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Grain boundary and surface energies of fcc metals

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Interfacial energies of five high-angle singular grain boundaries (GB's) in seven fcc metals—Ag, Al, Au, Cu, Ni, Pd, and Pt—are calculated employing lattice statics at 0 K using embedded-atom-method potentials. The results disagree with predictions of broken-bond models. The GB energies, however, exhibit a good linear relationship with the c_{44} elastic constants of these elements. This implies the existence of a characteristic GB length serving as a proportionality coefficient between GB energy and c_{44}. The results for GB energies are compared with theoretical results on surface/vacuum interfacial energies for the same metals. [S0163-1829(96)53540-X]

A grain boundary's (GB's) interfacial free energy per unit area γ is one of its fundamental properties as it determines all phenomena associated with GB's.[1,2] A great deal of experimental and theoretical effort has been devoted to elucidate the relationships between the crystallography of GB's with their energies.[3,4] Historically, consideration of GB energies starts with low-angle GB's consisting of regular arrays of primary GB dislocations (PGBD's). Classically the GB energy is divided into an elastic portion and a nonlinear elastic contribution from the dislocations' cores.[5] Significant progress has been made in describing analytically the elastic component for a wide range of situations.[6–8] The nonlinear elastic contribution, however, is normally treated as a parameter that may be extracted from a Read-Shockley plot. At high-angle misorientations the cores of the PGDB's overlap and the nonlinear elastic contribution is dominant. Additional insight is provided by incorporating secondary GB dislocations (SGBDs) within the Read-Shockley framework.[9] The energies, however, of high-coincidence low-energy singular GB's remain to be determined in a different manner.

Broken-bond models have been employed to try to understand GB energies.[10] Those models are, however, phenomenological ones that relate energies of crystalline defects to the number of broken-bonds–a quantity that is loosely defined; mainly first-neighbor bonds are considered, although extensions to higher-order neighbors are available. Given the nature of metallic bonding, a bond has no physical significance but is a geometrical construct. Additionally, a broken bond is assigned a fraction of the cohesive energy of the lattice, U_{coh}. The simplest approach is to divide U_{coh} by the number of nearest neighbors in a perfect crystal. If additional coordination shells are considered, U_{coh} is divided among the shells and then the energy of each shell is divided by the number of atoms in it. The ratios of the bond energies to U_{coh} need to be constant, at least within one metal, otherwise they are determined in an *ad hoc* manner and are not useful. It is often assumed that the ratios are constant in all metals with a specific crystal structure. Broken-bond models are thought to describe adequately surface energies.[11–13] The problem is that the experimental results used for this analysis are frequently from polycrystalline samples; that is, they are weighted averages over different $\{hkl\}$ orientations. For GB energies, broken-bond models have been suggested based on lattice statics calculations for GB's in copper using a Lennard-Jones potential and for gold using an EAM potential.[10]

Broken-bond models are extended to alloys and one of their important applications concerns interfacial solute-atom segregation.[14,15] The driving force for this phenomenon is provided by the decrease of γ according to

$$\Gamma_{\mathrm{solute}} = -\left(\frac{\partial\gamma}{\partial\mu'}\right)_{T,P}, \text{ specified DOF's;} \tag{1}$$

where Γ_{solute} is the Gibbsian interfacial excess of solute, μ' is the chemical potential of a solute atom in a binary alloy, and T and P are temperature and pressure. GB's have five macroscopic geometrical degrees of freedom (DOF) that are thermodynamic variables;[16] three are for the misorientation of the two grains and two are for the orientation of the interface. Within a broken-bond model a decrease in γ is achieved by increasing the number of low-energy bonds at an interface; that is, by increasing the concentration of the species with the lower cohesive energy at a GB. A realistic picture of solute segregation at GB's (or surfaces) is more complicated and often contradicts the predictions of broken-bond models.[17,18] The remedy is often sought by supplementing the broken-bond models with other possible physical contributions to the interfacial energy: for example, elastic strain, electronic, etc.[19–22] The question, however, remains as to the applicability of broken-bond arguments to GB or surface energies, even in pure metals, and this is the principal subject that we now address.

