Characterization of M_2X formed during 5 MeV Fe^{2+} Irradiation

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Abstract

The growth of M_2X phase in HT9 irradiated to high dpa was explored using self-ion irradiation. HT9 was pre-implanted with 10 appm He and irradiated with a raster-scanned Fe^{2+} beam with a damage rate of $\sim 1 \times 10^{-3}$ dpa/s at 460°C. The precipitation of M_2X was observed and a combination of high resolution transmission electron microscopy (HRTEM), energy filtered transmission electron microscopy (EFTEM) and diffraction analysis was used to characterize the Cr-rich carbide observed at 250 dpa and above. Cr_2C was determined to be semi-coherent with the matrix such that $100Cr_2C//100\alpha$ and $001Cr_2C//101\alpha$ with $a=2.71$ and $c=2.82$ Å.

Ion irradiations of prospective reactor materials have pushed damage levels beyond those observed in reactor [1–6]. Recent work has confirmed that the microstructure continues to evolve even at very high levels of damage [5,6]. Perhaps even more surprisingly is the observation of the nucleation and subsequent growth of the M_2X (ϵ) phase at 250 dpa and beyond [5]. M_2X (ϵ) has previously been observed by Borodin et al. [7] after ion irradiation 13Cr-2Mo-TiO₂ with 3 MeV Cr^{3+} to 30 dpa and 150 dpa at 500°C. Rod-like precipitates (M_2X) formed by 30 dpa and grew in size up to 150 dpa. Similar M_2X precipitates were also observed by Maziasz [8] in 12Cr-1MoVW (HT9) irradiated in HFIR at 500°C to 38 dpa with 87 appm He co-generated, indicating that the phase forms both in neutron and ion irradiation. M_2X was also observed by Wang et al. in 5 MeV Fe^{2+} in Chinese Nuclear Steel (CNS) II (Fe-12Cr) irradiated at 460°C to 450 dpa [9]. Both the Borodin et al. and the Wang et al. results suggested that M_2X forms coherently within the matrix, but characterization of the precipitate has been fairly limited.

More recently, M_2X formation was observed in HT9 pre-implanted with 10 appm helium (He) and then irradiated with 5 MeV Fe^{2+} at 460°C from 250 to 650 dpa [5]. A full description of the ion irradiation experiments that produced M_2X in ion irradiated HT9 is provided in [5], but a brief description of the irradiations is provided here. Heat 84425 of ferritic-martensitic alloy HT9 is an archival heat that was used in a fuel assembly duct in the Fast Flux Test Facility (FFTF) [10,11]. The alloy was heat treated

at 1065°C/30 min followed by air cooling to room temperature (RT), followed by tempering at 750°C/60min and air cooling to RT [12,13], which resulted in the characteristic tempered martensite structure.

Prior to irradiation, samples were mechanically polished with SiC paper up to a final grit of #4000 followed by mechanical polishing with 0.25 μm diamond solution. Samples were electropolished to remove mechanical damage using a 90% methanol/10% perchloric acid solution, which was kept between -40 and -50°C for 20 s, with an applied voltage of 35 V. Samples were pre-implanted at room temperature with He using a 400 kV ion implanter at energies of 80, 140, 220, 310 and 420 keV to produce an approximately flat He concentration profile between 300 and 1000 nm. Samples were irradiated with a 3 MV Pelletron accelerator at the Michigan Ion Beam Laboratory at the University of Michigan. Nominal damage was calculated at a depth of 600 nm using SRIM in quick Kinchin-Pease mode [14]. Damage rates varied between 0.6 and 1.2×10^{-3} dpa/s. The beam was raster scanned with a scan frequency of 255 Hz $\times$ 2061 Hz. Samples were irradiated to dpa levels of 188 to 650 at 460°C. Temperatures were monitored using a 2D thermal imager and the temperature was kept within $\pm 10^\circ\text{C}$. Chamber pressure before the start of the irradiation varied from 5 to 9×10^{-8} torr ensuring a high vacuum environment.

