CONF-810831--9

THE RESISTANCE OF $(Fe,Ni)_3V$ LONG-RANGE-ORDERED ALLOYS TO NEUTRON AND ION IRRADIATION*

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A series of $(Fe,Ni)_3V$ long-range-ordered alloys were irradiated with neutrons in the Oak Ridge Research Reactor (ORR) and with 4 MeV Ni ions at temperatures above 250°C. The displacement damage levels for the two irradiations were 3.8 and 70 dpa, and the helium levels were 29 and 560 at. ppm, respectively. Irradiation in ORR generally increased the yield strength and lowered the ductility of an LRO alloy, but produced relatively little swelling. The LRO alloys retained their long-range order after ion irradiation below the critical ordering temperature, T_c, and exhibited low swelling. Above T_c the alloys were disordered and showed greater swelling. Adjustment of alloy composition to prevent sigma phase formation reduced swelling.

1. INTRODUCTION

Long-range-ordered (LRO) alloys in the (Fe,Co, $Ni)_3V$ system have been developed recently at ORNL for potential use at elevated temperatures [1]. These alloys generally exhibit high strength, excellent ductility, low creep rates, and good fatigue properties at elevated temperatures below their critical ordering temperatures (T_c). Below these T_c temperatures, which vary from approximately 700 to 1000°C depending on composition, the alloys possess ordered cubic $L1_2$ structures. The first alloy to be developed was [illegible]$_3$V (designated LRO-1); its microstructural response to aging at elevated temperatures has already been reported [2]. The same alloy was irradiated with 4 MeV Ni ions to a dose of 70 dpa and exhibited very low swelling [3]. For fusion reactor applications, alloys with nickel instead of cobalt are more attractive, and a number of $(Fe,Ni)_3V$ LRO alloys have been developed (T_c = 670°C). An early alloy in this group was $(Fe_{0.61}Ni_{0.39})_3V$ or LRO-16; it was included in the ORR-MFE-2 reactor experiment that was completed in March 1980. The effect of that irradiation exposure at 250, 350, and 550°C on the microstructure and tensile properties of LRO-16 are presented in this paper. Also included are the main results of experiments using 4 MeV Ni ions where the radiation resistance of LRO-16 as well as newer $(Fe,Ni)_3V$ LRO alloys are compared to a 20%-cold-worked 316 stainless steel standard. These experiments employed simultaneous injection of helium and deuterium to better simulate fusion conditions and provided a rapid method of screening the LRO alloys.

2. EXPERIMENTAL

2.1 Alloy Preparation

Small (~0.4 kg) ingots of four LRO alloys were produced by arc melting under argon. The ingots were clad in molybdenum sheet, hot rolled at 1100°C, and cold rolled with intermediate anneals at 1100°C to a final sheet thickness of 0.76 mm. The composition and ordering heat treatment for each alloy are given in Table I. Also given is the composition of a 20%-cold-worked 316 SS sheet which was used in the ion irradiation experiments as a standard for comparison purposes. The LRO-35 alloy was prepared with two different heat treatments in an attempt to vary the amount of sigma phase produced in the microstructure.

2.2 Neutron Irradiation

Nine small sheet tensile specimens with 1.5-mm-wide gage sections (see ref. [4] for detailed specimen configuration) were fabricated from the LRO-16 sheet and exposed to neutrons in the ORR reactor at ORNL (MFE-2 experiment). Three specimens were heated with small electrical resistance furnaces at each of the irradiation temperatures of 250, 350 and 550°C. The environment in the specimen tube was helium gas. Irradiation temperatures were measured and controlled by thermocouples, and were within ±5°C of the desired temperature. The accumulated fluence was 4.8×10^{25} neutrons/m^2 (> 0.1 MeV), which produced a displacement damage level of 3.8 dpa. The amount of helium generated in the alloy was calculated to be approximately 29 at. ppm. Postirradiation tensile tests were conducted under vacuum (10^{-5} Pa) in an Instron tensile machine located in a shielded hot cell. The crosshead speed was 0.05 mm/min and specimens were tested at the same temperature used for the irradiation. Fracture surfaces were examined in a shielded SEM at 25 kV. Discs (3 mm dia) for TEM were electrical discharge machined (EDM) from the specimen shoulders and electropolished in a 12.5 vol % H_2SO_4 in methanol solution at −30°C and 27 V dc.

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*Research sponsored by the Office of Fusion Energy, U.S. Department of Energy, under contract No. W-7405-eng-26 with the Union Carbide Corporation.

