Grain-boundary structure and segregation behavior in a nickel-base stainless alloy

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Atom-probe tomography (APT) is utilized to obtain three-dimensional chemical information concerning grain boundary (GB) segregation in a Ni–Cr–Fe alloy 600 with atomic spatial resolution. Detailed crystallography of GBs is determined using an approach that combines electron backscatter diffraction and focused ion-beam microscopy to establish a GB’s five macroscopic degrees of freedom, followed by an APT GB composition analysis. Characterizations of GB microstructure and microchemistry are performed to improve our understanding of mechanisms controlling intergranular attack and stress-corrosion cracking.

Keywords: Grain boundary composition; Grain boundary structure; Segregation; Nickel-base alloy; Atom-probe tomography

Nickel-base stainless alloys are widely used in high-temperature, pressurized water nuclear-reactors (PWRs) because of their excellent corrosion resistance and small thermal expansion coefficients [1,2]. Despite these advantages, certain alloys (e.g. alloy 600) have exhibited intergranular stress-corrosion cracking (IGSCC) in service. One of the most important microstructural factors of IGSCC is grain boundary (GB) structure; for example, coincident site lattice (CSL) GBs are more immune to IGSCC than high-angle GBs [3]. GB structure is also closely linked with GB–solute interactions [4,5]. The degree of segregation at individual GBs depends on their structure and energy with the maximum enrichment occurring at random high-energy GBs, with minimal enrichment at coherent Σ3 twins in face-centered cubic metals, which have low interfacial energies.

Equilibrium segregation of a solute species, i, at a GB is described by the Gibbbsian interfacial excess [6], Γi, at constant temperature and pressure. Segregation at GBs has been most commonly performed using scanning Auger microscopy or analytical transmission electron microscopy (ATEM). Both techniques have significant limitations. An alternative approach is atom-probe tomography (APT), where a true three-dimensional (3-D) atomic-scale compositional analysis is capable of determining Γi, plus the distribution of solute atoms in individual atomic-planes with subnanoscale spatial resolution [7–9].

There are five macroscopic degrees of freedom (DOFs) needed to establish a GB’s phase space [10,11]: a unit rotation vector, c (two DOFs), the rotation angle, θ, about c (one DOF), and the unit normal, n, to the GB plane (two DOFs). The five DOFs of a GB are essential for making quantitative measurements of Γi, which is a thermodynamic quantity, but its experimental determination is a formidable task. One approach for determining the DOFs of a GB employs transmission electron microscopy (TEM), which can be utilized for a GB in an APT microtip [12,13]. TEM convergent-beam electron-diffraction (CBED) is utilized to characterize the complete crystallography of internal interfaces, which requires complex procedures. Electron backscatter diffraction (EBSD) offers another method to determine a GB’s crystallography by employing Kikuchi diffraction patterns [14,15]. In addition, 3-D EBSD in combination with dual-beam focused ion-beam (FIB) microscopy yields large data sets of the five DOFs of GBs [16]. Recently, site-specific analysis of solute–atom segregation was introduced for studying a CSL GB using EBSD/FIB in an APT experiment [17]. However, this does not provide a full description of the GB characterization.

This article presents measurements of GB segregation studies with APT for a GB, where its five macroscopic
DOFs have been determined by EBSD. The material studied is a commercial Ni-base alloy 600 (heat WF675), produced as forged thick-wall tubing with the nominal composition 16.05Cr–8.8Fe–0.81Mn–0.06C–0.45Si–0.02Cu–0.04Co–0.53(Al + Ti) at.%. The final thermal treatment for this tubing was reported as 820 °C for 2 h, and it has been shown to be susceptible to IGSCC in PWR primary water [18].

EBSD characterizations were performed with a field-emission gun scanning electron microscope (FEI Quanta 600F) equipped with an HKL Nordlys S camera. The accelerating voltage and working distance were 15 kV and 10 mm, respectively, with the sample stage tilted by 70° with respect to the surface normal. The EBSD sample surface was prepared by electro polishing in a 6% perchloric acid and 10% butoxy electrolyte at −30 °C. Ar+ ion milling (2 kV, 6 mA, 6° with respect to the surface) was then performed to remove residual chemicals.

