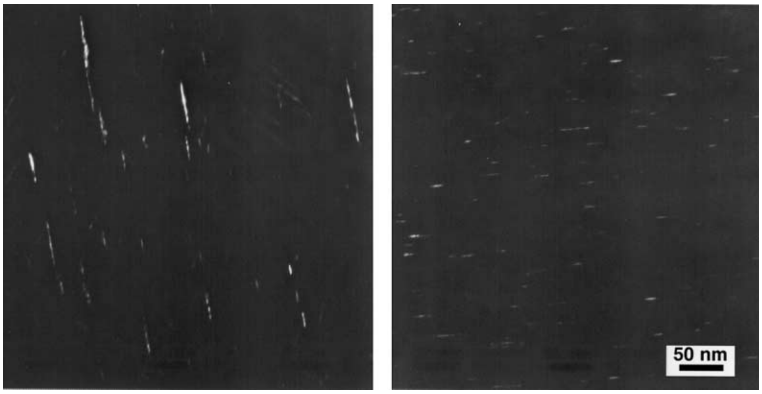

Fig. 2. Comparison of the precipitates observed in V–4Cr–4Ti irradiated to 4 dpa at 520 °C (left: constant temperature) vs. 360/520 °C (right: varying temperature). Centered dark field image.

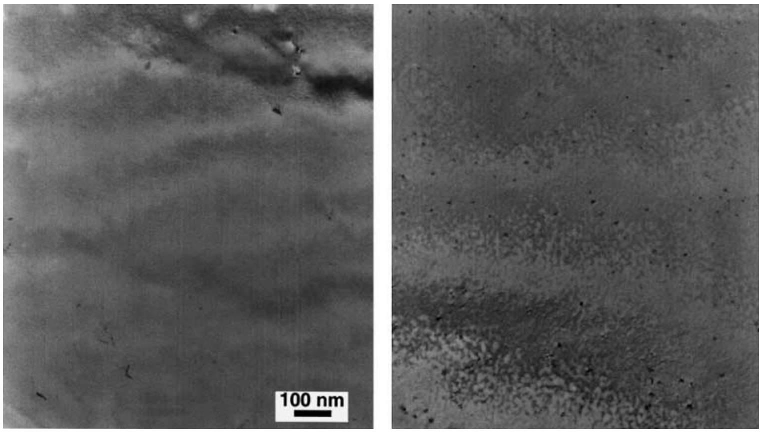

Fig. 3. Comparison of the defect clusters observed in stainless steel irradiated to 4 dpa at 520 °C (left: constant temperature) vs. 360/520 °C (right: varying temperature).

the two irradiation conditions. The varying temperature irradiation produced enhanced growth of defect clusters compared to the constant irradiation condition. Although the defect cluster density was $\simeq 3 \times 10^{21}$ m^{-3} for both irradiation conditions, the mean defect cluster diameter was significantly larger for the varying temperature condition (6 nm) compared to the constant temperature condition (2.5 nm).

As shown in Fig. 4, a low density of small cavities was observed in stainless steel at both irradiation conditions. The cavity number density appeared to be slightly higher and the cavity size was smaller for the varying temperature condition, but due to the low density of cavities (and accompanying spatial variability in the cavity density), statistically significant differences in the cavity size and density for the two irradiation conditions were not apparent. The amount of void swelling was very small (<0.01%) for both irradiation conditions. Higher dose irradiations would be needed to examine the possibility of statistically significant differences in the void swelling behavior for the constant vs. varying temperature irradiation conditions.

Irradiation of pure copper at a constant temperature of 340 °C produced a large amount of cavity swelling. The mean void diameter and density were 80 nm and 8×10^{19} m^{-3}, which yields a volume swelling of $\simeq$2.5%. The void density is about a factor of two larger than previously reported for copper irradiated to $\simeq$1 dpa at a constant temperature of $\simeq$350 °C [18,19]. There was no evidence for crystallographic ordering of the cavities in the present study. A very low density of small stacking fault tetrahedra was also observed. Fig. 5 shows an example of cavity formation adjacent to a grain boundary. The width of the zone denuded of cavities adjacent to the grain boundaries was $\simeq$0.45 μm, which is slightly less than the 0.7 μm width reported for copper irradiated

