ATOMIC SCALE STUDIES OF SOLUTE-ATOM SEGREGATION AT GRAIN BOUNDARIES: EXPERIMENTS AND SIMULATIONS

D. N. SEIDMAN, B. W. KRAKAUER AND D. UDLER

Department of Materials Science and Engineering and Materials Research Center, R. R. McCormick School of Engineering and Applied Science, Northwestern University, Evanston, IL 60208-3108, U.S.A.

Abstract—This paper presents two atomic scale approaches to study grain boundary (GB) segregation phenomena. The first is an experimental one that combines transmission electron microscopy (TEM) with atom-probe field-ion microscopy (APFIM) to measure quantitatively the Gibbsian interfacial excess of solute at GBs whose five macroscopic degrees of freedom are first measured by TEM; with this approach it is possible to explore systematically GB phase space. APFIM is also used to determine segregation profiles with atomic resolution. An application is presented for this combined experimental approach for a single phase FeSi alloy. The second involves Monte Carlo simulations of solute-atom segregation at GBs in bicrystals of single-phase f.c.c. alloys; this approach is also used to systematically explore GB phase space. The atoms are allowed to interact via long-range continuous embedded atom method potentials, and so-called transmutational ensemble is employed. The results show that, unlike the previously investigated Au-Pt system, the (002) twist boundaries are enhanced in solute atoms on both sides of the phase diagram. For low-angle (002) twist boundaries on the Pt-rich side the atomic sites enhanced in solute concentration are arranged in hourglass-like structures centered on the square grid of primary grain boundary dislocations. While for the same boundaries on the Ni-rich side the atomic sites enhanced in solute concentration are located in bipyramidal regions based on the squares cells of the same grain boundary dislocations. Thus, the atomic sites that are enhanced on one side of the phase diagram are not affected on the other side and vice versa.

Keywords: A. interfaces, A. metals, C. electron microscopy, D. defects, D. microstructure.

1. INTRODUCTION AND GENERAL BACKGROUND

The ultimate extent to which we can predetermine the properties of materials depends on our ability to control and tailor the properties of internal interfaces and surfaces [1-6]. This ability has resulted in a field called interfacial engineering [7-9], whose foundations are based on a fundamental knowledge of the phases, structure, chemistry and kinetics of internal interfaces. Interfacial engineering is a crucial component of materials design, particularly for tailoring the mechanical properties of structural materials—fracture mode, toughness, diffusional creep and creep cavitation embrittlement—that are frequently determined by phenomena occurring at internal interfaces under applied external stresses. More generally, processes occurring in the interfacial volume affect many important physical [10, 11] and technological properties of a wide range of bulk materials; these processes include phase transitions, short-circuit diffusion [12, 13], nucleation of new bulk phases, nucleation of voids in electromigration damage of metal interconnects, etc. These phenomena are sensitive to interfacial phases, structure and chemistry.

The interfacial region where two grains of a single-phase material meet is called a grain boundary (GB) or a homophase interface and similarly the region where two grains of two differing phases meet is denoted a heterophase interface or interphase interface. In the last 25 years a significant body of experimental and theoretical research has focused on the structures of homophase interfaces [14]. This work has emphasized both the dislocation structures and the positions of atoms at internal interfaces using transmission-electron (TEM) and high-resolution electron microscopes (HREM) as well as X-ray diffraction techniques [15-17]. There have also been efforts to correlate the structures and local chemistries of internal interfaces by employing energy dispersive X-ray and electron energy loss spectroscopies in conjunction with transmission electron or scanning transmission electron microscopy [18].
Interfacial segregation and phase transitions occur on an atomic scale, thus if one is to compare experimental results with computer simulations [19-22] one must use a probe with atomic scale resolution to determine the chemical identities and positions of individual atoms. Before addressing specific challenges, problems, and techniques toward this end, we consider general background material on the thermodynamics of interfaces, interface phases and GB phase transitions. This material provides a framework for our experimental and computer simulation studies.

Gibbs developed the concepts of the thermodynamics of interfaces [23] and defined the basic extensive thermodynamic properties. Cahn [24] extended Gibbs’ analysis to include the five macroscopic degrees of freedom (DOFs) that define the geometric character of a GB; he assumed that the three microscopic DOFs are relaxed to their equilibrium values. The five macroscopic DOFs are defined when a GB is “created” by taking a unit vector, c, in one of the two grains with direction cosines, c1 and c2, and then rotating grain 1 with respect to grain 2 about c by an angle, θ. The plane of the interface is defined by a unit normal vector, n. It is assumed that the microscopic DOFs of a GB are relaxed to values that minimize the total free energy of the GB. Cahn’s treatment results in a generalized expression for the interfacial free energy per unit area of interface, σ, or more simply the interfacial free energy:

\[ \sigma = \sigma(T, P, \mu, \text{strain}, c_1, c_2, \theta, n_1, n_2), \]  

where \( T \) and \( P \) are the temperature and pressure, \( \mu \) are chemical potentials of each of the components. The strain in eqn (1) refers to nonhydrostatic stresses and their concomitant strains [25]. Thus, \( \sigma \) is a function of many variables and, therefore, the phase space of an interface is in general a priori unknown and quite complex; each point in the multidimensional phase space represents a thermodynamic state. The exploration of this phase space is ideally achieved in a systematic manner by moving along a trajectory of one variable with all the remaining variables held fixed. We have performed both experiments and computer simulations utilizing this approach for the Gibbsian interfacial excess of solute (\( \Gamma_2 \)) in b.c.c. and f.c.c. alloys, respectively [26, 27]. The quantity \( \Gamma_2 \) is the basic measure of interfacial segregation; for example, for a GB in a single bulk phase containing only two components this quantity is:

\[ \Gamma_2 = -\left( \frac{\partial \sigma}{\partial \mu_2} \right)_T, \]  

where \( \Gamma_2 \) is the excess of the solute, 2, in an interfacial layer over what is present in a reference system containing the same amount of solvent. To explore a GB’s phase space properly and to obtain a physically meaningful value of \( \Gamma_2 \), careful attention must be paid to the five macroscopic DOFs-c, n, θ.

The quantity \( \Gamma_2 \) plays a central role, for example, in the Rice Thomson Wang theory of the effects of segregation on fracture [28]. The phenomenological picture of intergranular fracture is a transition between two limiting states: (a) a bicrystal and (b) two totally separated crystals with two new free surfaces. In a thermodynamic model this transition occurs reversibly under applied external forces that work against the forces of cohesion [29-31]. In the presence of a segregating solute species, the change in the free energy of the system due to GB decohesion can be written as:

\[ 2\Delta a_{\text{int}} = \sigma_g + \sigma_n - \sigma_{\text{GB}} - (\Delta g_2 - \Delta g_3)\Gamma_2, \]  

where \( \sigma_g \) and \( \sigma_n \) are the free energies of the two new surfaces, and \( \Delta g_2 \) and \( \Delta g_3 \) are the Gibbs free energies of segregation at a GB and a free surface, respectively. It follows from eqn (3) that for GB fracture the work of decohesion, \( 2\Delta a_{\text{int}} \), depends on both the crystallographic plane (n) along which the fracture occurs and on the misorientation of the two grains (θ and c or Σ). (The value of the quantity \( \Sigma \) is the inverse of degree of coincidence of the two grains comprising a bicrystal in three dimensions; for example, \( \Sigma = 5 \) implies one in five sites is in coincidence between the two three-dimensional grains.) Furthermore, eqn (3) demonstrates that a solute that segregates more strongly to the free surfaces than the GB embrittles that boundary, for example, Bi in Cu; whereas a species that segregates more strongly to a GB than to the free surfaces ductilizes that boundary, for example, B in Ni,Al [32]. Thus, the behavior of \( \Gamma_2 \) in GB phase space plays an important role in ultimately designing ductile materials.

