THE STRUCTURE AND COMPOSITION OF A Σ = 9 INTERFACE IN A Mo(Re) ALLOY VIA TRANSMISSION ELECTRON AND ATOM-PROBE FIELD-ION MICROSCOPES

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Introduction

We present the results of a combined classical transmission electron microscope (CTEM) and atom-probe field-ion microscope (APFIM) study of Re segregation at a grain boundary (GB), which is within Σ = 0.4° of a Σ = 9 coincidence-site lattice (CSL) orientation, in a Mo-5.4 at.% Re alloy; Re is used to improve the ductility and toughness of Mo [1]. The APFIM measurements show that the minimum Re concentration at this GB is Σ = 1.75x greater than its concentration in the single-phase matrix. This demonstrates in a direct and quantitative manner that a high-angle GB with a small Σ value (Σ = 9) exhibits segregation; i.e., at a so-called low-energy interface. This is consistent with our Monte Carlo simulations of solute-atom segregation to small Σ{001} twist and Σ = 5 tilt boundaries in a Pt-1 at.% Au alloy; the Au segregation is mainly to the cores of dislocations and the enhancement factors are in the range Σ = 1.2 to 3.5 [2].

Experimental Procedures

Specimen Preparation

The research was performed on a Mo-5.4 at.% Re alloy in the form of a wire (Σ = 0.2 mm diam.), which was first recrystallized at 1,773 K for one hour and then heat treated at 1,273 K for 35 h to induce solute-atom segregation; the calculated root-mean squared diffusion distance is Σ = 20 nm. The wire specimen was next electropolished to a sharply-pointed tip at 6 to 9 Vdc in an Σ = 0.013 vol.% solution of H₂SO₄ acid in methanol. The specimen was then systematically backpolished (Fig. 1) to move the GB to the tip’s volume, employing a versatile electropolishing (or etching) system [3]. Frequencies up to 20 kHz and a voltage of Σ = 8 Vac were used for backpolishing in the solution -- 15 cc deionized H₂O, 2 g potassium sulphite and Σ = 0.5 % hydroquinone.

The APFIM specimen was crystallographically analyzed utilizing a radically modified double-tilt stage [3] for an Hitachi H-700H 200 kV TEM. This double-tilt stage and TEM were also used to monitor the APFIM specimen during the course of the backpolishing procedure used to place a GB in the tip portion of an FIM specimen. Our approach for preparing FIM specimens has built on the pioneering work of Nordén et al. [4,5].

Chemical Analysis of the Grain Boundary

The GB is aligned so that its plane is centered symmetrically within the projection of the probe hole on the surface of the specimen. In addition, the GB plane contains the geometric axis of the cylinder of material analyzed. In this arrangement the mean composition of the cylinder of alloy is determined. For this well defined geometry there is a simple geometric correction to the measured composition of the interface, as the matrix contributes solute atoms in addition to the interface [6]. The value of <c₅s₅b> is given by the approximate equation, which obtains for the condition (2η/Dₕ) < 1 [6]:

\[
\langle c₅s₅b \rangle^* = \langle c₅s₅b \rangle + \left( \frac{\pi Dₕ}{8 \eta} \right) \left( \frac{1}{\langle c₅s₅b \rangle} - \frac{\pi Dₕ}{8 \eta} \right) \]

(1)

where <c₅s₅b> is the concentration of solute at the interface; <c₅s₅b> is the uncorrected mean value of the GB.
concentration-- i.e., the measured value; \( <c_s> \) is the mean solute concentration of the matrix; and \( D_a \) is the projected diameter of the probe hole, which is determined from an FIM image. In Eqn. (1) \( \eta \) is the half-width of a linear distribution, measured at the point where the concentration profile intersects the constant \( <c_s> \); [6]. The exact form of Eqn. (1) does not depend on the condition \( 2\eta/D_a < 1 \), but it is algebraically more complicated [6].

