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Impurity-induced van der Waals transition during decohesion

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We investigate the thermodynamics of impurity segration between the separating atomic planes of a decohering solid from first principles. We find that the traction curve for decohesion at constant impurity chemical potential differs qualitatively from that at constant impurity concentration. In fact, for hydrogen and oxygen segregation between separating (111) planes during decohesion of fcc aluminum, a first-order van der Waals transition is predicted above a critical impurity chemical potential that results in a dramatic drop in the maximum stress of decohesion.

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Current understanding of the mechanisms leading to mechanical failure of materials is far from complete. This has its origin in the immense complexity associated with an event such as fracture in which many phenomena operate at varying length scales. While dislocation nucleation and glide often play an important role, it is the propagation of cracks that ultimately leads to fracture. Crack growth results in the separation of atomic planes either along grain boundaries or through grains. Hence efforts have been made to relate the atomic-level description of bond breaking to fracture resistance and cohesion.[1–7]

The traction curve, a stress versus separation relation for uniform decohesion of a solid along a pair of adjacent atomic planes,[2] is one of the key constitutive relations entering in to macroscopic fracture models, in which a cohesive zone characterizing the crack region is embedded in a solid described by continuum plasticity.[3,4] The traction curve describes the response of the solid within the cohesive zone to stresses exerted by the surrounding medium, allowing crack growth to naturally emerge in continuum mechanics simulations, once the maximum stress for decohesion has locally been surpassed. Such heirarchical modeling schemes are invaluable in elucidating complex materials phenomena that are not amenable to a direct atomistic analysis. The focus of this paper is on the details of modification of the traction curve by mobile impurities.

It has long been known that impurities or volatile chemical species can drastically alter the fracture resistance of a solid. Elements such as hydrogen or sulfur are well-known embrittling agents of important structural materials such as steel. While the effect of impurities can modify fracture behavior in several ways, its effect on the traction curve of the cohesive zone are recognized to be of central importance.[8,9] For slow to moderate crack growth rates that are of the order of impurity diffusion lengths, impurities can dynamically equilibrate at the advancing crack tip.[10,11] Under these conditions, crack growth occurs at constant impurity chemical potential and the concentration of impurities will change near the crack as it is stressed. While the importance of impurities in modifying cohesive properties is widely recognized, it is not clear how impurities at constant chemical potential affect the traction curve for decohesion.

We present a first-principles thermodynamic model to study the effect of impurities *at constant chemical potential* on the traction curve of a uniformly decohering solid. We apply it to decohesion of fcc aluminum along a pair of (111) planes accounting for the presence of hydrogen or oxygen atoms in the decohering region at constant chemical potential. We find that while the tractions at constant impurity concentration have a form similar to those of previously explored systems,[1] a constant impurity chemical potential can lead to a discontinuity in the relation between decohesion distance and stress. This first-order transition in the stress-displacement diagram, reminiscent of a van der Waals transition, leads to an abrupt drop in the maximal cohesive stress once a critical impurity chemical potential is exceded. Instead of a gradual change in the resistance to crack growth with increasing impurity chemical potential, this result indicates that an abrupt change in crack growth mechanism should occur at a characteristic impurity chemical potential.

The traction curve for decohesion can be obtained as the derivative of the energy of a solid as two slabs of bulk material are uniformly separated along a pair of adjacent atomic planes. This stress-separation relation then serves as a first-principles input to describe the resistance to crack growth of the cohesive zone in continuum simulations of fracture.[3,4] Impurity atoms can segregate between the decohering atomic planes. Calculating the energy of decohesion as a function of slab separation from first principles is straightforward if the impurity concentration and arrangement between the separating atomic planes is kept fixed.[5–7] Obtaining the traction curve at constant impurity chemical potential though requires additional thermodynamic considerations.