Table I. Alloy Composition and Heat Treatment

Alloy	Content, wt %								Heat Treatment/ Condition
	Fe	Ni	V	Ti	Cr	Mo	Mn	C	
LRO-16	46.1	31.0	23.0	—	—	—	—	a	15 min at 1130°C, quench, aged at 605°C for 5.5 days
LRO-35	45.3	31.8	22.6	0.4	—	—	—	a	15 min at 1200°C, quench, aged 3 days at 650°C plus 30 h at 600°C plus 60 h at 500°C
LRO-35G	45.3	31.8	22.6	0.4	—	—	—	a	15 min at 1130°C, quench, aged 3 days at 650°C plus 30 h at 600°C plus 60 h at 500°C
LRO-20	37.6	39.5	22.9	—	—	—	—	a	15 min at 1200°C, quench, aged 4 days at 650°C plus 1 day at 600°C plus 2 days at 500°C
LRO-37	37.6	39.5	22.4	0.4	—	—	—	a	15 min at 1200°C, quench, aged 4 days at 650°C plus 1 day at 600°C plus 2 days at 500°C
316 SS	65.0	13.0	—	0.005	18	2.5	1.9	0.05	20% cold worked

[a]Carbon occurs as an impurity with levels from 100 to 200 wt ppm.

2.3 Ion Irradiation

Disks (3 mm dia) of the LRO alloys and the 316 SS were irradiated with 4 MeV nickel ions in the ORNL dual ion facility [5] to 70 dpa at 525, 570, and 625°C. A few disks were irradiated above T_c (670°C). Helium and deuterium ions were simultaneously injected at rates of 8 and 28 at. ppm/dpa, respectively. Since ion irradiation produced damage only in the surface layers of the disks, special techniques were needed to examine these layers by TEM [6].

3. RESULTS

3.1 Effect of Neutron Irradiation on Microstructure and Tensile Properties

The tensile properties of unirradiated and neutron-irradiated LRO-16 are given in Fig. 1. The ultimate tensile strength of unirradiated LRO-16 decreases slightly with increasing test temperature [Fig. 1(a)] while the yield strength actually increases across the same temperature range. The increase in yield strength is a feature of Fe,Ni,V LRO alloys which makes them potentially useful for elevated temperature application [7]. Stoloff and Davies [8] have shown that the increased yield strength is related to a decrease in the degree of order and have proposed that the dislocation movements in an LRO alloy with a low degree of order leave antiphase boundary tails which give rise to hardening. Neutron irradiation caused additional hardening of the alloy at the lower two temperatures by creating defects in the microstructure. At 550°C, the yield strength was unchanged by the irradiation. The irradiation also led to reductions in the ultimate tensile strength (except at 350°C) and rather dramatic losses in ductility [Fig. 1(b)].

Scanning electron micrographs of unirradiated LRO-16 fracture surfaces show the typical dimpled structure associated with ductile fracture [Fig. 2(a)]. The specimens irradiated and tested at 250°C exhibited a mixed ductile and intergranular fracture mode [Fig. 2(b)]. Those tested at 350°C were similar, but at 550°C a

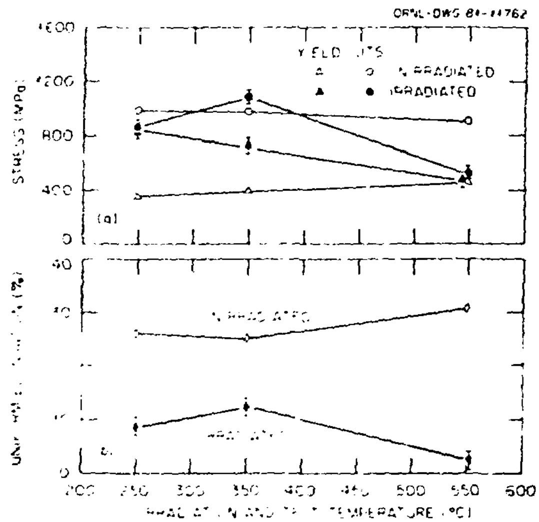

Fig. 1. Tensile properties of LRO-16 after neutron irradiation in HFIR (3.8 dpa) shown as a function of temperature (test temperature equals irradiation temperature).

higher percentage of the fracture surfaces were intergranular in nature. Figure 2(c) shows several exposed grain boundaries after testing at 550°C; the linear striations on the grain boundary surfaces are thought to be caused by the intersection of deformation bands with the grain boundary. These results indicate that the irradiation weakened a portion of the grain boundaries.