**Experimental Results**

**Transmission Electron Diffraction Analysis of the Grain Boundary**

Figure 2 exhibits a sequence of four selected area electron diffraction patterns (SADPs) which were used to determine the misorientation of the GB shown in Fig. 1. The quantities G1 and G2 denote the two grains. The letter B denotes the directions of the incident electron beam. Each grain was tilted to two low-index poles -- i.e., the 001 and 311 poles -- until the diffracted intensities were symmetric with respect to the 000 spot. Operationally this consisted of first obtaining an SADP (A) for G1 and then tilting 25.4° so \( B = [1,-1,3] \) -- see SADP (B). The same procedure was repeated for G2 -- see SADPs (C) and (D) -- except in this case the direction of tilt was in the opposite sense; note the signs of \( B \). The 180° ambiguity was removed by recording the direction of motion of the Kikuchi lines when tilting from one pole to another. The misorientation (\( \theta \)) of G1 with respect to G2 is \( \equiv 38.5^\circ \) about the \( \equiv (1/\sqrt{2})[1,1,0] \) axis (c); the latter is also the axis of the APFIM wire specimen. This result was verified by analyzing the FIM images. The GB normal was determined from the trace of the GB, and the orientation of the trace from an SADP. From this analysis the GB normal \( (n_1) \) is \( \equiv (1/3\sqrt{2})[-1,-1,4] \) with respect to G1. In summary, the GB plane is \( \equiv (-1,-1,4) \) and the misorientation is \( \theta = 38.5^\circ \) about the \( c_1 \equiv (1/2)[1,1,0] \) direction; this is within \( \pm 0.4^\circ \) of a \( \Sigma = 9 \) CSL orientation.

**Transmission Electron Microscope and O-Lattice Analyses of the Grain Boundary**

Figure 3 exhibits the GB whose \( n \) and \( c \) vectors we determined. The projected distance between the dislocations is \( \approx 11.0 \) nm and the actual distance is \( \approx 11.4 \) nm.\(^1\) For the bcc lattice the measured values of \( c \) and \( n \) are very close -- within \( \pm 0.4^\circ \) of the exact \( \theta \) value -- to the \( \Sigma = 9 \) CSL orientation; the exact CSL orientation is \( \theta = 38.94^\circ \) for \( \Sigma = 9 \) [9]. This GB is a mixed tilt-twist boundary; since the angle between \( c_1 \) and \( n_1 \) is 109.47° it is mainly a tilt boundary with a twist component.

The spacings between the primary grain boundary dislocations (PGBDs) are calculated using Bollmann's O-Lattice theory. The central equation of his theory [9] is:

\[
X_i = \left( I - A^{-1} \right)^{-1} b_i ;
\]

where the \( X_i \)'s are O-Lattice vectors, \( I \) is an identity matrix, \( A \) is an affine transformation matrix, and the \( b_i \)'s are the Burgers vectors of the PGBDs. For our case \( A \) is a rotation matrix (\( R \)) for the \( \Sigma = 9 \) boundary and it is given by:

\[
R = \begin{bmatrix}
8 & 1 & 4 \\
1 & 8 & 4 \\
4 & 4 & 7 \\
\end{bmatrix}
\]

Taking the \( b_i \)'s to be lattice vectors of the bcc lattice which are perpendicular to the tilt axis \( (1/\sqrt{2})[1,1,0] \) -- i.e., the two \( b \)'s are \( b_1 = (a/2)[1,-1,1] \) and \( b_2 = (a/2)[-1,1,1] \) -- we calculate the O-Lattice vectors \( X_1 \) and \( X_2 \) in the \((110)\) plane using Eqn. (2). The calculated O-Lattice vectors \( X_1 \) and \( X_2 \) are then projected onto the

\(^1\)The observed line contrast effects are due to dislocations -- not Moiré fringes -- as changing the diffraction conditions by tilting the specimen and noting that the image persisted even though the projected spacing between the lines changed [7,8]; it is expected that a Moiré pattern should change due to this procedure[8].
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(-1,-1,4) plane according to the following equation:

\[ X'_i = X_i + \frac{(X \times \mathbf{n})}{|\mathbf{n}|} \cdot \mathbf{c}. \quad \text{(4)} \]

Equation (4) is for the case where the O-Lattice vectors are perpendicular to the rotation vector \( \mathbf{c} \). The projections of the O-Lattice vectors are used to calculate the spacings between the PGBDs \( (d_1 \text{ and } d_2) \) in the (-1,-1,4) plane from the following equations:

\[ d_1 = \frac{|X'_1 \times X'_2|}{|X'_1|} \quad \text{and} \quad d_2 = \frac{|X'_1 \times X'_2|}{|X'_2|}. \quad \text{(5)} \]

The value of the lattice parameter \( a \) is 0.315 nm, and for the above \( b_i \)'s the values of \( d_1 \) and \( d_2 \) are 0.399 and 0.604 nm, respectively, for the PGBDs. It is impossible to observe these spacings employing a CTEM and, therefore, the dislocations in Figs. 2 and 3 must be secondary (S) GBDs.

