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ION IRRADIATION EFFECTS ON A MARTENSITIC
STAINLESS STEEL DESIGNED FOR REDUCED
LONG-LIFE RADIOACTIVITY

RD Griffin(a)
SJ Zinkle(b)
RA Dodd(a)
GL Kulcinski(a)
DS Gelles

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Pacific Northwest Laboratory
Richland, Washington 99352

(a) Univ. of Wisconsin
(b) Oak Ridge National Laboratory

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AUTHORS' NAMES:

Robin D. Griffin¹, Steven J. Zinkle², Richard A. Dodd³, Gerald L. Kulcinski⁴, and David
S. Gelles⁵

TITLE OF PAPER:

Ion Irradiation Effects on a Martensitic Stainless Steel Designed for Reduced Long-
Life Radioactivity

AUTHORS' AFFILIATIONS:

¹Research associate, Fusion Technology Institute, University of Wisconsin-
Madison, 1500 Johnson Drive, Madison WI, 53706.

²Research staff, Metals and Ceramics Division, Oak Ridge National Laboratory,
P.O. X, Bldg. 5500, MS A113, Oak Ridge, TN, 37831.

³Professor, Materials Science and Engineering, University of Wisconsin-Madison,
Madison, WI, 53706

⁴Professor of Nuclear Engineering and Director of the Fusion Technology Institute,
University of Wisconsin-Madison, 1500 Johnson Drive, Madison, WI 53706.

⁵ Staff Scientist, Battelle Pacific Northwest Laboratories, P.O. Box 999, M.S. P815,
Richland, WA 99352.

ABSTRACT: Alloys with reduced long-life radioactivity (low activation alloys) are being developed to increase the acceptability of fusion power. The phase stability and swelling resistance of a 12Cr-6.5Mn-1W-0.3V-0.1C martensitic steel were evaluated by transmission electron microscopy following 3.8 MeV Fe⁺⁺ ion irradiation with and without He coimplantation. Ion irradiations were performed at 450°C, 550°C, and 650°C to approximately 10, 20, and 40 dpa. At 550°C, approximately 20 appm He/dpa was coimplanted with the 3.8 MeV Fe⁺⁺ ions. The specimens were examined at a depth approximately halfway between the surface and the mean ion range in order to minimize the influence of the surface and of injected ions.

At all temperatures, M₂₃C₆, also present in the unirradiated structure, was the only precipitate present. A nonuniform distribution of loops also formed at all temperatures. After the 450°C and 650°C irradiations, no voids were present. At 550°C, the helium did not appear to have much effect. Very few faceted voids formed. At 20 and 40 dpa some bubbles were found but their density was very low. At 650°C, a structure similar to a heavily over-tempered steel was produced by the irradiation. At 550°C recovery was seen to a lesser extent. Little to no recovery was seen at 450°C.

KEY WORDS: martensitic stainless steels, radiation effects, microstructure, ion irradiation, low activation

Introduction

Structural alloys with reduced long-life radioactivity (low activation alloys) are being considered for fusion reactors. Normal alloy steels will need composition changes to reach this requirement. Such modifications were made to a martensitic stainless steel which was designed to be fully air hardenable. This alloy was subsequently ion-irradiated to test its ^{microstructural} stability. In this steel (designated L9) the elements nickel, molybdenum, and niobium, which produce long-lived radionuclides, have been eliminated. In Table 1, the composition of L9, the low activation alloy of this study, and the nominal composition of HT-9, a non-low activation counterpart are listed. It is to be noted that Ni, commonly used to eliminate delta ferrite from the structure, has been replaced with manganese. The carbon content was also decreased to increase the ductility of L9; the elimination of carbon was compensated for with additional manganese. Molybdenum, used for high temperature strength, is at least partially replaced with tungsten.

The stability of L9 has been previously tested with tempering and aging studies (1,2) and with neutron irradiations in the Fast Flux Test Facility in Richland, Washington (2). The tempering, aging, and neutron irradiation studies on L9 showed many similarities to the standard martensitic stainless steels. Essentially a fully martensitic structure formed upon air-cooling from the austenitic temperatures. The stable carbide was shown to be $M_{23}C_6$, with a metal composition 58%Cr, 27%Fe, 10%W, 2%Mn, and 2%V (wt%). The neutron irradiations showed the typical excellent resistance to void formation. The major difference between L9 and the standard steels was the formation of χ phase with the composition 58%Fe, 18%Cr, 16%Mn, and 8%W. The χ phase forms in L9 after aging for more than 1000 hours at 420°C and 520°C. Large amounts of χ phase also formed in L9 after neutron irradiation at 520°C to 14 and 48 dpa.