We first present results of 0-K lattice statics calculations of γ's of five high-angle GB's in seven fcc metals—Ag, Al, Au, Cu, Ni, Pd, and Pt. We utilized many-body interatomic potentials to calculate interatomic forces: see Ref. 23 for the Al EAM potential; the other six are the universal versions of the EAM potentials.[24] The singular GB's studied are listed in Table I; they all have low values of the inverse density of coincident sites Σ (a small planar repeat cell), and cusps in the γ versus misorientation dependence.[25] Their dislocation

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TABLE I. The values of the inverse density of coincidence sites (Σ), the misorientation angle (θ), the $\{hkl\}$ interface plane, and the coefficients of Eq. (2), L_{GB} and U_{GB}^0, obtained from a least-squares fit of the dependencies in Fig. 2. The rotation axis is [001] for all the GB's; for tilt GB's the rotation axis lies in the plane of the interface while for the twist GB's it is normal to it.

Σ	5	5	5	29	29
Type	twist	tilt	tilt	twist	tilt
GB plane	(002)	(310)	(210)	(002)	(730)
θ°	36.87	53.13	36.87	43.6	43.6
L_{GB} (nm)	0.0078	0.0089	0.0095	0.0078	0.0096
U_{GB}^0 (J m^{-2})	0.164	0.234	0.214	0.173	0.283

structures are simple and their structural units (SU's) occur in other GB's. For a summary of the structural unit model see Ref. 2; we have also reexamined the SU model.[26]

The computational cell used consists of two grains, with three-dimensional periodic border conditions. The two periodic lengths in the interface plane are held constant to avoid the effects of γ on small grains, while the periodic dimension normal to the interface plane is allowed to relax. There are two crystallographically identical GB's in the system and to avoid their elastic interaction the distance between them is 5.6–6.5 nm for the twist GB's, and 9.4–10.3 nm for the tilt GB's. The GB area is 14.9–20.1 nm^2 and 18.8–25.4 nm^2 for the twist and tilt GB's, respectively; the total number of atoms in a bicrystal is 7680–15 360. The GB energy is calculated as the excess over the energy of a single crystal, with the same number of atoms as the bicrystal, divided by the GB area.

Lattice statics calculations are sensitive to the choice of initial conditions. Generally, more than one energy minimum can be reached for a given set of macroscopic degrees of freedom.[27] For all GB's we sampled displacement vectors in the plane of the interface within one repeat cell.[26] We focus on the lowest-energy structures for each GB, noting that for each GB the lowest-energy structures are the same for all seven metals.

In the case when the ratios of the bond to cohesive energies are the same for all the metals, broken-bond models predict a linear dependence between $U_{\mathrm{coh}}a^{-2}$ (the cohesive energy divided by the square of the lattice constant) and γ.[10,13] The dependence of the GB energies on $U_{\mathrm{coh}}a^{-2}$ for five boundaries is exhibited in Fig. 1; the dependence is nonlinear and nonmonotonic. For those seven metals the γ values decrease as follows: $\Sigma=29/(730)/43.6°$, $\Sigma=5/(210)/36.87°$, $\Sigma=5/(310)/53.13°$, $\Sigma=29/(002)/43.6°$, $\Sigma=5/(002)/36.87°$.

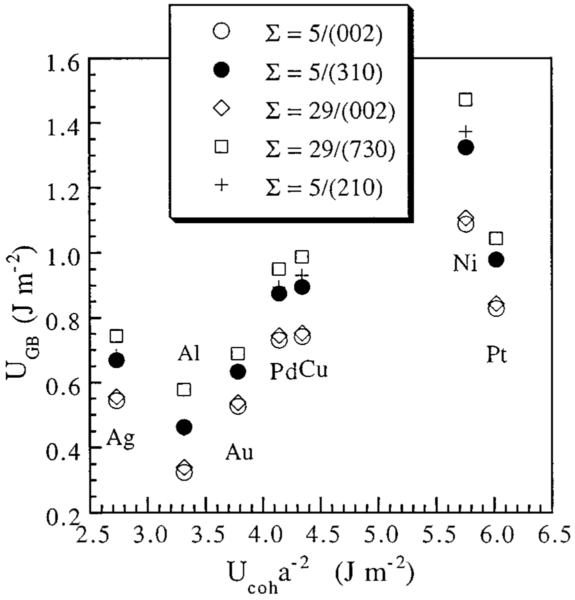

FIG. 1. The interfacial energies of the five GB's vs $U_{\mathrm{coh}}a^{-2}$. The open circles denote the $\Sigma=5/(002)/36.87°$; the solid circles are the $\Sigma=5/(310)/53.13°$; open diamonds are $\Sigma=29/(002)/43.6°$; open squares are $\Sigma=29/(730)/43.6°$; and plus signs are $\Sigma=5/(210)/36.87°$ GB's. The dependencies are neither linear nor monotonic.