A local-electrode atom-probe (LEAP) 4000X-Si tomograph was employed to measure GB composition on APT micro-tip samples prepared by lifting-out specimens from selected regions of the EBSD-characterized bulk sample. This was accomplished utilizing Ga+ ion milling in a FEI Helios FIB microscope with a final Ga+ energy of 2 kV at 24 pA. Ultraviolet laser light (355 nm wavelength) pulses were applied to the APT specimen at a pulse repetition rate of 2.5 kHz, 0.2 nJ pulse−1, and an average detection rate of 0.02 ions pulse−1. APT measurements were conducted under ultrahigh vacuum (<2 < 10−11 Pa), with the micro-tip at 66.8 ± 0.3 K. These conditions yield optimal compositional accuracy for a Ni–Al–Cr alloy [19]. Data analysis was performed on the 3-D reconstructions, utilizing Cameca’s IVAS 3.4.1 code. The detection efficiency is 50–60%, which is the same for all elements. Compositional information was obtained employing the proximity histogram methodology for APT, which does not involve detection efficiency [20].

Figure 1a displays an EBSD orientation map. The grains are specified by their misorientation, which is >5°, and colored according to their Euler angles. A twin boundary is characterized by a 60°/[111] angle/axis pair, with a 2° deviation, and indicated by white lines, grains nos. 3 and 4. The black spots in the GB between grains nos. 1 and 2 are unindexed regions, which are most likely carbide precipitates. From the EBSD Kikuchi pattern indexing, the rotation of each grain is calculated and displayed as Euler angles (φ1, Φ, φ2; Bunge notation) [21]. The angular relationship between two grains is expressed by a rotation matrix, g, which is computed from the Euler angles as follows:

\[
g = g(φ_2)g(Φ)g(φ_1) \quad (1)
\]

A rotation matrix, R12, between two grains is then calculated from g1 and g2:

\[
R_{12} = g_2 g_1^{-1} = \begin{pmatrix} r_{11} & r_{12} & r_{13} \\
 r_{21} & r_{22} & r_{23} \\
 r_{31} & r_{32} & r_{33} \end{pmatrix} \quad (2)
\]

R_{12} yields the angle (θ)/axis (ε) pair, which describes the rotation of a grain about a specific [hk] direction. In a cubic crystal, there are 24 possible symmetry rotations for two grains and one mirror imaging plane (m), yielding 1152 equivalent forms of R_{12}. The rotation with the smallest rotation angle between two grains in the standard stereographic triangle is the disorientation angle [22]. This minimum value of the angle (θ)/axis (ε) pair is found from R_{12}'s components:

\[
θ = \cos^{-1} \left( \frac{1}{2} (r_{11} + r_{22} + r_{33} - 1) \right) \quad (3)
\]

\[
c = \left[ c_1, c_2, c_3 \right] = \frac{1}{2 \sin θ} \left( r_{32} - r_{23}, r_{13} - r_{31}, r_{21} - r_{12} \right). \quad (4)
\]

From the angle (θ)/axis (ε) disorientation pairs, three DOFs are determined between two grains. The other two DOFs, the normal (n) to the GB plane, are obtained from the two-surface sectioning method [14]. This method is implemented using a dual-beam FIB microscope during APT micropit preparation. The GB line angle (z_M), from the x_o-axis, is determined using the EBSD map, while the other mutually perpendicular line angle (β_M), from the rotated axis (y') in the sectioned surface, is measured using FIB sectioning. The new y-axis (y') is rotated by the angle α from the y_o-axis, which is displayed in Figure 1b. The true GB line angles (α, β) are corrected for the SEM's tilt-angles (θ, φ) from the measured angles (z_M, β_M):

\[
α = \tan^{-1}(\tan z_M / \cos θ), \quad β = \tan^{-1}(\tan β_M / \cos (90 − φ)); \quad (5)
\]