It is important to recall that a GB contains many types of sites with local environments that differ appreciably from those of the bulk lattice; those sites may either attract or repel solute atoms. Thus, the distribution of segregated solute atoms at a GB can be heterogeneous on an atomic scale. Solute–atom segregation may be examined experimentally at an atomic scale employing atom-probe field-ion microscopy (APFIM), or alternatively, via various computer simulation techniques, for example, Monte Carlo (MC) or molecular dynamics (MD) [33, 34]. Simulations play an important role in studying segregation as they sample the C + 6 dimensional phase space in a systematic manner; our efforts have con-
centrated on studying f.c.c. binary alloys for which reliable embedded atom method (EAM) potentials are available [35]. For example, we have performed detailed MC studies of solute segregation in (002) twist boundaries, for dilute alloys in the Au–Pt and Ni–Pt systems for $0^\circ < \theta < 45^\circ$ (by symmetry $0^\circ < \theta < 360^\circ$). The picture of the atomistics of segregation obtained via MC simulations presents an extraordinary experimental challenge [36, 37]. Experimentally, we have measured directly via APFIM, for example, $\Gamma_{\text{Ga}}$, in $\alpha$-Fe as a function of $c$, $n$, $\theta$. These are the first absolute measurements of $\Gamma_2$ for GBs with a known structure in any alloy [38]. The tomographic atom probe holds the tantalizing potential of determining two- or three-dimensional chemical maps on the 0.5–1.0 nm scale [39]. This may ultimately enable us to compare MC simulations with experiments on an atom-by-atom basis.

GBs are two-dimensional structures that consist of one or more interface phases, and thus phase transitions are possible. It is only recently, however, that the study of GB phases and their transitions has occurred. There are two basic reasons for this. First, experimentally it is considerably more difficult to access a buried GB than a free surface. And, second, the number and type of processes that can occur at a GB is vast and difficult to quantify due to the larger number of thermodynamic variables. To elaborate, the GB has a local phase rule that includes the five geometric DOFs. For example, for the case of a GB in thermodynamic equilibrium with single-phase grains, this phase rule is given by [40]:

$$\psi = C + 7 - \varphi;$$

where $\psi$ is the number of independent variables, $\varphi$ the number of GB phases, $C$ the number of components in the system and 7 is $T$, $P$ and the five macroscopic DOFs of the GB. Equation (4) demonstrates that the exploration and construction of GB phase diagrams is a formidable experimental challenge as one needs to explore a $C + 6$ dimensional phase space.

In spite of the complexity of interface phase diagrams a number of transitions at GBs have been enumerated theoretically or observed experimentally. Cahn classified GB transitions as either congruent or noncongruent. For the former, the transitions occur with no change in boundary orientation—the interface remains planar with its core structure changing. For the latter, a change in boundary orientation is requisite. Few boundary orientations transform congruently, thus, an understanding of, for example, the faceting transition that describes a change in GB orientation, becomes important. In particular, this noncongruent transition results from a change of the inclination of the original interface plane with all other thermodynamic variables fixed [41]. This transition, also denoted roughening, is analogous to the roughening transition observed at free surfaces [42]. GB roughening can be induced by heating a specimen with a faceted interface [43]. Phase transitions producing new structures can also be induced by segregation of solute atoms to an interface. For example, the segregation of Nb to stacking faults in Co produces two coexisting phases in the plane of the fault—a random two-dimensional solid-solution and a two-dimensional ordered phase Co,Nb [44]. Also, the segregation of Au, Sb or S solute atoms to (002) twist boundaries in Fe results in the formation of a new network of dislocations; their cores possibly act as preferential sites for Au segregation [45, 46]. GBs thus exhibit many fascinating and intriguing transitions.

The subject of interface phases and their transitions is well developed for solid/vacuum surfaces, and there are many analogies between the phenomena occurring at GBs and free surfaces [47, 48]. For example, dissolution of a solute [49] at a metal/vacuum interface (surface) creates an interfacial region whose chemistry differs from that of the bulk. Pyramidal superstructures of solute, analogous to those that we observe at GBs via MC simulations, are calculated. Although the kinetics of dissolution has been the subject of theoretical work, little accompanying experimental research exists [50–52]. In order to search for correlations between dissolution and GB segregation on an atomic scale it is necessary to employ APFIM to chemically map this interfacial region.

First, in this paper we focus on a methodology to measure experimentally the value of $\Gamma_2$. Our approach involves a combination of TEM to measure the five macroscopic DOFs and APFIM to determine $\Gamma_2$ directly for the same GBs—see Section 2. An application of this methodology is presented for a series of GBs in a dilute Fe(Si) alloy. It is demonstrated that this approach allows one to directly access GB phase space. Second, an approach is presented for studying GB segregation employing Monte Carlo (MC) simulations—see Section 3. The results of a MC study of solute–atom segregation in the Ni–Pt system are presented for a series of (002) twist boundaries. The emphasis is on extracting a detailed atomic scale picture of the segregation patterns, and how they are affected by the twist angle. In this manner a trajectory in GB phase space is accessed. Both approaches are shown to yield new and unanticipated information about GB segregation.
2. ABSOLUTE ATOMIC SCALE MEASUREMENTS OF THE GIBBSIAN INTERFACIAL EXCESS OF SOLUTE AT GRAIN BOUNDARIES

2.1. Introduction

The methods widely used to study segregation involve exposing a GB surface by in situ fracturing of a polycrystalline or bicrystal specimen. This is limited to metals that fail intergranularly, and, moreover, the atomic arrangement at a GB is necessarily disturbed; also the orientation relationship is lost after fracture. Furthermore, techniques applied to solid/vacuum interfaces, for example, Auger electron spectroscopy, do not yield direct quantitative measures of $\Gamma_i$. Other techniques that indirectly measure $\Gamma_i$ involve measuring the free energy of a GB as a function of composition and then applying the Gibbs absorption isotherm equation \[ \Gamma_i = \frac{N^\text{vol}}{A} = \frac{1}{A} (N^\text{vol}_i - N^\text{f}_i - N^\text{a}_i) \]

where $N^\text{vol}_i$ is the excess number of atoms associated with an interface, and $A$ is the interfacial area over which $\Gamma_i$ is determined. The quantities $N^f_i$ and $N^a_i$ are the number of atoms of element $i$ in phases $\alpha$ and $\beta$, assuming that the two phases exist up to the Gibbs dividing surface, $\xi$. The excess is, therefore, defined by comparing the total number of atoms of element $i$ in the actual system containing the interface ($N^\text{vol}_i$), to a comparison system where the two phases making up the interface extend to the position of $\xi$. The quantities $C^\alpha_i$ and $C^\beta_i$ are the atomic concentrations of element $i$ in the homogeneous regions of phases $\alpha$ and $\beta$, that is, the bulk regions of the two phases. The quantity $C^\text{vol}_i$ is the atomic concentration of element $i$ in the total volume of material containing the internal interface, and $N^\text{vol}$ is the total number of all elements in the same volume.

The quantity $\Gamma_i$ is defined such that its value depends upon the position of the dividing surface \[ \Gamma^{(0)}_i = \Gamma_i - \Delta \xi, \] which is the result that we apply to GBs in Fe(Si).

When the APFIM is used to chemically analyze a heterophase 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 and temporal order in which the atoms are detected is preserved. This data is then plotted in the form of an integral profile, as shown schematically in 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
Fig. 1. Three-dimensional schematic drawing exhibiting an atom-probe field-ion microscope specimen containing a heterophase internal interface. This heterophase interface separates two different phases (α and β) with the atomic concentrations \( C_i^\alpha \) and \( C_i^\beta \) of element \( i \) in the homogeneous regions of phases α and β, that is, the bulk regions of the two phase phases. The quantity \( C_i^\text{vol} \) is the atomic concentration of element \( i \) in the total volume of material containing the heterophase interface. The unit vector \( n \) is normal to the plane of the interface, \( l \) is the unit vector parallel to the direction of the atom-probe analysis, and \( \phi \) is the angle between the vectors \( n \) and \( l \). The maximum depth resolution of an integral profile is achieved when \( \phi \) is zero.

