

Comparing grain boundary energies in face-centered cubic metals: Al, Au, Cu and Ni

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The energy of 388 grain boundaries in Al, Au, Cu and Ni were calculated using atomistic simulations. Grain boundary energies in different elements are strongly correlated. Consistent with a dislocation model for grain boundary structure, the boundary energy scales with the shear modulus. Boundaries with substantial stacking fault character scale with the stacking fault energy. There is more scatter in the data for Al, which has a high stacking fault energy, than for the low stacking fault energy elements.
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Understanding the relationships between structure, composition and properties is a fundamental principle of materials science. Because structure and composition are interdependent, it is not always easy, or even possible, to separate their effects. Computational modeling provides opportunities for deconvoluting structure and composition, at least in part, in order to better understand the contributions of each to the resulting material properties.

In this paper, we use a high-throughput atomistic method to examine the grain boundary energy for several hundred boundaries in four elemental, face-centered cubic (fcc) metals: Au, Cu, Ni and Al. We compare boundaries with the same macroscopic structure to determine how much of the variation in grain boundary energies is due to chemical composition. We find that boundary structure is the dominant influence upon boundary energy for materials with the same crystal structure; given a macroscopic structure, the magnitude of the boundary energy is proportional to a composition-dependent scalar.

The method for efficiently constructing infinite, planar grain boundaries and minimizing their energies has been described in detail previously [1]. We apply this

method to 388 grain boundaries in Au, Cu, Ni and Al, which represents a complete catalog of the boundaries that can be constructed in a periodic box of size $15a_0/2$, where a_0 is the lattice parameter. Grain boundary energies are calculated via the molecular statics method using embedded atom method (EAM) interatomic potentials [2]. The particular potentials used were Foiles Au1 for Au [3]; Mishin Cu EAM1 for Cu [4]; Foiles and Hoyt EAM Ni for Ni [5]; and Ercolessi and Adams EAM Al for Al [6]. Table 1 gives an overview of properties predicted by these potentials. These potentials have been used successfully in other simulations of defect properties.

For each macroscopic boundary structure (representing a misorientation with five macroscopic degrees of freedom) we construct several hundred to several thousand configurations with different microscopic structures using the method detailed in Ref. [1]. We minimize each configuration using a conjugate gradient method in the LAMMPS code [7].

For some boundaries, we observe a large number of configurations that minimize to nearly the same low energy; in some boundaries, we find a small number of configurations with uniquely low energies. In either case, we select the lowest-energy configuration as the minimum. Note that we repeat this procedure for each element studied, so there is no guarantee that for a given macroscopic boundary structure, the minimum energy configuration in one element is identical to that in another element.

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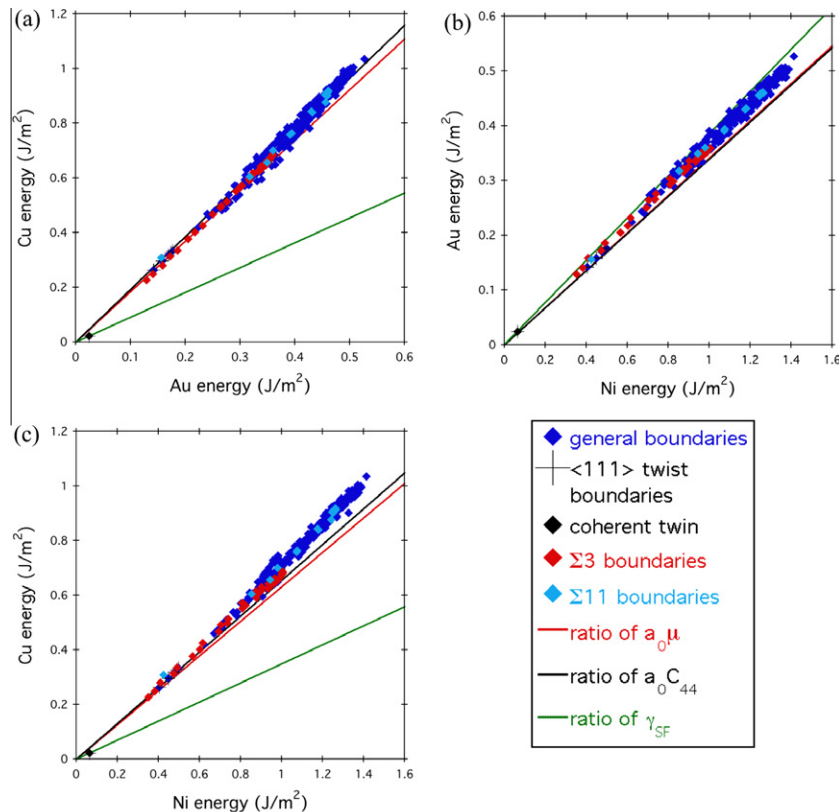
Table 1. Material properties calculated from EAM interatomic potentials for Au, Cu, Ni and Al.

