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# Irradiation-induced microchemical changes in highly irradiated 316 stainless steel

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ABSTRACT

Cold-worked 316 stainless steel specimens irradiated to 74 dpa in a pressurized water reactor (PWR) were analyzed by atom probe tomography (APT) to extend knowledge of solute clusters and segregation at higher doses. The analyses confirmed that those clusters mainly enriched in Ni–Si or Ni–Si–Mn were formed at high number density. The clusters were divided into three types based on their size and Mn content; small Ni–Si clusters (3–4 nm in diameter), and large Ni–Si and Ni–Si–Mn clusters (8–10 nm in diameter). The total cluster number density was 7.7 × $10^{23}$ $m^{-3}$. The fraction of large clusters was almost 1/10 of the total density. The average composition (in at%) for small clusters was: Fe, 54; Cr, 12; Mn, 1; Ni, 22; Si, 11; Mo, 1, and for large clusters it was: Fe, 44; Cr, 9; Mn, 2; Ni, 29; Si, 14; Mo,1. It was likely that some of the Ni–Si clusters correspond to $\gamma'$ phase precipitates while the Ni–Si–Mn clusters were precursors of G phase precipitates. The APT analyses at grain boundaries confirmed enrichment of Ni, Si, P and Cu and depletion of Fe, Cr, Mo and Mn. The segregation behavior was consistent with previous knowledge of radiation induced segregation.

## 1. Introduction

It is well known that structural components made of stainless steels (SSs) located near the core region of light water reactors (LWRs) become susceptible to irradiation assisted stress corrosion cracking (IASCC) in coolant water. IASCC is caused by changes in material properties such as strength, ductility, deformation mode and corrosion resistance, which are induced by microstructural and microchemical changes under neutron irradiation. The characteristics of microscopic changes and their role in property changes have been extensively studied [1–3] mainly by using transmission electron microscopy (TEM). Recent atomic-scale studies using atom probe tomography (APT) [4–12] have provided new findings on microchemical evolution in neutron irradiated SSs, cold-worked 316 SS to 12 dpa [4,5], 304 SS to 24 dpa [8,9], 304L and 316L SSs to 3–13 dpa [10], and in proton irradiated 304 SS to 10 dpa [7,12] and in heavy ion irradiated 304 and 316 SSs up to 260 dpa [11]. The APT analysis at grain boundaries [5–7,9] revealed the same segregation trends of Fe, Cr, Ni, Si and Mo as those confirmed by TEM measurements and the theory of radiation-induced segregation. A high resolution of APT analysis also provided data on behavior of minor elements such as enrichment of B and Cu in some SSs [7]. Segregation to dislocation loops or dislocation segments, enrichment of Ni and Si and depletion of Fe and Cr were also evidenced in the APT analysis [6,7,10,12].

The APT studies commonly confirmed the formation of solute clusters in the grains, which mainly contained Ni and Si and had cluster diameters less than 20 nm. Solute clusters in irradiated stainless steels found in the literature were summarized in Table 1. It was also found that some clusters contained P and Mn in 304 SS irradiated to 24 dpa [8]. Furthermore, clusters containing Al and Cu were found in some SSs [7,10,12]. Although the clusters containing Ni and Si (often referred to as Ni–Si clusters) were believed to have some relationship with known precipitates containing Ni and Si such as γ' ($Ni_3Si$) and G-phase ($M_6Ni_{16}Si_7$, M = Mn, Mo) precipitates, the exact nature of the clusters has not been clarified. A wide variety of cluster compositions observed in irradiated SSs is likely to originate from the varieties of material type and irradiation conditions. However, general understanding of the microchemical evolution in SSs under irradiation based on metallurgical knowledge has not been established yet. Further analytical studies of irradiated SSs are needed to get such understanding. In this study,

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**Table 1**
Solute clusters in irradiated stainless steels.

| Material | Particle | T (K) | Dose (dpa) | Solute clusters | Ref. |
|---|---|---|---|---|---|
| CW316 SS | Neutrons | 633 | 12 | Si atmospheres<br>Ni–Si enriched clusters | [4] |
| 304 SS | Neutrons | 573 | 24 | Ni–Si ppts<br>Mn & P enrichment in some ppts | [8] |
| 304 SS | Neutrons | 561 | 5.5 | Ni/Si-enriched and C-enriched clusters | [10] |
| 304L SS | Neutrons | 561 | 3.6–13 | Ni/Si-enriched, Ni/Si, Al-enriched, Cu-enriched, and C-enriched clusters | [10] |
| 316L SS | Neutrons | 561 | 6.7 | Ni/Si-enriched and Ni clusters | [10] |
| 304 SS | Protons | 633 | 10 | Cu and Ni–Si rich clusters | [12] |
| 304 SS | Protons | 633 | 5 | Ni/Si-rich and Cu-rich clusters | [7] |
| 304L &316 SS | Fe ions | 653 | 46,260 | Ni/Si-rich clusters | [11] |

cold-worked 316 SS specimens irradiated to 74 dpa in a pressurized water reactor (PWR) were analyzed by APT to extend knowledge of solute clusters and segregation at higher doses. Such knowledge is important to understand irradiation induced degradation of core internals during extended operation of PWRs.