The microstructure of the unirradiated LRO-16 is shown in Fig. 3(a). It consists of an ordered matrix and a fine dispersion of fcc vanadium carbide (VC) particles having diameters of ~25 nm. The carbide particles have a larger lattice parameter and lower coefficient of thermal expansion than the matrix and, therefore, produced strain contrast in the micrograph. The carbides showed an epitaxial, cube-on-cube relationship with the matrix. The alloy also contained a

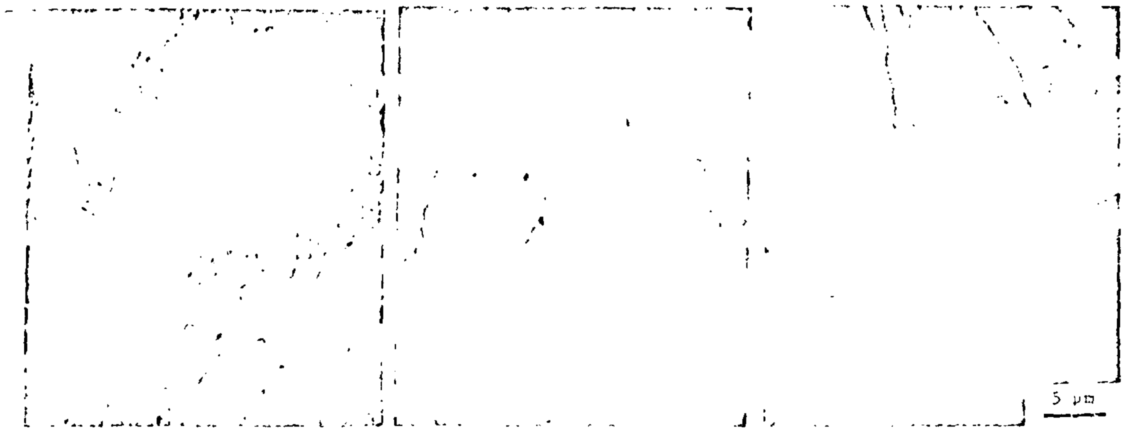

Fig. 2. Scanning electron micrographs of LRO-16 fracture surfaces before and after testing. (a) Unirradiated, tested at 550°C; (b) irradiated and tested at 250°C; and (c) irradiated and tested at 550°C.

small amount of sigma phase. The sigma phase was present as widely scattered patches containing small, highly faulted grains. STEM microanalysis showed it to be a Fe-V phase containing some nickel, and SAD showed it to be tetragonal with a_o = 0.88 nm and c_o = 0.46 nm. Figure 3(b) shows the ordered domains and antiphase boundaries (APBs) in the unirradiated LRO-16. Only two-thirds of the APBs are imaged in dark field with the (1[illegible]) superlattice reflection; when all APBs are imaged simultaneoulsy, the domains appear equiaxed in shape. Irradiation at the lower temperatures produced about four times more dislocations than were found in the unirradiated material as shown in Fig. 3(c) for 250°C. Most of the dislocations were small loops. Fewer, but larger sized faulted loops were found in specimens irradiated and tested at 550°C [Fig. 3(d)]. Contrast analysis experiments using TEM showed that the loops were interstitial in nature. The micrograph in Fig. 3(d) also shows that many of the VC particles in the matrix must have dissolved while the VC particles in the high-angle grain boundaries have coarsened. Apparently the cascade processes [illegible] back into [illegible] the matrix precipitate phase [9]. In competition with this were the normal thermal processes of VC precipitation, but these prevailed only in the grain boundaries where diffusion was more rapid. Since the specimens were reheated back to their respective temperatures for tensile testing, it was not possible to determine the effect of the irradiation on the degree of order. However,