In order to fabricate very thin (<50 nm) samples suitable for high resolution transmission electron microscopy (HRTEM), focused ion beam (FIB) liftout samples were cleaned using a final low energy (5 keV) step. For even thinner samples, several liftouts were then flash electropolished. The electropolishing solution used was 4% perchloric acid/96% ethanol. Samples were polished with an applied voltage of 12 V for 0.1 s followed by washing with cold methanol. The cold methanol wash was performed three times in total.

Energy filtered transmission electron microscopy (EFTEM) mapping was used to confirm the composition of M_2X . Supplementary X-ray energy dispersive spectroscopy (XEDS) was used to confirm stoichiometry. Coherency was assessed with a JEOL 3100 AEM in STEM HAADF and LAADF mode. Both nanodiffraction and fast Fourier transform (FFT) techniques were utilized to determine diffraction patterns and orientation relationships between M_2X and the matrix.

Low angle annular dark field (LAADF) imaging was used to examine the evolution of the precipitates with a representative image shown in Figure 1a. The image was taken near the $\mathbf{a} \langle 100 \rangle$ direction of the matrix, which shows bright plate-like features with different widths and lengths lying perpendicular to each other. Figure 1b shows the length, width, thickness, number density and volume fraction as a function of dpa. The size saturated with damage at approximately 450 dpa. The number density peaked at 450 dpa, then decreased leading to a corresponding decrease in the volume fraction.

To measure the precipitate composition, EFTEM element mapping was performed on the sample irradiated at 460°C and 450 dpa as shown in Figure 2. Figure 2a is a bright field (BF) image showing Moiré fringes indicating the location of the precipitates. Figure 2b-d are carbon, chromium and nitrogen maps, respectively, which suggest that the precipitates consist of Cr and C without no detectable N. To further confirm this observation, XEDS spectra of the much thinner flash polished samples were taken and a sample spectrum is shown in Figure 3 along with an inset showing X-ray peaks from 0 to 1 keV. The spectra confirm that the precipitate consists of mainly C and Cr. The Fe and O peaks may be from the surrounding un-etched matrix with some surface oxide. The measured composition is consistent with the data from EFTEM confirming the formation of a chromium carbide phase. It should be mentioned that N is an interstitial type solute that behaves similarly to carbon and has been observed in precipitates like M_2X in other ferritic steels [15,16]. However, no nitrogen was observed in the precipitates in the present study, which is probably due to the low nitrogen content (0.006 wt%) of this alloy [11].

To identify the crystal structure of the carbide, a tilt series of selected area electron diffraction (SAED) patterns were obtained from a single precipitate by tilting the sample along one direction to several degrees as shown in Figure 4a-c. Based on the patterns in this tilt series, the lattice structure was determined to be orthorhombic with reciprocal lattice parameters of $a^*=0.369 \text{ \AA}^{-1}$, $b^*=0.221 \text{ \AA}^{-1}$ and $c^*=0.436 \text{ \AA}^{-1}$, respectively, shown in Figure 4d. A simple real space orthorhombic unit cell is then obtained with $a_{Or}=2.71 \text{ \AA}$, $b_{Or}=4.52 \text{ \AA}$ and $c_{Or}=4.66 \text{ \AA}$. Considering that a hexagonal cell can also be drawn as orthorhombic with the relationship between those two cells of: $a_H=a_{Or}$, $b_{Or}=b_H+a_H$, and $c_H=c_{Or}$, a hexagonal cell will be approximately obtained with lattice parameters of $a = 2.71 \text{ \AA}$ and $c = 4.52 \text{ \AA}$. This means that the carbide may have a similar crystal structure as M_2X with a HCP structure [15,16] confirming that the plate-like precipitates are Cr_2C phase. Wang et al. [9] determined lattice parameters of $a=2.79 \text{ \AA}$, $c=4.4 \text{ \AA}$ for alloy CNS II, a Chinese analogue for HT9.