Atom-Probe Field-Ion Microscope Analysis of the Grain Boundary

Figure 4 is an integral profile displaying the data taken from the single-phase matrix. The local fluctuations about this mean represent random solid-state fluctuations caused by the size of the sample [6]. The slope of the profile is equal to \( \langle c_s \rangle \); its value is 5.6 \pm 0.3 at.% Re, which is good agreement with the nominal concentration of 5.4 at.% Re supplied by the manufacturer. (A chemical analysis of a bulk specimen by Ledoux & Co. yielded a Re concentration of 6.1 \pm 0.33 at.%; the furilidioxime spectrophotometric method was employed.) The \( \pm \) uncertainty value stated for each integral profile is calculated from \( \sqrt{N_i} / \Sigma N_i \), where \( N_i \) is the number of Re atoms detected and \( \Sigma N_i \) is the number of Mo plus Re atoms; \( \sqrt{N_i} \) is equal to \( \pm \) one standard deviation. The data presented in Fig. 5 were taken with the GB placed at the periphery of the probe hole; i.e., at the distance \( \lambda \), which is \( \approx \) a few-tenths of a nm -- see the schematic diagram in the upper right-hand corner. The mean concentration is 5.6 \pm 0.9 at.% Re; this value clearly indicates that the width of concentration profile must be very narrow, as it is essentially the same as \( \langle c_s \rangle \) [6].

Figure 6 is an integral profile for a portion of the GB presented in Fig. 3. The mean slope of this integral profile is 7.1 \pm 0.8 at.% and this value is the quantity \( \langle \delta_{GBRe} \rangle_u \) in Eqn. (1). Thus the uncorrected Re concentration of the GB is \( \approx \) 1.27 times or 27% greater than the Re concentration of the matrix -- this value represents the minimum segregation enhancement factor, as it includes some solute atoms from the matrix [6].

The uncorrected concentration of the GB is corrected for the contribution of the matrix employing Eqn. (1). The value of \( D_a \) was measured from the FIM images and is equal to \( 3a (0.9438 \text{ nm}) \). Therefore, the only quantity to be specified in Eqn. (1) is \( \eta \). We have taken \( \eta \) to be equal to the magnitude of the Burgers vector of the PGBDs -- \( a\sqrt{3}/2 \). Thus the GB can be taken to be a slab of thickness \( 2\eta = a\sqrt{3} \), with the solute atoms residing in the cores of the PGBDs. There may also be solute atoms in the cores of the SGBDs. (The SGBDs, however, are more widely spaced than the PGBDs and they also have a smaller Burgers vectors.) This is a reasonable physical assumption, as a Monte Carlo simulation of solute-atom segregation -- employing embedded-atom method potentials -- to a dissociated edge dislocation in a Ni-10 at.% Cu alloy demonstrates that most of the segregating Cu atoms reside in the cores of the partial dislocations bounding the stacking fault, which separates the partials, and with the maximum solute-atom concentration at the center of their cores [10]. We have also shown for a Pt-1 at.% Au alloy -- employing Monte Carlo simulations and embedded atom method potentials [2] -- that for [001]-twist boundaries the Au atoms segregate mainly to the cores of the PGBDs; also simulations of Au atom segregation to a \( \Sigma = 5 \) tilt boundary indicates a similar result [2]. Employing \( \eta = a\sqrt{3}/2 \) we obtain a value of \( \langle c_{GB} \rangle_u \) equal to \( 9.8 \text{ at.% Re} \), which implies a minimum segregation enhancement factor of 1.75 with respect to \( \langle c_s \rangle \). This is a minimum value, as the Monte Carlo simulations indicate that \( \eta \) is \( \approx 0.88b \) [2].

Summary and Discussion

Detailed results are presented for a GB in a Mo-5.4 at.% Re alloy which was studied employing the
CTEM and APFIM techniques [11]. A bulk specimen which had been recrystallized at 1,773 K was annealed at 1,273 K for 35 h to induce solute-atom segregation to GBs; the calculated root mean-squared diffusion distance is \( \approx 20 \) nm. The following points are enumerated.

