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Quantitative atom probe tomography characterization of microstructures in a proton irradiated 304 stainless steel

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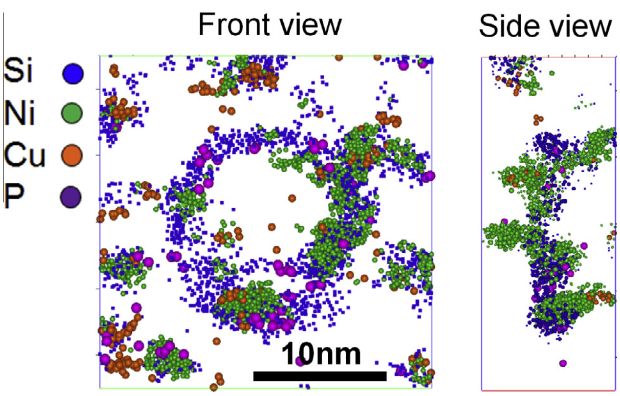
GRAPHICAL ABSTRACT



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ABSTRACT

Irradiation of 304 stainless steels induces complex microstructural changes such as solute clustering, precipitation, and segregation to dislocations, which have been best characterized by atom probe tomography. However, reliably and reproducibly quantifying these localized chemical changes can be challenging. To this end, an approach for quantitative cluster and dislocation analysis of the atom probe tomography data is proposed. The method is applied to the quantification of Cu clusters, Ni–Si rich clusters and Si, Ni and P segregation to dislocations that are observed in a 304 stainless steel that was proton irradiated at 360 °C to 10 dpa.

1. Introduction

Most structural materials in nuclear reactors are subjected to irradiation-induced degradation phenomena, which have become a critical issue in the context of life-time extension campaigns for the existing fleet of reactors [1]. Commonly observed consequences of irradiation are hardening, embrittlement, and dimensional instability including creep and swelling [2]. The microstructural changes that may be responsible for these mechanical property changes include dislocation loops, black dots, solute clustering, precipitation, and irradiation induced segregation to grain boundaries [3]. Establishing direct and quantitative relationships between microstructure and properties is not trivial because of the complexity of the microstructure involved and the challenges involved in characterizing such microstructures at the relevant nano-scale.

One of the major degradation concerns is irradiation assisted stress corrosion cracking (IASCC) [4]. IASCC is a common issue for various types of stress-bearing components including welds

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subject to residual stress that are exposed to high neutron fluences in corrosive environments [5]. It is believed that microstructural and micro-chemical modifications such as irradiation-induced segregation and precipitation are at the origin of IASCC. For decades, efforts have been pursued to understand IASCC by investigating proton or neutron-irradiated microstructures [6]. While performing mechanical property assessment can be a challenging and costly proposition, microstructural characterization may be an easier task in principle. The ultimate goal would therefore be the ability to assess or predict IASCC susceptibility or hardening based on microstructural observations of small volumes of materials. In turn, this proposition would require accurate and reproducible measurements of dislocation loops, clusters, black dots, and segregation behaviors.

Transmission electron microscopy (TEM) has been widely used for structural characterization of irradiated microstructures [7–9]. A significant number of studies regarding the influence of irradiation on size and density of precipitates, voids and dislocations, and on grain boundary chemistry can be found in the literature [3,10]. TEM is the technique of choice for measuring dislocation size and density, e.g. [11]. However, the spatial resolution of TEM limits the size of the objects that can be imaged, and the clear distinction between contrasts originating from dislocations or clusters is not always possible. In addition, the chemistries of clusters and dislocations are rarely determined due to inherent projection limitation and chemical sensitivities of electron energy loss spectrometry (EELS) or energy dispersive spectrometry (EDS) measurements. More recently, high spatial and chemical resolution microanalyses based on atom probe tomography (APT) have provided significant new insights into elemental distributions in irradiated steels. While a significant number of APT reports are available for reactor pressure vessel (RPV) ferritic steels, particularly on the formation of Cu and Ni/Si clusters, e.g. [12,13], fewer results exist regarding the presence of such features and dislocations in irradiated austenitic stainless steels [14,15]. Of note, Toyama et al. found that the Ni/Si cluster density in a high purity 304 steel measured by APT measurements [15] was one order of magnitude higher than that measured by TEM [16], highlighting the experimental issues associated with such measurements. Jiao et al. also found that the size and number density of Ni/Si clusters depend on the alloy Si concentration [14], thereby adding additional complexities to our understanding of microstructures under irradiation.