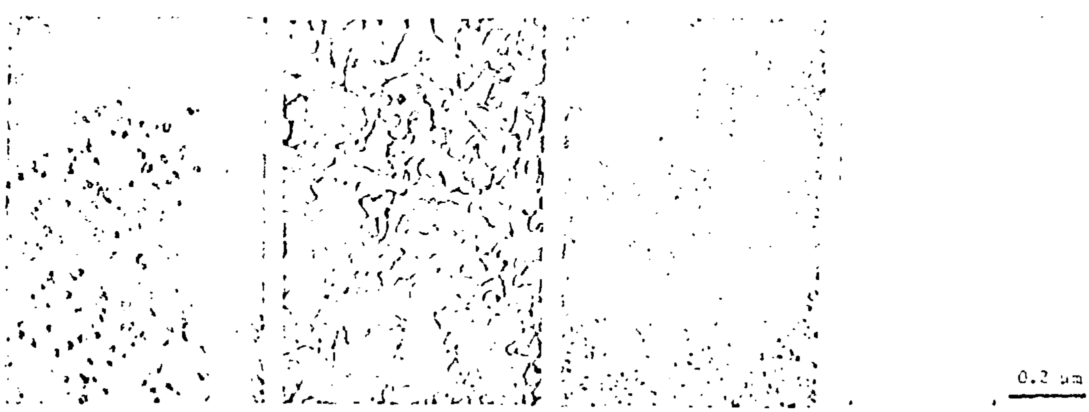

Fig. 3. LRO-16 microstructure (a) before irradiation showing VC particles (b) before irradiation showing ordered domains and APBs (c) after neutron irradiation (3.8 dpa) at 250°C. (d) After neutron irradiation (3.8 dpa) at 550°C.

the specimens tested at 250°C showed only weak superlattice reflections and must have been disordered to some extent by the irradiation. Only a few cavities were observed at 350 and 550°C, with calculated swelling values of 0.009 and 0.07%, respectively. There were no cavities observed at 250°C.

The results of the tensile tests and microstructural evaluations indicate that at 250 and 350°C neutron irradiation hardens the alloy by producing small interstitial dislocation loops and other dislocations. The fracture surfaces of the irradiated specimens also exhibited some intergranular separation which was found to increase in specimens tested at 550°C. Possible explanations for the weakened grain boundaries include the radiation-induced segregation of elements such as helium to the grain boundaries. At the temperatures, doses, and helium production rates encountered in this experiment, cavity production was very low or nonexistent which indicates that the alloy is relatively low swelling. However, the presence of sigma phase in the LRO-16 was generally undesirable and for this reason, several other $(Fe,Ni)_3V$ LRO alloys with different compositions have been produced in an attempt to eliminate this phase. The results of radiation screening experiments on some of these newer alloys will be described next.

3.2 Effect of Ion Irradiation on Microstructure

The [illegible] of [illegible] the 3?6 alloys [illegible] are [illegible] as a function of irradiation temperature in Fig. 4. A vertical line is drawn at T_c. Looking first at the results below T_c, it is seen that all of the LRO alloys had less swelling than the 316 SS (20% CW) standard. Very low swelling was observed in LRO-35 as compared to LRO-16. Since the two alloys were of the same composition except that LRO-35 had a small titanium addition, one is tempted to conclude that titanium increased the resistance to swelling. However, with higher nickel contents as in the LRO-20 LRO-37 pair, the titanium addition had little effect on the swelling. LRO-16 had considerable sigma phase in its microstructure while LRO-35 contained a much smaller amount. LRO-20 and LRO-37 were completely free of sigma phase. Since LRO-16 had greater swelling than the other LRO alloys, it would appear that the presence of sigma phase tended to increase swelling. Even more convincing is the comparison of the swelling results between LRO-35 and LRO-35G. Both groups of specimens were fabricated from the same alloy, but LRO-35G was heated to produce a greater amount of sigma phase in the microstructure. With more sigma phase present, the swelling was greater than in LRO-35 (Fig. 4) but still less than LRO-16. With the exception of LRO-35 and LRO-35G, all of the LRO alloys had high values of swelling above T_c (Fig. 4). It is believed that this sharp increase in swelling was due to the loss of order above T_c rather than a fortuitous rise in the swelling curves for these LRO alloys. All of the LRO alloys irradiated below T_c retained their long-range-ordered structures as shown by the presence of superlattice reflections in their electron diffraction patterns. Experimental evidence that significant reordering did not occur after the irradiation [illegible] shown [illegible] by the fact that the [illegible] irradiated above T_c remained disordered upon cooling to room temperature.

