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Effect of the Character of High-Angle Grain Boundaries on Segregation: An Elastic Model

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Abstract: We introduce a model for high-angle grain boundaries in the form of a two-dimensional array of compressive forces. Segregation profiles driven by the stress field around the boundary are calculated for several levels of translational order. We find an enhancement of segregation with increasing degree of translational disorder, in agreement with experimental observations.

1. Introduction

The phenomenon of segregation of impurities to grain boundaries is strongly influenced by the physical characteristics of the grain boundaries. Segregation to low-angle grain boundaries is the problem of interaction between solute atoms and the elastic strain field of dislocations [1]. The structure of high-angle grain boundaries in contrast to the low-angle ones cannot be described as arrays of dislocations. The difficulty in structural characterization of grain boundaries in the high-angle regime renders the study of a correlation between structure and segregation difficult. A few trends supported by experimental evidences were drawn [2]. In particular, segregation to general grain boundaries appears to be more important than to boundaries with special character. Special boundaries are defined as those with a particularly high degree of order. More specifically, they are represented by a periodic sequence of short structural units [3]. General grain boundaries are those that possess a low degree of structural order. Some may be described as a periodic sequence of very long structural units. However, the tendency for grain boundary energy minimization results in a decomposition of the long structural units into periodic sequences of short units representative of special delimiting grain boundaries. By delimiting, it is meant that the misorientation of the general boundary is bound by those of the special boundaries in which it decomposes. Others are quasiperiodic grain boundaries with no translational symmetry but orientational symmetry. They may also be represented as quasiperiodic sequences of structural units [3, 4]. Finally, the most disordered case may correspond to completely aperiodic interfaces.

The purpose of this paper is to quantify the effect of grain boundary structural disorder on the phenomenon of segregation. Of interest is the relation between translational periodicity and the extent of segregation. A simple model for a high-angle grain boundary as a planar array of point sources of compression is used. The degree of structural order is varied by altering the location of the point sources. We employ the linear thermochemical theory for stressed solids

[5] to relate the grain boundary stress field to the chemical segregation profile. We show that the range of segregation increases significantly with small reductions in structural order.

In section 2, we introduce the model for high-angle grain boundaries. The calculation of the stress field in the vicinity of the boundary is performed in the frame of continuous linear elasticity of isotropic media in section 3. The stress field generated by grain boundaries with various degrees of translational disorder is related to segregation profiles. We draw some general conclusions regarding the effect of disorder within the grain boundary plane on the extent of segregation in section 4.

2. Model

We consider a system containing a high-angle grain boundary. The system is a binary interstitial solid solution in equilibrium with a chemical reservoir. The grain boundary is not defined as a discontinuity in the solid network but as a source of stress. In absence of the interface and therefore stress, the composition of the solid is c_0. The phenomenon of segregation to this grain boundary is amenable to the linear theory of thermochemical equilibrium of solids under stress developed by Larché and Cahn [5]. In the case of small variations in concentration, Larché shows that the elastic problem can be separated from the thermochemical one. The composition field resulting from the grain boundary stress field is given in the case of isotropic media, by:

$$\Delta c = \chi k_1 trT, \tag{1}$$

where the symbol trT stands for the trace of the stress tensor T.

In the case of interstitial solid solution, the number of immobile atoms, ρ_0', per unit volume in the stress free solid is a constant. χ is related to the chemical potential of the solid per immobile site, μ^p, by:

$$\frac{1}{\chi} = \rho_0' \frac{\partial \mu^p}{\partial c}. \tag{2}$$

A change in composition of the stress-free solid gives rise to a spherical strain tensor $E_c = k(c)I$ where I is the identity matrix. k_1, is defined as the first derivative of $k(c)$ with respect to composition evaluated at the composition c_0.

The stress tensor, T, can be calculated in the frame of an ordinary elastic problem. However the elastic constants take the values of the elastic constants of the solid at composition c_0.

