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Relationship between lath boundary structure and radiation induced segregation in a neutron irradiated 9 wt.% Cr model ferritic/martensitic steel

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ABSTRACT

Ferritic/Martensitic (F/M) steels with high Cr content posses the high temperature strength and low swelling rates required for advanced nuclear reactor designs. Radiation induced segregation (RIS) occurs in F/M steels due to solute atoms preferentially coupling to point defect fluxes which migrate to defect sinks, such as grain boundaries (GBs). The RIS response of F/M steels and austenitic steels has been shown to be dependent on the local structure of GBs where low energy structures have suppressed RIS responses. This relationship between local GB structure and RIS has been demonstrated primarily in ion-irradiated specimens. A 9 wt.% Cr model alloy steel was irradiated to 3 dpa using neutrons at the Advanced Test Reactor (ATR) to determine the effect of a neutron radiation environment on the RIS response at different GB structures. This investigation found the relationship between GB structure and RIS is also active for F/M steels irradiated using neutrons. The data generated from the neutron irradiation is also compared to RIS data generated using proton irradiations on the same heat of model alloy.

1. Introduction

Ferritic/Martensitic (F/M) steels with a body-center-cubic (BCC) structure and 9–12 wt.% Cr alloying addition are under consideration as structural materials in the next generation of fusion and fission nuclear reactor designs. F/M steels' low swelling rate under irradiation, high strength, and corrosion resistance lend themselves to the high doses, elevated temperatures, and corrosive environments of these advanced nuclear reactor designs [1]. Although they exhibit excellent materials properties, F/M steels have been shown to be susceptible to radiation induced segregation (RIS) at grain boundaries. Segregation of Cr to grain boundaries in F/M steels due to RIS could alter the steels' performance during service depending on the magnitude of segregation. Therefore, a need exists to understand the underlying mechanisms for RIS in F/M steels.

A significant portion of the published studies on the mechanisms for RIS in F/M studies has been conducted using ion irradiations [2–15] or modeling [13,16–20] with a minority of the studies using in-reactor neutron irradiations [21–23]. Throughout these works, no consensus has been drawn on the dominant mechanisms for RIS in F/M steels. Recently, systematic ion irradiation studies on model and commercial systems have been conducted in conjunction with modeling efforts to determine the phenomena driving the RIS response in F/M steels [11–15,19]. These works have reported variability in the segregation response from boundary to boundary within the same irradiated specimen.

Recent theoretical and experimental studies on austenitic stainless steels have demonstrated the variability in the RIS response for specimens irradiated under the same conditions could be due to variances in grain boundary structure [24–26]. These findings indicate grain boundary structure, in concert with grain boundary energetics, alters the local sink efficiency resulting in changes in the point defect absorption cross section at grain boundaries. Low angle and low-Σ coincident site lattice (CSL) boundaries were found to have reduced RIS responses compared to general high angle grain boundaries due to their higher coherency, and hence low grain boundary energetics.

Work on the relationship between grain boundary structure and RIS for austenitic stainless steels has been extended to ion irradiated F/M steels [13,14]. The same dependencies found in austenitic stainless steels where found to hold true for F/M steels within these limited studies. Furthermore, the theoretical work of Duh et al. was extended to the F/M steels to develop a 1D rate theory model to capture the sink efficiency effect at different irradiated grain boundary structures in relation to RIS. For a detailed

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discussion on the rate theory model and underlying mechanisms the reader is referred to the author's previous work in Ref. [13] and the work of Barnard et al. [20] and Duh et al. [26]. These works utilized ion irradiations and modeling to evaluate the relationship between grain boundary structure and RIS, but limited work has been conducted on neutron irradiated F/M steels. This study builds on the foundation established by the ion irradiation studies and investigates the relationship between RIS and lath boundary structure in a neutron-irradiated model F/M steel in the Advanced Test Reactor (ATR).

2. Materials and methods

2.1. Experimental procedure

This study utilized the same heat of 9 wt.% Cr model steel as in Refs. [13,15]. The same heat was investigated in this study to eliminate any heat-to-heat variations. A simple model steel was used to provide a fundamental understanding of Cr segregation under irradiation without interference from other minor alloying elements. The composition of the steel is 0.015 wt.% O, 0.72 wt.% C, 8.68 wt.% Cr, and balance Fe. The steel was heat treated after arc melting by austenitizing at 950 °C for 60 min in an Ar atmosphere and cooled to room temperature followed by tempering at 750 °C for 60 min and air-cooled. Transmission electron microscopy (TEM) samples were punched to a 3 mm diameter and polished to 800 grit from the bulk material before being placed in the rodlet assemblies.

