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APPLICATION OF THE EMBEDDED ATOM METHOD TO THE FRACTURE OF INTERFACES

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ABSTRACT

A modern theory of metallic bonding, the Embedded Atom Method (EAM) provides a simple but accurate method of evaluating the energy and forces in a cluster of atoms. As an example of the utility of the EAM, surface segregation in Ni-Cu alloys and reconstruction of fcc(110) surfaces will be predicted and compared to experiment. Using energetics from the EAM and a Monte Carlo procedure, the structure and cohesive energy of grain boundaries in nickel and Ni₃Al are predicted. The brittle fracture strength of these boundaries at room temperature is determined using molecular dynamics calculations.

Introduction

The study of interfaces is a critical area in the design of engineering materials. One specific subset of this area, the intergranular fracture of metals, will be discussed here. If detailed understanding of fracture is to be obtained, specific atomistic processes must be considered. There have been numerous previous atomistic studies of the structural properties of grain boundaries (see Ref. 1 for a review) using pair potential interactions. These interactions, however, are not applicable to the fracture problem, as explained below.

Recently the Embedded Atom Method (EAM) has been developed to handle atomistic calculations at surfaces and interfaces. The EAM is a semi-empirical method based on electron density theory which has been shown to accurately describe a large number of properties in metals, e.g. defects, liquids, surfaces, alloys, mechanical properties, and hydrogen on surfaces. This paper will first review the EAM and discuss the types of calculations we perform. Then two specific examples of application of the EAM to surface segregation and to surface reconstruction will be given. The surface examples are chosen because in contrast to grain boundaries direct straightforward comparison to experiment is available. The paper will then turn to the fracture process. An important part of the ductile fracture process is dislocation motion. Thus molecular dynamics simulation of dislocation motion in nickel will be presented and compared to continuum theory. Finally the fracture of a grain boundary in nickel and Ni₃Al will be compared.

Calculational Method

Recently a new method has been developed at Sandia National Laboratories which has been used to investigate the atomic behavior of metals. We have called this procedure the Embedded Atom Method (EAM) since in a metal the primary contribution to the energy of an atom results from "embedding" an atom into the sea of electrons produced by its neighbors. The formalism of the method has been derived from electron density theory, but in specific applications we have used a semi-empirical approach which requires the knowledge of experimental materials properties. The EAM overcomes an important deficiency of previous calculations which employed pair-wise interactions which are valid only in cases where the atoms are contained in a definable volume. Unfortunately this limitation precludes the interesting case of fracture, during which new surfaces are formed.

(a) Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences.
In the EAM, the total energy, \( E \), of a configuration of atoms is given as:

\[
E = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i<j} \phi_{ij}
\]

(1)

where the embedding function, \( F_i \), depends on the type of atom, \( i \), and the electron density at that site, \( \rho_i \). A pair potential contribution, \( \phi_{ij} \), is included to represent electrostatic repulsion. The electron density is taken to be a linear superposition of atomic electron densities. A complete description of the EAM may be found in the references quoted above. The functions \( F \) and \( \phi \) for transition metals are determined by requiring that the calculated lattice constant, elastic constants, sublimation energy, vacancy formation energy, and equation of state for homogeneous deformation agree with experiment. For the Ni-Al system the lattice constants and sublimation energies of NiAl and Ni\(_3\)Al are also fit.

The atomistic calculations start with a simulated metal lattice of thousands of transition metal atoms with either periodic boundaries or free surfaces depending upon the problem of interest. Three procedures are then used to investigate the evolution of the system. In the first, the minimum energy configuration is found by moving the atoms so that the forces on all atoms are reduced to zero. The second procedure uses the calculated forces to solve Newton's equations of motion for each atom. These molecular dynamics calculations actually follow the motion of each atom and are useful for examining dynamic processes such as dislocation motion or fracture. For the thousands of atoms we typically examine, such calculations can take hours of computing time on our CRAY1-S computer. The third type of calculations presented here are Monte Carlo simulations. They are used to produce the thermal equilibrium atomic distribution of the atoms. These simulations allow for atomic motion around the lattice sites. In addition, the calculations are performed in an isobaric, grand canonical ensemble where the relative value of the chemical potentials of the two species is held constant. The simulations allow the atomic species of an atom to change in accord with the change in the total energy relative to the chemical potential as described previously. This procedure produces rapid convergence of the equilibrium compositional distribution since the need for actual atomic diffusion is bypassed. The desired pressure \( P \) is maintained by allowing the volume of the computational cell to change by a uniform dilation \( \Delta V \) of the system. The volume change is accepted based on the change in energy relative to \( P\Delta V \).

