Absolute atomic-scale measurements of the Gibbsian interfacial excess of solute at internal interfaces

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A method consistent with the Gibbs' formalism is presented for measuring the Gibbsian interfacial excess of solute (Γ) at an internal interface using atom-probe field-ion microscopy (APFIM). The values of Γ are measured directly, that is, *without* deconvolution procedures. The relationships between Γ and the thermodynamic-state variables of an internal interface are studied using the techniques of APFIM and transmission electron microscopy (TEM). Examples are given of the application of APFIM-TEM to the measurement of Γ at grain boundaries in an Fe(Si) alloy.

The presence of solute atoms at internal interfaces influences the physical properties of the interfaces and this, in turn, affects the bulk physical properties.[1,2] It is, therefore, important to be able to predict and measure quantitatively the level of equilibrium solute-atom segregation at internal interfaces. The classical thermodynamic quantity that represents the amount of equilibrium solute-atom segregation is the Gibbsian interfacial excess of solute (Γ).[3] In our laboratory, one type of internal interface of interest is a grain boundary (GB)—a homophase boundary—for which the values of Γ are a function of temperature, pressure, bulk composition, and GB type: the thermodynamic-state variables of a GB.[4] The GB type is defined by the five macroscopic geometric degrees of freedom (DOF's):[5,6] the unit rotation axis (c), the rotation angle (θ) about c, and the unit GB plane normal (n). This paper explains the principles of an analysis for measuring the value of Γ at a general internal interface, either homophase or heterophase, and demonstrates the analysis for GB's in an Fe(Si) alloy.

While numerous studies of segregation (or adsorption) at solid/gas interfaces have been performed using systematic and quantitative methods, the same cannot be said for solid/solid interfaces. The reason for this disparity is that of the techniques used to study solid/gas interfaces, only atom-probe field-ion microscopy (APFIM) can directly access an internal interface with atomic-scale resolution.[7] The method used most widely to study equilibrium solute-atom segregation at GB's is to expose a GB surface by *in situ* fracturing of a polycrystalline specimen or a bicrystal. This technique is, however, restricted to those materials that fail intergranularly, and, moreover, the atomic arrangement at the interface is necessarily disturbed. Furthermore, the techniques applied to these solid/vacuum interfaces, e.g., Auger electron spectroscopy (AES), do not yield quantitative measures of the level of solute-atom segregation—in particular, the value of Γ. A technique that indirectly measures Γ, involves measuring the free energy of an internal interface as a function of bulk composition and then applying the Gibbs adsorption isotherm equation.[8,9] Those investigations are restricted to high temperatures, and the identity of the segregating species must be known *a priori*. Because of the limitations of the latter two methods, there is

no experimental study that has considered all of the thermodynamic-state variables required to properly assess the nature of equilibrium solute-atom segregation at GB's in a specific alloy.

APFIM has demonstrated its capability to measure directly the level of equilibrium solute-atom segregation as a function of temperature at stacking faults.[10] To extend this capability of APFIM to other types of internal interfaces, requires the use of APFIM in combination with transmission electron microscopy—APFIM-TEM—because TEM is needed to precisely determine the geometric thermodynamic-state variables of the more general type of internal interface.[11] The technique of APFIM-TEM has always had the potential to systematically and quantitatively study equilibrium solute-atom segregation at internal interfaces, but until recently the advantages have not been realized because of experimental difficulties. In our laboratory, we have made two important advances. First, by identifying key factors required to analyze a GB via both APFIM and TEM,[12,13] we have demonstrated with the W (Re) (Ref. 14) and Fe (Si) (Ref. 15) alloy systems that a wide range of GB types can be systematically analyzed via APFIM-TEM. Our second contribution is the realization and demonstration

FIG. 1. Three-dimensional schematic drawing of the volume analyzed via APFIM. The spatial resolution of an analysis is maximized when $\phi = 0°$.

FIG. 2. Hypothetical integral profile (line $ABCD$) showing how the excess number of solute atoms is determined from an APFIM analysis of a volume of material as in Fig. 1.

that the APFIM directly extracts absolute measures of the Gibbsian interfacial excess of solute at internal interfaces.[15]