We construct a high-angle grain boundary in an infinite isotropic medium by removing some atoms in a thin planar region. This planar region possesses a lower atomic density than the rest of the solid. Relaxations of the lattice around the voids give rise to compressive forces. We assume that relaxation parallel to the planar region is complete and that the compressive forces exist only in a direction perpendicular to this region. We call x_3, this direction. The high-angle grain boundary is therefore modeled as a discrete array of distribution of forces of compression in the form:

$$F_3(\vec{r}) = A \sum_i \frac{\partial}{\partial x_3} \delta(\vec{r} - \vec{r}_i). \tag{3}$$

δ is the usual delta function; and A measures the strength of the compression and has dimension of a force times a length. The summation is taken over the sites in the planar region where the voids are located.

By changing the positions, $\vec{r}_i$, of the voids, we can vary the character of the high-angle grain boundary. A periodic array of point sources of compression corresponds to a special grain boundary. General boundaries are modeled by disordering the array.

Let us now calculate the elastic stress field around such a model of high-angle grain boundaries.

3. Stress Field

In a first phase, we calculate the stress field around a single force of compression located at some origin. We determine initially the displacement field produced by this single force of compression.

A continuous distribution of forces $F_j(\vec{r})$ in an infinite elastic medium causes displacements:

$$u_i(\vec{r}) = \int u_{ij}(\vec{r} - \vec{r}') F_j(\vec{r}') d^3\vec{r}', \qquad i, j = 1, 2, 3, \tag{4}$$

where $u_{ij}(\vec{r})$ is the tensor Green's function [6] at the position $\vec{r}$ and is given, for an isotropic medium, by:

$$u_{ij}(r) = \frac{1}{8\pi\mu}\left[\frac{2}{r}\delta_{ij} - \left(\frac{\lambda+\mu}{\lambda+2\mu}\right)\frac{\partial^2 r}{\partial x_i \partial x_j}\right], \quad (5)$$

where λ and μ are the usual Lamé coefficients, and δ_{ij} is the Kronecker's symbol. Here we consider a single force of compression located at the origin of the form:

$$F_3(\vec{r}) = A\frac{\partial}{\partial x_3}\delta(\vec{r}). \quad (6)$$

Introducing equation (6) in equation (4) gives:

$$u_i(r) = A\frac{\partial}{\partial x_3}u_{i3}(r). \quad (7)$$

From equation (5), we deduce the expressions of $u_{13}(r)$, $u_{23}(r)$, and $u_{33}(r)$. Using equation (7) we obtain the displacements $u_1(r)$, $u_2(r)$ and $u_3(r)$.

On the other hand, the components of the strain tensor E are determined in the limit of small strain from the usual relation of linear elasticity:

$$E_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right). \quad (8)$$

We are only interested in the trace of the stress tensor T which for isotropic media takes the form:

$$trT = (3\lambda + 2\mu)trE. \quad (9)$$

We finally arrive at the following expression for the trace of T:

$$trT = \frac{-A(3\lambda+2\mu)}{4\pi(\lambda+2\mu)}\left[\frac{1}{r^3} - \frac{3x_3^2}{r^5}\right]. \quad (10)$$

In a second phase, we consider a periodic array of compressive forces. Sources of compression are located on a square grid. This could be a representation of a $\Sigma 5$ [100] twist boundary. The square grid is isomorph to the coincident sites lattice with the sites of compression situated in the regions of poor atomic registry. The period of the array is D. A typical special grain boundary in a f.c.c. crystal such as aluminium has D on the order of 10 Å.

In other words, in the structural unit model [3] of grain boundaries, the sites for compression would correspond to some cavities in each structural unit.