In this study, L9 was ion-irradiated with Fe^{++} ions to further test its stability in an irradiation environment. The effect of helium on the swelling resistance of L9 was tested by simultaneously irradiating with He^+ and Fe^{++} , at a temperature close to the peak swelling temperatures in martensitic steels.

Experimental Procedure:

The initial heat treatment for the steel was $1000^\circ\text{C}/20 \text{ hr}/\text{AC} + 1100^\circ\text{C}/10 \text{ min}/\text{AC} + 700^\circ\text{C}/2 \text{ hr}/\text{AC}$. The steel was ion-irradiated at the Oak Ridge National Laboratory, using a facility equipped with two accelerators so that irradiation with both heavy and light ions could be accomplished simultaneously (3). The 3.8 MeV Fe^{++} ions were produced with a vertical CN Van de Graff accelerator equipped with a Model 910 Physicon ion source. Figure 1 shows the calculated displacement damage versus depth curve for 3.8 MeV Fe^{++} ions in iron along with the range at which He^+ was implanted. The calculations were performed using the E-DEP-1 code (4). The He^+ ions were provided by a horizontal AN Van de Graaff accelerator. A uniform distribution of He^+ implantation was obtained by varying the accelerating voltage from 200 to 400kV. Nine TEM disks were loaded into the sample chamber for simultaneous irradiation, and the dose rate was approximately $3 \times 10^{-3} \text{ dpa/sec}$ so that the samples were held for approximately four hours at temperature. The steel was irradiated at 450°C and 650°C with Fe^{++} ions only, while at 550°C , the steel was irradiated with both He^+ and Fe^{++} ions. Table 2 summarizes the ion irradiation conditions.

The samples were back-thinned to a depth of 400 nm. This depth was chosen as it lay within the region where helium was injected. This depth was also approximately halfway between the area where surface effects dominate (5) and the area where injected interstitials may reduce swelling (6). The first 400 nm of the irradiated surface of the steel was removed by electropolishing for 38 seconds at 0.03 A/cm^2 in a

solution of 10% perchloric acid, 90% butyl alcohol at -50°C. The samples were then back-thinned by painting the irradiated surface with a chemical resistant laquer and jet-thinning in a solution of 10% perchloric acid, 90% acetic acid at 15°C, 65V. At each temperature, one of the samples did not have the irradiated side laquered off during the thinning process, so that the irradiated region was removed during jet thinning. These samples then served as thermal controls for the study. Microstructural analysis was performed using a JEOL 200CX TEM/STEM electron microscope equipped with a Tracor Northern-Energy Dispersive X-Ray system.

Results:

The thermal control samples showed the expected lath structure with $M_{23}C_6$ carbides and a high dislocation density present. At 550°C and 650°C, the structure became somewhat more equiaxed, but the lath and dislocation structure are still readily visible (Figure 2). The lath width remained constant at all three temperatures while the carbides coarsened somewhat (Table 3).

There were few differences between the 450°C thermal control sample and the 450°C irradiated samples. Figure 3 shows a set of TEM images of L9 irradiated at 450°C to 8, 24 and 47 dpa. No voids were found in the samples irradiated at 450°C. The only precipitate present was $M_{23}C_6$, which was also present in the unirradiated condition. The carbide diameter, the grain (lath) width, and the aspect ratio of the grains length to width stayed fairly constant with irradiation (Table 3). The dislocations which were present prior to the irradiation remained at all displacement levels, and the lath shaped structure was also still dominant. At 47 dpa there was some evidence that irradiation was leading to additional recovery of the subgrains, as the dislocations showed a definite tendency to line up in arrays (Figure 4). But in most areas the lath shape of the grains was still present. The only other changes caused by the irradiation

at 450°C, was the formation of small dislocation loops at 24 and 47 dpa (Figure 5). These loops had an average diameter of 2 nm. They were not uniformly distributed in the two samples as most grains were loop free.

Irradiation at 650°C led to a dramatic decrease in the dislocation density up to 30 dpa, with little additional reduction at 40 dpa (Figure 6). Grain coarsening appeared to saturate at 6 dpa as reflected by the grain width measurements (Table 3). The aspect ratio of the subgrain length to width decreased with irradiation up to 17 dpa. Carbide coarsening also did not increase past 17 dpa (Table 3). Again, $M_{23}C_6$ was the only precipitate found in the 650°C ion irradiated steel. A few dislocation loops with an average size of 30 nm were found at 30 and 40 dpa (Figure 8b). At this temperature no voids were found.