The elastic properties of the alloy are important to the mechanical behavior of the material. While the elastic properties of the pure metals are used in the fitting process, the elastic constants of the alloys are not necessarily correct. Therefore the comparison of the elastic constants computed from this model with the experimental values is a crucial test of the empirical functions used here and a good indicator of their predictive value. We have therefore calculated the elastic constants of Ni\(_3\)Al in Table I. The phonon modes of Ni\(_3\)Al have been calculated by computing the dynamical matrix from Eq. (1) as was done for pure metals by Daw and Hatcher. The extension of this procedure to heteronuclear systems is straightforward, albeit algebraically tedious. From the long-wavelength limit of the acoustical phonon modes, the elastic constants can be computed. The longitudinal and transverse modes along the [100] direction and one of the transverse modes along the [110] direction are sufficient to determine \( C_{11}, C_{12}, \) and \( C_{44} \), and the other modes along [110] and [111] are used as checks. The calculated elastic constants are compared to experiment in Table I. The agreement is quite good and again gives confidence in the reliability of the empirical functions.
TABLE I. Calculated elastic constants of Ni$_3$Al and experimental values. The elastic constants are in $10^{12}$ ergs/cm$^3$.

<table>
<thead>
<tr>
<th></th>
<th>Theory (EAM)</th>
<th>Experiment (Ref. 14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>2.516</td>
<td>2.302</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>1.370</td>
<td>1.493</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>1.262</td>
<td>1.316</td>
</tr>
</tbody>
</table>

Application to Surfaces

In earlier work$^{11}$, the segregation of Ni-Cu alloys at low index surfaces was studied in detail. Here we describe the general results and how these results compare with the experimental data. All of the calculations were performed for a temperature of 800K. The calculated compositions for the (100) and (111) surfaces were found to be very similar. The composition of the top three atomic planes are presented as a function of bulk composition for the (111) surface in Figure 1. The top atomic layer is strongly enriched in Cu with the composition of the top layer being >90% for bulk compositions in excess of about 5%. The surprising feature of the results is the composition of the near surface atomic layers. The second layer is enriched in Ni with a composition of about 80% Ni for a bulk composition of 50%. The third layer composition is close to the bulk value but again somewhat enriched in Ni. The oscillations of the composition are unexpected because in the Ni-Cu alloy system the individual elements tend to cluster so that one would have expected Cu to have been enriched near the surface as well as on the top layer. This prediction of composition oscillation is in agreement with the field ion microscopy results of Ng et al.$^{15}$ For the (111) face of a NiCu (5%) alloy, they found strong enrichment of Cu in the surface layer and depletion of Cu from the near surface layer. The results for the (110) face also show a non-monotonic composition variation with depth. There the top two atomic layers are enriched in Cu while the third through fifth atomic layers are somewhat enriched in Ni.

The top layer compositions are compared in Figure 1 with various experimental results. The Auger results of Webber et al.$^{16}$ are for a temperature of 850-920K. They studied various low index faces and reported that their results did not depend on the orientation. The ion scattering results of Brongersma et al.$^{17}$ are for polycrystalline samples at a temperature of 780K, and the field ion microscopy results of Ng et al.$^{15}$ are for (111) surfaces at 820K. The agreement between theory and experiment is quite encouraging.

As an example of reconstruction we will consider the (110) surface of fcc materials. The (110) surface of Pt, as well as Au and Ir, is known to reconstruct to a (1x2) symmetry$^{18}$. Initially, two prominent models for the reconstruction were the "missing row" and "sawtooth" geometries. While early LEED studies were unable to differentiate these structures, recent work with a variety of techniques shows that the missing row structure is preferred$^{19}$. Total energy LCAO calculations$^{20}$ show that the sawtooth structure is definitely higher in energy than the missing-row structure on Pt(110), although the unreconstructed surface is found to be marginally lower in energy in that work.