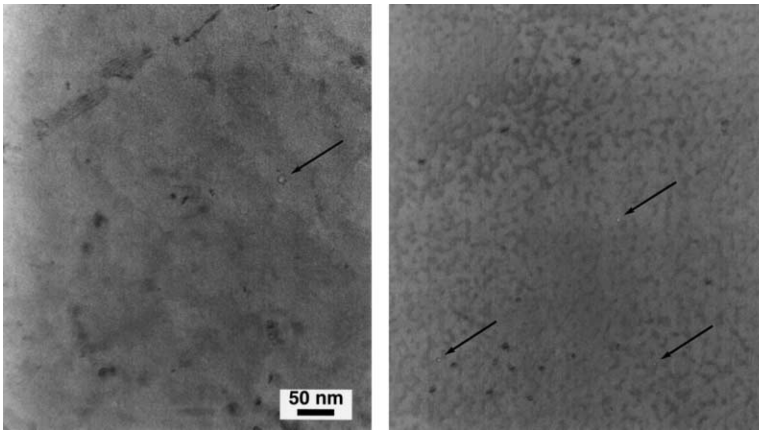

Fig. 4. Examples of the small cavities observed in stainless steel irradiated to 4 dpa at 520 °C (left: constant temperature) vs. 360/520 °C (right: varying temperature).

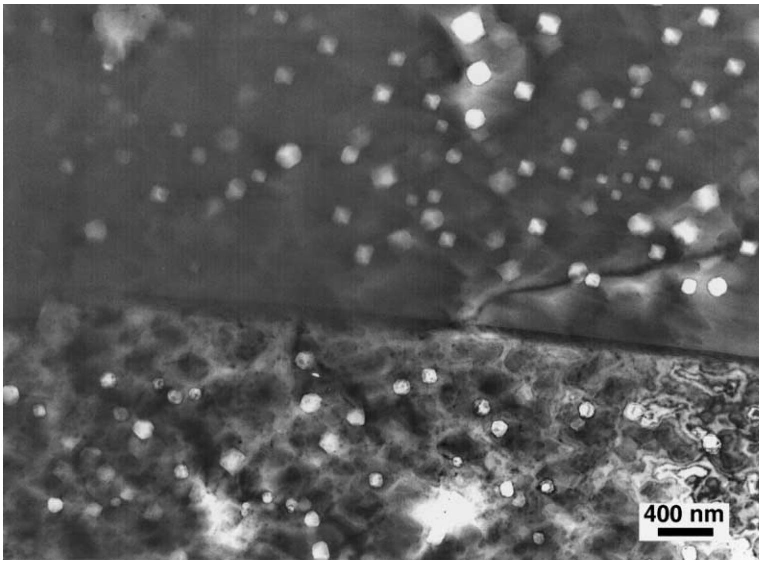

Fig. 5. Cavity swelling adjacent to a grain boundary in copper irradiated to 5 dpa at 340 °C.

with neutrons at 327 and 350 °C [18]. The higher cavity density and smaller grain boundary denuded zone width in the present study compared to previous constant temperature irradiation studies at 350 °C [18,19] may be in part attributable to the higher damage rate in this study.

4. Discussion

Qualitatively similar microstructures were observed in V–4Cr–4Ti and stainless steel for the constant and varying temperature irradiation conditions investigated in this study. In quantitative terms, the varying (360/520 °C) temperature irradiation generated a higher density of smaller precipitates in V–4Cr–4Ti and a larger average defect cluster size in stainless steel compared to the constant (520 °C) irradiation. The precipitate density observed for V–4Cr–4Ti (4×10^{21} and 12×10^{21} m^{-3}) was slightly higher than that observed in the same alloy heat following a constant temperature neutron irradiation to 0.1 dpa at 505 °C (2.6×10^{21} m^{-3}) [14]. As mentioned in the introduction, 360 °C is near or higher than the Stage V recovery temperature for V–4Cr–4Ti and austenitic stainless steel. Therefore, more pronounced differences between the constant and varying temperature irradiation conditions might have occurred if the low temperature portion of the irradiation was performed at lower temperatures.

