Effect of Impurity Bonding on Grain-Boundary Embrittlement

L. Goodwin, R. J. Needs, and Volker Heine
Cavendish Laboratory, Cambridge CB3 0HE, United Kingdom
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We have explicitly tested, using pseudopotential total-energy techniques, the effect of two representative embrittling impurities on the grain-boundary cohesion of a metal. We find that substitutional Ge and As impurities increase the Al[111] interlayer energy of cohesion both at the impurity-doped layer and one layer into the bulk. Our calculations do not support either the first-layer or the second-layer decohesion models of impurity-promoted grain-boundary embrittlement.

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It is seen experimentally[1-3] that nonmetallic impurities, such as S and As, having poor solubility in a host metal tend to segregate to grain boundaries which can lead to brittle intergranular fracture. As these impurities form very stable compounds with the metals, they might be expected to strengthen the metal rather than weaken it. Recent studies have used both empirical[4,5] methods, based on improved pair potentials,[4] and quantum-mechanical methods.[6,7]

In this paper we present the first quantum-mechanical calculations with a realistically large supercell which show explicitly the effect of different impurities on the energy to fracture a metal. We consider a well defined problem such that the impurities sit in substitutional sites within a perfect crystal with no appreciable volume mismatch between the host and impurity atoms. It is seen experimentally that the segregation of impurities, in particular P in a NiCr steel,[8] is not uniform. The NiCr steel boundaries with large free volumes contained large concentrations of segregant while boundaries containing no free volume, such as coherent twin boundaries, contained no segregant.[8] We suggest that the impurities segregate to grain-boundary sites such that the volume mismatch is reduced. It is conceivable that the mechanism of impurity embrittlement is strongly dependent on grain-boundary geometry and on any impurity-host volume mismatch. Nevertheless, the widespread nature of embrittlement suggests to us that this is not the case, i.e., that changes in the geometries used will change the energies but not the qualitative features of the impurity effect.

A number of models have been proposed to explain impurity-promoted embrittlement. One of the earliest[9] proposed that the embrittling impurity forms bonds with the host metal that are weaker than the surrounding host-host bonds. We refer to this model as first-layer decohesion (FLD) as it implies a reduction in cohesion between an impurity-doped layer and the neighboring undoped layers. Indeed, Sayers[10] has demonstrated decohesion within a metal cluster using an empirical tight-binding model. Yet despite the elegance of his approach it has not been shown that the results are stable with respect to variations in the parameters.

A somewhat different and perhaps more plausible model is suggested by calculations on metal impurity clusters by Briant and Messmer.[11] Their work suggests that *interstitial* S in Ni weakens Ni—Ni bonds, i.e., S—Ni bonds appear to be favored at the expense of Ni—Ni bonds. We refer to this model as second-layer decohesion (SLD) as it suggests that fracture occurs not at the grain boundary but one layer into the pure metal. As Briant and Messmer confined themselves to a rather small tetrahedral cluster of four metal atoms surrounding one interstitial impurity, the applicability of their results is questionable. Furthermore, they did not calculate an energy, only a charge density, so that decohesion had to be inferred. In fact, recent quantum-mechanical calculations[6] have shown that *interstitial* B and S impurities *increase* the binding energy of small clusters of Ni atoms (a fracture energy was not calculated). In addition B, a cohesive enhancer, was seen to increase the maximum sustainable restoring force associated with an isotropic dilation. S, an embrittler, was seen to reduce this force.

Haydock[12] has proposed a third model which introduces the idea of bond mobility. When directional covalent bonds are formed between an impurity atom and a host metal there will be a reduction in the ease of atomic rearrangement relative to the case of the more uniform valence charge density in the pure metal. These rigid localized bonds embrittle by impeding stress release at the atomic level, thus favoring the breaking of bonds. One might expect the degree of covalency of the bonds between the impurity and the metal to correspond to the impurity's efficacy as an embrittler.

In this paper we present results of calculations that are motivated by the model of Haydock and aim to test directly the ideas of FLD and SLD for a representative metal and impurity elements possessing some covalent character. Thus we test the Briant and Messmer model for the case of substitutional impurities (their calculations were done with an interstitial impurity). These are self-consistent with a plane-wave basis set and local pseudopotentials of the Heine-Abarenkov form.[13] The calculations are performed in reciprocal space within a density-functional scheme with use of the Ceperley-

TABLE I. Calculated and experimental binding energies. Values calculated with our local pseudopotentials and with *ab initio* norm-conserving pseudopotentials are listed for comparison. Energies are in units of electronvolts per atom for Al and Ge, and electronvolts per pair of atoms for AlAs.

	fcc Al	Diamond Ge	Zincblende AlAs
Calc. (local)	3.68	5.31	8.83
Calc. (*ab initio*)	3.67[a]	4.50[b]	8.2[c]
Expt.	3.40[d]	3.85[e]	7.7[f]

[a] Reference 16.
[b] Reference 17.
[c] Reference 18.
[d] Reference 19.
[e] References 19 and 20.
[f] Reference 21.