The quantity \( N_i^{\text{vol}} \) is the total number of atoms plotted on the ordinate. This graphical construction is simple and does not require any assumptions. The value of \( A \) is given by:

\[
A = \frac{\pi D_{ph}^2}{4 \cos \phi},
\]

where \( D_{ph} \) is the diameter of the probe 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:

\[
\Gamma_i = \frac{4 \cos \phi}{\eta \pi D_{ph}^2} \left[ N_i^{\text{vol}} - N_i^\alpha - N_i^\beta \right] = \frac{4 \cos \phi}{\eta \pi D_{ph}^2} N^{\text{vol}} \left( \langle C_i^\alpha \rangle - \langle C_i^\beta \rangle \right) \xi - \langle C_i^\beta \rangle (1 - \xi).
\]

The atomic concentrations are expressed as averages, because the APFIM measures these averages. The quantity \( \eta \) is the detection efficiency of the chevron detector of the APFIM. The value of \( \eta \) equals the fractional open area of a chevron detector and is typically 0.55. The value of \( \phi \) is given by:

\[
\phi = \cos^{-1}(\mathbf{n} \cdot \mathbf{l}),
\]

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 \( \mathbf{l} \) 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 [62]. The value of \( D_{ph} \) is then determined directly from information in an FIM image. For the experiments reported here, the value of \( \cos \phi \) is unity, as \( \mathbf{n} \) is parallel to \( \mathbf{l} \) and therefore the projection of the probe hole is a circle.

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 \( N_i^{\text{vol}} \). 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 Gibbs 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 \( C_i^\beta \) in eqn (6).

The schematic diagram in Fig. 3(a) shows an atomic scale picture of the analysis for a GB in an Fe(Si) alloy; this figure corresponds to the situation where \( \mathbf{n} \) is parallel to \( \mathbf{l} \). To extract \( \Gamma_{Si} \), the excess number of Si atoms, \( N_{Si}^{\text{excess}} \), in the volume and area,
A, over which it is determined, is measured; $\Gamma_{ni}$ is given by:

$$\Gamma_{ni} = \frac{N_{\text{re}}}{A} = \frac{4 \cos \phi}{\eta \pi D_{ph}^2} \left( N_{\text{re}}^{\text{vol}} \right) \left( N_{\text{ni}} - N_{\text{ni}}^{\text{vol}} \right)$$

$$= \frac{4 \cos \phi}{\eta \pi D_{ph}^2} \left( C_{\text{ni}}^{\text{vol}} - C_{\text{ni}}^{\text{vol}} \right) \xi$$

$$- \left( C_{\text{Si}}^{\text{vol}} \right) \left( 1 - \xi \right),$$

(11)

where the quantities $N_{\text{re}}^{\text{vol}}$ and $N_{\text{ni}}^{\text{vol}}$ are the number of Si atoms in grains 1 and 2; the two grains exist up to a Gibbs dividing surface, $\xi$. The quantities $\langle C_{\text{Si}}^{\text{vol}} \rangle$ and $\langle C_{\text{ni}}^{\text{vol}} \rangle$ are the average atomic concentrations of Si in the homogeneous bulk regions of grains 1 and 2; $\langle C_{\text{ni}}^{\text{vol}} \rangle$ is the average atomic concentration of Si in the total volume of GB material. All the quantities in eqn (11) are indicated on Fig. 3(b).

2.2.2. Locating an internal interface for atom-probe spectroscopy. The general approach to observe a specific internal interface is to prepare an FIM specimen from a bulk specimen that was process to produce a desired microstructure. The FIM specimen is then prepared by electropolishing, electroetching, ion-beam milling, or a combination of those processes. One specific approach we employ involves electrolytic backpolishing to an internal interface, employing a versatile system for systematically preparing atom-probe specimens. This systematic approach incorporates a.c. electroetching or d.c. electropolishing in automated or manual modes [63]. The a.c. waveforms available are sine or triangular or square in either the one shot or continuous wave modes. The d.c. electropolishing mode produces pulses with widths in the range from 0.5 ms to 500 s. The power supply provides 0 to $\pm 48 \text{ V.d.c.}$ at up to 1 A.

In our laboratory an atom-probe specimen is examined by TEM utilizing a radically modified double-tilt stage for an Hitachi H-700H 200 kV transmission electron microscope; this stage is vibrationless at a magnification of 310,000 $\times$. It has a tilting range of $\pm 30^\circ$ for the $x$-tilt and $\pm 27^\circ$ for the $y$-tilt; this range is sufficient to analyze crystallographically an internal interface. This double-tilt stage and transmission electron microscope are also used to examine atom-probe specimens during the course of a backpolishing treatment to place selectively an internal interface in an FIM tip.

We have employed this approach extensively to study segregation at GBs in binary metal alloys and presently in Ni-based intermetallics. If, however, the interfacial area per unit volume is sufficiently large ($> 10^8 \text{ m}^2 \text{m}^{-3}$) it is possible to perform a random area analysis to locate an internal interface; this obviates the need to use TEM to place an interface in the field of view.

2.2.3. Measurement of the Gibbsian interfacial excess of Si at GBs in an FeSi alloy. First, the study of equilibrium solute-atom segregation in an FeSi alloy requires that the starting materials must have utmost purity to minimize the influence of impurity-atom segregation of the interstitial elements carbon, phosphorous, sulfur, nitrogen or oxygen. Thus the starting materials were Fe of 99.9945 at.% purity and Si of 99.9999 at.% purity. The Fe-3 at.% Si alloy was arc melted in an atmosphere of argon of high purity. The ingot was swaged and cold drawn to 185 $\mu\text{m}$ diameter wire. Next the specimens were encapsulated in a quartz tube backfilled with Ar of high purity. Then they were annealed at 823 K for 14.5 or 72.5 h and quenched into a brine solution at 273 K. Two annealing times were used to ascertain that the equilibrium concentration of Si was achieved at the GBs. These annealing times produce root-mean-square diffusion distances of 0.055 and 0.123 $\mu\text{m}$, respectively.

Figure 4(a) exhibits a transmission electron micrograph of a GB near the tip of an Fe 3 at.% Si wire.
Solute-atom segregation at grain boundaries

Fig. 4. (a) A transmission electron micrograph of an Fe-3 at.% Si specimen after GB analysis and backpolishing. (b) A field-ion microscope 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 aligned so that its perimeter is concentric with that of the GB image: \( \phi = 0^\circ \) and \( D_\text{e} = 11.5 \) nm. This Fe-3 at.% Si specimen had been annealed at 823 K for 14.5 h.

That was backpolished to produce a tip with the requisite geometry to locate a GB and analyze it via atom-probe microscopy. Figure 4(b) shows an FIM micrograph of the same tip. No signs of precipitation are observed in the bulk or at GBs by either transmission electron or atom-probe microscopy. Figure 5 is the corresponding integral profile; the abscissa represents the cumulative number of Fe plus Si atoms collected from a cylinder of material 11.5 nm in diameter. A pulse fraction \( (f) \) of 0.15—\( f \) is the ratio of \( V_p \) to \( V_{dc} \)—and a specimen temperature of 35 K were employed (see Krakauer and Seidman [64]). The value of \( \Gamma_{si} \) is \( 0.378 \pm 0.12 \times 10^{14} \) atoms cm\(^{-2}\).

Fig. 5. Integral profile of the GB analyzed in Fig. 4. The value of \( N_{\text{vol}} \) is 8915 atoms. The pulse fraction \( (V_p/V_{dc}) \) employed was 0.15, the temperature was 35 K, and the pulse frequency was 60 Hz.
The five macroscopic geometric degrees of freedom are: \(e = [0.85, 0.52, 0.06], \theta = 25.28^\circ, n_1 = [0.04, 0.68, 0.73], \) and \(n_2 = [0.21, 0.36, 0.91].\) Figure 6 is a layer profile calculated from the data displayed in Fig. 5. Each silicon concentration data point plotted on the ordinate is based on a total of 300 atoms/layer; note that the data points are 0.05 nm apart, and that there is a slight depletion of silicon on the left-hand side of this GB. This type of profile is the experimental version of the segregation profiles calculated via MC simulations, see Section 3.3.

