FURTHER STATISTICAL ANALYSIS OF THE COMPOSITION OF A Σ ≈ 9/(−1,−1,4) GRAIN BOUNDARY IN A Mo(Re) ALLOY STUDIED BY ATOM-PROBE FIELD-ION MICROSCOPY

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Introduction

We have recently performed a combined transmission electron microscope (TEM) and atom-probe field-ion microscope (APFIM) investigation of Re segregation to a single grain boundary (GB) that is within ±0.4° of a Σ = 9 coincident site lattice (CSL) orientation in a Mo-5.58±0.31 at.% Re alloy [1,2]; specifically the misorientation is θ = 38.5° about the c1 = (1/2)[1,1,0] direction, and the plane of the GB is = (-1,-1,4); this GB is mainly a tilt GB with a twist component. The primary conclusion of our paper [1,2] with respect to GB segregation is that this specific GB studied has an "uncorrected" Re concentration which is = 1.27 or 27% greater than the Re concentration of the matrix -- this value represents the minimum segregation enhancement factor,3 as it includes some solute atoms from the matrix."[3,4] In this letter we recapitulate briefly our experimental procedure, the results obtained, and we then consider in detail the question of the statistical uncertainties involved. This detailed statistical analysis confirms the original conclusions made in reference 1 with respect to the uncorrected Re concentration at the GB, as well as the corrected Re concentration.

Recapitulation of Experiments Performed and the Results Obtained

We now recapitulate briefly the experiments performed and the results obtained. A schematic diagram of the basic geometry employed is exhibited in Fig. 1. For the geometry of Fig. 1 the plane of the GB is parallel to the long axis of the APFIM, and as field evaporation of the FIM specimen proceeds the chemical identities of the atoms in the individual planes perpendicular to the GB plane are analyzed on an atom-by-atom basis. With the GB plane in this orientation the measurements integrate over the segregation concentration profile that is normal to the plane of the GB interface. The principles of these experiments have been presented and analyzed in detail elsewhere.[3,4] Figure 2 illustrates the three basic measurements made and the results obtained. Figure 2(a) is a reference measurement and is made at a point which is far enough away from the GB -- >10 nm -- that the GB's presence does not affect the value of the Re concentration measured; the Re concentration measured for this case is 5.58±0.31 at.% Re based on ≈5680 Mo plus Re atoms. Figure 2(b) is the arrangement used to measure the Re segregation enhancement factor. In this geometry the Re concentration measured is denoted <C_{gb}^{Re}>u, where the u denotes a

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3That is, it is a lower bound to the actual segregation enhancement factor or excess Re at the GB.
concentration uncorrected for the contribution of the matrix. The measured diameter \( D_a \) of the projection of the probe hole on the surface of the tip is 0.9438 nm for the measurements illustrated in Figs. 2(b) and 2(c). The value of \( \langle C_{B_{Re}} \rangle_u \) is 7.11±0.82 at.% Re based on ∼ 984 Mo plus Re atoms. And therefore the minimum uncorrected segregation enhancement factor is \( (7.11±0.82 \text{ at.\% Re})/(5.58±0.31 \text{ at.\% Re}) = 1.27±0.16 \) \(^4\) Figure 2(c) represents the third measurement performed; in this case the GB is displaced to the periphery of the probe hole by tilting the FIM specimen with the aid of a goniometer. The purpose of this measurement is to assess how quickly the Re concentration profile perpendicular to the GB interface falls off with distance. For this experiment the value of the measured Re concentration is 5.57±0.87 at.% Re based on 700 Re plus W atoms; the uncertainty is larger for this data set because of the smaller sample size used. This value is essentially the same as the matrix concentration -- 5.58±0.31 at.% Re -- and indicates that the width of the concentration profile associated with the GB must be very narrow. We emphasize strongly that this data was not used to calculate the segregation enhancement factor of 1.27 given in reference [1].

**Statistical Considerations**

A very common situation in experimental studies is that error bars overlap, and this is the case for the results presented in Figs. 2(b) and 2(c). Does this mean that we should neglect the discrepancies in the mean values and assume absence of evidence for segregation? To answer this question we present some statistical considerations. We start with the assumption of an ideal solution which implies a binomial distribution of solute atoms. Therefore we identify the true concentration with the probability of the binomial distribution and the observed experimental concentrations with frequencies in a series of binomial trials. The most likelihood estimator for the Re concentration is then:

\[
c_{Re} = \frac{N_{Re}}{N_{Re} + N_W}.
\]

The estimate for the standard deviation is:

\[
\sigma_c = \frac{\sqrt{N_{Re}N_W}}{(N_{Re} + N_W)^{3/2}}.
\]

These values are the uncertainties presented in Fig. 2. In references 1 and 2 an approximate relation for dilute alloys was used:

\[
\sigma_c^{\ast} = \frac{\sqrt{N_{Re}}}{N_{Re} + N_W}.
\]

A numerical comparison of \( \sigma_c^{\ast} \) with \( \sigma_c \) demonstrates that the difference between the two values is tiny in our case.