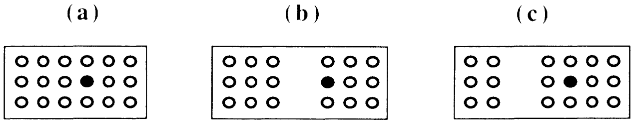

FIG. 1. Schematic depiction of the supercells for bulk and fractured material with six [111] layers of three atoms per layer. The open circles are Al atoms and the filled circles impurity atoms. (a) Unfractured bulk material. (b) Fractured at the impurity-doped layer to test the FLD model. (c) Fractured one layer distant from the impurity for testing the SLD model.

Adler[14] form of the local-density approximation for the exchange and correlation energy.

Al was chosen as a representative host metal with Ge and As as impurities. Ideally a transition metal such as Fe should be the host metal but the depth of the Fe pseudopotential is such as to require an unmanageably large plane-wave basis set. Al is thus a compromise though brittle intergranular fracture has been seen in alloys containing approximately 90% Al.[15] The core radius and the depth of the potential in the core region were adjusted so as to reproduce the experimental lattice spacings of Al, Ge, and As (4.02, 5.62, and 5.62 Å, respectively) while keeping the first zero of each pseudopotential in reciprocal space equal to the value tabulated by Cohen and Heine.[13] Thus we set the calculated atomic volumes equal to the experimental values while ensuring that the other properties of the pseudo atoms are close to those of the real atoms. The calculated bulk moduli of Al, Ge, and AlAs agree with experiment to within 8%. In addition Table I lists calculated and experimental binding energies. The binding energies calculated with *ab initio* and local pseudopotentials are in quite close agreement but both show the consistent overbinding that is normally ascribed to the use of the local-density approximation. Table II lists some phonon frequencies calculated with our local pseudopotentials for Al, Ge, and AlAs, showing good agreement with the experimental values.

We have tested the FLD and SLD models by taking a regular crystal structure with and without a dilute layer of substitutional impurities and calculating the strength of the first- and second-layer bonds. To maximize symmetry and to minimize the degree of surface relaxation we have chosen to consider cohesion of the Al[111] atomic planes. LEED measurements have shown that the only significant relaxation of the Al[111] surface is a 0.9% outward displacement of the topmost layer.[24] Two hexagonal unit cells, both containing eighteen atoms, are employed (Fig. 1). The first consists of six layers with three atoms per layer, the packing and spacing being that of fcc Al [Fig. 1(a)]. The second cell is the same but with an extra region of vacuum between two layers of width equal to one and a half layer spacings [Fig. 1(b) or 1(c)]. In all cases the lattice spacing used was that of bulk Al at zero temperature, i.e., 4.02 Å. Separate calculations have shown that one and a half layers adequately approximates an infinite separation. Thus the difference in energy between the two cells gives the energy to fracture the material creating two free surfaces with a total area equal to that of six atoms. Our idealized grain boundary is a single close-packed layer of enhanced impurity concentration with one substitutional impurity atom per three atoms and no impurities in the bulk (Fig. 2). By breaking at the impurity-doped layer we test the FLD model [Figs. 1(a) and 1(b)] and by breaking it one layer further along we test the SLD model [Figs. 1(a) and 1(c)].

TABLE II. Calculated and experimental phonon frequencies in units of 10^{13} rad/s.

	Mode	ω_{calc}	ω_{expt}
fcc Al	L(X)	5.68	6.08[a]
	T(X)	3.11	3.65[a]
Diamond Ge	TO(Γ)	5.64	5.73
	TA(X)	5.73[b]	1.51[b]
Zincblende AlAs	TO(X)	5.86	6.30
	TA(X)	6.30[c]	2.05[c]

[a] Reference 22.
[b] Reference 23, p. 106.
[c] Reference 23, p. 166.