Figure 2 displays the dependence of U_{GB} on the elastic constant c_{44}. Experimental values of c_{44} are used for the plot; they are very close to the EAM values—see Ref. 24. A good linear relation is observed throughout the whole c_{44} range for the seven fcc metals: that is,

$$U_{\mathrm{GB}}=U_{\mathrm{GB}}^0+L_{\mathrm{GB}}c_{44}, \tag{2}$$

where U_{GB} is a GB's internal energy at 0 K and the constant L_{GB} is a characteristic length for a given GB type; values of L_{GB}, for a least-squares linear fit, are listed in Table I. U_{GB}^0 is the linear intercept at $c_{44}=0$ obtained by an assumed linear extrapolation; this intercept is simply a mathematical quantity used to describe a straight line and does not have a physical meaning as crystalline fcc metals have, of course, nonzero values of c_{44} at all temperatures. The values of L_{GB} for twist GB's are somewhat smaller than those for tilt GB's, but since only seven points are available along the c_{44} axis it is difficult to state that there is a significant difference among them. The existence of characteristic bulk and surface lengths smaller than lattice constants has been suggested for a universal cohesive relation.[28,29] The relation between those lengths and L_{GB} remains to be elucidated. We also unsuccessfully tried fitting our results to the values of

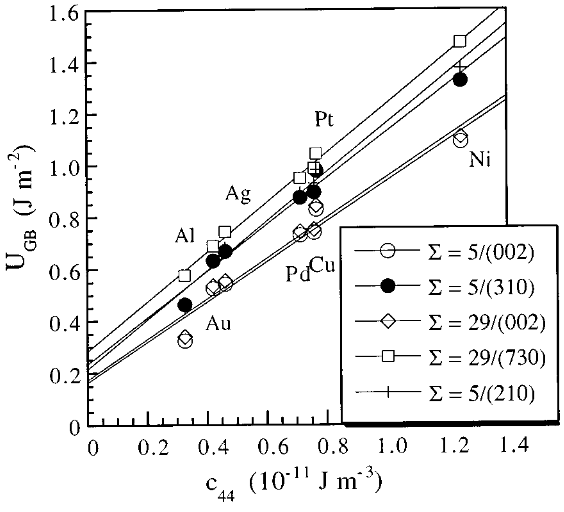

FIG. 2. The interfacial energies of five singular GB's vs c_{44}. The notation is the same as in Fig. 1. Note that a fairly good linear relation is observed.

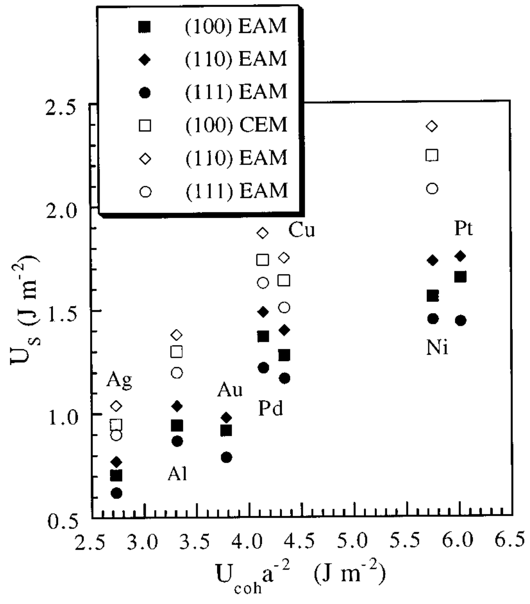

FIG. 3. The surface energies of three low-index $\{hkl\}$ surfaces vs $U_{\mathrm{coh}}a^{-2}$. The solid symbols denote EAM results (Refs. 23 and 29) and the open ones are for CEM results (Ref. 32). The relation is not linear for the EAM potentials, but the number of points is not sufficient to determine reliably the behavior of the CEM results.