Atom probe tomography provides three-dimensional reconstructions of atoms within small volumes of materials. The technique is ideally suited for the analysis of spatial distribution and chemical composition of solute clusters. While the spatial resolution is not sufficient to determine the crystallographic structure of defects, defects such as dislocations decorated by solute elements can be visualized by APT measurements [17,18]. A summary of existing APT data analysis techniques is available in Refs. [19,20]. Nonetheless, let us summarize the maximum separation method (MSM), which is the most common method applied to APT data to identify and analyze solute clusters [21–23]. The method assigns two solute atoms to the same cluster if these atoms are separated by a distance smaller than a user-defined distance (d_{max}). Optimal selection of d_{max} is often based on the value that minimizes cluster splitting (if d_{max} is too small some clusters may be detected as multiple clusters) and cluster aggregation (if d_{max} is too large some clusters may be merged). In order to exclude possible small clusters due to random fluctuations in the matrix, clusters under a chosen critical size (N_{min}) are considered as artificial clusters and removed from the data [24]. Moreover, Stephenson et al. proposed a logical extension employing higher order nearest neighbors where a nearest neighbor distance at order of N means that the Nth nearest neighbor solute atom is located at the given distance [24]. After the core solute atoms in clusters have been defined by d_{max} an algorithm is then applied to identify other elements that may also be part of the identified clusters. In this process all atoms located within a distance L to a clustering atom will be added to that cluster [22]. L is usually called the envelope parameter. In general the same value is used for d_{max} and L. However, this step often includes parts of the matrix located at the interface. Therefore, an eroding algorithm involving a third distance, d_e, is used to remove interfacial atoms [22].

The MSM method was initially designed to investigate strong clustering behavior in dilute alloys and the output is sensitive to the choice of input parameters, which are often chosen by experience. Only limited work has been published investigating methodologies for the selection of the values for the parameters [24–27]. Quantification can become more challenging if different types of clusters involving the same solute species co-exist, if the interface between clusters and matrix is broad, or if the compositional difference between matrix and clusters is not large. The irradiated microstructures found in 304 stainless steels present all these challenges, thereby questioning the use of traditional cluster search methods to analyze such microstructures. Procedures for optimizing key parameters are proposed and the present study intends to provide a systematic and quantitative analysis of the microstructures developing in a proton-irradiated 304 stainless steel, which can be compared to TEM analysis and may ultimately be used for mechanical property and materials behavior predictions.

2. Materials and methods

2.1. Experimental

The material investigated in this study is a commercial purity 304 stainless steel (CP304). The nominal and APT-measured compositions are listed in Table 1. The irradiation experiments were conducted using protons to a dose of 10 dpa at 360 °C at a dose rate of 1×10^{-5} dpa/s at the Michigan Ion Beam Laboratory. The damage profile calculated using SRIM with full damage cascades indicates a 10 dpa damage plateau over 10 μm in depth, and a stopping distance of 20 μm [28].

Samples for scanning transmission electron microscopy (STEM) were prepared by the standard lift-out and ion beam milling procedure. STEM observations were conducted on a JEOL 2010F operated at 200 kV using a probe size of 0.2 nm with images collected by a Gatan circular bright-field detector using a camera length of 15 cm.

Needle-shaped APT specimens were prepared by the standard lift-out method and focused ion beam milling on a FEI Helios Nanolab dual beam microscope [29]. Specimens were prepared from the relatively flat dose rate region at about 10 μm under the irradiated surface. Prior to the lift-out procedure, Pt was deposited to protect the material from ion beam damage. A final 5 kV clean-up procedure was utilized to minimize the Ga damaged regions and reduce the tip radius to ~50 nm. A few APT specimens were mounted on 3 mm diameter Cu half grids allowing TEM observations prior and following APT data collection from these specimens. APT specimens were analyzed using a LEAP-4000XHR microscope operated in electrical mode with a voltage pulse fraction of 20%. Specimen temperature was maintained at 35 K and detection rate was kept constant at 0.005 atom/pulse. Reconstruction of the relative atom positions from the raw data was performed using the commercial software, IVAS 3.6.4 from CAMECA™. Whenever possible, specimens were imaged by TEM before and after APT analysis and the observed tip shapes were used for data reconstruction. A sphere-cone radius ratio of 1.55 was used to match the length of the evaporated volume [30]. When TEM observations were not possible, the data was reconstructed assuming that clusters have a spherical