Now we seek a probabilistic interpretation of the situation where the uncertainty bounds overlap. The usual way is provided by De Moivre’s theorem, [6] which states that the quantity (\( z \)):

\[\text{4The uncertainty was calculated using propagation of error theory for independent errors. [5]}

characterizing the deviation of the observed concentration value \( \hat{c} \) from the true one \( c \), in a set of \( n \) trials (atoms), has a normal distribution function given by:

\[
\Phi(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-x^2/2} \, dx.
\]

This allows, for example, one to calculate the confidence limits for any given probability \( 1 - \alpha \); this implies that the true value of concentration with a given probability is confined within these limits. In fact the range of \( z \) is given by:

\[
P[-z_{\alpha/2} \leq \frac{\hat{c} - c}{\sqrt{nc(1-c)}} \leq z_{\alpha/2}] = 1 - \alpha;
\]

where \( z_{\alpha/2} \) is the value such that \( \Phi(z_{\alpha/2}) = 1 - \alpha / 2 \). The inequality in the square brackets is equivalent to:

\[
n(\hat{c} - c)^2 \leq z_{\alpha/2}^2 c(1-c);
\]

which leads to the equation whose roots are the confidence limits:

\[
c^2 \left( n + z_{\alpha/2}^2 \right) - c \left( n \hat{c} + z_{\alpha/2}^2 \right) + n\hat{c}^2 = 0.
\]

The 95% confidence limits for the statistically most representative situation in Fig. 2(a) are:

\[
0.050 < c_{Re} < 0.062.
\]

This implies approximately that the probability of a random fluctuation which would bring the concentration value in this case to the value given in Fig. 2(b) is less than 2.5%; it is <2.5% and not <5% because we made the estimate with respect to a value which is greater than the matrix concentration.

We may, however, employ a more rigorous approach, taking into account possible fluctuations in both compared data sets.[6] To do this we have to substitute the unknown true concentration with the "pooled" estimator

\[
\hat{c}_p = \frac{n_1 \hat{c}_1 + n_2 \hat{c}_2}{n_1 + n_2};
\]

where \( n_1, \hat{c}_1, \) and \( n_2, \hat{c}_2 \) are the numbers of atoms and concentrations in the both data sets, hence:

\[
z = \frac{\hat{c}_1 - \hat{c}_2}{\sqrt{\hat{c}_p (1 - \hat{c}_p) \left( \frac{1}{n_1} + \frac{1}{n_2} \right)}};
\]

where \( c \) is set equal to \( c_p \). Thus, the probability \( (1 - \beta) \) that two observed concentrations of the same ideal solid
solution would differ by less than \( |c_1 - c_2| \) is given by \( \Phi(z) = 1 - \beta / 2 \); this value of \( \Phi(z) \) corresponds to the "two-sided" alternative. So, in a general sense, \( (1 - \beta) \) gives us a "confidence estimate" for the conclusion that \( c_1 \) and \( c_2 \) belong to two solid solutions with different concentrations, and \( \beta \) to the opposite conclusion.

**Conclusions**

First, we compare the three integral profiles employing the "two-sided" alternative which is a worst case confidence estimate of the data. For the integral profiles in Fig. 2(a) and 2(b) we get \( z = 1.90 \) and \( (1 - \beta) \) is in excess of 94%; i.e., this large a value of \( (1 - \beta) \) allows us to distinguish this GB concentration from the matrix concentration. However, for the profiles in Fig. 2(a) and 2(c) we obtain \( z = 0.01 \) and \( (1 - \beta) = 0.008 \); this implies that we can consider the measured concentrations to be identical with a very "good confidence." Physically this implies the GB concentration profile is very narrow; and this justifies the correction we made for the matrix contribution to the data exhibited in Fig. 6 of reference 1, to obtain a minimum corrected segregation enhancement factor of 1.75 with respect to the matrix concentration.\[1,2\] Finally for the profiles in Figs. 2(b) and 2(c) \( z = 1.27 \) and \( (1 - \beta) \) is about 80%; this implies that with a fairly "good degree of confidence" we can distinguish the concentrations. Once again this is consistent with the point that the Re concentration profile is highly localized at the GB. Therefore it is justified to employ the "one-sided" alternative "equal" vs. "greater than." For the "one-sided" alternative \( (1 - \beta) \) equal to 94, 0.008, and 80% become \( (1 - \beta) \) equal to 97, 0.004 and 90%. In summary, a more detailed statistical analysis of all the data presented in reference 1 -- also see Fig. 2 of this paper -- is consistent with all the conclusions we reached earlier.\[1,2\]

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**References**

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FIG. 1. The geometry employed for analyzing this GB. The plane of the GB is perpendicular to the plane of the probe hole (Dₐ). The value of Dₐ is 0.9438 nm for this GB.

\[ <C_{\text{Re}} > = 5.58 \pm 0.31 \text{ at. % Re} \]
\[ <C_{\text{Re}} >_u = 7.11 \pm 0.82 \text{ at. % Re} \]
\[ <C_{\text{Re}} > = 5.57 \pm 0.87 \text{ at. % Re} \]

(a) \hspace{1cm} (b) \hspace{1cm} (c)

\( d > 10 \text{ nm} \) \hspace{1cm} \( d = 0 \text{ nm} \) \hspace{1cm} \( d < 1 \text{ nm} \)

d: distance from GB to the center of the probe hole.

FIG. 2. A summary of the principle results obtained in reference 2. (a) The mean Re concentration of a cylinder of alloy measured at a distance (d) > 10 nm from the GB. (b) The Re concentration measured with the GB in the center of the probe hole. (c) The Re concentration measured with the GB at the periphery of the probe hole. In (b) and (c) the plane of the GB is perpendicular to the plane of the projection of the probe hole. The diameter of the probe hole is Dₐ.