Several previous studies have investigated the effect of constant vs. varying temperature on the microstructure of irradiated austenitic stainless steel [4–6,8,20], vanadium [7,10], and vanadium alloys [7,21]. In some cases, rather spectacular differences were observed. For example, Yoshida et al. [5] observed that varying temperature (either 200/400 °C or 300/450 °C) neutron irradiation of Fe–16Cr–17Ni-0.25Ti austenitic stainless steel produced dramatically higher void swelling levels compared to constant temperature irradiation at 400 °C for damage levels of 0.13–0.2 dpa. Similarly, enhanced void nucleation has been observed in numerous binary vanadium alloys that were preirradiated at low temperature, compared to constant temperature irradiation (total accumulated dose $\simeq$0.13 dpa) [7]. Low temperature preirradiation has been observed to cause an enhancement in the defect cluster density in many cases [5,6], but in some cases either no effect [8] or a decrease in loop density [10] has been observed compared to the constant temperature irradiation condition. Nita et al. [21] observed that varying temperature irradiation was significantly different from constant temperature irradiation for vanadium alloys irradiated 220/420 °C, whereas relatively minor differences were observed for 340/530 °C temperature combination. It should be noted that the damage levels in these early pioneering studies were mainly 0.1–0.3 dpa, with a maximum investigated dose of 2 dpa.

A recent study on companion specimens in the same HFIR irradiation capsule reported that, for the irradiation conditions examined (340 °C constant irradiation temperature vs. 225/340 °C varying temperature), the cyclic low-temperature irradiation had a relatively modest effect on the microstructural evolution of pure V, V–4Cr–4Ti, Fe–16Cr–17Ni austenitic ternary alloy, and pure copper [22]. The 225/340 °C varying temperature irradiation was reported to induce a higher cavity density and a lower defect cluster density in Fe–16Cr–17Ni compared to the constant 340 °C irradiation. The loop density and cavity size were similar in the 225/340 °C and 340 °C Fe–16Cr–17Ni specimens. The density of precipitates in the 225/340°C vanadium alloy specimens was higher compared to the 340 °C constant temperature case.

5. Conclusions

Periodic low temperature excursions produced a moderate enhancement in the nucleation of radiation-induced defects (precipitates, dislocation loops) in V–4Cr–4Ti and stainless steel. The quantitative effect of low-temperature excursions was relatively small for the materials and conditions investigated in the present study (eight cycles of varying 360/520 °C temperature vs. constant 520 °C temperature, with 0.05 dpa at the lower temperature and 0.45 dpa at the higher temperature for each cycle). Further work is needed to investigate the quantitative influence of varying temperatures under other irradiation conditions (different temperatures, different doses at low temperature, etc.).

Acknowledgements

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References

[1] M. Kiritani, J. Nucl. Mater. 160 (1988) 135.
[2] M. Kiritani et al., J. Nucl. Mater. 174 (1990) 327.
[3] M. Kiritani et al., J. Nucl. Mater. 179–181 (1991) 1104.
[4] M. Kiritani et al., J. Nucl. Mater. 212–215 (1994) 241.
[5] N. Yoshida, Q. Xu, H. Watanabe, Y. Miyamoto, T. Muroga, J. Nucl. Mater. 212–215 (1994) 471.
[6] Q. Xu et al., J. Nucl. Mater. 212–215 (1994) 258.
[7] H. Matsui et al., J. Nucl. Mater. 212–215 (1994) 784.
[8] Q. Xu et al., J. Nucl. Mater. 233–237 (1996) 1057.
[9] T. Muroga et al., J. Nucl. Mater. 258–263 (1998) 130.
[10] K. Ochiai et al., J. Nucl. Mater. 271&272 (1999) 376.
[11] N. Yoshida et al., J. Nucl. Mater. 191–194 (1992) 1114.
[12] S.J. Zinkle et al., J. Nucl. Mater. 206 (1993) 266.
[13] M. Horiki, M. Kiritani, J. Nucl. Mater. 239 (1996) 34.
[14] P.M. Rice, S.J. Zinkle, J. Nucl. Mater. 258–263 (1998) 1414.
[15] S.J. Zinkle, Radiat. Eff. Def. Solids 148 (1999) 447.
[16] A.L. Qualls, T. Muroga, in: Fusion Materials Semiannual Progress Report for Period ending 30 June 2000, DOE/ER-0313/28, Oak Ridge National Lab., 2000, p. 266.
[17] D.T. Hoelzer, S.J. Zinkle, in: Fusion Materials Semiannual Progress Report for Period ending 31 December 2000, DOE/ER-0313/29, Oak Ridge National Lab., 2000, p. 19.
[18] S.J. Zinkle, K. Farrell, J. Nucl. Mater. 168 (1989) 262.
[19] S.J. Zinkle et al., J. Nucl. Mater. 168 (1991) 262.
[20] D.J. Mazey et al., J. Nucl. Mater. 154 (1988) 186.
[21] N. Nita et al., J. Nucl. Mater. 271&272 (1999) 376.
[22] T. Muroga et al., J. Nucl. Mater. 299 (2001) 148.