The Gibbsian interfacial excess of element i (Γ_i) is defined as

$$\Gamma_i = N_i^{\text{excess}}/A = (1/A)(N_i^{\text{vol}} - N_i^{\alpha} - N_i^{\beta})$$
$$= (1/A)N^{\text{vol}}[C_i^{\text{vol}} - C_i^{\alpha}\xi - C_i^{\beta}(1-\xi)] , \quad (1)$$

where N_i^{excess} is the excess number of atoms associated with an interface, and A is the interfacial area over which Γ_i is determined. The quantities N_i^{α} and N_i^{β} are the number of atoms of element i in phases α and β, assuming that the two phases exist up to the Gibbs dividing surface (ξ). The excess is, therefore, defined by comparing the total number of atoms of element i in the actual system containing the interface (N_i^{vol}), to a reference system where the two phases making up the interface extend to the position of ξ. The quantities C_i^{α} and C_i^{β} are the atomic concentrations of element i in the homogeneous re-

gions of phases α and β, i.e., the bulk regions of the two phases. The quantity C_i^{vol} is the atomic concentration of element i in the total volume of material containing the internal interface and N^{vol} is the total number of all elements in the same volume.

The quantity Γ_i is defined such that its value depends upon the position of the dividing surface.[16] This dependence is eliminated by defining a so-called relative Gibbsian interfacial excess of component i with respect to component 1 ($\Gamma_i^{(1)}$):

$$\Gamma_i^{(1)} = \Gamma_i - \Gamma_1(C_i^{\alpha} - C_i^{\beta})/C_1^{\alpha} - C_1^{\beta} . \quad (2)$$

For a homophase bicrystal, Eq. (2) becomes

$$\Gamma_i^{(1)} = \Gamma_i - \Gamma_1 C_i^{B}/C_1^{B} , \quad (3)$$

where C_i^{B} is the atomic concentration of element i in the bulk. For a substitutional binary alloy, under the condition of a dilute solution, $\Gamma_2^{(1)} \approx \Gamma_2$.

When the APFIM is used to chemically analyze an interface, a volume of material is probed as in Fig. 1. The APFIM determines the chemical identity of individual atoms, one at a time, in a cylinder of material on an atomic layer-by-layer basis. The spatial order in which the atoms are detected is preserved. These data are then plotted in the form of an integral profile (Fig. 2), which is a plot of the cumulative number of atoms of element i versus the cumulative number of all of the atoms collected. The data are plotted in the order in which the ions are collected. The slope between any two points, therefore, corresponds to the average atomic composition of element i of a particular plane or series of planes in the volume of analyzed material. From the integral profile, we can directly determine the value of N_i^{excess}, using Eq. (1). The values of N_i^{α} and N_i^{β} are determined by linearly extending the average bulk compositions of the α phase and the β phase to the Gibbs dividing surface. The quantity N_i^{vol} is the total number of atoms plotted on the ordinate. This graphical construction is simple and does not
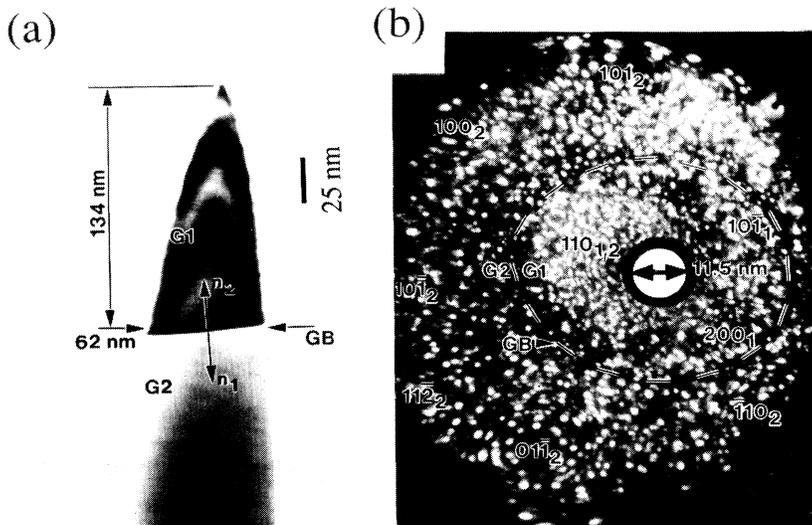
FIG. 3. (a) TEM micrograph of an Fe–3 at. % Si specimen after GB analysis and back-polishing. (b) FIM image of the same specimen as in (a). The tip has been field evaporated so that the image of the GB perimeter is circular. The probe hole is then aligned so that its perimeter is concentric with that of the GB image: $\phi = 0°$ and $D_{\text{ph}} = 11.5$ nm.
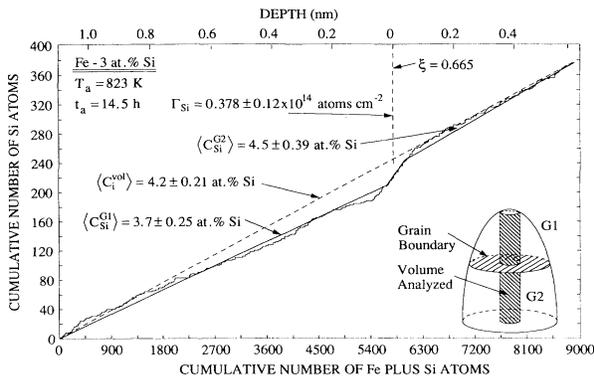
FIG. 4. Integral profile of the GB analyzed in Fig. 3. The value of N^{vol} is 8915 atoms.