- It is possible to electrolytically backpolish an FIM specimen -- in a highly controlled and systematic manner -- to a specific GB and to also analyze it crystallographically in detail using CTEM techniques. And then subsequently to analyze the same GB by the APFIM technique; also see [5,12]. The diameter of the cylinder of alloy analyzed chemically is 0.9438 nm.
- The specific GB studied is within \( \pm 0.4^\circ \) of a \( \Sigma = 9 \) CSL orientation. The plane of the GB is \( \pm (-1,-1,4) \), and its misorientation is \( \theta \equiv 38.5^\circ \) about the \( c_1 = (1/\sqrt{2})(1,1,0) \) direction. This GB is mainly a tilt boundary with a twist component.
- The APFIM results show that this GB experienced an appreciable solute-atom enrichment, even though the solid solubility of Re in Mo is \( \approx 27.8 \) at.% at 1,273 K. The corrected minimum segregation enhancement factor is \( \approx 1.75 \) for a half-width \( \eta = a\sqrt{3}/2 \) (this is the magnitude of the PGBD Burgers vector) -- see previous section. And this demonstrates that the dislocation structure of an interface plays an important role in determining the enhancement factor for solute-atom segregation. It is emphasized that the exact value of the enhancement factor depends upon the value of \( \eta \), and \( \eta \) can be less than one \( \{1\} \) [2].
- The experimental results also demonstrate that Re segregation can occur at a GB which is near to a high coincidence-site lattice orientation -- \( \Sigma = 9 \) in this case. Thus even a so-called low-energy interface can exhibit solute-atom segregation.
- The measurements are in reasonable agreement with our Monte Carlo simulations of solute-atom segregation to low CSL \( \Sigma \) values [001]-twist boundaries and a \( \Sigma = 5 \) tilt boundary in a Pt-1.0 at.% Au alloy [2]. The Monte Carlo simulations show that the segregating atoms are highly localized at the cores of the PGBDs and the enhancement factors are \( \approx 1.2 \) to 3.5 for high coincidence boundaries (low \( \Sigma \)).

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References

FIG 1: Backpolishing sequence of a Mo-5.4 at.% Re specimen. The left-hand TEM micrograph is denoted as zero time. The times in ms indicate the total time electroetched with respect to the left-hand micrograph. Note the total period of electroetching is short between CTEM observations. The final electroetching step is only one period at 20 kHz. The linear magnification of the two right-hand micrographs is a factor of two greater than for the two left-hand ones.

FIG. 2: A sequence of the four SADPs used to determine the misorientation of the GB displayed in Fig. 1; see Fig. 3 for a magnified picture of the GB. The quantities G1 and G2 denote the two grains which are contiguous with the GB. The schematic diagrams next to the SADPs indicate the procedure.

Fig. 3: This is the same GB which is displayed in Fig. 1; i.e., the one labeled 0.3 ms. Note the presence of the SGBDs which have a projected separation of ~11 nm. This GB was analyzed employing the SADPs exhibited in Fig. 2. The APFIM was also used to chemically analyze this same GB -- see Figs. 5 and 6.
FIG. 4: The Re integral profile for the Mo-5.4 at.% Re alloy used in the experiment. The data were taken from the matrix far from the GB; see schematic diagram in the upper right-hand corner. The temperature of the specimen ($T_f$) was 45 K, and the pulse fraction ($f$) was 0.10. The quantity $f$ is the ratio of the pulse voltage to the steady state dc voltage.

FIG. 5: The Re integral profile for the situation where the GB is placed just on the periphery of the probe hole; see schematic diagram in the upper right-hand corner. The distance $\lambda$ is a few-tenths of a nm; see [6] for a detailed description of the analysis of this situation. The temperature of the specimen ($T_f$) was 45 K, and the pulse fraction ($f$) was 0.10. The quantity $f$ is the ratio of the pulse voltage to the steady state dc voltage.

FIG. 6: The Re integral profile for the same GB as exhibited in Fig. 5. This profile was recorded with the GB in the center of the probe hole; see schematic diagram in the upper right-hand corner. The temperature of the specimen ($T_f$) was 45 K, and the pulse fraction ($f$) was 0.10. The quantity $f$ is the ratio of the pulse voltage to the steady state dc voltage.