## 2. Experimental procedures

A flux thimble tube (FTT) made of 15% cold-worked SUS316 (CW316) SS that had been used for core neutron monitoring in a PWR for 16 cycles was examined. The FTT had an outer diameter of 7.62 mm, inner diameter of 5.14 mm and wall thickness of 1.24 mm. The chemical composition (wt%) was: C, 0.04; Si, 0.62; Mn, 1.63; P, 0.022; S, 0.006; Ni, 12.61; Cr, 16.94; Mo, 2.22. The material was solution annealed at 1038 to 1177 °C and then cold worked to 15% thickness reduction. The average grain size was ~10 μm. The initial dislocation density was $3 \times 10^{15}$ $m^{-2}$. Data on the microstructure obtained by TEM and material properties such as IASCC behavior and mechanical properties have already been published in the literature [13–19]. In this study, specimens for APT analysis were prepared from the selected region of the FTT where the irradiation dose was 74 dpa. The dose rate and temperature were $1.5 \times 10^{-7}$ dpa/s and 305 °C, respectively.

Two small blocks that included one grain boundary each were cut from the FTT by focused ion beam (FIB) processing. These grain boundaries were high-angle boundaries with a misorientation angle of 27° and 49°, which were selected by using electron back scattering diffraction (EBSD) measurements. Needle specimens for APT analysis were prepared with a FIB/SEM apparatus (Hitachi NB-5000). Needle specimens containing the grain boundary were processed in such a way that the grain boundary was located at a distance of 100–200 nm from the tip by repeated FIB processing with position confirmation by TEM observations. A final 2 kV procedure was utilized to minimize the Ga damage regions.

APT analysis was conducted using a local electrode three-dimensional atom probe (LEAP 3000X HR) by CAMECA. Standard measuring conditions were as follows: laser pulse mode, specimen temperature of 35 K, laser output of 0.3 nJ, and initial pulse frequency of 200 kHz. The resulting data, which were determined by mass-to-charge ratios using specialized software, were used to generate three dimensional atom maps for each of the chemical elements, such as Fe, Cu, Ni, Fe/Ni-58, Mn and Si. For the reconstruction process, an evaporation field of 30.0 V/nm was used to optimize the length in the z-direction in the atom map. The reconstruction parameters have been optimized by the direct comparison of the arrangement of grain boundaries in between the TEM image from TEM observations and the atom map from APT analysis. Elements with an indicated mass of 58, were regarded to be Ni in this measurement. This was the most reasonable assumption based on the bulk concentrations and isotope ratios.

## 3. Results

### 3.1. Solute clusters in the grains

Fig. 1 shows an example of atom maps in a grain obtained from a specimen. There were areas where Ni and Si were enriched, forming solute atom clusters. These clusters were observed in all specimens, indicating that solute atom clusters formed inside grains at high densities. The clusters were roughly of two sizes; a few larger clusters of ~10 nm in diameter, and many smaller clusters of ~5 nm. Some of the larger clusters also had enrichments of Mn and P. Fig. 2 is the atom map of Si showing a circular shaped enrichment area. Enrichment of Ni and depletion of Fe and Cr were also observed at the same circular region that showed Si enrichment. This type enrichment is likely to correspond to radiation induced segregation to a dislocation loop as observed in numerous previous APT studies [4–7,10–12]. Fig. 2 shows such an example for a relatively large dislocation loop (~20 nm in diameter).

Cluster analysis was performed on the measurement results using a recursive search method based on the maximum separation method [20]. This method is used to extract solute atom clusters with a diameter of several nm that form in steels of reactor pressure vessels due to neutron irradiation. In this analysis, cluster core elements are defined, and clusters are extracted targeting the neighboring core atoms within the given distance. Then, all the atoms existing within the given distance from each core atom are extracted (hereinafter 'surrounding atoms'). Finally, the number of core atoms existing within the given distance from each surrounding atom is counted to eliminate surrounding atoms that have an insufficient number of core atoms around them. In this analysis, Si was defined as a core element of a cluster, and with a core atom extraction threshold distance of 0.7 nm, only the aggregates with more than 20 core atoms in this 0.7-nm range were treated as clusters. The core atom extraction threshold distance was determined based on the fact that when the threshold distance is set to 0.5 nm, larger clusters tend to be divided for extraction because the distance is too close. A threshold distance of 0.6 nm was considered still too close because while large and clear clusters could be extracted almost always properly, it was impossible to extract small clusters or diffuse clustering. However, with too large thresholds, multiple clusters were extracted as one. Thus, 0.7 nm was thought to be an appropriate threshold. Ni atoms also clearly cluster and are therefore thought to be core atoms, however, proper extraction of Ni clusters was not possible. This is because; Ni is a major constituent of stainless steel and it is contained in the studied material at high concentrations, and therefore, when extracting Ni clusters based on the assumption that a Ni atom is a core atom, small clusters that resulted from the Ni concentration variation were extracted in large numbers, and at the same time, multiple clusters often tended to be extracted as one cluster. For this reason,