Thermodynamically, the decohering region can be considered as a subregion of the solid characterized by excess extensive quantities[8] as in the standard thermodynamic description of surface properties. The excess internal energy for the decohering region per unit area (of the separating atomic planes) u is related to the other excess extensive quantities according to

$$du = T ds + \sigma d\delta + \mu d\Gamma, \tag{1}$$

where s is the excess entropy and Γ is the excess number of impurity atoms on the separating atomic planes per unit area.

The extent of decohesion, δ, is the elongation of the decohering solid in excess of the elongation of each separating slab assuming that this elongation is homogeneous. T, σ, and μ refer to the temperature, the stress perpendicular to the decohering atomic planes, and the impurity chemical potential, respectively. (We neglect work modes that stretch the decohering planes in their own plane as a result of the Poisson effect during elongation of slabs). The excess energy u, with its natural variables s, δ, and Γ is an impractical thermodynamic potential and a more appropriate potential with natural variables T, σ, and μ can be defined by successive Legendre transforms. The relevant potential at constant T, σ, and μ, conditions that specify the state of a decohering region in an actual solid, is the grand-force potential, $\phi = u - Ts - \sigma\delta - \mu\Gamma$.

In this work, we used first-principles total-energy calculations to parametrize a lattice model Hamiltonian[12,13] that describes the energy of different impurity configurations on the decohering atomic planes as a function of the distance, δ, between these planes. Solving the lattice model Hamiltonian within the mean-field approximation or with Monte Carlo simulations yields a Gibbs free energy g (per unit area of decohered planes) as a function of impurity concentration and δ. The relation between g and the physically relevant thermodynamic potential ϕ can again be obtained with Legendre transforms according to $\phi = g - \sigma\delta - \mu\Gamma$.

We considered the effect of hydrogen, an important embrittling agent of metals, on the decohesion of adjacent (111) planes in fcc aluminum. In bulk aluminum, dilute hydrogen energetically prefers the tetrahedral sites (within the local-density approximation, LDA)[6] that in the fully decohered state, become the fcc surface sites that rest above a triangle of aluminum atoms of the exposed (111) plane. Between adjacent (111) planes, the tetrahedral sites form an undulating honeycomb lattice formed by a pair of interpenetrating two-dimensional triangular lattices.

We used a lattice model Hamiltonian that includes the nearest-neighbor and second-nearest-neighbor interactions on the honeycomb lattice between the pair of decohering aluminum (111) planes. We obtained numerical values for the interaction parameters at each separation δ by requiring the Hamiltonian to reproduce first-principles total-energy values of four different hydrogen arrangements between the decohering (111) planes. These energies were calculated within the local-density approximation[14] with ultrasoft pseudopotentials[15] using a periodic supercell of fcc Al. The supercell consisted of a slab of 12 (111) planes, the periodic images of which were separated by a gap with a width δ that was systematically varied. The (111) planes of adjacent slabs that define the boundaries of this gap constitute the decohering planes and δ is a measure for the extent of decohesion. In these calculations, the hydrogen atoms between the pair of decohering planes were allowed to relax, though, the aluminum atoms within the slabs were held fixed. We found that while relaxations in the slabs affect the total energy of the system considerably, its effect on the excess properties of the decohering region are small.

The nearest-neighbor pair interactions for the lattice model Hamiltonian are small for all separations, never exceeding 10 meV, and favoring hydrogen-vacancy ordering (i.e., the interactions are positive within the Ising formalism). At room temperature, the hydrogen atoms between the decohering planes exhibit solid solution behavior and we found that the mean-field approximation at this temperature essentially yields the same results as the more accurate Monte Carlo simulations.