Irradiation at 550°C also caused the dislocation density to decrease and produced more equiaxed subgrains, but not as dramatically as was seen in the sample irradiated at 650°C (Figure 7 and Table 3). No appreciable change in the aspect ratio occurred after 18 dpa. In all the 550°C irradiated samples the aspect ratio remained higher than that of all the samples irradiated at 650°C, indicating that less recovery occurred. Some grain coarsening occurred, but beyond 6 dpa the coarsening did not additionally increase. Again, the only precipitate present in these samples was $M_{23}C_6$ which did not appear to coarsen with the 550°C irradiation (Table 3). More dislocation loops were found at 550°C than were found at 650°C, but their distribution was still nonuniform. Most of the Burger's vectors were determined to be $a\langle 100 \rangle$ type. Their average diameter was 12nm. The dislocation loops were often found in grains which also contained dislocation lines. This meant that there were grains with a relatively low dislocation density, and those with both dislocation lines and loops (Figure 8a). Cavities were only seen in the 18 and 40 dpa samples, none were present at 6 dpa. Only three areas containing relatively large, faceted voids were found in the 16 and 40 dpa samples irradiated at 550°C. The overall swelling was found to be $\ll 0.01\%$. In

the three areas where voids were found, the highest local swelling was found to be 0.1% (Figure 9a). In the other two areas the local swelling was found to be 0.02% (Figure 9b). At the two higher fluences a low density of bubbles with an average diameter of 3 nm were also present. In the 18 dpa sample, the bubble distribution was quite uneven, while at 40 dpa the bubbles were more uniformly distributed. The number density at 40 dpa was approximately $4 \times 10^{13}/\text{cm}^3$. The bubbles did not appear to be preferentially associated with any microstructural features, but could be seen at lath boundaries, subgrain boundaries, and within grains (Figure 10). None were found at carbide/matrix boundaries.

Discussion

The addition of manganese to a 12% chromium martensitic stainless steel does not appear to reduce its swelling resistance. In both neutron irradiation studies on L9 (2) and the present ion irradiation study, little swelling occurred. No cavities were found at 450°C and 650°C when L9 was ion irradiated without the presence of helium. HT-9 also exhibited this swelling resistance when ion irradiated without helium to 25 dpa between 350°C-600°C (7) and to 60 dpa between 300 to 600°C (8). In the present study, cavity formation only occurred at 550°C, where helium was coimplanted. The swelling was very low in spite of this being close to the peak swelling temperature in ion-irradiated ferritics (9), and there being helium present to promote cavity formation. HT-9 also shows excellent swelling resistance when ion irradiated with helium present (10).

At 450°C and 550°C, L9 showed irradiation enhanced recovery similar to that of ion irradiated HT-9 (8, 10). But at 650°C, the irradiation enhanced recovery of L9 deviated from that of HT-9. In L9, there was a substantial difference between the structure of the irradiated samples and that of the thermal control sample (Figures 2

and 6). The ion irradiated L9 samples showed a dramatic dislocation density decrease, more equiaxed subgrains, and some carbide coarsening. This showed a marked difference from HT-9, which when ion irradiated at 600°C (6), exhibited essentially no difference between the irradiated and control microstructures. This indicates that irradiation effects dominate the microstructure to higher temperatures in L9 than they do in HT-9.

It appears that L9 is more resistant to loop formation than HT-9 as the loop density at all temperatures remained low and nonuniform. This may be due to a difference in the pre-irradiation structures. The starting dislocation density in L9 may be different than in the standard alloys. This, in turn can change the time it takes for dislocation loops to form.

There were no phase changes found in the ion-irradiated L9 at any temperature. The only carbide found was $M_{23}C_6$, which was also the only carbide present in the unirradiated sample. In a sample of L9 which was neutron irradiated at 600°C (2), there was one large area where large amounts of austenite were present. It was tentatively concluded that the austenite was present prior to the irradiation because of a local composition inhomogeneity. This is supported by the complete lack of austenite formation found in the sample ion-irradiated at 650°C.

Thermal and irradiation studies on Ni-stabilized martensitic stainless steels such as HT-9 have shown that χ phase is not thermally stable, but is an irradiation induced phase. No χ phase was found in heat-treated HT-9 (11) or in other Ni-stabilized martensitic stainless steels which were aged for up to 9000 hours (12). Ion irradiation of HT-9 did lead to the formation of χ phase (8,10). At 50 dpa, 12 nm diameter χ phase with a number density $10^{20}/m^3$ formed within the HT-9 grains (approximately 0.01% χ). But subsequent thermal annealing dissolved it (8). Neutron irradiation of HT-9 also led to χ phase formation with a diameter of approximately 100 nm (13, 14).

