Annual Report: DOE Contract # DE-FG02-88ER45367

Atomistic And Elastic Analyses Of

Defects And Small Structures

PI: David J. Srolovitz, University of Michigan

Over the past year, we have been working on several problems associated with defects in crystal and small structures. In one series of studies, we have been investigating the structure and energetics of surfaces as a function of surface orientation. All but a countable number of free surfaces consists of flat sections (terraces) separated by steps. In one study, we examine the structure and energy of 22 different surfaces (all containing the [011] direction) of both gold and copper at three different temperatures using the Free Energy Minimization method. Using this data, we construct a surface free energy plot in polar coordinates. This plot is then used directly in the Wulff construction in order to predict the equilibrium shape of a crystallite. We found that the equilibrium shape of a gold particle along the $\langle 011 \rangle$ projection consists entirely of {111} and {100} facets, copper crystals also exhibit very small {110} facets. Although both surface relaxation and atomic vibration reduce the surface free energy, they have no discernible effect on the equilibrium shape of the crystallites. This work is detailed in R. Najafabadi and D. J. Srolovitz, "The Effect of Surface Relaxation and Atomic Vibration on the Equilibrium Shape of Gold and Copper Crystallites", Journal of Computer-Aided Materials Design **1**, 187-197 (1994).

The energy of vicinal (stepped) surfaces has contributions from the terrace energy, the step energy and step-step interactions. Several authors (including us) have shown that step-step interactions are mediated by elastic interactions with the bulk of the crystal. These elastic analyses have employed linear elasticity and a simple model for the step source of strain to find that the step-step interaction energy decays as the inverse square of the step spacing. We have performed a series of simulations to determine the actual interaction between steps without making these assumptions. These calculations were performed at $T=0$ in Ag, Au, Cu, Ni, Pd and Pt for (01n) and ($\bar{1}$ lm), for $1 \leq n \leq 71$ and $1 \leq m \leq 41$ (i.e., [100] and [110] steps on an (001) surface). We found that the simple model for the atomic displacements assumed in the elastic theories are a poor approximation to the true displacement fields about each step and that the main features of the displacement fields surrounding the cores of the steps do not show any significant variation with step spacing. The step-step interaction energies are determined by subtracting the terrace and step energies (determined in separate calculations) from the total surface energy. We found that the simple inverse square decay of the interaction energy with step separation is valid for separations smaller than about 3 lattice parameters. Inside this cut-off, elastic theory can still be used provided that higher order terms in the moment expansion of the step source of strain are included. When this is done, the elastic analysis can provide a reasonable description of the elastic interaction energy down to spacings as smaller than a single lattice parameter. We also showed that a [100] step on the (001) surface of Au and Pt (but not Ag, Cu, Ni, or Pd) will lower its energy by transforming into a zig-zag pattern of $\langle 110 \rangle$ steps. This work is detailed in R. Najafabadi and D. J. Srolovitz, "Elastic Step Interactions on Vicinal Surfaces of FCC Metals", Surface Science **317**, 221-234 (1994). We are currently performing a detailed analysis of the strain field associated with surface steps in order to provide an analytical description of the elasticity of steps, akin to that which was done for dislocations in the 1940's - 1960's.

One of the goals in our present research is to model non-topological defects in crystals and very small structures using elastic models as parameterized using atomistic calculations. In order to do this, we need to make sure that the atomistic and elastic models describe the same bulk system. To this end, we have developed a set of Embedded Atom Method interatomic potentials that produce an elastically isotropic perfect fcc crystal. This is convenient since elastic analyses are routinely performed assuming that the material is elastically isotropic. This work is detailed in R. Najafabadi and D. J. Srolovitz, "Interatomic Potentials for Elastically Isotropic Solids", *Modelling and Simulation in Materials Science and Engineering*, in press.

Many of our past calculations performed under DOE funding were based upon the Free Energy Minimization (FEM) method. This method provides a very computationally efficient method for determining the thermodynamic properties of crystals and defects in single component and alloy systems at finite temperature. Recently, two papers have been published which call into question the accuracy of this method. Because of this, we have performed a series of simulations using the more accurate, but very expensive Thermodynamic Integration Monte Carlo (TIMC) and FEM methods to examine the free energies of crystals and defects using a series of different interatomic potentials. We found that in nearly all cases the FEM method accurately reproduced the TIMC results in high symmetry situations and qualitatively reproduced the correct behavior in low symmetry situations. Further, we demonstrated that the poor results obtained in the other studies could largely be traced to the unphysically large anharmonicity of the interatomic potentials employed in those studies. This work is reported in R. Najafabadi and D. J. Srolovitz, "Evaluation of the Accuracy of the Free Energy Minimization Method", *Physical Review B*, submitted.