The depth scale on the upper abscissa of Fig. 5 is determined from a knowledge of \(\rho, \) and the atomic density of Fe (\(\rho_{Fe} = 84.879\) atoms nm\(^{-3}\)); note well that each tick mark corresponds to 0.2 nm. The ultimate depth resolution of an atom-probe compositional analysis is equal to the mean interatomic planar spacing (\(d_{\text{m}}\)) 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 \(\approx 0.07\) 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 atom-probe analysis. An example of an easily identifiable pole is \(\{110\}\) for which the depth resolution is 0.02 nm. The error bar for \(\xi\) is determined by propagating the errors of each quantity in eqn (6). The error in \(N_{\text{excess}}\) is determined by assuming that the measured atomic concentrations are binomially distributed [65]. The error in \(D_{\text{m}}\) is empirically determined to be \(\pm 7\%\). The value of \(\Gamma_{\text{gb}}\) corresponds to a fractional monolayer coverage of \(\Theta = 0.22\) monolayers by assuming a saturation value for \(\Gamma_{\text{gb}}\) of \(\rho_{Fe}d_{\text{m}},\) which equals \(1.70 \times 10^{14}\) atoms cm\(^{-2}\). If we assume that the solute–atom segregation behavior obeys a Langmuir–McLean type adsorption isotherm, then the free energy of segregation for this GB is \(-15.1\) kJ mol\(^{-1}\).

2.2.4. The grain boundary phase space of an Fe(Si) alloy. Thirteen GBs were analyzed as described in the previous section. As \(\Gamma_{\text{gb}}\) is a function of \(e, \theta,\) and \(n,\) at fixed \(T, P,\) and bulk composition, the data spans a six-dimensional space. In Fig. 7, five DOFs are folded into two axes to display \(\Gamma_{\text{gb}}\) in a three-dimensional plot. Four of these DOFs are folded into the abscissa \(\cos(\theta, n),\) while the fifth DOF, the disorientation angle, \(\theta_{\text{dis}},\) is displayed along the second axis. This corresponds to the degree of twist or tilt of a GB. Figure 7 shows that \(\Gamma_{\text{gb}}\) rapidly increases from 0 at \(\theta_{\text{dis}} = 0^\circ\) to \(1.0 \times 10^{13}\) atoms cm\(^{-2}\) at the transition from low- to high-angle. Beyond this transition, \(\Gamma_{\text{gb}}\) increases to \(2.5 \times 10^{13}\) atoms cm\(^{-2}\) (\(\theta_{\text{dis}} = 68^\circ\)). (For \(\sin((\theta_{\text{dis}}/2) = 0\) the value of \(\Gamma_{\text{gb}}\) is zero.) Also, the GBs with \(e \cdot n = 1\) (pure twist) have higher values of \(\Gamma_{\text{gb}}\) than do GBs with \(e \cdot n = 0\) (pure tilt). This demonstrates that twist GBs exhibit a higher level of segregation than do tilt GBs in this alloy. This is the first experimental evidence that twist and tilt GBs exhibit different absorptive capacities for solute atoms. We have recently obtained some evidence for this same fact employing Monte Carlo simulations on \(\Sigma = 5\) twist and tilt boundaries for a dilute Pt(Au) alloy [66].

2.3. Conclusions

1. A direct, quantitative and absolute methodology has been developed to determine the Gibbsian interfacial excess of solute, \(\Gamma_2,\) at preselected GBs.
2. The approach involves the combined use of TEM and atom-probe microscopy—APFIM/TEM. TEM is used to first determine the five macroscopic degrees of freedom, DOFs, of a GB in an atom probe specimen, employing a specially developed double-tilt stage that holds 1 cm long field-ion microscope wire specimens. The same specimen is then electrolytically backpolished to the GB, and transferred to an atom probe.

3. We have applied this methodology to GBs in single-phase alloys of the W(Re) and Fe(Si) systems.

4. Results are presented for a high-purity Fe-3 at.% Si alloy that was recrystallized and annealed at 823 K for 14.5 or 72.5 h; these annealing times correspond to root-mean-squared diffusion distances of 0.055 and 0.123 μm respectively.

5. For this Fe(Si) alloy Γs was measured for GBs with different structures. A three-dimensional plot of Γs vs cos(Ł, n) and sin(Ł, n) is used to present the results; in this manner all five macroscopic DOFs are folded into two axes—see Fig. 7. This figure constitutes the phase space of GBs for this alloy.

6. Figure 7 shows that for large values of θ, that Γs saturates for all the GBs studied. Although the saturation value depends on the character of the GB. In particular, for this alloy the saturation value is larger for pure twist boundaries, cos(Ł, n) = 0, than it is for pure tilt boundaries cos(Ł, n) = 1. This is the first experimental measurement that demonstrates that there is a difference in the absorptive capacities of tilt and twist boundaries.

7. Atomic scale segregation profiles normal to the GB plane are measured for specific GBs, see Fig. 6.

3. MONTE CARLO SIMULATIONS OF SOLUTE-ATOM SEGREGATION AT (002) TWIST BOUNDARIES IN DILUTE FCC ALLOYS

3.1. Introduction

In spite of numerous experimental, theoretical and simulation studies our basic knowledge about GB segregation is still rather fragmentary. This is a result of the enormous complexity of the 6 + C dimensional phase space in which this phenomenon occurs. Besides the conventional state variables—temperature, pressure and composition—the five macroscopic DOFs of a GB are postulated to be thermodynamic state variables. The three microscopic DOFs, that is, the rigid body translation vector between two grains, are assumed to be fully relaxed to minimize the Gibbs free energy of a bicrystal. We have investigated solute-atom segregation in detail at (002) symmetrical twist boundaries in dilute Au–Pt and Ni–Pt alloy. And in this section we present an abbreviated account that outlines the important features of segregation in the Ni–Pt system, focusing on low-angle (002) symmetrical twist boundaries [67]. The Ni–Pt system is of particular interest for several reasons:

1. It exhibits a clear tendency to ordering with three ordered phases (Ni,Pt, NiPt and NiPt,) in the bulk phase diagram [68]; this is in sharp contrast to the Au–Pt system which exhibits a miscibility gap.

2. There is a considerable size misfit between the two elements in contradistinction to the elements Au and Pt; the room temperature values of the lattice parameters are 0.352 and 0.392 nm for Ni and Pt, respectively, while for Au it is 0.408 nm.
3. Oscillatory solute-atom segregation profiles are observed in Ni-Pt alloys near different free surfaces [69], at a mixed $\Sigma = 5$ twist–tilt boundary [70], and at an (002) twist boundary.

All the simulations were performed at a temperature, $T = 850$ K, that is high enough to be reproduced experimentally (in terms of diffusion times) but low enough to observe substantial solute–atom segregation effects. The solute–atom concentrations on both sides of the phase diagram were chosen to lie in single-phase solid-solution regions. The solute-atom concentrations are high enough to give adequate statistics but the alloys can still be considered to be dilute.

The main questions of concern are:

- What is the structural dependence of solute–atom segregation? that is, the dependence of the Gibbsian interfacial excess of solute on the twist angle of the boundaries.
- What is the detailed spatial arrangement of solute atoms at a grain boundary as a function of twist angle for low-angle boundaries?
- How is the solute–atom segregation behavior related to the thermodynamic properties of the alloy system?

3.2. Computational procedures

The computational methodology employed is MC simulation, which is well suited for atomistic simulations of equilibrium phenomena in solids [71, 72]. We utilize the fundamental algorithm of Metropolis et al. [73] as it provides a reasonably good convergence to equilibrium and efficient sampling of the equilibrium configurational space. The choice of the statistical ensemble was dictated by the necessity to simulate a GB in a single-phase solid solution that is in equilibrium with a quasi-infinite reservoir of solute atoms in a bulk reference crystal. The most suitable approach for this situation is the so-called transmutational ensemble. The parameters held constant are temperature, the total number of atoms and the difference in the so-called excess chemical potentials [74]. Atoms are, however, allowed to change their chemical identities, so that the atomic fraction of each component is variable. In addition, the volume of the simulation cell is allowed to relax, thereby yielding a constant pressure.

