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On the interaction of solutes with grain boundaries

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ABSTRACT

Solute segregation to grain boundaries is considered by modeling solute atoms as misfitting inclusions within a disclination structural unit model describing the grain boundary structure and its intrinsic stress field. The solute distribution around grain boundaries is described through Fermi–Dirac statistics of site occupancy. The susceptibility of hydrogen segregation to symmetric tilt grain boundaries is discussed in terms of the misorientation angle, the defect type characteristics at the grain boundary, temperature, and the prescribed bulk hydrogen fraction of occupied sites. Through this formalism, it is found that hydrogen trapping on grain boundaries clearly correlates with the grain boundary structure (i.e. type of structural unit composing the grain boundary), and the associated grain boundary misorientation. Specifically, for symmetric tilt grain boundaries about the [0 0 1] axis, grain boundaries composed of both B and C structural units show a lower segregation susceptibility than other grain boundaries. A direct correlation between the segregation susceptibility and the intrinsic net defect density is provided through the Frank–Bilby formalism. Overall, the present formulation could prove to be a simple and useful model to identify classes of grain boundaries relevant to grain boundary engineering.

1. Introduction

Solute-atom segregation to grain boundaries (GBs) and other microstructural line defects such as dislocations substantially affects their fundamental physico-chemical properties, e.g. grain boundary energy [1–3], grain boundary mobility [4–7], and grain boundary cohesion [8–10], which in turn impacts a wide range of material behaviors including strain aging [11–13], intergranular fracture [14,15], recrystallization [16,17], and creep [18,19]. The chemical equilibrium distribution of solutes in a solid determines the interaction between these solutes and defects already existing in a material system and plays a key role in the nature of the subsequent mechanisms governing the behaviors listed above.

It has been established, both experimentally [8,20–22] and theoretically [11,23–27], that solute equilibrium depends on the intrinsic character of the defect considered and its associated pre-existing stress field. Of particular theoretical interest, Cai et al. [27] recently clarified the formalism of how the equilibrium configuration of solutes should depend on the stress field in an isotropic elastic solid. This formulation models the chemical equilibrium distribution of point defects as non-overlapping spherical inclusions with purely positive dilatational eigenstrain. This formulation excludes the *self-stress* of the inclusions (hydrostatic stress found *inside* the inclusion), but accounts for the *image stresses* introduced to satisfy the boundary conditions in a finite solid. The solute distribution around a given defect *d* follows Fermi–Dirac statistics on the hydrostatic stress field produced by the defect considered, the stress fields generated by other defects, and stress field generated by external loads. This non-uniform distribution of solutes around a defect *d* is accompanied by a coherency stress preserving the coherency of the crystal lattice. In an infinite isotropic elastic medium it has been shown [24,27] that the coherency stress is directly proportional to the local concentration of solutes and the solute distribution throughout the entire solid.

Most of the theoretical treatments concerning the interaction between solute atoms and defects focus on dislocation-type defects [11,24,27–32]. For example, Cottrell and Bilby [11,28,29] and later work extended by others [24,27,31,32] have examined the equilibrium solute distribution around a single infinitely long straight dislocation. In the case of an edge dislocation, the total depletion of solutes shows a logarithmic dependence beneath the glide plane. Webb [30] extended this theory to the case of dislocation walls or small angle grain boundaries by summing the contributions of an array of individual lattice dislocations as classically defined in

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dislocation theory [33]. However, dislocation-type analyses are limited to simple representations of low-angle boundaries and are not adequate for large-angle boundaries, low symmetry crystals, very short boundaries of any angle and other types of more complex defects like triple junctions.

Another paradigm which can be used to model more complicated grain boundary structures in terms of linear defects instead constructs grain boundaries using disclinations [34–41]. Disclination-based models are fully equivalent to dislocation models in terms of their stress and strain fields, and are also particularly advantageous for obtaining the mechanical field of a general grain boundary where dislocation cores would overlap as is the case for large angle GBs. Similarly, models of other complex defects such as triple junctions [40] or the structure of zigzag tilt GBs [38] can be constructed using disclinations. Such defects are of particular interest since they constitute stress concentrators within any given microstructure potentially providing additional driving force for solute segregation.

The present analysis, which is based on the formalism suggested by Cai et al. [27], treats solute atoms as misfitting spherical inclusions and considers their interactions with (tilt) grain boundaries (about the [0 0 1] axis). The adopted model accounts for the complex structure of grain boundaries through disclination-based models and considers the material as linear, elastic, and isotropic. Hydrogen segregation to grain boundaries is explored for a wide variety of grain boundaries. Of particular interest, correlations between grain boundaries' segregation susceptibility, the grain boundary misorientation and the grain boundary structural character is investigated. The susceptibility to hydrogen segregation of symmetric tilt grain boundaries is discussed in terms of the misorientation angle and the intrinsic grain boundary defect type characteristics.

The manuscript is thus organized as follows. Section 2 details the construction of grain boundaries using disclination theory and the resulting solute distribution. Section 3 discusses the correlation between solute concentration and the grain boundary defect characteristics. Conclusions are drawn concerning the application of this model in Section 4.