One of the goals of the present research is to understand the effect of small system size on the behavior of materials. To that end, we have been performing simulations on the structure and thermodynamics of small spherical clusters of atoms (less than 50,000 atoms) and thin films, as a function of system size. In single component metals, we atomistically validated the continuum concept of the development of internal pressure resulting from surface stress (i.e., the Laplace pressure) for clusters as small as 4 lattice parameters. We have also shown that for clusters of varying size, the surface stress and structure does not vary significantly down to this same size. Since spherical clusters expose all possible surfaces, we were able to use these results, in the large cluster size limit, to obtain polycrystalline average surface energies. This is important since nearly all surface science studies focus on high symmetry surfaces while most materials are polycrystalline. This work is discussed in S. Swaminarayan, R. Najafabadi and D.J. Srolovitz, "Polycrystalline Surface Properties From Spherical Crystallites: Ag, Au, Cu and Pt", *Surface Science* **306**, 367-380 (1994).

Recently, we have extended these calculations on small systems to alloys where the appropriate focus is on surface segregation. We have considered both thin films and spherical clusters. We have performed atomistic simulations of spherical Cu-Ni clusters of between 10^3 and 10^4 atoms as a function of concentration and temperature. We find that the segregation is extraordinarily surface site specific. Increasing cluster size results in increasing surface concentration, especially in the small bulk concentration limit. The Laplace pressure relation, described above, was shown to still be valid as the surface stress is modified by segregation. The manuscript describing this work is in preparation. We have repeated these simulations in a thin film geometry for films of between one and ten fcc lattice parameters thick. We found that the same size effects on segregation behavior

observed in the clusters is also found in the films. We have developed an analytical theory to describe the effect of system size on surface segregation. Comparison of our simulation results with our analytical theory shows excellent agreement over wide ranges of concentration and temperature with NO adjustable parameters. This is particularly significant because we can now predict the segregation behavior of nanoscale systems based upon measurements made on bulk materials. This is very important in such applications as bimetallic catalysts, where the selectivity for different reactions is dictated by surface composition. This work is described in S. Swaminarayan and D. J. Srolovitz, "Surface Segregation in Thin Films", *Acta Metallurgica et Materialia*, in press.

In the course of our finite size system segregation studies, we noted that the phase diagrams for these systems can vary significantly from that of the bulk equilibrium phase diagram. In order to examine this effect, we performed a series of simulations of small spherical clusters in the miscibility gap system, Au-Pt. Although it is difficult to identify phase transitions in small, finite systems, we were able to show that as the system size decreases the equilibrium phase boundaries are pushed toward the Au-rich side of the diagram and to higher temperatures. We then showed that most of this effect is associated with the depletion of the bulk Au concentration by Au segregation to the particle surface. The Laplace pressure, which scales inversely with particle radius, has little effect on the phase boundaries. This work is to be submitted to the *Journal of Catalysis* within the next two weeks.

Finally, we have been working to understand the effects of strain energy on the thermodynamics of a new class of highly distorted materials - nested fullerenes. Experimental and theoretical work has shown that as the number of atoms increases, fullerenes change from single layer to multilayer structures. We have applied linear elastic analyses to understand the competing role of bending and bonding on this transition and the equilibrium morphology of these interesting materials. In our first paper, D. J. Srolovitz, S. A. Safran and R. Tenne, "Elastic Equilibrium of Curved Thin Films", *Physical Review E* **49**, 5260-5270 (1994), we worked out the elasticity associated with the bending of these types of materials. In a later paper, D. J. Srolovitz, S. A. Safran and R. Tenne, "Morphology of Nested Fullerenes", *Physical Review Letters* **74**, 1779 (1995), we experimentally demonstrated the validity of these ideas in metal dichalcogenide nested fullerenes. We plan on performing atomistic simulations to confirm our predictions in detail.

There have been several changes in the personnel involved with this project. First, Dr. Najafabadi, who has been working with us on this project for several years took up a permanent position in a DOE laboratory. We are searching for a post-doc to replace him. One student on this project left, before completing his degree, and another will finish his Ph.D. this summer. Last fall, we added a new student on this project - now looking at surface step elastic problems, and plan on adding a new student this coming fall.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.