The large size of the unit cells necessitates a large number of plane waves in the basis set for each electron

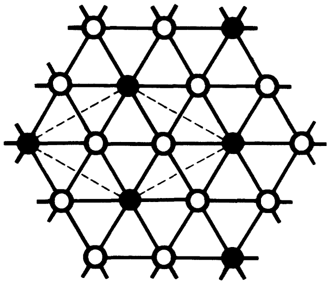

FIG. 2. A section of the plane of the grain boundary, idealized as an fcc[111]-type layer with a one-third concentration of impurity atoms. Dotted lines indicate the unit cell.

state (about 2000). The calculations for pure Al and for As-doped Al included in the basis set all plane waves with kinetic energy up to 9 Ry exactly, while those with kinetic energy between 9 and 14 Ry were included within second-order perturbation theory. For the calculations involving Ge we have treated all plane waves with kinetic energy up to 14 Ry exactly using a new diagonalization algorithm.[25] To test the basis-set convergence we have performed separate calculations with smaller cells and a wide range of basis-set energy cutoffs. For the calculations with As impurity atoms we estimate that the errors in the energy differences between 18 atom cells due to basis set truncation are less than 0.03 eV. The basis-set convergence of the calculations with Ge and Al is expected to be much better than this since the Ge and Al pseudopotentials are smoother than that of As. The wave functions were sampled at $4\times4\times2$ points on a regular mesh in the Brillouin zone. Separate calculations with different mesh sizes indicated that the error from the Brillouin-zone sampling was less than 0.015 eV per eighteen-atom cell.

In all our calculations we have kept the atoms fixed at regular fcc lattice sites but with a gap introduced in the structures of Figs. 1(b) and 1(c). For the Al[111] surface Needs[26] has calculated, using *ab initio* pseudopotentials, the relaxation energy of the atomic planes perpendicular to the surface to be 10^{-4} eV/Å^2. For our eighteen-atom cells having six surface atoms this corresponds to about 4×10^{-3} eV per cell, which is much smaller than the estimated error due to basis-set truncation and Brillouin-zone sampling. As Ge and As atoms are nearly the same size as Al atoms the relaxation energies for the structures with impurity atoms will also be small. Separate calculations for which a Ge-doped surface was relaxed have confirmed that the neglect of relaxation results in negligible error, especially in the energy differences between structures.

Our results are shown in Table III. We give the energies to fracture pure Al and impurity-doped Al both at the impurity-doped layer and one layer into the Al. The energy to fracture at the impurity-doped layer is the difference in total energy per unit cell between the structure shown in Fig. 1(a) and that in 1(b) (E_a and E_b, respectively), and similarly for fracture one layer into the Al. Thus the fracture energy is the energy required to create a crack of area equal to 3 atoms. For the surface energy of Al[111] we obtained a value of 0.30 eV per surface atom corresponding to a fracture energy of 1.80 eV. This is somewhat smaller than the value of 0.42 eV per surface atom obtained by Needs[17] in a calculation using a nine-layer slab with six layers of vacuum, *ab initio* pseudopotentials, and a large basis set. The experimental value of 0.515 eV per surface atom[27] is again a little higher but this is the energy of an "average" high-index surface, whereas the Al[111] surface is expected to have the lowest energy of all Al surfaces because of its high coordination.

TABLE III. Energies of fracture, E_γ, for pure and for impurity-doped Al calculated as the difference in energy between the unit cells of Figs. 1(a), 1(b), or 1(c) where E_a denotes the total energy per unit cell of the structure shown in Fig. 1(a), etc. Hence E_γ is the fracture energy to create a crack of area equal to three atoms or 21.0 Å^2.

Impurity	E_γ (eV)
Al	$E_a-E_b=1.80$
As	$E_a-E_b=1.94$
As	$E_a-E_c=1.88$
Ge	$E_a-E_b=1.82$
Ge	$E_a-E_c=1.89$

It is clear from our results that both As and Ge increase interlayer cohesion both for the impurity-doped layer and one layer into the metal on either side of the doped layer. In each case the fracture energy is increased, by up to 8%, by the presence of impurities. Thus what we see is increased cohesion, as allowed in the Haydock model of embrittlement, and not FLD or SLD. As, with the higher valency of the two impurities, exhibits the stronger enhancement of cohesion. We predict on the basis of our results that Si and P as substitutional impurities would give enhancement of cohesion comparable to Ge and As, respectively, and that S would show an even stronger effect.

In conclusion, our calculations for the fracture energy of the Al[111] surface with and without substitutional Ge and As impurities do not support either the FLD or the SLD models, as an explanation of embrittlement by segregated substitutional impurities. We see neither an overall weakening of the bonding between the impurity-doped layer and its neighbors nor an overall weakening of the interlayer bonding one layer into the metal. Because our results are contrary to the predictions of the widely quoted FLD and SLD models, we suggest that these models should be replaced by new ones based on the broad ideas discussed by Haydock.[12] To investigate these ideas it is necessary to calculate the ease with which atomic rearrangement can take place at a grain boundary and not just to calculate fracture energies as presented in this paper. These calculations should include the response of the structure to both applied tensile and shear stresses. Furthermore, to increase our understanding of the impurity-host interaction, calculations are needed with different geometries and other impurities for which there exists an impurity-host volume mismatch.

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