The stress field generated by the array of compressive forces is simply the superposition of the stress field due to each force. The trace of the total stress tensor is given by a discrete summation over all the grid sites. Let mD and nD define the position of the grid sites ($\vec{r}_i(mD, nD, 0)$ where m and n are two integer parameters). The value of the trace of T at some position $\vec{r}(x_1, x_2, x_3)$ becomes:

$$trT = \frac{-A(3\lambda+2\mu)}{4\pi(\lambda+2\mu)}\sum_m\sum_n \times\left\{\frac{1}{\left[(x_1-mD)^2+(x_2-nD)^2+x_3^2\right]^{3/2}} - \frac{3x_3^2}{\left[(x_1-mD)^2+(x_2-nD)^2+x_3^2\right]^{5/2}}\right\}. \quad (11)$$

This expression shows that the composition field depends not only on the distance from the grain boundary but also on the position parallel to the grain boundary. The composition in a plane parallel to the boundary is periodic with period D. Because of difficulties in measuring experimentally variations in composition parallel to the boundary on a scale less than 10 Å and for the sake of comparison with available experimental data on segregation profiles perpendicular to the boundary plane, we average the composition field at each position x_3, over a surface $D \times D$. The average composition field at a distance x_3 from the boundary takes the following form:

$$\Delta c = \chi k_1\left[\frac{A(3\lambda+2\mu)}{4\pi(\lambda+2\mu)}\right]\frac{1}{D^3}\sum_m\sum_n \times\{I_{m,n} + J_{m,n} + K_{m,n} + L_{m,n}\}, \quad (12)$$

where:

$$I_{m,n} = \frac{(1-n)(1-m)}{[(1-n)^2+X_3^2]} \cdot\frac{\sqrt{(1-m)^2+(1-n)^2+X_3^2}}{[(1-m)^2+X_3^2]} \cdot\left\{1+\frac{X_3^2}{[(1-m)^2+(1-n)^2+X_3^2]}\right\}, \quad (13a)$$

$$J_{m,n} = \frac{(1-n)m}{[(1-n)^2 + X_3^2]} \cdot \frac{\sqrt{m^2 + (1-n)^2 + X_3^2}}{(m^2 + X_3^2)} \cdot \left\{1 + \frac{X_3^2}{[m^2 + (1-n)^2 + X_3^2]}\right\}, \quad (13b)$$

$$K_{m,n} = \frac{n(1-m)}{(n^2 + X_3^2)} \cdot \frac{\sqrt{(1-m)^2 + n^2 + X_3^2}}{[(1-m)^2 + X_3^2]} \cdot \left\{1 + \frac{X_3^2}{[(1-m)^2 + n^2 + X_3^2]}\right\}, \quad (13c)$$

$$L_{m,n} = \frac{nm}{(n^2 + X_3^2)} \cdot \frac{\sqrt{m^2 + n^2 + X_3^2}}{(m^2 + X_3^2)} \cdot \left\{1 + \frac{X_3^2}{[m^2 + n^2 + X_3^2]}\right\}, \quad (13d)$$

and

$$X_3 = \frac{x_3}{D}.$$

This average value is equal to zero. This was predictable knowing that the expression given in equation (10) for the trace of the stress tensor of a single compression force is a Legendre's polynomial. An integral over a period of such a polynomial results in a null value because of the orthogonality of the Legendre's polynomials. This observation is also at the origin of the calculation of the vanishing value of the elastic energy of interaction of a point defect with an infinite plane of dilation or compression [7].

The contribution of a force on the square grid to the average composition is inversely proportional to the distance from the center of the surface element $D \times D$. The convergence of the double summation in equation (12) is ensured by canceling contributions from grid points diametrically opposed.

This periodic model for a special grain boundary does not give rise to a driving force for segregation.

Let us now consider the case of more general angle grain boundaries. Aperiodic interfaces can be produced from the preceeding array of compressive forces by displacing randomly the forces from their periodic location. One controls the degree of disorder by imposing constraints on the magnitude of the random displacements. Our aperiodic array of forces possesses the following properties:

(i) The distance between any two grid points is greater than some positive number.
(ii) Every grid point lies within some distance d of another grid point.

The aperiodic grid does not possess the other properties of a quasiperiodic lattice as defined by Levine and Steinhardt [8]. Our model is therefore restricted to representing the most disordered case of general grain boundary.

Concentration profiles are still obtained from equation (12) where m and n are replaced by $m' = m \pm \mathcal{E}_m$ and $n' = n \pm \mathcal{E}_n \cdot \mathcal{E}_m$ and $\mathcal{E}_n$ are random numbers distributed according to a normal distribution generated numerically. They are restricted in absolute value to an interval $[0; \alpha]$ where α determines the degree of disorder.