Where θ is the EBSD sample tiltangle (70°) and φ is the FIB’s ion and electron-gun tilt angle (52°). Figure 1b displays a stereogram illustrating the calculation of n1 of grain 1 by tracing the two points of the line directions (0.5°, 64.3°). Table 1 lists the three Euler angles, GB line angles (α, β), and the five DOFs of the GB for four different grains (yellow arrow in Fig. 1a). The measurement...
strongest segregant at the GB, and is sensitive to elastic strain fields because of its small size and electrical covalent bonding with Ni [26]. Phosphorous also exhibits a weak asymmetric concentration profile. This asymmetry may also be affected by the UV laser-assisted evaporation of atoms because of the different evaporation fields of the alloying elements. Simultaneous Ni-enrichment and Cr-depletion are observed near this GB; this is related to the formation of an adjacent Cr-rich carbide and is not due to equilibrium segregation [27]. Many other elements, e.g. Si, C, Ti, B and P, are only enriched at the GB, consistent with local equilibrium segregation.

The equilibrium Gibbsian interfacial excess of an element \( i \), \( \Gamma_i \), is defined by the excess number of solute atoms \( i(N_i^{\text{excess}}) \) per unit area (A). \( \Gamma_i \) can be calculated for an arbitrary interface using a proxigram and is defined by [20]:

\[
\Gamma_i = N_i / A = \rho \Delta x \sum_{j=1}^{p} (c_j^i - c_0^i),
\]

where \( \rho \) is the atomic density (90.17 atoms \( \text{nm}^{-3} \) for a Ni–Cr alloy); \( \Delta x \) is the distance between the \( p \)-layers in the proxigram; and \( c_0^i \) is the average concentration of element \( i \) in the

**Table 1.** Measured Euler angles, GB line angles \( (\alpha, \beta) \), and calculated five DOFs for the four different GBs indicated in Figure 1.

<table>
<thead>
<tr>
<th>Grainno numbers</th>
<th>Euler angles ( (\phi_1, \Phi, \phi_2) )</th>
<th>GB angles ( (\alpha, \beta) )</th>
<th>5 DOFs of GB ( (c, \theta, n_1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63.6, 47.5, 60.7</td>
<td>0.5, 64.3</td>
<td>[201], 36.5, (365)</td>
</tr>
<tr>
<td>2</td>
<td>165.0, 29.8, 75.8</td>
<td>25.4, 98.4</td>
<td>[221], 43.6, (8T7)</td>
</tr>
<tr>
<td>3</td>
<td>41.3, 16.3, 2.1</td>
<td>0.3, 77.7</td>
<td>[T11], 60. (T11)</td>
</tr>
<tr>
<td>4</td>
<td>301.1, 43.5, 41.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 2.** The dual-beam FIB microscope lift-out technique procedure for preparing an APT micro-tip: (a) wedge-shaped piece \( (30 \times 5 \mu m^2) \) cut from the region-of-interest to measure the vertical angle \( \beta_M \) of a GB; (b) rotation of sample to set a horizontal GB plane; (c) welding and cutting the sample to a Si micropost; and (d) Ga\(^+\) ion-milling to form a sharp APT microtip.

<table>
<thead>
<tr>
<th>Grainnumber</th>
<th>GB plane</th>
<th>GB angle ( (\alpha, \beta) )</th>
<th>5 DOFs of GB ( (c, \theta, n_1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[201]</td>
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<td>4</td>
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</table>

**Figure 3.** 3-D APT reconstruction, containing \( 3.1 \times 10^8 \) atoms, and elemental distributions in the GB: (a) 3-D APT reconstruction display of the GB with nickel (small green spots), carbon (black spheres), silicon (dark green spheres), boron atoms (blue spheres), and phosphorous (purple spheres); and (b) Concentration profiles for each atomic species obtained using a proximity histogram (proxigram) analysis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 2.** Atomic concentrations of solute atoms and Gibbsian interfacial excesses \( \Gamma_i \) at the GB between grain nos. 1 and 2, which is described by \( c = [201], \theta = 36.5, n_1 = (365) \).

