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Defect sink characteristics of specific grain boundary types in 304 stainless steels under high dose neutron environments[☆]

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Abstract—Radiation induced segregation (RIS) is a well-studied phenomena which occurs in many structurally relevant nuclear materials including austenitic stainless steels. RIS occurs due to solute atoms preferentially coupling with mobile point defect fluxes that migrate and interact with defect sinks. Here, a 304 stainless steel was neutron irradiated up to 47.1 dpa at 320 °C. Investigations into the RIS response at specific grain boundary types were used to determine the sink characteristics of different boundary types as a function of irradiation dose. A rate theory model built on the foundation of the modified inverse Kirkendall (MIK) model is proposed and benchmarked to the experimental results. This model, termed the GiMIK model, includes alterations in the boundary conditions based on grain boundary structure and expressions for interstitial binding. This investigation, through experiment and modeling, found specific grain boundary structures exhibiting unique defect sink characteristics depending on their local structure. Such interactions were found to be consistent across all doses investigated and to have larger global implications, including precipitation of Ni–Si clusters near different grain boundary types.

Keyword: Steel; Grain boundary; Irradiation; Segregation; Misorientation

1. Introduction

Numerous light water reactor (LWR) nuclear power plants in the United States with operating licenses for 40 years have undergone license renewal processes to extend their operational lifetimes up to 60 years. The drive for these life extensions has been, in part, due to the high capital cost for new nuclear power plant construction in the United States. Recently, success in proving the viability of operating LWR plants up to 60 years and limited change (or no change) in the cost of new builds has sparked interest in life extensions to 80 years and beyond. Such long operational lifetimes would significantly increase the radiation dose absorbed by core internals in these nuclear power plants.

Additionally, an interest in fast neutron fission reactors and fusion power reactor technology has pushed the radiation dose design envelope of nuclear grade materials to displacement damage dose levels greater than typical LWR conditions [1,2]. Such high doses, for any nuclear power technology, could lead to significant changes in known radiation-induced processes such as radiation hardening and embrittlement, radiation-induced/enhanced precipitation, radiation-induced segregation (RIS), irradiation creep, volumetric swelling, and helium embrittlement [2]. Hence, new materials and/or novel processing routes capable of producing materials with enhanced radiation tolerance must be developed and verified.

A review by Zinkle et al. has shown the development of materials with point defect sink strengths above $\sim 10^{16}$ m^{-2} can significantly suppress several of the radiation-induced processes seen in nuclear materials, such as radiation-induced hardening [3]. Such studies have shown the importance of the sink density to irradiation resistance, particularly when high dose applications are desired. Studies have also shown the importance of the defect sink-matrix interface in determining the strength of a particular type of defect sink [4–7]. Therefore, the irradiation resistance of a

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material can be a superposition of both the density and the sink strength of any particular defect sink in the material of interest.

Several approaches have been applied/proposed to control both the sink density and/or the sink strength in metallic nuclear materials, including the addition of a high density of nano-scaled oxide particles in steels such as oxide dispersion strengthened (ODS) steels [8–18], grain boundary engineering to increase the density of grain boundaries of a certain type [19–21], and grain refinement to develop grain sizes approaching the nanometer scale level [22–24]. RIS can serve as a metric to assess the viability of such approaches because the phenomenon is directly related to the mobile point defect flux and annihilation/absorption to/at a defect sink or cluster of sinks. RIS in its simplest form is the segregation of solute and solvent at a defect sink that has occurred due to the preferential coupling of specific alloying elements to the interstitial and/or vacancy flux at said defect sink. By comparing the magnitude of the RIS response at different defect sinks where the diffusion and irradiation parameters remain known, the variances in the point defect interactions occurring at different defect sinks can be determined. Through the coupling of modeling and experiment, further information can be extracted about the relationship between mobile point defects and defect sinks, including mechanisms such as defect sink biasing, sink–defect interaction distances, and solute–defect diffusion rates.