We do not displace the grid points at the vertices of the surface element $D \times D$, that is, we calculate the average composition field over a structural unit of the original periodic grain boundary.

The double summation in equation (12) converges only very slowly. The contributions from the grid points which were diametrically opposed in the periodic array do not cancel anymore in the aperiodic array. These contributions diminish with the distance γ from the center of the surface element. The number of contributions from points at some distance γ is proportional to the distance γ leading to an apparent divergence of the double summation. In the limit of very large distances the number of contributions to the trace of T becomes so large that convergence is statistically achieved by the existence for each positive contribution of a negative contribution of same magnitude.

For numerical reasons, we compute concentration profiles from a large but finite number of compressive forces. We have verified that if we take m and n in the interval $[-2000, +2000]$ the occurrence of convergence is frequently observed for various series of random numbers.

We study three cases: $\alpha = 0.05, 0.1, 0.15 \times D$, which correspond to an increasing degree of dis-

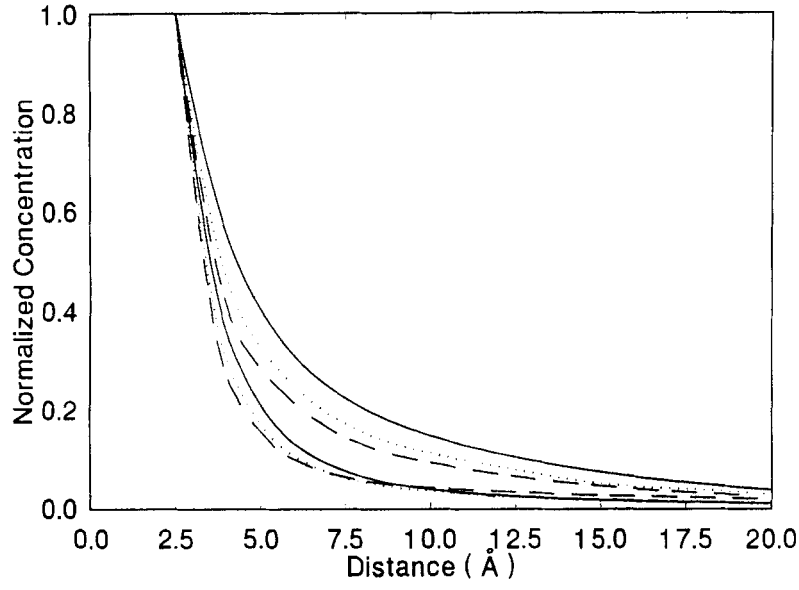

Fig. 1. Envelopes of the normalized concentration profiles in three different cases: solid: $\alpha = 0.15 \times D$; dots: $\alpha = 0.10 \times D$; and long dash: $\alpha = 0.05 \times D$.

order. In each case, we generate 20 sequences of random numbers, that is, 20 different grain boundary structures. The calculated concentration profiles are reported as $(c-c_0)/(c_1-c_0)$ where c_1 is the concentration at a distance 2.5 Å from the grain boundary core. We chose to do this in view of the limitation of continuous elasticity to represent phenomena at the scale of atomic distances [9]. We chose 2.5 Å as the half-thickness of a typical high-angle grain boundary [10].

In figure 1, we plot the envelopes of the normalized concentration profiles produced in the three cases. These profiles are in reasonable agreement with experimental data obtained for a variety of materials [11]. They are short range, rapidly decaying after a distance of approximately 15 Å.

We note that while the minimum profiles remain closely related, the extent of segregation in the maximum profiles increases significantly with disorder. Our calculation also shows that the enrichment at the grain boundary as measured by $(c_1 - c_0)$ increases with the degree of disorder. This demonstrates the correlation between grain boundary character and segregation. Segregation is unlikely to special grain boundaries. Segregation to general grain boundaries is more important to highly disorder interfaces.