<table>
<thead>
<tr>
<th>Solute atom</th>
<th>( c_i^{\text{extr}} ) (at.%)</th>
<th>( c_0^i ) (at.%)</th>
<th>( \Gamma_i ) (atom ( \text{nm}^{-2} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>9.50 ± 0.10</td>
<td>8.97 ± 0.13</td>
<td>-2.45 ± 0.27</td>
</tr>
<tr>
<td>C</td>
<td>0.23 ± 0.02</td>
<td>0.65 ± 0.02</td>
<td>1.89 ± 0.34</td>
</tr>
<tr>
<td>Si</td>
<td>0.52 ± 0.03</td>
<td>1.04 ± 0.03</td>
<td>1.93 ± 0.35</td>
</tr>
<tr>
<td>Ti</td>
<td>0.25 ± 0.02</td>
<td>0.51 ± 0.02</td>
<td>1.24 ± 0.23</td>
</tr>
<tr>
<td>B</td>
<td>0.02 ± 0.006</td>
<td>1.13 ± 0.04</td>
<td>10.39 ± 0.47</td>
</tr>
<tr>
<td>P</td>
<td>0.006 ± 0.002</td>
<td>0.14 ± 0.01</td>
<td>0.63 ± 0.05</td>
</tr>
</tbody>
</table>
matrix. The concentrations in grain no. 1 and at the GB (maximum at.% and $\Gamma_5$ at the GB between grain nos. 1 and 2) are listed in Table 2. Fe has a negative value of $\Gamma_5$ (depletion), while Si, C, Ti, B and P, exhibit positive $\Gamma_i$ values (segregation). Boron is segregated significantly at the GB with a maximum $\Gamma_B$ of 10.39 ± 0.47 at. % nm$^{-2}$. The elements Fe, C, Si, Ti and P segregate with $\Gamma_i$ values of $-2.45 \pm 0.27$, $1.89 \pm 0.34$, $1.93 \pm 0.35$, $1.24 \pm 0.23$ and $0.63 \pm 0.05$ at. % nm$^{-2}$, respectively. These $\Gamma_i$ values at the GB are local-thermodynamic equilibrium values; this specific GB is described by its Gibbsian excess employing 3-DAPT experiments. The concentrations in grain no. 1 and at the GB (maximum at.) are listed in Table 2. Fe has a negative value of $\Gamma_5$ (depletion), while Si, C, Ti, B and P, exhibit positive $\Gamma_i$ values (segregation). Boron is segregated significantly at the GB with a maximum $\Gamma_B$ of 10.39 ± 0.47 at. % nm$^{-2}$. The elements Fe, C, Si, Ti and P segregate with $\Gamma_i$ values of $-2.45 \pm 0.27$, $1.89 \pm 0.34$, $1.93 \pm 0.35$, $1.24 \pm 0.23$ and $0.63 \pm 0.05$ at. % nm$^{-2}$, respectively. These $\Gamma_i$ values at the GB are local-thermodynamic equilibrium values; this specific GB is described by its Gibbsian excess employing 3-DAPT experiments.

GB characterization and its associated Gibbsian interfacial excess of a solute species are important for understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC.

In this article, a novel approach for determining the five macroscopic DOFs of a GB in conjunction with measuring its Gibbsian excesses employing 3-DAPT experiments is presented. Combined EBSD/FIB techniques yield a full macroscopic description of a GB in an APT microtip. GB characterization and its associated Gibbsian interfacial excess of a solute species are important for understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC. GB segregation phase-space is a function of GB structure, i.e. the five macroscopic DOFs, which enables understanding GB properties and physical behavior, specifically IGSCC.

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