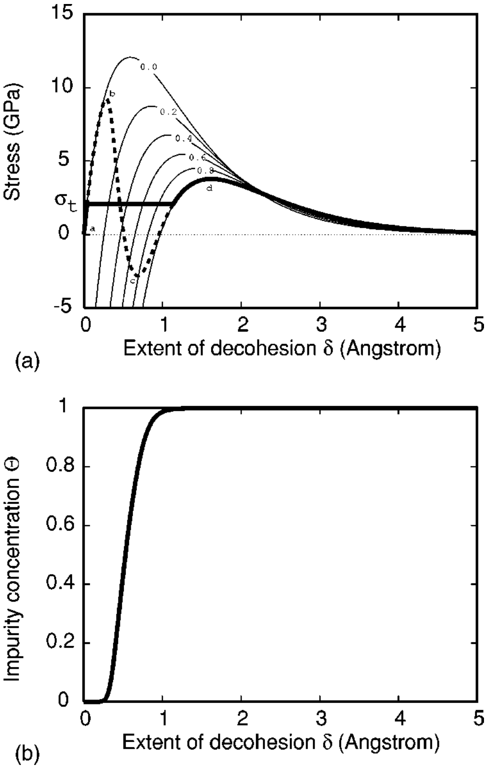

FIG. 1. (a) Traction curves calculated at different hydrogen concentrations Θ (thin lines). Θ is indicated along the traction curve. Superimposed is the traction curve at constant μ (thick dashed line) greater than μ_c. The thick solid line corresponds to the part of the traction curve with minimal grand-force potential. (b) Variation of Θ with slab separation δ for a constant chemical potential above μ_c.

Figure 1(a) illustrates traction curves calculated at fixed hydrogen concentration $\theta = \Gamma/\Gamma_s$ (Γ_s is the excess concentration when the hydrogen sites between the pair of decohering aluminum (111) planes are fully saturated by hydrogen atoms) for a range of θ values (thin lines). As the hydrogen concentration increases, the maximum stress decreases. The equilibrium width between decohering planes (determined by $\sigma = 0$), and the values for δ at which σ peaks, increases with θ. The maximum cohesive stress ranges from 12 GPa in the absence of hydrogen to ≈ 4 GPa when the region between decohering planes are fully saturated with hydrogen.

At fixed hydrogen chemical potential μ, the hydrogen concentration θ changes with separation δ. At very low μ, the hydrogen adsorption is negligible and the traction curve closely follows that for $\theta = 0$. For higher μ, θ increases with δ. Figure 1(b) illustrates, for an intermediate value of μ, a surge in hydrogen concentration in a narrow interval of δ. The rapid change in θ causes the stress to follow a trajectory in the shape of a double-humped camel's back as illustrated

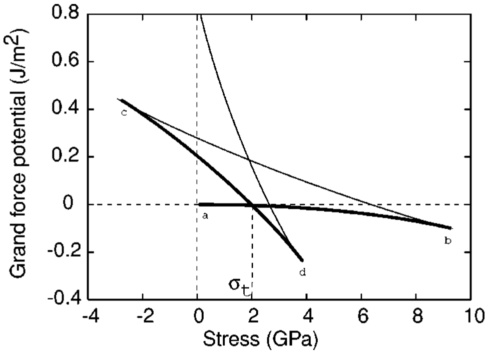

FIG. 2. Grand-force potential ϕ for the traction curve of Fig. 1(a). Bold portions of the curves denote thermodynamically stable states.

by the dashed line in Fig. 1(a). This trend persists as the chemical potential increases further, though the onset of the sudden rise in θ occurs for lower δ. Not all portions of the σ-δ traction curves of Fig. 1(a) are thermodynamically stable. A straightforward stability analysis shows that the crack region is thermodynamically stable with respect to infinitesimal fluctuations in δ in regions for which $(\partial\sigma/\partial\delta)_{T,\mu}$ is positive. Hence, the constant chemical potential traction curve at intermediate to high chemical potential has two stable segments. These correspond to the initial stages of each hump for which $(\partial\sigma/\partial\delta)_{T,\mu}>0$, i.e., between a-b and c-d in Fig. 1(a). When the decohering region of the solid is in a state between a-b, we refer to it as in the *dilute cohesive-zone* (DCZ) phase, while if it is in a state between c-d, we refer to it as in the *saturated cohesive-zone* (SCZ) phase.