HRTEM was primarily used to examine coherency and orientation relationship between the Cr_2C precipitate and the matrix. Figure 5a is a HRTEM image taken from an area with both Cr_2C and the matrix along the [011] direction of the matrix. Figure 5b is a FFT pattern from the outlined region in Figure 5a showing two sets of patterns; one from the Cr_2C and one from the matrix. To index the patterns, simulated SAED patterns were obtained from the α -Fe phase and the hexagonal Cr_2C precipitate and are shown in Figure 5c. The overlap pattern of the $001Cr_2C//011\alpha$ matches well to the FFT patterns from the two phases shown in Figure 5b where green and red diffraction spots represent the Cr_2C and matrix, respectively. The orientation relationship between the precipitate and the matrix was then determined to be $001Cr_2C//101\alpha$ or $0001Cr_2C//101\alpha$; $100Cr_2C//101\alpha$ or $1120Cr_2C//101\alpha$. These growth directions of Cr_2C were consistent with recent results from Wang *et al.* in FM alloy CNS II [9]

and were also consistent with results from unirradiated, thermally aged ferritic steels with high ($\geq 17\%$) chromium content [15,16].

From the simulated SAED patterns, it is observed that the $[020]$ spot from the Fe matrix had $d=0.141$ nm and was coincident with the $120\text{Cr}_2\text{C}$ spot from Cr_2C , which had $d=0.136$ nm, a 3.5% mismatch. Furthermore, the $d[10\bar{1}]$ from the matrix and $d[100]$ from the Cr_2C precipitate were coincident with $d=0.202$ nm and $d=0.235$ nm, respectively, indicating a 16% mismatch, which indicates semi-coherency rather than true coherency. Furthermore, the growth directions of $[100]$ and $[110]$ explain the plate-like shape (Figure 1a) which was oriented on the $\{100\}$ family of planes as Cr_2C forms by growth along the $[100]$ and $[110]$ directions.

Thus, the orientation relationship between the Cr_2C precipitate and the matrix is $100\text{Cr}_2\text{C} // 100\alpha$ and $001\text{Cr}_2\text{C} // 101\alpha$. There is a mismatch in the a lattice parameter ($a=2.71$ and $c=2.82$ Å in Cr_2C and the matrix, respectively) of 3.5%, and a mismatch of 16% along the $[011]$ direction. Considering the size of the mismatch, the size of the precipitates (up to 100 nm in length) and the fact that the precipitate and matrix have different crystal structures, the precipitate is best characterized as semi-coherent with the matrix. The growth directions of the Cr_2C precipitate are along $[010]$ and $[10\bar{1}]$, which also explains the plate-like shape lying on the $\{100\}$ planes of the matrix.

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Figures

Figure 1: M_2X formed under 5 MeV Fe^{2+} irradiation at 460°C to 450 dpa with 10 appm He pre-implanted. b) M_2X evolution with damage in HT9 irradiated with 5 MeV Fe^{2+} at 460°C (from [5])

Figure 2: BF (a) and EFTEM maps (b-d) indicating Cr/C rich precipitate formation in HT9 irradiated with 5 MeV Fe^{2+} at 460°C to 450 dpa.

Figure 3: XEDS spectrum of M_2X confirming Cr_2C composition. No nitrogen observed.

Figure 4: Tilt series showing SAED patterns at tilt angles of a) 0° b) 27° and c) 43° in HT9 irradiated with 5 MeV Fe^{2+} at 460°C to 650 dpa, and d) the reconstructed reciprocal lattice from the tilt series.

Figure 5: a) HR-HAADF image of HT9 irradiated to 650 dpa at 460°C, b) FFT and c) FFT with simulated SAED pattern overlaid indicating consistency of observed pattern with simulation along the [011] direction. Green and red diffraction spots represent the Cr_2C and matrix, respectively.

(a)

(b)

Figure 1: M₂X formed under 5 MeV Fe²⁺ irradiation at 460°C to 450 dpa with 10 appm He pre-implanted. b) M₂X evolution with damage in HT9 irradiated with 5 MeV Fe²⁺ at 460°C (from [5]).

Figure 2: BF (a) and EFTEM maps (b-d) indicating Cr/C rich precipitate formation in HT9 irradiated with 5 MeV Fe^{2+} at 460°C to 450 dpa.

Figure 3: XEDS spectrum of M_2X confirming Cr_2C composition. No nitrogen observed.

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