The energies of candidate structures are given in Table II for the EAM calculations using the functions of Ref. 3 and the LCAO calculations in Ref. 20. These energies are very similar to those reported by Daw$^5$ using slightly different EAM functions for Pt. The energies are reported
Fig. 1. Calculated Cu concentration by layer as a function of bulk concentration at 800 K for the (100) face of Ni-Cu alloys. The solid curve is the top layer, the long dashed curve is the second layer, and the short dashed curve is the third layer. The symbols (x) and (+) are the experimental values for the top layer composition obtained by Auger, Reference 16, and by ion scattering, Reference 17, respectively. The symbols (o) and (θ) are the experimental first and second layer compositions, respectively, determined by field ion microscopy, Reference 15.

relative to the energy of the relaxed 1x1 structure. The "missing row" structure is lower in energy than the 1x1 and the "sawtooth" is clearly too high in energy to be considered. (The sawtooth structure energy relative to the 1x1 structure is a large fraction of the 1x1 surface energy.) The energies are comparable to those calculated by Tomanek et al.20, except that our energies show the missing row to be preferred over the 1x1.

The energy of both the unreconstructed (1x1) surface structure and of the (1x2) missing-row reconstruction for the metals Cu, Ag, Au, Ni, Pd, and Pt have been computed both for the unrelaxed and fully relaxed surface geometries21. The differences between the surface energies of the relaxed reconstructed and unreconstructed surfaces are presented in Fig. 2. These energy differences correctly predict that Au and Pt should reconstruct and that Ni and Cu should not. However, they also predict that Pd and Ag should reconstruct in contradiction with experiment19 though the computed energy differences are small.

Dislocation Calculations

Calculations of dislocation motion have been carried out to test the EAM in a dynamical situation6. Shear stresses are achieved by applying external forces on the surface atoms in the
The Embedded Atom Method Shows the Missing-row Geometry to be the Lowest in Energy for Pt(110) Structure

<table>
<thead>
<tr>
<th>Structure</th>
<th>E(1x2) - E(1x1) (meV/Å²)</th>
<th>EAM</th>
<th>LCAOa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Missing row</td>
<td>-2.10</td>
<td>+3.68</td>
<td></td>
</tr>
<tr>
<td>Sawtooth</td>
<td>+32.6</td>
<td>+33.6</td>
<td></td>
</tr>
<tr>
<td>Hollow-on-facet</td>
<td>Unstable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ridge</td>
<td>+66.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paired-row</td>
<td>Unstable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buckled paired-row</td>
<td>Unstable</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quasi-hexagonal</td>
<td>Unstable</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

E(1x1) = 94.2 meV/Å²

a Reference 20

Fig. 2. The Embedded Atom Method shows a trend toward the (1x2) reconstruction for (110) fcc surfaces as one goes down the periodic table. The solid bars represent the surface energy differences between the missing row and unreconstructed surfaces for Ni, Pd, and Pt while the other bars represent Cu, Ag, and Au.
slip direction. In the dislocation dynamics calculations, the stresses quoted are applied at the 
beginning of the runs and held constant. Under energy minimization, the unstressed dislocation 
separates into two partial dislocations approximately 12Å apart. (The reader should note that 
this separation distance is one of the parameters which is used to determine the functions. This 
separation is therefore not a prediction.) This separation does not change significantly during 
molecular dynamics runs even with stresses applied.

We can apply a shear stress to the dislocation and watch the resulting dislocation motion. As 
one would expect, the dislocation starting at rest slowly accelerates to a terminal velocity, which 
is close to the speed of sound in the material. The actual limiting velocity, which we obtain from 
these calculations, is determined by the appropriate sound velocity for the finite slab which is 
dominated by the propagation of surface waves. The calculations shown22 were performed at 
T = 0 K, but can also be performed at finite temperature. In Fig. 3 we show the velocity of a 
dislocation at three stresses: 0.015%, 0.06%, and 0.24% of C_{44}. The data points are from the 
molecular dynamics simulations. The solid lines are a comparison to a continuum calculation that 
will be described next.

![Dislocation Motion at 0K](image)

Fig. 3. Edge dislocation velocity, in the slip direction [110] for nickel under various shear 
stresses. The points are from the molecular dynamics calculations, and the solid lines are the fit 
from elastic continuum theory (see text). The low, medium, and high stresses are 0.015%, 0.06%, 
and 0.24% of the shear modulus. The dislocation accelerates to a terminal velocity, but in the 
lower stress cases the time illustrated is insufficient for the velocity to reach its terminal value.
The isotropic elastic continuum equation of motion for a dislocation under stress at T = 0 K is\(^{23}\):

\[
\frac{d}{dt} \left( \frac{m^*v}{\sqrt{1 - \frac{v^2}{c^2}}} \right)^1/2 = \sigma b
\]  