At each MC step an atom is chosen at random and a decision is made whether or not a certain attempt is accepted—the latter is based on the Metropolis algorithm. The following sequence of attempts is performed:

1. The chemical identity of an atom is changed; this step is for modifying the local composition of an alloy, and it is basic to the phenomenon of solute–atom segregation.
2. The displacement of an atom from its position by a random vector with a magnitude smaller than 0.01 nm; this step allows for relaxations on an atomic scale. Note well that steps 1 and 2 are made simultaneously.
3. After, on the average, all the atoms in a bicrystal have undergone the above two attempts an overall volume relaxation is implemented that involves a change in one or more periodic lengths, and a corresponding rescaling of coordinates of all the atoms in the bicrystal by a small random quantity. This procedure changes the volume of the computational cell to maintain the bicrystal at constant pressure.
4. A relative translation of the two grains in the plane of the interface by a random vector is attempted with the same time periodicity as step 3. It allows complete relaxation of all microscopic degrees of freedom of the boundary. No significant displacements from the coincident site lattice (CSL) structure were, however, observed for the low-angle boundaries.

The total value of the internal energy $E_{\text{tot}}$ is calculated using the embedded atom method (EAM) potentials that have been developed for six face-centered cubic elements (Ag, Au, Cu, Ni, Pd and Pt). The EAM potentials are empirical many-body continuous potentials that have been used extensively for studying different physical problems in materials science [75–78].

Prior to simulations for GBs, similar simulations are run for a perfect single crystal (4000 atoms) to determine the value of $\Delta \mu$—the difference in the excess chemical potentials—corresponding to the requisite value of solute–atom concentration. The equilibrium lattice constants for given concentrations are also obtained from those runs ($10^4$ MC steps per atom).

The computational cell represents a bicrystal with three-dimensional periodic boundary conditions. The two grains are rotated about an [001] direction to obtain a given twist angle; hence, only one of the five macroscopic geometric DOF is varied. Physically, there are two crystallographically identical GBs separating the two grains. This arrangement is valuable because it eliminates the free surface, and improves the statistics by having two GBs in a given bicrystal. Also a sufficiently large separation is necessary between the two GBs to exclude the interaction of the stress fields of the two GBs in the middle of the bicrystal, where it is necessary to maintain the properties of the bulk single crystal. We find empirically
that commencing with 16 (002) planes between the two interfaces this condition is met for the lowest-angle boundary—that is, the one having the longest range elastic stress fields—we investigated. Normally in our MC simulations we use a computational cell that is approximately (4-5) nm × (4-5) nm in the plane of the interface—this corresponds to between 200-300 atoms in one atomic plane and is about 6.3 nm in the direction normal to the (002) GB plane.

Thus, the overall number of atoms in the system varies between 6400-9600. The first $2.5 \times 10^3$ MC steps per atom of each run were used for equilibration. The averaging was performed over the next $3 \times 10^3$ or $10^4$ MC steps per atom, depending on the boundary. The time step for averaging was of the order of 10 MC steps per atom to avoid temporal correlation effects.

Another important effect is the surface tension of a GB that acts in the plane of an interface to reduce its cross-sectional area. This effect causes stresses that cannot relax locally—due to the periodicity in the plane of the interface—so that the entire bicrystal has to accommodate these stresses. In our case the stresses are accommodated by means of a lattice expansion normal to the GB plane. The magnitude of the effect is approximately proportional to the fraction of the total system volume belonging to the GB phase; that is, essentially the inverse of the distance between the two GBs in our bicrystals. The typical "thickness" of a GB is approximately one to two atomic planes.

Thus in a normal polycrystalline specimen this effect most likely does not exist; it may, however, exist in nanograin material. In a MC simulation this effect may be quite large if a bicrystal is too small.

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**Fig. 8.** A plot of the Gibbsian interfacial excess of solute ($\Gamma$) vs $\sin(\theta/2)$ for Pt-3 at.% Ni (open squares) and Ni-3 at.% Pt (solid circles) at 850 K. The quantity $\sin(\theta/2)$ is directly proportional to the primary grain boundary dislocation density via the Read–Shockley equation. The error bars indicate plus or minus one standard deviation.

**Fig. 9.** Solute-atom segregation profiles normal to the geometric (002) interface plane for the nine boundaries studied at 850 K. The left-hand column corresponds to Pt-3 at.% Ni and the right-hand one to Ni-3 at.% Pt. Each plot contains two crystallographically identical periodic interfaces—ther planes lying between planes 16-17 and 32-1. (a) For the twist angles ($\theta$) $5^\circ$, $10.4^\circ$, $16.3^\circ$ and $22.6^\circ$. (b) For $\theta = 28.1^\circ$, $33.9^\circ$, $36.9^\circ$, $41.1^\circ$ and $43.6^\circ$. The error bars correspond to plus or minus one standard deviation.
straightforward but computationally inefficient solution is to increase the separation between the GB planes. We employ an alternative solution, where the total area of the interface is held constant at a given equilibrium value, the latter is determined by the equilibrium value of the lattice parameter found from simulation runs for a single crystal. Thus, only the periodic length normal to the interface is allowed to relax. We have demonstrated that either employing much larger bicrystals—40 (002) planes between the GBs—or fixing the cross-sectional dimensions of an interface yields the same quantitative results.

The bicrystal employed is one where the [001] direction is perpendicular to the plane of the (002) interface plane; the geometric interface lies between two (002) planes and it contains no atoms. All possible (002) twist boundaries lie in the angular range $\theta = 0^\circ$ to $45^\circ$ about the [001] direction; the point group for this interface is 4mm. Of the five macroscopic geometric degrees of freedom only $\theta$ is varied. The angular values studied correspond to the following CSL boundaries: $5^\circ$ ($\Sigma = 265$), $10.4^\circ$ ($\Sigma = 61$), $16.3^\circ$ ($\Sigma = 25$), $22.6^\circ$ ($\Sigma = 13$), $28.1^\circ$ ($\Sigma = 7$), $33.9^\circ$ ($\Sigma = 289$), $36.9^\circ$ ($\Sigma = 5$), $41.1^\circ$ ($\Sigma = 77$) and $43.6^\circ$ ($\Sigma = 29$). The choice of CSL boundaries is not restrictive, because the boundaries cover the entire range of possible misorientations. The atomic structures of the (002) grain boundaries have been extensively studied experimentally by X-ray diffraction techniques, geometrically by the packing of hard spheres [79], anisotropic elasticity theory [80], lattice statics [81,82], molecular dynamics [83] and free-energy minimization [84] techniques.

Relaxed low-angle (002) twist boundaries in cubic metals consist of a square grid of localized orthogonal screw dislocations. The resulting twist boundary is in a state of pure shear with no long range stress fields [85]. This description appears to be an excellent one for twist boundaries in metals. The screw dislocations are the so-called primary grain boundary dislocations (PGBDs) whose Burgers vectors (b) are $(a/2)(110)$-type ($a$ is the lattice parameter) in the face-centered cubic lattice. The spacing of the grid is given by the Read–Shockley relation:

$$d = \frac{|b|}{2 \sin(\theta/2)} = \frac{a/\sqrt{2}}{2 \sin(\theta/2)}.$$  \hspace{1cm} (12)

![Fig. 10. Patterns of Ni atom segregation at the four successive (002) planes nearest the geometric interface for a $\theta = 5^\circ$ twist boundary in a Pt-3 at.% Ni alloy. Atomic sites with an average Ni concentration that is one or more standard deviations above the bulk Ni concentration are indicated by solid black circles and the remaining sites are gray circles.](image-url)
The deviation from an exact CSL orientation produces a grid of secondary grain boundary dislocations (SGBDs) with the spacing given by the same Read–Shockley relation, with \( \theta \) replaced by \( |\Delta \theta| \); where \( \Delta \theta \) is the deviation angle measured from the exact CSL orientation [86]. The intersections of the PGBD lines form patches of the \( \Sigma = 5 \) structure. The localization of the misfit falls off with the distance from the interface, and the dislocation cores become broader and less pronounced. At sufficiently large angles (\( \theta \geq 22.6^\circ \)) the areas of the regions of “good” atomic fit become comparable to those of the intersection regions, and more complicated high-angle twist boundaries appear that can be described by a structural unit model [87, 88]. The atomic displacements within the square cells of the PGBDs are rotations around the elements of Bollmann's O-lattice.