	Foiles AuI [3]	Mishin Cu EAM1 [4]	Foiles and Hoyt EAM Ni [5]	Ercolessi and Adams EAM Al [6]
Cohesive/sublimation energy (eV)	3.93	3.54	4.45	3.36
Melting point (K)	865	1327	1565	939 ± 3
Lattice constant (Å)	4.08	3.615	3.52	4.032
Stacking fault energy (mJ m ⁻²)	30.7	44.4	127	104
Bulk modulus (GPa)	167	138.3	180.4	80.9
Voight average shear modulus (GPa)	29.1	55.2	90	33
C ₁₁ (GPa)	185.8	169.9	240.5	118.1
C ₁₂ (GPa)	157.1	122.6	150.3	62.3
C ₄₄ (GPa)	38.9	76.2	119.2	36.7
C' (GPa)	14.4	23.7	45.1	27.9
(111) surface energy at 0 K (J m ⁻²)	1.094	1.239	1.953	0.870
(100) surface energy at 0 K (J m ⁻²)	1.176	1.345	2.060	0.942
(110) surface energy at 0 K (J m ⁻²)	1.282	1.475	2.375	1.037
Vacancy formation energy (eV)	0.97	1.272	1.76	0.69

Because throughput is our goal, we do not examine the microscopic structure of each boundary studied. However, for the few boundaries we have analyzed, the minimum energy configurations often differ between elements. While variations in boundary structure could reflect composition dependence, they can also arise from computational artifacts. Since most boundaries possess a large number of nearly degenerate configurations [8], small numerical differences can cause the minimization method to find different optimum structures. The tiny variations in atomic arrangement and bonding that cause one configuration to be slightly favored may arise from details of the interatomic potential functions. For

example, when we compared minimum energy configurations generated by two different Al potentials [6,9], we found that the optimum Al boundary structures coincided with each other about as frequently as each coincided with optimum structures in Au. Nonetheless, while the minimum energy microscopic configurations may differ in detail, the large number of nearly degenerate configurations suggests that the energies extracted from these structures should provide a good approximation of the actual grain boundary energy.

Figure 1 shows pairwise comparisons of grain boundary energies for Au, Cu and Ni, which all have low to moderate stacking fault energy. Points represent the

**Figure 1.** Comparisons of grain boundary energies for low to moderate stacking fault energy fcc metals. Data points represent pairs of boundaries that share the same macroscopic structure. Lines show scaling predicted by various material parameters. (a) Cu vs. Au. (b) Au vs. Ni. (c) Cu vs. Ni.

grain boundary energy in one element vs. that in the other element for boundaries with identical macroscopic degrees of freedom. The data fall on a line that passes through the origin, indicating a strong correlation between grain boundary energies in each element.

The linear relationship between boundary energies in different materials suggests first that boundaries with the same macroscopic structure tend to take on energetically similar microscopic configurations, and second that there is an element-dependent proportionality constant that scales boundary energy. That is, given a macroscopic boundary structure, a composition-dependent scalar determines the grain boundary energy. A number of material parameters could be plausibly linked to this scaling. We have examined the properties listed in Table 1, each multiplied by the appropriate power of the lattice parameter so as to give the same units as grain boundary energy (energy per length squared). With three exceptions, the slopes resulting from the ratios of these properties do not match the observed slopes of the lines in Figure 1. The exceptions are the stacking fault energy, γ_{SF} , and two shear moduli: the C_{44} elastic constant and the Voigt average shear modulus μ . The scaling predicted by ratios of γ_{SF} , $a_0 C_{44}$ and $a_0 \mu$ are shown as lines in Figure 1. The stacking fault energy scales the energies of boundaries with substantial stacking fault character. In Figure 1, this includes only the lowest energy boundary, the $\Sigma 3$ coherent twin, which lies directly on the line representing the stacking fault energy ratio between the elements.

The remainder of the boundaries scale with the shear moduli, with the ratio of $a_0 C_{44}$ providing a slightly better fit than the ratio of $a_0 \mu$, as shown in Figure 1. As suggested by others [1,10,11], scaling grain boundary energy with shear modulus is compatible with a dislocation model for grain boundary structure. The elastic energy of a dislocation is proportional to a shear modulus [12]. If boundaries are comprised of an array of dislocations [11], the boundary energy should remain proportional to the shear modulus. This is reflected in the familiar Read–Shockley model for the energy of low misorientation boundaries [13], which has been empirically observed to apply to high misorientation boundaries as well [11,14]. Indeed, scaling with the shear modulus is best for low and medium energy boundaries; the highest energy boundaries, which might be expected to deviate from ideal dislocation structures, diverge slightly from the $a_0 C_{44}$ scaling.