(2)

where \( m^* \) is the effective mass, \( c \) is speed of sound, \( \sigma \) is the external stress, and \( b \) is the Burgers vector. The effective mass cannot be determined by continuum theory, but is a material parameter (like the speed of sound). The effective mass parameter is related to the energy of a dislocation at rest, and also to its dynamics through Eq. 2. We can, however, determine the effective mass from atomistic calculations, either by directly calculating the energy of a dislocation at rest or by calculating the dynamics of the dislocation. The solution to Eq. 2 is

\[
v = \frac{ct}{\sqrt{t^2 + \tau^2}}
\]

(3)

with \( \tau = m^*c/\sigma b \). Now we can fit this solution to the results of the molecular dynamics simulations, where we have one parameter to fit to three functions. The fit determines the effective mass, (we get \( m^* = 1.6 \times 10^{-3} \) eV-\( \text{psec}^2/\text{Å}^3 \) which is 0.65 of an atomic mass per Burgers vector) and results in the solid lines in Fig. 3. The fact that the fit is good is quite encouraging, in that the atomistic and continuum calculations are consistent. The effective mass tells us that the inner cut-off of continuum theory (the point where local elastic continuum theory breaks down) is about 1 Burger's vector. A similar number is obtained by comparing to the rest energy of a dislocation, which gives \( m^* = 3.9 \times 10^{-3} \) eV-\( \text{psec}^2/\text{Å}^3 \). In short, the continuum equation of dislocation motion (Eq. 2) works surprisingly well.

Grain Boundary Calculations

We now consider the main topic of interest for this conference, grain boundaries. The grain boundaries of Ni\(_3\)Al are of interest due to its propensity for intergranular fracture. As a first step toward understanding the mechanical properties of the boundaries, the equilibrium structure of various ideal grain boundaries have been computed\(^{24}\) using Monte Carlo simulations at a temperature of 1000 K. Two types of ideal boundaries will be considered here, symmetric twist boundaries and a symmetric tilt boundary. The two twist boundaries are the \( \Sigma=5 \) and the \( \Sigma=13 \) twist boundaries which are constructed by rotating one half of a crystal around the (100) axis normal to the boundary plane by 36.90 and 22.60 respectively. The tilt boundary is a \( \Sigma=5 \) symmetric tilt boundary. The two lattices on each side of this boundary are rotated around a cubic axis parallel to the boundary plane such that the boundary plane is parallel to a (210) plane in each lattice. These boundaries were chosen because they have relatively small unit cells and so are amenable to computer simulation. The simulations treat a bi-crystalline slab which is periodically repeated in the plane of the slab. The linear dimensions of the periodic cell were different for each boundary but were about 15-20 Å in each direction and the slabs were about 35Å thick. For each geometry, the simulations were performed with chemical potentials corresponding to a Ni-rich bulk, an Al-rich bulk and an ideal stoichiometric bulk. The initial condition for each simulation was an ideal coincidence site structure consisting entirely of Ni atoms.

The compositional structure determined by the simulations for the twist boundaries at ideal stoichiometry is very simple. The (100) planes of the Ni\(_3\)Al structure alternate between pure Ni and an equal mix of Ni and Al. At the grain boundary, this alternating pattern of the (100) planes parallel to the boundary continues uninterrupted through the boundary. Thus the compositional ordering is the same that would be obtained by taking an ideal Ni\(_3\)Al crystal and rotating the two halves to form the boundary. This result is not surprising since the interactions favor the presence of Ni-Al nearest neighbor pairs and this structure accomplishes that. The interplanar spacing normal to the boundary increases due to the lattice misorientation. For the \( \Sigma=13 \) boundary at ideal stoichiometry, the calculated net expansion normal to the boundary is 0.3 Å.
The structure of the tilt boundary is more complicated. The atoms originally in the (210) plane on each side of the boundary combine to form one dense plane with little compositional order. The next (210) plane on each side of the boundary is close to its structure in the bulk crystal and is separated by 1.4Å from the middle of the central plane. (The (210) interplanar spacing is 0.81 Å.) Thus there is a net expansion of about 0.4 Å normal to the boundary. (Note that the central plane of the boundary would normally be two separate (210) planes.)