For (002) twist boundaries only symmetrical structures exist. A displacement, however, of the upper grain with respect to the lower grain—parallel to the plane of the interface—may lead to a change of the symmetry of the boundary. For twist boundaries crystallographically nonequivalent displacements of the two grains are limited to the cell bounded by the two shortest nonparallel displacement shift complete (DSC) vectors, \( b_1 \) and \( b_2 \), in the boundary plane. Bristowe and Crocker have shown by means of molecular statics at 0 K, for a \( \Sigma = 5 \) twist boundary in pure Ni or Cu that the only displacements leading to stable structures are \((1/2)b_1\) or \((1/2)b_2\) and \((1/2)[b_1 + b_2]\); these structures are denoted type I and type II. Recently, a free-energy minimization study, in the local-harmonic approximation [89], revealed a phase transition from the CSL to type I structure in a \( \Sigma = 5 \) high-angle twist boundary in gold at about 315 K. In our previous papers [90] Monte Carlo simulations were performed for the type I and type II as well as the CSL \( \Sigma = 5 \) high-angle boundaries in a Pt-1 at.% Au alloy at 850 K. The type I structure reverted to the CSL structure and the type II structure remained metastable. There were, however, no significant differences between the solute–atom segregation profiles of the type II and CSL structures. We have recently discovered a phase transition in the \( \Sigma = 5/(002) \) twist boundary in the Pt(Ni) system. This

![Fig. 11. The pattern of Ni atom segregation at the three successive (002) planes nearest to a \( \theta = 10.4^\circ \) twist boundary in a Pt-3 at.% Ni alloy. Atomic sites with an average Ni concentration that is one or more standard deviations greater than the bulk concentration are indicated by solid black circles and the remaining sites are gray.](image-url)
transition occurs when the bulk concentration of Ni exceeds \( \approx 6 \text{ at.\%} \); it involves a change from the CSL structure to the type II structure \([91]\). A drastic change in the distribution of solute concentrations at different GB sites accompanies this transition.

3.3. Solute-atom segregation behavior

As discussed in Section 2.2.1 \( \Gamma_2 \) is the most general measure of solute-atom segregation—it applies to any solid/solid interface. For analyzing the results of the simulations on GBs we define \( \Gamma_2 \) in terms of dimensionless units of solute monolayers by:

\[
\Gamma_2 = \frac{2}{n_{pl}} \sum_{i=1}^{n_{pl}} (c_i - c_b),
\]

where \( n_{pl} \) is the number of (002) planes in the bicrystal and \( c_i \) and \( c_b \) are average solute-atom concentrations, in units of atomic fraction, in plane \( i \) and in the bulk of the bicrystal, respectively.

The dependence of \( \Gamma_2 \) on \( \sin(\theta/2) \) is exhibited in Fig. 8 for the Ni-3 at.\% Pt and Pt-3 at.\% Ni alloys. The dislocation density is simply the reciprocal of \( d \) in eqn (12), hence the quantity \( \sin(\theta/2) \) is proportional to the PGBD dislocation density. For both alloys \( \theta/2 \) increases with increasing dislocation density, that is, with increasing \( \theta \). The value of \( \Gamma_2 \) increases monotonically for both alloys, and then saturates at about half of the angular interval \( (\theta > 22.6^\circ) \). This angle corresponds to the dislocation density at which the dislocation cores start to overlap. The magnitude of the effect is about a factor of two larger for the Ni-rich alloy.

The solute-atom segregation profiles normal to the (002) GB plane yield the next most detailed level of information. These profiles for nine GBs are exhibited in Figs 9(a) and 9(b) in order of increasing \( \theta \). The left-hand column is for the Pt-3 at.\% Ni alloy, and the right-hand column is for the Ni-3 at.\% Pt alloy. The two geometric interfaces are located between the 16th and 17th (002) planes and the 1st and 32nd (002) planes.
Solute-atom segregation at grain boundaries

planes; the presence of two GBs is due to the periodic boundary conditions. The 1st to 16th (002) planes belong to one grain of the bicrystal, while the 17th to 32nd (002) planes belong to the other grain. Solute-atom segregation is expected to be symmetrical with respect to the (002) interface planes because the GB is a symmetrical twist boundary. The concentration values plotted on the ordinate scale are the average solute-atom concentrations integrated over the area of each (002) plane. The error bars represent plus or minus one standard deviation, and are of different magnitudes for different GBs because of different durations of the simulation runs. The planes in the region between the two interfaces constitute the bulk of a bicrystal, and they are unaffected by solute-atom segregation; this region has a constant solute-atom concentration that corresponds to the bulk concentration of each alloy. The solute concentration is highest near the interface, with the exception of the \( \theta = 5^\circ \) boundary in the Pt-3 at.\%Ni alloy; this boundary exhibits a Ni concentration in the first (002) plane adjacent to the interface that is slightly lower than in the second (002) plane. The solute-atom concentrations in the (002) planes adjacent to the interface increase steadily until saturation occurs at \( \theta \approx 22.6^\circ \). Simultaneously the width of the segregation profiles decreases with increasing twist angle; the profiles are fairly sharp for the Pt-3 at.\%Ni alloy, and even sharper for the Ni-3 at.\%Pt alloy.

Now we examine visually the spatial distribution of atomic sites enhanced in solute atoms near the interface for low-angle boundaries. Figure 10 displays the first four (002) planes adjacent to a \( \theta = 5^\circ \) twist boundary in a Pt-3 at.\%Ni alloy. The atomic sites with a solute-atom concentration greater than one standard deviation above the equilibrium bulk value are black while the remaining sites are gray. The sites enhanced in Ni atoms are situated predominantly in rows along the dislocation cores—the (1/2)<110>-type directions—and the region of enhanced solute concentration widens with increasing distance from the (002) interface. Note carefully, however, that the average solute-atom concentrations at the enhanced sites decrease concomitantly with increasing distance from the (002) interface. The sites in the middle of the dislocation grid are essentially unaffected by

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Fig. 13. The pattern of Pt solute-atom segregation at the four successive (002) planes nearest to the \( \theta = 5^\circ \) interface in a Ni-3 at.\%Pt alloy. Atomic sites with an average Pt concentration that is greater than the bulk value by more than one standard deviation are indicated by solid black circles and the remaining sites are gray circles.
the process of solute-atom segregation. A similar physical picture is found for the $\theta = 10.4^\circ$ boundary (Fig. 11).

To better visualize the spatial distribution of enhanced sites, a projection onto a $\{110\}$-type plane normal to the plane of the interface is shown in Fig. 12(a). The regions with the dislocations parallel to the plane of the projection have been deleted, so that only the two dislocation cores normal to the plane of the projection remain. Five (002) atomic planes on both sides of the geometric (002) interface, denoted by I—I, are displayed with the sites enhanced in solute denoted by large spheres, and those unaffected by solute-atom segregation by points. Due to the small ($\theta = 5^\circ$) misorientation between the upper and the lower grains, the points representing rows of atoms are slightly shifted in the (002) planes normal to the interface. The cross-section of the atomic sites enhanced in solute atoms has an hourglass-like shape for both dislocations; the same description also applies to the two dislocations not displayed. This figure provides an explanation for the oscillatory segregation profile in this boundary (Fig. 9). The first (002) plane has a smaller number of enhanced sites than the second one, while for the third (002) plane the increase in the number of enhanced sites is compensated for by a decrease in the average concentrations at those sites—the average solute-atom concentration decreases with increasing normal distance from the (002) interface. Figure 12(b) is the same image as in Fig. 12(a) but it is rotated by $6^\circ$ around the [001] direction normal to the (002) interface plane, denoted by I—I, to display the three-dimensional character of the solute-atom distribution.