require any assumptions. The value of A is given by

$$A = \pi D_{ph}^2 / 4 \cos\phi , \qquad (4)$$

where D_{ph} is the diameter of the probe hole projected onto an FIM surface. The value of A is determined by projecting the probe hole onto a GB plane; this projection is, in general, an ellipse, thus:

$$\Gamma_i = (4 \cos\phi / \eta \pi D_{ph}^2)[N_i^{vol} - N_i^\alpha - N_i^\beta]$$
$$= (4 \cos\phi / \eta \pi D_{ph}^2)N^{vol}[\langle C_i^{vol} \rangle$$
$$- \langle C_i^\alpha \rangle \xi - \langle C_i^\beta \rangle (1 - \xi)] . \qquad (5)$$

The atomic concentrations are expressed as averages, because the APFIM measures these averages. The quantity η is the detection efficiency of the Chevron detector of the APFIM. The value of η equals the fractional open area of a Chevron detector and is typically 0.55. The value of ϕ is given by

$$\phi = \cos^{-1}(\mathbf{n} \cdot \mathbf{l}) ; \qquad (6)$$

where $\mathbf{n}$ is the unit normal to the interface plane, $\mathbf{l}$ is the

unit vector parallel to the direction of APFIM analysis, and is determined by indexing the center of an FIM image of the projection of a probe hole. The image is indexed by determining the rotation matrix from a TEM analysis.[7,15] The value of D_{ph} is then determined directly from information in an FIM image.[10] For the experiments reported here, the value of $\cos\phi$ is unity, as $\mathbf{n}$ is parallel to $\mathbf{l}$.

For a homophase bicrystal the bulk compositions on each side of a GB are identical, so that the location of a dividing surface does not influence the value of N_i^{excess}. For the Fe(Si) alloy, experimental measurements show, however, that the bulk compositions do vary slightly due to the statistical nature of a compositional analysis. To account for these variations a dividing surface is placed at the center of the region that constitutes a GB. This placement is equivalent to using the average of the bulk compositions of both grains for the value of C_i^B in Eq. (3).

To study equilibrium segregation in the Fe(Si) alloy, the starting materials must have the utmost purity to minimize the influence of impurity-atom segregation of the interstitial elements C, P, S, N, or O. The starting materials are Fe of 99.9945 at. % purity and Si of 99.9999 at. % purity. The Fe–3 at. % Si alloy is arc melted in an atmosphere of Ar of high purity. The ingot is swaged and cold drawn to 185 μm diam wire. Specimens are encapsulated in a quartz tube backfilled with Ar of high purity. Next, they are annealed at 823 K for 14.5 or 72.5 h and then quenched into a brine solution at 273 K. Two annealing times are used to ascertain that the equilibrium concentration of Si is achieved at the GB's. Those annealing times produce root-mean-square diffusion distances of 0.055 and 0.123 μm, respectively.

Figure 3(a) exhibits a TEM micrograph of a GB near the tip of an Fe–3 at. % Si wire that was backpolished to produce a tip with the requisite geometry to locate a GB and analyze it via APFIM. Figure 3(b) shows an FIM micrograph of the same tip. No signs of precipitation are observed in the bulk or at GB's by either TEM or AP-FIM. Figure 4 is the corresponding integral profile; the
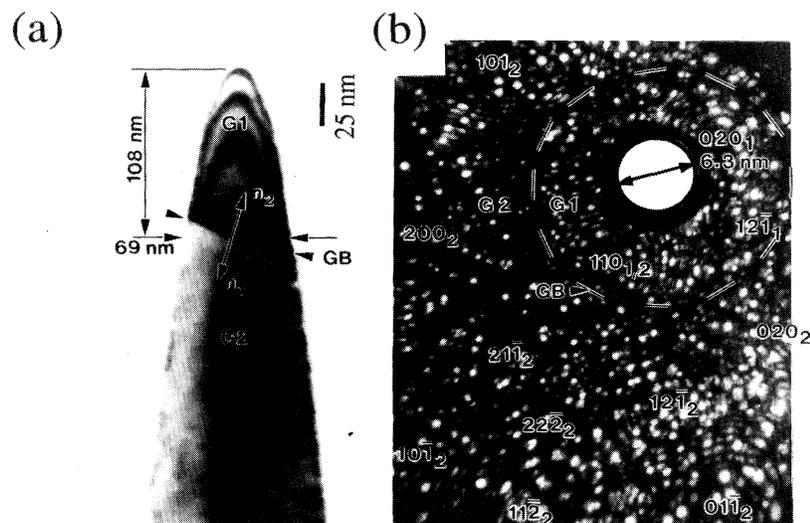
(a)   (b)