A state that is thermodynamically stable is not necessarily the one that will appear in thermodynamic equilibrium. Some states may be *metastable*. True equilibrium at constant T, σ, and μ is characterized by a minimum of ϕ. The evolution of ϕ with σ for the traction curve at constant μ of Fig. 1(a) (dashed curve) is illustrated in Fig. 2. The concave down-portions correspond to the stable branches of the humps of the traction curve. At low impurity chemical potential, the DCZ phase is thermodynamically favored for all forces, while the SCZ phase is metastable. Above a critical impurity chemical potential μ_c, the grand-force potential ϕ for the SCZ phase (c-d) dips below ϕ for the DCZ phase (a-b) at a stress σ_t significantly below the maximal stress along a-b as illustrated in Fig. 2. This crossover in ϕ signifies a first-order phase transition (van der Waals transition) at constant stress, during which the DCZ phase transforms to the SCZ phase. Hence, during this phase transition, decohesion progresses under constant applied stress, whereby a *dilute* decohering phase transforms to a *saturated* decohering phase.

The significance of the first-order phase transition is that the maximal stress for decohesion is no longer that of the first hump along a-b in Fig. 1(a), but the significantly lower maximal stress of the second hump along c-d corresponding to full saturation by hydrogen of the decohering planes. For $\mu<\mu_c$, the first-order phase transformation does not occur and σ tracks the first hump to maximal stress. The existence of a critical $\mu=\mu_c$, above which a transition occurs leads to a discontinuity in the maximal stress for decohesion as a function of chemical potential. This is illustrated in Fig. 3 which shows the maximal stress along the traction curve as a function of the chemical potential. Figure 3 also illustrates the result of a similar analysis for oxygen segregation between the pair of decohering (111) planes of aluminum. The pair interactions between oxygen atoms between the decohering planes favor phase separation (i.e., island formation) which is qualitatively different from the interactions between hydrogen atoms. For both hydrogen and oxygen segregation to the decohering region, the critical chemical potential (which is impurity specific) was arbitrarily set to zero. Even for $\mu<\mu_c$, hydrogen reduces the maximum stress while this is not the case for oxygen. The effect of oxygen is more pronounced in reducing the maximal stress than hydrogen, reducing it by a factor of almost 10. (It is difficult to estimate the partial pressures corresponding to the critical chemical potentials μ_c since LDA makes large errors in relative energies between a molecular state and the solid state. This complicates the comparison between calculated impurity chemical potentials on a solid and in molecular form in the gas phase.)

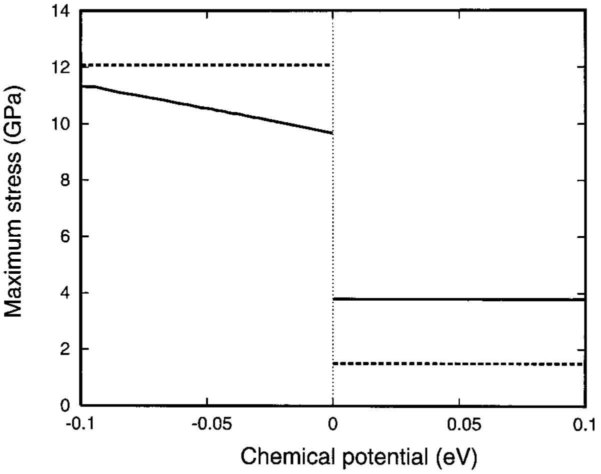

FIG. 3. Critical stress as a function of chemical potential relative to μ_c (arbitrarily set to zero). Solid line is for hydrogen and dashed line is for oxygen.

Our results indicate the following picture for decohesion under constant impurity chemical potential above μ_c. Stress builds up in the solid ahead of the crack tip with only a very small increase in impurity concentration. Once the critical stress σ_t (for that given impurity chemical potential) is reached, the atomic planes near the crack can further separate at constant stress by influx of impurities. At this point, growth of the crack is limited by the supply of impurities. The heavily saturated crystal planes are then further separated to full decohesion, but at a stress significantly lower than is required in the absence of the impurity.