For the Ni-3 at.% Pt alloy two-dimensional plots of the solute-atom distribution in the first three (002) planes parallel to the geometric interface are displayed in Figs 13 and 14 for the $\theta = 5^\circ$ and $\theta = 10.4^\circ$. For this alloy the solute atoms tend to segregate to regions that are complementary to those in the Pt-3 at.% Ni alloy. Rows of atoms along the dislocation cores are virtually unaffected by solute-atom segregation, while the areas inside the dislocation grid are enhanced in solute atoms. Away from the (002) interface plane the rims of the unenhanced regions broaden and the enhanced sites move toward the

![Fig. 14. The pattern of Pt solute-atom segregation at the three successive (002) planes nearest to the $\theta = 10.4^\circ$ interface in a Ni-3 at.% Pt alloy. Atomic sites with an average Pt concentration that is greater than the bulk value by more than one standard deviation are indicated by solid black circles and the remaining sites are gray circles.](image-url)
Fig. 15. (a) A projection of atomic sites in a Pt-3 at% Ni alloy—for a $\theta = 5^\circ$ twist boundary—normal to the (002) interface and to one of the two orthogonal sets of screw dislocations along the (110)-type directions; this is similar to the projection in Fig. 12(a). The distance between the two screw dislocation lines is 11.5 nm. The first six (002) planes on both sides of the interface, denoted I—I, are displayed. The sites enhanced in solute are depicted by large red spheres and all the others by small points. The black color corresponds to solute-atom concentrations less than the bulk concentration plus one standard deviation, that is, less than 4 at.% solute. The concentration of solute at enhanced sites (with concentrations of solute greater than 4 at.%) is represented by the density of color. The darkest red corresponds to concentrations of solute in excess of 10 at.%. The enhanced sites are arranged in bipyramidal patterns above and below the screw dislocation lines. The solute concentration at an individual enhanced site decreases with increasing distance from the interface. The rotation angle between the upper and lower grains is seen from the projections of atomic rows. (b) The same picture rotated by $9^\circ$ around an [001] axis normal to the interface to exhibit the three-dimensional character of the pattern.
center of the square grid of dislocations. When projected onto a \{110\}-type plane, in the same manner as in Fig. 12(a), the enhanced regions are found to form bipyramidal regions centered on the same square grid of dislocations—see Fig. 15(a). For better resolution in Fig. 15(a) and (b) different levels of solute concentrations are represented by a color scale. The first six (002) planes on both sides of the interface, denoted I—I, are displayed. The sites enhanced in solute are depicted by large red spheres and all the others by small points. The black color corresponds to solute-atom concentrations less than the bulk concentration plus one standard deviation, that is, less than 4 at.% solute. The concentration of solute at enhanced sites (with concentrations of solute greater than 4 at.%) is represented by the density of color. The darkest red corresponds to concentrations of solute in excess of 10 at.%. The rotation angle between the upper and lower grains is seen from the projections of atomic rows. Figure 15(b) is the same picture as in Fig. 15(a) except that it is rotated by $9^\circ$ around the [001] direction normal to the (002) interface plane to exhibit the three-dimensional character of the solute-atom distribution.

### 3.4. Discussion and summary

A systematic investigation has been performed of the phenomenon of solute–atom segregation at (002) symmetrical twist boundaries in dilute single-phase solid-solution alloys on both sides of Ni–Pt phase diagram at 850 K. The following is a discussion and summary of the results presented in Section 3.3.

#### 3.4.1. Chemistry of the alloy

The interfacial regions are enhanced in solute atoms on both sides of the Ni–Pt phase diagram. From the point-of-view of classical thermodynamics of the Gibbsian interfacial excess of solute is defined by eqn (2). The sign of $\Gamma_2$ can be either positive or negative, depending on the fundamental thermodynamic properties of the solid-solution. A major challenge is to be able to infer at least the sign of $\Gamma_2$ from the properties of the bulk phase diagram. One of the simplest suggestions is that the pure element with the lower surface free energy is enhanced at a GB. This implies that the sign of $\Gamma_2$ always changes on opposite sides of a phase diagram. This has been found to be true for simulations of solute–atom segregation at symmetrical twist (002) boundaries in the Au–Pt [92], Cu–Ni [93, 94] and Au–Pd [95] systems. For all three alloy systems Au and Cu are enhanced on both sides of the phase diagrams, respectively. For all three alloy systems the element with the lower melting point—that is, the element with the lower surface tension segregates to GBs. The present results introduce, however, a different trend, with the sign of $\Gamma_2$ being positive for the solute species on both sides of the Ni–Pt phase diagram. Other systems with similar behavior are Au–Cu [96] and Cu–Pt [97]; these systems also have large values of the size misfit parameter.

We now attempt to interpret our observations for the Ni–Pt and Au–Pt systems. The real situation may, of course, be much more complicated than the simple model we are presenting. Within the framework of elasticity theory the interaction of a solute atom with a twist boundary [98] arises from two effects. The size misfit effect is a $pA/V$ type of interaction, and it arises from local expansions at screw dislocation cores and the resulting net compression is derived from nonlinear elasticity theory. The inhomogeneity effect is due to a difference of the elastic constants of the solute and solvent atoms and it comes from linear elasticity theory. Both effects are second order in the distance from a dislocation line. The size misfit effect parameter, $\epsilon_s$, is proportional to the fractional change of the lattice constant with concentration of the solute species and it is given by $\epsilon_s = a^{-1}(da/dc)$. The inhomogeneity effect parameter, $\epsilon_a$, is given by $\epsilon_a = \mu^{-1}(d\mu/dc)$, where $\mu$ is a shear modulus. Due to the size misfit effect oversized atoms should be repelled from twist boundaries, while undersized ones should be attracted to them. Similarly, due to the inhomogeneity effect “harder” atoms should be repelled from GBs, and “softer” ones should be “attracted”. In the Ni–Pt system, where the size misfit parameter is fairly large and the inhomogeneity factor is small, the larger Pt atoms should be repelled from the interface on the Ni-rich side of the phase diagram and the smaller Ni atoms should be attracted to a GB on the Pt-rich side. This is inconsistent with the simulations, and, therefore, doesn’t explain the results. Alternatively, the explanation in terms of the inhomogeneity effect seems to work for the Pt–Au system, where the size misfit parameter is small and the inhomogeneity factor is large, that is, the “softer” Au atoms tend to be attracted to a GB on both sides of the phase diagram. The exact relation, however, between the magnitudes of the two elastic effects is determined by the value of an unknown dimensionless parameter, $q$.

The above discussion demonstrates that at present we cannot formulate a reasonably simple criterion to predict even the sign of the interfacial segregation! The connection between a bulk phase diagram of an alloy and interfacial phase diagrams for the same system is an intriguing and high priority area of research that can be resolved only on the basis of more detailed and accurate information than we presently have available.

#### 3.4.2. Structural features

One macroscopic geometric DOF—the twist angle $\theta$—was systematically...
varied for the (002) symmetrical twist boundaries investigated. We find (see Fig. 2) that $\Gamma_{\text{cros}}$ steadily increases with increasing $\theta$ until saturation occurs at about $22.6^\circ$ on both sides of the phase diagram. The effect is, however, a factor of two larger on the Ni-rich side. The widths of the segregation profiles normal to the interface decrease systematically with increasing $\theta$. This is indicative of an elastic interaction between a GB and a solute atom—at least at low angles. The volume expansions at the GBs scale with the amount of solute-atom segregation.