FIG. 5. (a) TEM micrograph of an Fe–3 at. % Si specimen after GB analysis and backpolishing. (b) FIM image of the same specimen as in (a). The tip has been field evaporated so that the image of the GB perimeter is circular. The probe hole is then aligned so that its perimeter is concentric with that of the GB image: $\phi = 0°$ and $D_{ph} = 6.3$ nm.

abscissa represents the cumulative number of atoms collected from a cylinder of material 11.5 nm in diameter. The value of Γ_{Si} is $0.378\pm0.12\times10^{14}$ atoms cm^{-2}. The five macroscopic geometric DOF's are: $c=[0.85,\overline{0.52},\overline{0.06}]$, $\theta=25.28°$, $n_1=[0.04,0.68,0.73]$, and $n_2=[0.21,0.36,0.91]$.

The depth scale on the upper abscissa of Fig. 4 is determined from a knowledge of D_{ph} and the atomic density of Fe ($\rho_{Fe}=84.879$ atoms nm^{-3}). The ultimate depth resolution of the APFIM compositional analysis is equal to the mean interatomic planar spacing (d_m) along n, and is approximately equal to 0.02 nm. Because the probe hole covers approximately 3.5 atomic planes, the actual depth resolution is ≈0.07 nm. Since the vector n is not along an identifiable low-index pole in the FIM image, the Miller indices can only be assumed for this APFIM analysis. An example of an easily identifiable pole is 110, for which the depth resolution is 0.2 nm. The error bar in Γ_{Si} is determined by propagating the errors of each quantity in Eq. (5).[17] The error in N_i^{excess} is determined by assuming that the measured atomic concentrations are binomially distributed.[18] The error in D_{ph} is empirically determined to be $\pm7\%$.[10] The value of Γ_{Si} corresponds to a fractional monolayer coverage of $\Theta=0.22$ monolayers by assuming a saturation value for Γ_{Si} of $\rho_{Fe}d_m$, which equals 1.70×10^{14} atoms cm^{-2}. If we assume that the segregation behavior is of the Langmuir-McLean type, then the free energy of segregation (ΔG) for this GB is -15.1 kJ mol^{-1}.

Figures 5 and 6 are another example of an APFIM-TEM analysis. The integral profile shows that the number of atoms collected from the GB region is much less than for the example of Figs. 3 and 4 and yet the signal is still detectable via APFIM; The value of D_{ph} is 6.3 nm, and the depth resolution is ≈0.05 nm. The value of Γ_{Si} is $0.46\pm0.22\times10^{14}$ atoms cm^{-2}. The corresponding macroscopic geometric DOF's are $c=[0.69,0.54,0.48]$,
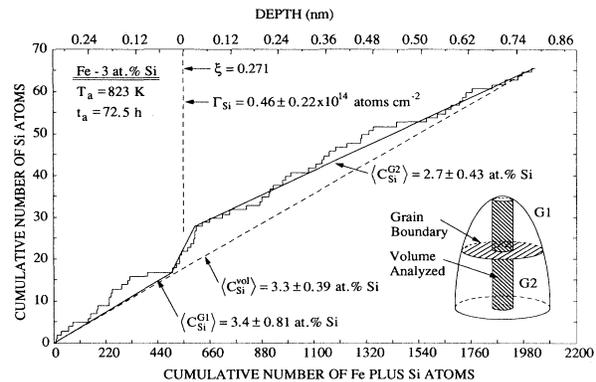

FIG. 6. Integral profile of the GB analyzed in Fig. 5. The value of N^{vol} is 2025 atoms.

$\theta=58.88°$, $n_1=[\overline{0.36},\overline{0.05},0.93]$, and $n_2=[\overline{0.21},\overline{0.36},0.91]$. The value of $\Theta=0.27$ monolayers and ΔG equals -17.0 kJ mol^{-1}.