To quantify further the relationship between the extent of segregation and disorder, we introduce an order parameter. This order parameter is defined as follows:

$$S(\vec{k}) = \frac{\sum_m \sum_n \cos(\vec{k}.\vec{r}_k)}{N} \tag{14}$$

where $\vec{k}$ and $\vec{r}_k$ are two-dimensional vectors of components $2\pi(1, 1)/D$ and $D(m', n')$, respectively, and N is the total number of grid sites. The order parameter is equal to 1 in the case of the periodic array of forces and decreases to 0 with increasing disorder.

In Figure 2, we plot the concentration at four locations of the upper limit of the envelopes of concentration profiles versus the order parameter. This figure clearly shows that disorder influences the extent of segregation in the near vicinity of the grain boundary. The effect is less pronounced at longer range.

4. Conclusion

We have developed a simple model of high-angle grain boundaries which allows us to relate the ex-

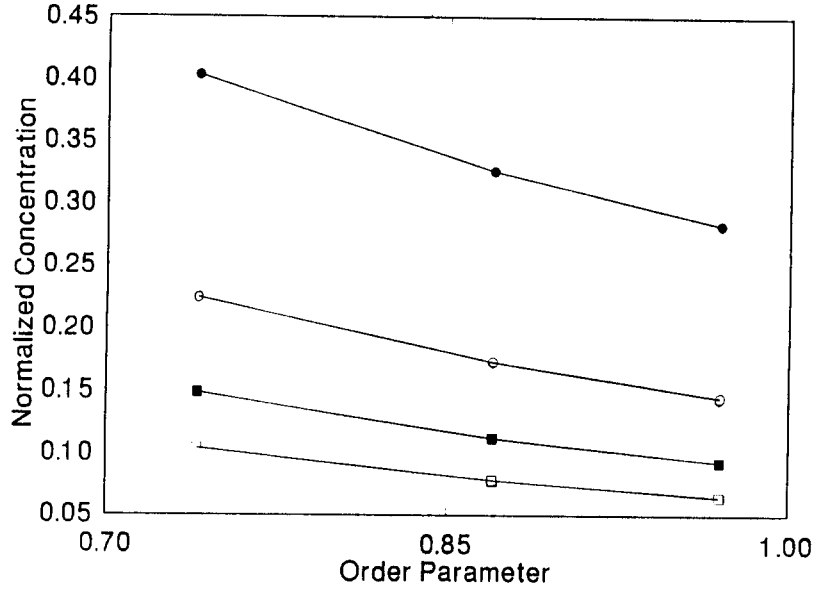

Fig. 2. Normalized concentration of the upper limit of the envelopes of concentration profiles versus the order parameter: •: distance from the grain boundary core = 5 Å; ○: distance from the grain boundary core = 7.5 Å; ■: distance from the grain boundary core = 10 Å; and □: distance from the grain boundary core = 12.5 Å.

tent of segregation to the character of the grain boundary. More specifically we focus on the relationship between order in the grain boundary and segregation profiles. We show that the periodicity of special grain boundaries annihilates the effect of local sources of compression in the boundary as a driving force for segregation. On the other hand, compressive forces in aperiodic interfaces drive solute atoms to segregate to the boundary. The influence of the degree of disorder in the boundary is more pronounced in the close vicinity of the interface.

We finally note that the stress field arising from the array of compressive forces is only one contribution to the phenomenon of segregation among many others. More specifically in another publication [12], we have shown that the self-strain energy as well as the electronic energy of a point defect in the vicinity of a planar defect may provide a strong driving force for segregation. In this model for a grain boundary, the planar defect is constructed as a thin slab inserted between two homogeneous isotropic media and the grain boundary is characterized by its physical parameters such as elastic constants and atomic density.

We have proved that the grain boundary atomic density and the variation of the elastic constants of the grain boundary with respect of the elastic constants of the homogeneous media are the fundamental physical parameters for segregation. It is found that the general grain boundaries with high excess volume have then a strong tendency for segregation. The model also suggests the possibility of strong segregation to higher atomic density special interfaces.

In light of these results, the translational disorder in the grain boundary may act as an enhancement of segregation.

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