Figure 2 shows boundary energy comparisons for Au, Cu and Ni with Al, which is a high stacking fault energy material. Although the linear trend is still evident, there are considerably more outliers and scatter than for the lower stacking fault energy materials in Figure 1.

The coherent twin energy remains proportional to the stacking fault energy, and for the bulk of the boundaries, $a_0 C_{44}$ is a reasonable scaling parameter, with $a_0 \mu$ also plausible. The $\langle 111 \rangle$ twist boundaries, and to a lesser extent the low energy $\Sigma 3$ boundaries, have higher energy in Al than would be predicted from their energy in the lower stacking fault energy elements. This might

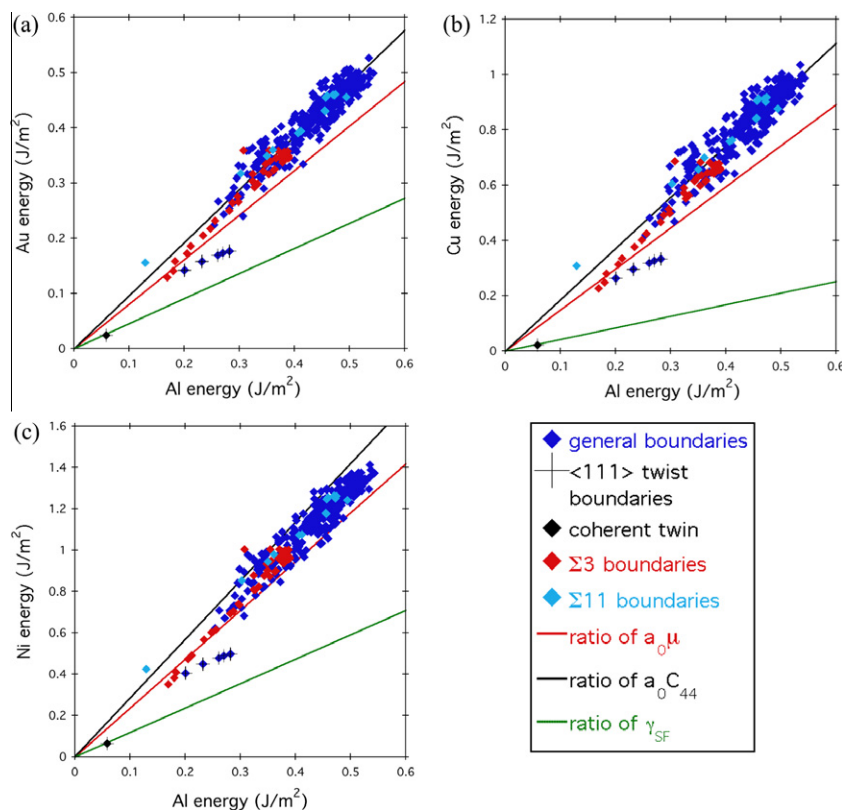


Figure 2. Comparisons of grain boundary energies for low to moderate stacking fault energy fcc metals with Al, which has high stacking fault energy. Data points represent pairs of boundaries that share the same macroscopic structure. Lines show scaling predicted by various material parameters. (a) Au vs. Al. (b) Cu vs. Al. (c) Ni vs. Al.

indicate that these boundaries, which all have some stacking fault character, are able to attain a more favorable structure in low stacking fault energy materials than in Al. Conversely, the $\Sigma 11$ symmetric $\langle 011 \rangle$ tilt boundary with $\{311\}$ normals has lower energy in Al than in Au, Cu or Ni.

The greater degree of scatter in the data for comparisons with Al indicates that there are more differences in grain boundary structure when materials differ widely in stacking fault energy. Trivalent Al has strong electron density fluctuations that affect bonding and are responsible for its unique properties, including low elastic anisotropy and high stacking fault energy. This also complicates the development of interatomic pair potential functions for Al, which must take a different functional form than for lower stacking fault energy elements. Thus, it is reasonable for Al grain boundaries to differ structurally and energetically from Au, Cu and Ni.

Common sense would suggest that the energy of a grain boundary depends on its structure. Grain boundary structure, in turn, is assumed to depend primarily on crystallography. Thus, it is not surprising that boundaries in different fcc metals that share a common crystallography have energies proportional to one another. However, this study is the first to verify this supposition using a large set of boundary energy data for macroscopically identical boundaries in several pure metals. Similarly, while a dislocation model for grain boundary structure suggests energy should scale with the shear modulus, this study confirms this scaling over a wide range of macroscopic boundary structures and provides further evidence that C_{44} is the most relevant one. Finally, although the stacking fault is often considered to be related to the grain boundary, the stacking fault energy does not scale the grain boundary energy except in certain special cases, most notably the coherent twin boundary. While these ideas have been discussed previously, high-throughput atomistic simulations provide new data to clarify and validate models for grain boundary energy.

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