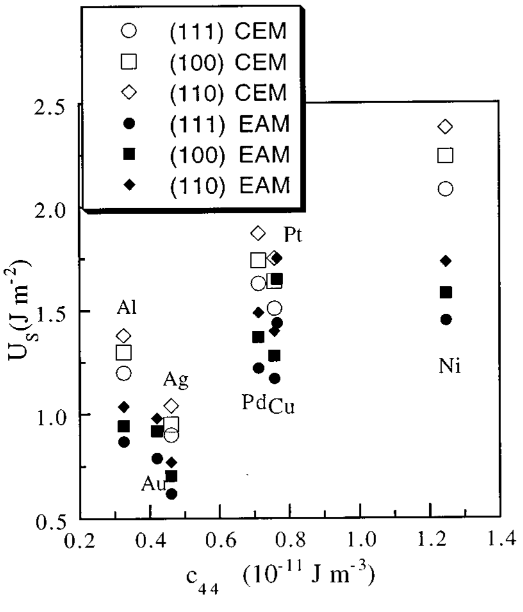

FIG. 4. The surface energies of three low-index surfaces vs c_{44} employing the same notation as in Fig. 3. The dependencies are not linear.

bulk and interfacial length scales from Ref. 28, as well as different anisotropic elasticity parameters[30] and many other physical parameters.

For comparison we examine the same dependencies as in Figs. 1 and 2 for surfaces (surface/vacuum interfaces). Theoretical results for low-index (100), (110) and (111) (1×1) surfaces are presented in Fig. 3. The full symbols refer to results obtained by lattice statics minimization with EAM potentials [Al (Ref. 23) and other metals[31]]. EAM potentials underestimate surface energies due to the neglect of the large gradient of the charge density near a surface.[32,33] The trends for different metals, however, are believed to be preserved.[33] We also plot theoretical results obtained with the more precise corrected effective medium (CEM) method.[34] These theoretical results—shown by open symbols—are available for Ag, Al, Au, Cu, Ni, and Pt. First, the dependencies are nonlinear for the EAM results. Second, for the CEM values, it is difficult to state definitely the dependence because the number of points is too small. It follows that the applicability of simple broken-bond models to surfaces, at least based on the EAM results,[13] is problematic. Figure 4 shows the dependencies of U_s on c_{44} for the EAM potentials and CEM method and neither set of results exhibit a linear relationship. Therefore, a linear dependence on c_{44} appears to be a feature of GB's and not surfaces.

The results obtained for five singular high-angle GB's by lattice statics calculations at 0 K, using EAM potentials, lead to the following conclusions.

(i) The dependence of U_{GB} on $U_{\mathrm{coh}}a^{-2}$ is nonlinear, in disagreement with the broken-bond model. This is most likely a result of extensive atomic-scale structural relaxations at GB's. Consequently, it is difficult to extend simple broken-bond models to models of solute-atom segregation at GB's.

(ii) A linear relation is observed between U_{GB} and c_{44} and the proportionality coefficient L_{GB} is approximately 0.01 nm for both twist and tilt GB's (see Table I). In view of this result it is important to (a) verify this relation experimentally by measuring energies of singular GB's in different pure metals, (b) to determine if L_{GB} has a universal value or if it has different values for different types of GB's, (c) provide a physical explanation for this relation. In linear elasticity theory the elastic constants—in different combinations—enter relations for GB energies. For high-angle GB's, however, linear elasticity is inapplicable because of the large contribution of dislocation cores. It is also important to (d) investigate, theoretically and experimentally, the validity of this relation to GB's in alloys in the presence of solute-atom segregation.

(iii) The applicability of simple broken-bond models for surfaces is problematic, especially for the EAM potential results.[13] This question requires more extensive experimental and theoretical investigations.

(iv) A linear relation is not observed between U_s and c_{44} for solid surface/vacuum interfaces; therefore, this relation is a special feature of GB's.

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