The thermal and irradiation studies on L9 have shown substantial differences in the

stability of the χ phase which can form. The difference between χ phase formation in L9 and HT-9 does not appear to be due to the simple replacement of Mo with W. Similar Fe-Cr-Mo and Fe-Cr-W χ phases are documented (15, 16). Instead, it is the additional Mn in L9 which appears to be altering the stability of the χ phase. In Table 4, the composition of χ phase in L9 and HT-9 is listed. Note that no χ was found in L9 which also did not contain substantial amounts of Mn. Aging studies have shown that in L9, χ is thermally stable, although long anneals are necessary before it forms (1, 2). In neutron irradiation studies of L9 which combine the long time anneal with irradiation, χ phase formation was certainly irradiation enhanced (2). Much more χ formed in L9 than formed in neutron irradiated HT-9. At 520°C. the average diameter of the χ was 550 nm. At 14 dpa, approximately 10% of the structure was found to be χ . At 48 dpa, the amount had increased to approximately 20%. But the present ion irradiation study indicates that irradiation alone may not be enough to lead to its formation as χ phase formation did not occur during these relatively short time irradiations.

Conclusions

- 1) Cavities did not form in L9 which was ion-irradiated at 450°C to 47 dpa and at 650°C to 40 dpa, without the presence of helium.
- 2) At 550°C, with helium present, some cavities formed, but the overall swelling resistance of L9 was still excellent.
- 3) Ion irradiation did not lead to the formation of any new phases in L9 within the experimental conditions studied. Both long time aging and neutron irradiation led to χ phase formation in L9 (1,2). These results suggest that χ phase formation in L9 does not occur without the presence of long time anneals.
- 4) Up to 650°C, irradiation is still dominating the dislocation recovery and the transformation to equiaxed subgrains in L9. This result differs from HT-9 (8), where the thermal effects begin to dominate at 600°C.

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TABLE 1--Composition of L9 and HT-9 (wt%)

Composition	Cr	C	Ni	Mn	Mo	W	V
L9	12	0.1	---	6.5	---	0.9	0.3
HT-9	12	0.2	0.5	0.6	1.0	0.5	0.3

TABLE 2--Irradiation Conditions

Temperature	Displacement Levels (dpa) at 400 nm	Helium (appm)/dpa at 400 nm
450°C	8	---
	24	---
	47	---
550°C	6	35
	18	26
	40	27
650°C	6	---
	17	---
	30	---
	40	---

TABLE 3--Carbide Diameter, Lath Width, and Aspect Ratio for the Thermal Control and Irradiated Samples

Temperature (°C)	Displacement Level (dpa)	Carbide Diameter (nm)	Grain (lath) Width (nm)	Aspect ratio (grain length/width)
450°C	0 (thermal control)	50	300	> 10
	8	*	300	> 10
	24	*	400	> 10
	47	50	400	> 10
550°C	0 (thermal control)	70	300	> 10
	6	*	500	4
	18	*	700	3
	40	70	600	3
650°C	0 (thermal control)	80	300	> 10
	6	110	900	3
	17	130	800	2
	30	120	800	2
	40	120	800	2

TABLE 4--Composition of χ Phase in L9 and HT-9

Alloy	Reference	Condition	Composition of χ Phase (wt %)							
			Fe	Cr	Ni	Mn	Si	W	Mo	V
L9	1,2	1	58	18	---	16	---	8	---	---
HT-9	13	2	56	26	7	---	6	---	6	---
HT-9	14	3	59-65	24-28	---	---	---	3-8	6-11	---
HT-9	14	4	39-50	16-33	---	---	---	9-14	17-23	0-1

Condition 1: Aged for 1000 to 10,000 hours at 420°C and 520°C. Neutron irradiated to 48 dpa at 520°C.

Condition 2: Neutron irradiated at 400 to 650°C to fluences up to approximately 90 dpa.

Condition 3: Neutron irradiated at 520°C to fluences up to approximately 34 dpa. Most of χ within delta ferrite.

Condition 4: Neutron irradiated at 600°C to fluences up to approximately 34 dpa. Most of χ within martensite.

Figure Captions

Fig. 1--Displacement damage versus depth for 3.8 MeV Fe⁺⁺ ions in L9, martensitic steel.

Fig. 2--TEM micrographs of the thermal control samples.

Fig. 3--Microstructure of L9 after ion irradiation at 450°C.

Fig. 4--Dislocation structure in L9 after ion irradiation to 45 dpa at 450°C.

Fig. 5--Small dislocation loops in L9 irradiated to 45 dpa at 450°C.

Fig. 6--Microstructure of L9 after ion irradiation at 650°C.

Fig. 7--Microstructure of L9 after ion irradiation at 550°C.

Fig. 8--Dislocation loops in the sample ion irradiated at a) 550°C and b) 650°C.

Fig. 9--Faceted cavities found in L9 after simultaneous irradiation with Fe⁺⁺ and He⁺ ions at 550°C. a) 18 dpa b) 40 dpa.

Fig. 10--Bubbles found in L9 after after simultaneous irradiation with Fe⁺⁺ and He⁺ ions at 550°C.

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Figure 10: Bubbles
ions at 550°C.

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