The 9 wt.% Cr model steel specimens were irradiated to 3 dpa with a target irradiation temperature of 500 °C in the Advanced Test Reactor (ATR) National Scientific User Facility at the Idaho National Laboratory (INL) as part of a pilot neutron irradiation campaign [27]. Specimens were loaded into a non-instrumented, inert gas filled rodlet-capsule enclosure, inserted into a cadmium neutron filter basket, and placed in ATR East Flux Trap where the maximum fast flux was approximated at 9.7×10^{13} n/cm^2 s ($E > 1$ MeV). Dose calculations assumed a dose of 3 dpa in a stainless steel is approximately equivalent to a neutron fluence of 2.1×10^{21} n/cm^2. Based on this assumption, the average dose rate was $\sim 1 \times 10^{-7}$ dpa/s with the reactor operating for 250 Effective Full Power Days (EFPD). This dose rate is lower than light ion irradiation dose rates that are typically in the range 10^{-5}–10^{-6} dpa/s. The rodlet containing the samples did not have instrument leads or passive temperature monitors and therefore the exact average irradiation temperature cannot be reported here. Simulations calculated the average irradiation temperature to be expected between 523–526 °C, but an adjacent rodlet during the irradiation campaign was determined to be ~100 °C lower than the simulated temperature as determined by passive SiC temperature monitors. Another adjacent rodlet did show excellent agreement between predicted and observed temperatures [28].

Scanning transmission electron microscopy (STEM) samples were fabricated using focused ion beam (FIB) lift-out techniques. The low net volume of the FIB lift-out specimens reduced the overall observed radioactivity of the samples and electron beam aberrations resulting from specimen magnetism during STEM investigations. A FEI Quanta 3D FEG DualBeam™ FIB housed at the Center for Advanced Energy Studies (CAES) was used to create three cross-sectional FIB lift-out samples from the surface of the irradiated specimens. A low angle, low keV milling was completed after thinning the samples to electron transparency to reduce gallium contamination and damage induced from the FIB.

A FEI Tecnai F30-FEG S-TWIN operated in STEM mode with an accelerating voltage of 300 kV and equipped with an EDAX energy dispersive X-ray spectroscopy (EDS) detector housed at CAES was utilized in this study to investigate microchemical variations within the irradiated specimens near lath boundaries. Lath boundaries were investigated using 2D EDS spectrum imaging. Spectrum images used a region of interest size of 48×96 nm containing 32×64 pixels, an incident probe size of ~1–2 nm at full width at half-maximum, a 1 s dwell time per pixel, and drift corrected every 32 pixels. Spectrum images were binned 32 pixels along the boundary direction to generate 1D concentration profiles from each boundary and increase counting statistics. Composition at each point was calculated assuming a normalized Fe–Cr binary system using the Cliff–Lorimer equation with experimentally determined 'k' factors. Error bars reported in 1D concentration profiles was calculated using a 99.7% confidence based on the Gaussian counting statistics of the binned EDS acquisition. 1D experimental profiles were fitted with a single Gaussian peak function to determine the segregation profiles' FWHM and peak Cr and Fe content.

The structure of each lath boundary was determined by calculating the misorientation angle and axis using diffracted Kikuchi pattern analysis. Patterns were taken in STEM mode immediately following the microchemical investigation. Diffracted Kikuchi patterns were taken at a calibrated camera length of 259 mm at the CCD. Details of the analysis to determine the misorientation between the two laths which comprised the lath boundary via Kikuchi pattern analysis can be found in Ref. [29]. Calculated misorientation angle and axis were then evaluated to determine if they met low-Σ CSL boundary criterion [30].

3. Results

Low angle, general high angle, and low-Σ coincident site lattice (CSL) boundaries were investigated after neutron irradiation. All the investigated low-Σ CSL boundaries were found to be Σ3 or near the Σ3 condition. A summary of the lath boundaries observed and their boundary classification are provided in Table 1. No prior segregation was found at either lath or prior austenite boundaries as reported in Refs. [13,15]. Neutron irradiation led to experimentally observed enrichment of Cr at lath boundaries complemented by depletion of Fe for all lath boundaries investigated, although the magnitude and width of segregation varied depending on the lath boundary structure.

Fig. 1 shows the 1D segregation profiles of select boundaries from each lath boundary type. The largest RIS response was observed in general high angle boundaries with the highest on-boundary Cr segregation at 16.7 ± 1.4 wt.% ($\theta = 47.1$ $\langle \bar{1}01 \rangle$). Low angle boundaries and near Σ3 boundaries showed similar responses with the on-boundary Cr content lower than the observed Cr segregation at general high angle boundaries. The lowest observed segregation was at the Σ3 condition with the on-boundary Cr segregation observed at 10.7 ± 0.9 wt.%.

The shape of the profiles varied from those observed in previous ion irradiation studies. Fig. 1 shows distinct regions of Cr depletion near the enrichment peak in the neutron-irradiated studies with the depleted region more pronounced at general high angle boundaries. These regions are not always observed in ion-irradiated boundaries but one explanation is if the magnitude of the depleted region is below ~0.5–1 wt.% Cr it would reside within the error of the STEM–EDS analysis technique preventing accurate detection. The Cr depleted zone near the boundary for the neutron-irradiated boundaries was observed in all boundary types as shown in Fig. 1.

The FWHM of each segregation profile was also investigated. Trends in the width of segregation mirrored the magnitude. The sharpest profiles were seen in the general high angle boundary regime while low angle grain boundaries showed a decreasing FWHM value with increasing misorientation and two out of the three low-Σ CSL boundaries having the broadest segregation