Our measurements of equilibrium solute-atom segregation in the W(Re) and the Fe(Si) alloy systems demonstrate that the values of Γ vary with the GB type, even in the high-angle regime. The complete understanding of the nature of solute-atom segregation in these systems will, however, require measuring Γ as a function of temperature and bulk composition, for a fixed GB type, so that models of statistical thermodynamics can be applied.[19,20] The application of APFIM-TEM provides a quantitative and systematic approach to this important experimental problem.

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(a)

134 nm

25 nm

62 nm

G1

G2

n_2

n_1

GB

(b)

101_2

100_2

101_1

110_{12}

11.5 nm

G2 \ G1

$10\bar{1}_2$

GB

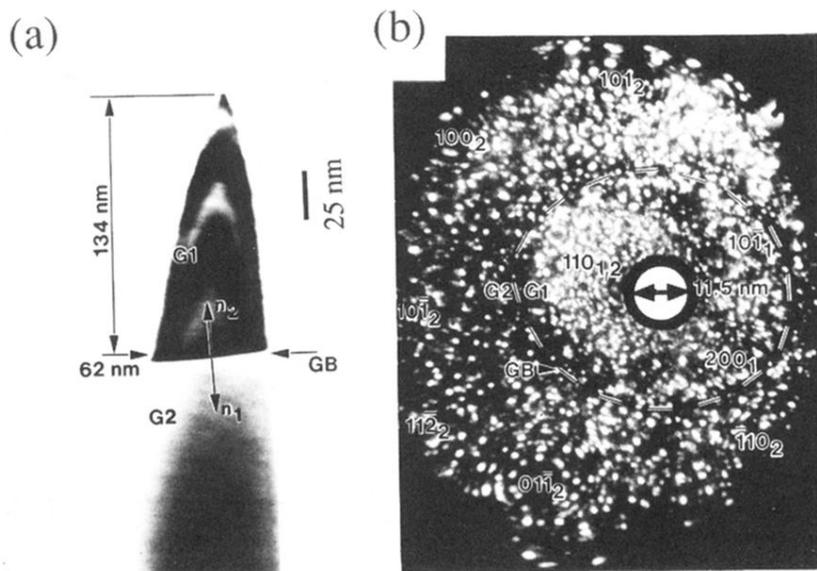200_1
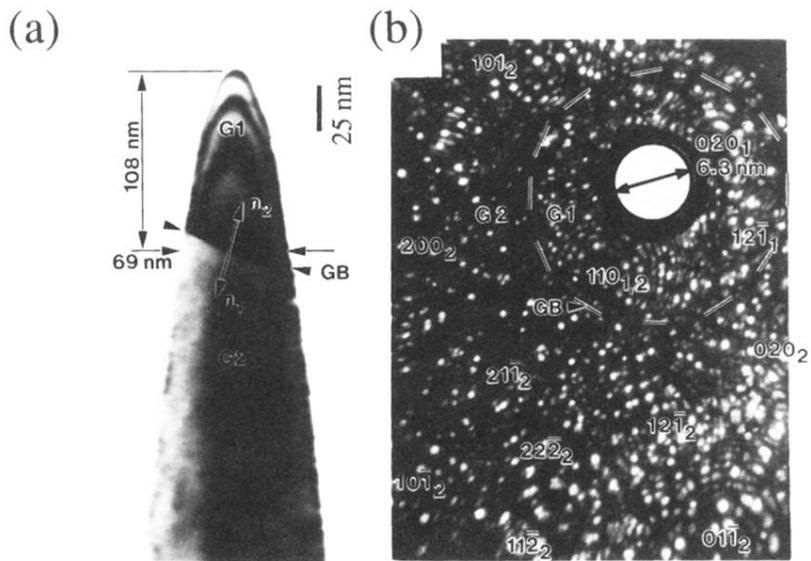
$11\bar{2}_2$

110_2

$01\bar{1}_2$

FIG. 3. (a) TEM micrograph of an Fe–3 at. % Si specimen after GB analysis and back-polishing. (b) FIM image of the same specimen as in (a). The tip has been field evaporated so that the image of the GB perimeter is circular. The probe hole is then aligned so that its perimeter is concentric with that of the GB image: $\phi = 0°$ and $D_{ph} = 11.5$ nm.

(a)

(b)

FIG. 5. (a) TEM micrograph of an Fe-3 at. % Si specimen after GB analysis and back-polishing. (b) FIM image of the same specimen as in (a). The tip has been field evaporated so that the image of the GB perimeter is circular. The probe hole is then aligned so that its perimeter is concentric with that of the GB image: $\phi = 0°$ and $D_{ph} = 6.3$ nm.