2. Solute distribution around grain boundaries

As mentioned in Section 1, so-called superatomic (mesoscopic) disclination-based models provide a convenient way of representing grain boundary behavior under various loading conditions using linear theory of defects. Wedge disclination dipoles are the basic ingredients of such models [39]. As illustrated in Fig. 1 (a), disclinations are linear rotational defects [42] for which, similar to the way dislocations are characterized in continuum mechanics using the Burgers vector, the strength of a disclination is related to an axial pseudo vector $\vec{\omega}$ (Frank's vector) defining the rotation between two cut surfaces. The elastic fields of straight disclinations in an elastic infinite isotropic medium can be found in analytical form based on the general linear elastic theory of defects [43,44]. Following deWit [43], the stress field $\sigma_{ij}^{\triangleright}(x,y)$ of a pure wedge disclination located at the origin with a Frank's (pseudo) vector magnitude (or strength) ω (see Fig. 1) is given in a Cartesian coordinate system by:

$$\sigma_{xx}^{\triangleright}(x,y,\omega) = D_0\omega\left(\ln\sqrt{x^2+y^2} + \frac{y^2}{x^2+y^2}\right) = D_0\omega\left(\ln r + \frac{y^2}{r^2}\right), \tag{1}$$

$$\sigma_{yy}^{\triangleright}(x,y,\omega) = D_0\omega\left(\ln\sqrt{x^2+y^2} + \frac{x^2}{x^2+y^2}\right) = D_0\omega\left(\ln r + \frac{x^2}{r^2}\right), \tag{2}$$

$$\sigma_{xy}^{\triangleright}(x,y,\omega) = -D_0\omega\frac{xy}{x^2+y^2} = -D_0\omega\frac{xy}{r^2}, \tag{3}$$

$$\sigma_{zz}^{\triangleright}(x,y,\omega) = \nu\left[\sigma_{xx}^{\triangleright}(x,y) + \sigma_{yy}^{\triangleright}(x,y)\right], \tag{4}$$

where $r^2 = x^2+y^2$, μ is the shear modulus, ν is the Poisson's ratio and $D_0 = \mu/2\pi(1-\nu)$.

Note that the logarithmic divergence of the long-range stress fields of a wedge disclination implies that disclinations can exist only in a screened state by configuring straight disclinations in dipoles or other multipole configurations. The stress field of such arrangements can be found by superposition of the contributions from individual straight disclinations. As such, the stress field $\sigma_{ij}^{\bowtie}(x,y)$ of a disclination dipole (ω, L) centered at $y=0$ with positive disclination $+\omega$ at $(0, L)$ and negative disclination $-\omega$ at $(0, -L)$ (see Fig. 1(b)) is given by:

$$\sigma_{ij}^{\bowtie}(x,y,\omega,L) = \sigma_{ij}^{\triangleright}(x,y-L,\omega) - \sigma_{ij}^{\triangleright}(x,y+L,\omega). \tag{5}$$

2.1. Construction of grain boundaries using the disclination structural unit model (DSUM)

Originally proposed by Shih and Li [34,35] and later improved by Gertsman et al. [36], the disclination structural unit model (DSUM) constructs a (non-favored) grain boundary with a misorientation angle θ by decomposing it into a contiguous and alternating sequence of special (favored) m majority and n minority structural units with associated misorientation angles θ_m and θ_n respectively such that $\theta_m < \theta < \theta_n$. Favored boundaries are grain boundaries that have a structure characterized by a repeating sequence of only one type of structural units. As a result the boundary is represented in the form of a complex wall of disclinations combined into dipoles associated with the minority structural units (see Fig. 2(a)). The strength of the disclination dipoles associated with the minority structural unit is equal to $\pm\omega = \pm(\theta_n - \theta_m)$, the arm of the dipoles is fixed and set to L'_n, and the period of the grain boundary is given by $H = (md'_m + nd'_n) = 2(mL'_m + nL'_n)$.

As illustrated in Table 1 [45–47], all symmetric tilt grain boundaries about the [0 0 1] axis can be decomposed into primary structural units that are consistent with the four favored [0 0 1] symmetric tilt grain boundaries: the A structural unit Σ1 (1 1 0)/$\theta = 0°$ perfect lattice, the B structural unit Σ5 (2 1 0)/$\theta = 36.87°$ grain boundary, the C structural unit Σ5 (3 1 0)/$\theta = 53.13°$ grain boundary, and the D structural unit Σ1 (1 0 0)/$\theta = 90°$ perfect lattice. Thus, all symmetric tilt grain boundaries about the [0 0 1] axis with a misorientation $0° \le \theta < 36.87°$ are composed of only A and B structural units, all boundaries with a misorientation $36.87° \le \theta < 53.13°$ are composed of only B and C structural units, and all boundaries with a misorientation $53.11° \le \theta < 90°$ are composed of only C and D structural units. Additionally due to the geometric distortions of the (favored) elementary structural units composing a given (non-favored) grain boundary (see Fig. 2(b)), the dimensions L'_m and L'_n can be evaluated from the rest length of the structural units L_m and L_n through the geometric relation [48],

$$L'_m = L_m\cos\left(\frac{\theta-\theta_m}{2}\right), \quad L'_n = L_n\cos\left(\frac{\theta_n-\theta}{2}\right), \tag{6}$$

while the average misorientation angle θ is given by,

$$\sin(\theta/2) = \frac{[2mL_m\sin(\theta_m) + 2nL_n\sin(\theta_n)]}{H}. \tag{7}$$