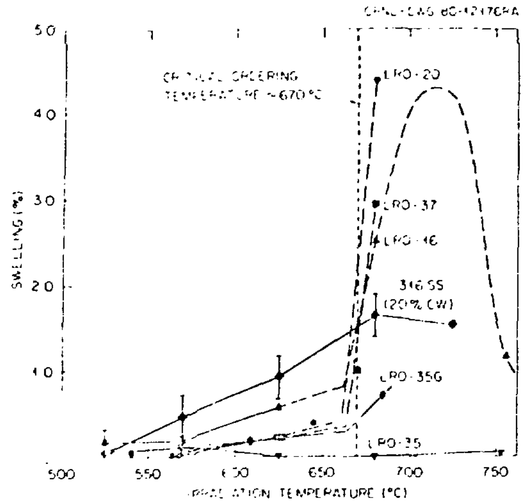

Fig. 4. Swelling measured in LRO alloys and 316 SS (20% CW) after nickel ion irradiation (70 dpa) with simultaneous helium and deuterium injection.

The nickel ion irradiation screening experiments indicate that increasing the nickel content of the $(Fe,Ni)_3V$ LRO alloys permits one to fabricate ordered alloys that are free of sigma phase and somewhat more resistant to swelling than those with lower nickel containing sigma phase. The presence of sigma phase may have increased the susceptibility of LRO alloys to swelling by removing specific elements from the matrix, upsetting the stoichiometry and reducing the degree of order. With a lower degree of order, vacancy migration would be enhanced and interstitial vacancy recombination lessened. (Schulson has proposed that recombination should be enhanced in ordered alloys [10].) Such a mechanism would encourage cavity growth. Similarly, enhanced vacancy migration with losses in recombination might also explain why swelling increased dramatically when the alloys were irradiated in their disordered state above T_c. The addition of titanium to the alloy was more effective in reducing swelling in the LRO-16–LRO-35 comparison when the nickel content was ~31%. However, the mechanism enabling the reduced swelling was clouded by the fact that a titanium addition also tended to reduce the amount of sigma phase present. Therefore, one cannot be sure whether (1) titanium was acting intrinsically in some way to restrict cavity formation and/or growth, or (2) the titanium was merely moving the alloy compositionally away from the sigma phase field. The fact that the swelling measured in LRO-20 and LRO-37 was nearly identical below T_c and neither contained sigma phase tends to support the second explanation. At the irradiation temperatures used, it appears that bulk diffusion was rapid enough to enable the LRO alloys to reorder. At lower temperatures, irradiation may quickly disorder an LRO alloy. The use of nickel ion irradiation with simultaneously injected helium and deuterium is a rapid and convenient method to screen LRO alloys with regard to their radiation resistance in fusion environments. Detailed response of the alloy's microstructure to radiation can be studied with virtually no hazards of radioactivity, and preliminary optimization with regard to thermomechanical treatment and/or composition can be conducted. When used in conjunction with reactor irradiations, ion irradiation can shorten the total time in developing reactor materials.

4. CONCLUSIONS

The $(Fe,Ni)_3V$ alloy, LRO-16, was irradiated in ORR at 250, 350, and 550°C to damage and helium levels of 3.8 dpa and 29 at. ppm, respectively.

1. The reactor irradiation generally "hardened" or increased the yield strength of LRO-16 by [illegible] interstitial loops and other dislocations.

2. The irradiation lowered the ductility of LRO-16 at all three temperatures. The losses may be due to a combination of radiation hardening and radiation-induced segregation to grain boundaries.

3. The amount of swelling measured in 250, 350, and 550°C specimens was relatively low with values of [illegible], [illegible]9, and [illegible].07%, respectively.

Disks of $(Fe,Ni)_3V$ alloys were irradiated to 70 dpa with 4 MeV Ni ions above 570°C and simultaneously injected with 3 at. ppm/dpa He ions and 28 at. ppm/dpa D to simulate fusion reactor conditions.

1. All of the LRO alloys remained ordered when irradiated below the critical ordering temperature (T_c = 670°C).

2. All of the LRO alloys had less swelling due to cavities than 316 SS (20% CW) below T_c. Above T_c, most of the LRO alloys exhibited higher swelling probably because the alloys were disordered.

3. The LRO alloys, LRO-20 and LRO-37, that contained higher nickel contents to prevent sigma phase formation also exhibited lower swelling. The presence of sigma phase is thought to lower the degree of order in the alloy and decrease interstitial/vacancy recombination. The titanium additions appear to improve the swelling resistance of the LRO alloys by preventing or minimizing sigma phase formation.

ACKNOWLEDGMENTS

The author appreciates the work of B. L. Cox, G. A. Potter, N. Rouse, C. G. McKamey, and J. T. Houston for specimen preparation and/or testing, L. Shrader for SEM work, M. B. Lewis and R. A. Buhl for the ion irradiations, and F. A. Scarboro for typing the manuscript.

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