The solute concentrations at different sites near the boundaries are found to be very inhomogeneous both for low- and high-angle boundaries. At low-angle boundaries some sites have concentrations of solute atoms significantly greater than in the bulk, that is, these sites are enhanced in solute, while other sites are unaffected by solute-atom segregation. At high-angle boundaries a considerable fraction of the sites have a concentration that is less than the bulk concentration, while other sites are very strongly enhanced. A more detailed discussion of solute-atom segregation at high-angle twist boundaries is given elsewhere [99].

The spatial distribution of sites affected by the solute-atom segregation at low-angle boundaries is found to be complementary on both sides of the phase diagram. On the Pt-rich side the enhanced sites are arranged in rows, above and below the cores of the PGBDs, in the form of an hourglass-like pattern based on the square grid of screw dislocations. Alternatively, on the Ni-rich side the enhanced sites are arranged in the shape of a stepped bipyramid that is based on the same square grid of PGBDs. The sites on the outer surfaces of each bipyramid are more strongly enhanced in solute atoms than sites inside them. The hourglass-like structures account for the nonmonotonic segregation profile of the $\theta = 5^\circ$ boundary in Pt-3 at.% Ni, as the average concentrations in the second (002) plane are higher than at the first (002) plane. In both cases the concentration of solute atoms at enhanced sites decreases with increasing distance from the interface. The spatial extent of the two geometric arrangements of solute atoms—hourglass-like structures and stepped bipyramids—decreases with increasing $\theta$; this effect points to the importance of elastic interactions as the penetration depth of the elastic stress field associated with twist boundaries is inversely proportional to the periodicity of the dislocation grid by St Venant's principle.

The results presented in this paper show abrupt changes in the solute-atom segregation behavior near the cores of the primary GB screw dislocations. On the Ni-rich side there is an abrupt transition from the highest level of enhancement at the surface of stepped bipyramids to no enhancement at all beyond these surfaces. Alternatively, on the Pt-rich side the hourglass-like structures above the dislocation cores are strongly enhanced in Ni but the effect disappears abruptly when crossing into the bipyramidal region. One possible explanation may be that the solute-atom segregation behavior is completely different in a dislocation's core from its behavior in the elastic region beyond the core. This possibility appears unlikely, however, because the abrupt transitions occur in the 2nd, 3rd and 4th planes from the (002) geometric interface, and this is well beyond the possible radius of influence of a dislocation core. Another possible explanation is based on a competition between the inhomogeneity and size misfit effects as these effects have different laws of decay. When these effects have different signs and are of comparable magnitude, the areas with the strongest interaction energies can be shifted from the dislocation cores. We cannot make any better prediction, because only an order of magnitude estimate for the dimensionless parameter, $q$, in this model is presently available.

The same low-angle twist boundaries in dilute Au–Pt alloys exhibit a stepped bipyramidal pattern of segregation on both sides of the phase diagram, that is, the bipyramidal structures are enhanced in Au on the Pt-rich side and are depleted in Pt on the Au-rich side. The remaining hourglass-like structures above the dislocation lines are virtually unaffected by solute-atom segregation.

Bipyramidal patterns of solute-atom segregation are also observed in MC simulations of (001) semicoherent heterophase boundaries in binary Cu–Au [100] and ternary Cu–Ag–Au [101] alloys. The effect is larger in the latter case, where pyramids of a silver-rich phase form that penetrate deeply in the copper-rich phase. The bipyramids are based on the cells of a square grid of the geometrically necessary misfit dislocations.

A direct correlation between the local hydrostatic pressure and chemical composition was observed in Ag monolayers deposited on Cu substrates. A tight-binding molecular dynamics study [102, 103] showed that the larger Ag atoms tend to occupy atomic sites in tension, while the smaller Cu atoms preferentially go to compressed sites forming a hexagonal grid.

Recently, the effect of local stresses on solute–atom segregation at (002) boundaries was investigated for a Cu-5 at.% Ni alloy by the free-energy minimization technique in the local-harmonic approximation [104]. It was found that enhancement in Cu, which has a slightly larger lattice parameter, than Ni—$c_0 = 0.2233$ for Ni(Cu) [105]—correlates strongly with tensile
stresses and is not affected by shear stresses. On the other hand, at a low-angle boundary in the same alloy substantial solute-atom segregation was observed in the 2nd and 3rd planes from the interface with a bipyramidal pattern. From the point of view of elasticity theory, there can be no tensile stresses there.

From the above we conclude that the conventional wisdom [106] about the atomic sites near the interface being essentially of two types—"good fit" ones where there is almost no distortion of the crystalline lattice and "bad fit" ones where distortions are large (in the cores of GB dislocations)—is inadequate to describe the atomic-scale picture of solute-atom segregation. In our case some "bad fit" sites are strongly affected by solute-atom segregation, while others are not. Accurate calculations of local stresses at each site can be very helpful in understanding interfacial segregation phenomena. These results are to be presented elsewhere.

3.5. Conclusions

1. Monte Carlo simulations were performed of solute-atom segregation at symmetrical (002) twist boundaries, as a function of the twist angle, for dilute single-phase alloys on both sides of the Ni-Pt phase diagram at 850 K.

2. The Monte Carlo simulations exhibit solute-atom enhancement at twist boundaries for both the Pt-3 at.% Ni and Ni-3 at.% Pt alloys. This result is in qualitative agreement with solute-atom segregation at free surfaces in the same alloy system (see discussion in [72] and references therein). The magnitude of the enhancement for the grain boundaries studied is approximately a factor of two greater on the Ni-rich side as measured by the Gibbsian interfacial excess of solute.

3. In both alloys the value of the Gibbsian interfacial excess of solute increases with increasing \( \theta \) and it saturates at approximately one-half of the 45° interval, that is, at about the angle at which the cores of the primary grain boundary dislocations begin to overlap.

4. The widths of the solute-atom segregation profiles normal to the (002) geometric interface narrow with increasing \( \theta \) from three to two planes on each side of an interface until saturation occurs. This is consistent with the fact that the penetration depth of the elastic stress fields associated with a twist boundary decreases with increasing \( \theta \). At the smallest value of \( \theta \) studied (5°), on the Pt-rich side of the phase diagram, an oscillatory segregation profile is observed that disappears with increasing \( \theta \). On the Ni-rich side oscillatory segregation profiles are not observed.

5. At low-angle boundaries on the Pt-rich side of the phase diagram solute atoms tend to segregate in hourglass-like structures based on the square grid of primary grain boundary screw dislocations. For the same boundaries on the Ni-rich side a spatially-complementary type of segregation pattern is observed, with the regions enhanced in solute atoms forming a stepped bipyramidal pattern that is centered on the same square grid of primary grain boundary screw dislocations.

6. The height of the stepped bipyramidal and hourglass regions—that is, the number of (002) planes where solute-atom segregation is observed—decreases with increasing \( \theta \) from about five atomic planes each side of the interface to two atomic planes in the high-angle regime; in the latter regime the patches of perfect crystal become comparable to the areas of dislocation cores and their intersections. This is consistent with elasticity theory considerations [98].

7. A comparison with the previously studied Au-Pt system, where a reversal of the sign of the Gibbsian interfacial excess of solute occurs when changing sides of the phase diagram, demonstrates that the bulk thermodynamics of an alloy as well as the structure of a grain boundary plays an important role in determining the detailed atomic-scale behavior of solute-atom segregation.

8. A comparison with other available simulation results on solute-atom segregation at grain boundaries, heterophase boundaries and free surfaces suggests that hourglass and bipyramidal patterns of solute-atom segregation are quite common, and are related to the stress-field pattern associated with interfaces.

9. No significant differences with respect to solute-atom segregation are observed between the so-called "special" high coincidence boundaries, as opposed to "general" boundaries. This contradicts common expectations that "special" boundaries, due to a higher degree of order, should have weaker solute-atom segregation. The "special" boundaries are known to possess peculiarities in interfacial tensions and kinetic properties, but equilibrium segregation is determined by the partial derivative of the interfacial free energy of an interface with respect to the chemical potential of solute atoms [eqn (2)], and not the absolute value of the interfacial free energy.

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