In addition to the composition of the boundary region, the compositional order of the boundary is also affected by the bulk composition. This is most easily seen for the twist boundaries. For boundaries that are Al-rich, the excess Al could either be placed in the Ni plane or in the Ni sites of the mixed composition plane. However, the simulations show that the majority of the excess Al are placed on the Ni plane and that the mixed composition plane actually contains slightly less than 50% Al. For the Ni-rich case, one would simply expect to replace the Al atoms on the mixed composition plane with Ni atoms. The simulations show, though, that in addition there is a reduction in the ordering of the mixed plane. For the Σ=13 boundary at a bulk composition of 24.5% Al, there are three times more anti-site defects in the mixed composition plane than are required by the reduced Al concentration in that plane. In addition, the Ni plane in this boundary is found to contain 4% Al atoms even though the system is deficient in Al. Thus away from ideal stoichiometry, there is a tendency to smear out the alternating composition of the (100) planes at the boundary. These effects are discussed more fully in Ref. 24.

The EAM can also be used to investigate the energetics of the grain boundary. This is of interest because the propensity of Ni3Al to intergranular fracture could be attributed to a low cohesive energy of the grain boundaries. The energy of the tilt boundary has been computed at zero temperature for the Σ=5 grain boundary for both pure Ni as well as for Ni3Al. In both cases the grain boundary energy is about 1250 ergs/cm². The cohesive energy represents the energy required to cleave the boundary and so is the sum of the surface energy of the two free surfaces that are created minus the energy of the grain boundary which is cleaved. For this tilt boundary, the surfaces created have a (210) orientation. The energy of this surface is 1830 or 1940 ergs/cm² for Ni and 1830 or 1940 ergs/cm² for Ni3Al depending on whether the exposed surface plane is the pure Ni plane of the mixed composition plane. Thus one would expect about the same cleavage energy for this boundary in both Ni and Ni3Al, namely about 2400 ergs/cm². This value was compared for the case of Ni3Al to the finite temperature simulation results by cleaving various of the configurations produced during the simulation of the boundary and comparing the initial and final energies. The cleavage energy computed in this manner was 2500-2600 ergs/cm². The difference between the energies computed by cleaving typical boundaries and that estimated from surface and grain boundary energies probably reflects the fact that the surfaces produced are not ideal. These results indicate that the cohesive energy of grain boundaries in nickel aluminate are not significantly different than for pure Ni which implies that the tendency to intergranular fracture is not simply due to poor cohesion of the boundaries. Similar results have been obtained from calculations performed by Chen, et al.25.

Once the equilibrium structure and composition of a grain boundary is known, we use this information to initiate the dynamic fracture calculations. The geometry we have chosen for the calculations presented here is a Σ=5 (210) tilt boundary (see Fig. 4). We start with a boundary in pure nickel. Three atoms per plane are removed to form an initial planar crack nucleus. By slowly increasing the tensile stress normal to the grain boundary in a static calculation, we find the approximate fracture stress. We then apply a stress below this level (being careful not to introduce shock waves) and follow the motion of the atoms using molecular dynamics. Initial velocities are randomly chosen and the temperature is held at 600 K. We have found the fracture stress for nickel at 600 K is 7% of C44 and for Ni3Al 7% of C44. The shear modulii for nickel and Ni3Al are essentially the same.

A series of snapshots of the atom positions is shown in Fig. 4a. The applied stress is 10% of C44. This very high stress is necessary because our initial crack is so small. Note that as the grain boundary fractures, secondary cracks open up along the boundary. These cracks then coalesce as the fracture progresses.
Fig. 4. Snapshots of atom positions in a $\Sigma=5(210)$ tilt boundary in a) nickel and b) Ni$_3$Al. The temperature is held at 600 K and the stress is at 10% of $C_{44}$ during the molecular dynamics runs. The times (in psec) are indicated below each snapshot. For Ni$_3$Al, the Al atoms are darkened. The horizontal direction is a [125] direction while the direction out of the plane is a [121].
For the case of Ni$_3$Al, we start with atom positions and types characteristic of an equilibrium boundary at 1000 K. The snapshots (Fig. 4b) show fracture proceeding slightly more rapidly than in nickel and without the secondary cracks. Certainly these initial calculations are not sufficient to explain the large differences seen experimentally in the fracture behavior of nickel and Ni$_3$Al. Continuing work in this area is in progress to better understand these profound differences.

Conclusions

We have shown that the EAM is a powerful technique for calculations of structural and segregation effects at surfaces and grain boundaries. The surface calculations agree with experiments quite well. Calculated dislocation mobility is shown to agree with continuum theory and in fact is; able to determine the effective mass of the dislocation. Predictions are made for the structure and composition of grain boundaries in Ni$_3$Al. The fracture strength of a grain boundary in nickel and Ni$_3$Al are calculated and found to be quite similar. The fracture mechanism in nickel, however, includes secondary cracking while in Ni$_3$Al it does not.

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