The predicted van der Waals transformation during decohesion constitutes a mechanism by which impurities can embrittle a solid. This transition can be viewed as a stress-induced phase transformation in the presence of mobile impurities. In the present model, the new phase is restricted to form between the pair of decohering planes, but in real materials, the new phase could also encompass many atomic planes. Above a critical stress and impurity chemical potential, it becomes thermodynamically more favorable for the metal to fill interstitial sites with impurity atoms. The new phase with interstitial sites saturated by impurities has a different cohesive stress.

Whether a crack separates under constant impurity chemical potential or under constant impurity concentration depends on the rate of impurity transport as compared to the mechanical loading rate. While impurities can diffuse to the crack from the bulk, impurity supply from the faces behind the crack tip is probably more relevant. In essence, these surfaces, when saturated, behave as a reservoir of impurities for the growing crack at relatively constant chemical potential. Dislocations offer another rapid impurity diffusion path to the crack tip. Hydrogen diffusion coefficients in metals are difficult to measure experimentally.[16] Nevertheless, first-principles calculations of hydrogen mobility in bulk aluminum and on aluminum (111) surfaces predict that the length scale for hydrogen diffusion is of the order of a micron per second.[6] Hence, for crack growth rates less than this value (i.e., state I and II of stress corrosion cracking in moist environments and fatigue cracking in the near threshold regime[10,11]), decohesion should occur under conditions of constant impurity chemical potential.

In conclusion, this work demonstrates that the traction curve at constant impurity chemical potential differs in important ways from that calculated for a constant impurity concentration segregated on the decohering atomic planes. In fact, a first-order van der Waals transition is predicted above a critical impurity chemical potential for decohesion of fcc aluminum in the presence of hydrogen or oxygen. This phase transformation leads to a dramatic reduction of the maximal stress for decohesion and offers significant insights as to how impurities can embrittle solids for regimes of slow crack growth. The sudden drop in the maximal stress for decohesion above a critical chemical potential means that a change in the environmental conditions could significantly alter the crack growth mechanism.

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[1] J.H. Rose, J. Ferrante, and J.R. Smith, Phys. Rev. Lett. **47**, 675 (1981); J.H. Rose, J.R. Smith, and J. Ferrante, Phys. Rev. B **28**, 1835 (1983).

[2] A. Needleman, J. Appl. Mech. **54**, 525 (1987).

[3] H.H.M. Cleveringa, E. Van der Giessen, and A. Needleman, J. Mech. Phys. Solids **48**, 1133 (2000).

[4] V.S. Deshpande, A. Needleman, and E. Van der Giessen, Acta Mater. **49**, 3189 (2001).

[5] E.A.A. Jarvis, R.L. Hayes, and E.A. Carter, ChemPhysChem **2**, 55 (2001).

[6] G. Lu, D. Orlikowski, I. Park, O. Politano, and E. Kaxiras, Phys. Rev. B **65**, 064102 (2002).

[7] R. Wu, A.J. Freeman, and G.B. Olson, Science **265**, 376 (1994).

[8] J. R. Rice, in *Effect of Hydrogen on Behavior of Materials*, edited by A. W. Thompson, and I. M. Bernstein (The Metallurgical Society of AIME, Warrendale, PA, 1976), p. 455.

[9] J.R. Rice and J.S. Wang, Mater. Sci. Eng., A **107**, 23 (1989).

[10] N.J.H. Holroyd and D. Hardie, Corros. Sci. **23**(6), 527 (1983).

[11] R.S. Piascik and R.P. Gangloff, Metall. Trans. A **22A**, 2415 (1991).

[12] J. M. Yeomans, *Statistical Mechanics of Phase Transitions* (Clarendon Press, Oxford, 1992).

[13] D. de Fontaine, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic Press, New York, 1994), p. 33.

[14] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[15] We implemented the VASP ultrasoft pseudopotential code. See G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[16] J.R. Scully, G.A. Young, and S.W. Smith, Mater. Sci. Forum **331-337**, 1583 (2000).