RIS has been successfully used to investigate the sink characteristics of specific grain boundary types in both austenitic and ferritic/martensitic steels using experiments and modeling [25–36]. These studies have shown the grain boundary type, whether a low-angle grain boundary, random high-angle grain boundary, or low-Σ coincident site lattice (CSL) boundary, will have different sink characteristics due to the local structure of the grain boundary and can be correlated to their coherency and hence grain boundary energetics. The majority of these studies were conducted using either ion irradiations or electron irradiations with no investigations at doses greater than 10 dpa. Such data provides an initial understanding on grain boundaries as sink interfaces but limits the ability to draw conclusions on the effectiveness of custom tailoring the density of grain boundary types for high-dose neutron environments such as those expected in life extended LWRs, fast fission reactors, and fusion power reactors. This study expands on these works by investigating the low to high dose (∼50 dpa) response of specific grain boundary types in a neutron irradiated 304 stainless steel irradiated at 320 °C and relates the findings toward the tailoring of the grain boundary network of a metallic material to increase the radiation tolerance of a material for high dose applications. A 304 stainless steel was used due to its well-known characteristics under irradiation and well-developed models for RIS.

2. Materials and methods

2.1. Experimental procedure for RIS quantification

This study used an industrial grade AISI 304 austenitic stainless steel from core shroud material. The nominal composition in weight percent was 19.95% Cr, 10.8% Ni, 1.82% Mn, 0.56% Si, 0.53% Mo, 0.023% C, bal. Fe. The stainless steel specimens were annealed prior to being irradiated. The alloys were irradiated in the BOR-60 fast reactor at ∼320 °C to 5.5, 10.2, and 47.1 dpa with an average dose rate of $\sim 8 \times 10^{-7}$ dpa/s [37]. The irradiated specimens are part of a cooperative research program on irradiation-assisted stress corrosion cracking (IASCC) [37,38]. In previous reports of this program [39–47], the alloy of interest is referred to as "Alloy A" or "Heat A" with AS13 referring to the 5.5 dpa specimen, AS18 to the 10.2 dpa specimen, and AS23 to the 47.1 dpa specimen, for reference. Samples were prepared for scanning transmission electron microscopy (STEM) by mechanically polishing 3 mm diameter discs punched from acquired parent material to a thickness less than ∼100 μm followed by electropolishing at −12 °C in a methanol:sulfuric (7:1) solution using a Struers Tenupol polishing unit.

A Philips CM200 FEG S/TEM operated in STEM mode with an accelerating voltage of 197 kV that is equipped with an EDAX energy dispersive X-ray spectrometer (EDS) detector was used. The accelerating voltage is the result of a post column energy filter being activated during STEM-EDS acquisition. Grain boundaries were investigated using 2D EDS spectrum maps. Spectrum images were taken with a 50 nm × 50 nm region-of-interest using 25 × 25 pixels with the grain boundary orientated running top to bottom in the image. An incident probe size of 1.5 nm with ∼1 nA of probe current was used, and acquisition was taken with 1.5 s dwell times and a drift correction every 19 pixels. Quantification of elements was completed using the Cliff–Lorimer quantification scheme assuming a normalized alloy composition with Fe, Cr, Ni, Mn, and Si. Experimentally determined '*k*' factors were calculated assuming the normalized alloy composition. Spectrum images were binned parallel to the boundary to increase counting statistics and provide an average 1D profile along the length of the grain boundary. Conditions were selected in an attempt to balance the EDS counting statistics during acquisition against issues with specimen drift and maintaining reasonable total acquisition times. Average profiles were fitted to a single Gaussian peak to determine peak height and profile full-width-at-half-maximum (FWHM). Error bars are reported using one standard deviation of the mean through binning.

The grain boundary type was determined by calculating the misorientation angle and axis using the diffracted Kikuchi patterns of each grain taken immediately following spectrum imaging. Diffracted Kikuchi patterns were taken at a calibrated camera length of 119 mm at the CCD. Patterns were indexed assuming a face-centered cubic (fcc) grain boundary structure using custom software [48]. Calculated misorientation angle/axis pairs were evaluated using the Brandon criteria [49] to determine whether random high angle (HA) grain boundaries were low-Σ (<27) CSL grain boundaries.

2.2. GiMIK rate theory model description

2.2.1. MIK model and GiMIK model

The modified inverse Kirkendall (MIK) model for Fe–Cr–Ni alloys by Allen et al. [50] has been widely used to predict RIS in irradiated austenitic (fcc) stainless steels. The MIK model was developed from the Perks' model [51]. Both models assume that RIS is due to an inverse Kirkendall mechanism. These two models are essentially