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DOE/ER/45367--6

PROGRESS REPORT

DOE Grant # DE-FG02-88ER45367

During the past 2 1/4 years of our current DOE/BES/DMS research contract, we have focused on understanding interfacial segregation and the effect of interfacial segregation on interfacial phase stability. We have developed an efficient, approximate method for performing atomistic simulations in alloys which accounts for equilibrium solute redistribution and allows for the determination of all thermodynamic properties. This method is based upon the minimization of an approximate free energy functional with respect to atom position and composition profile. We have validated this approach by performing and comparing with more rigorous simulations and experiments on metastable phases. Examination of surfaces and grain boundaries in metals show that the classical models for interfacial do not, in general, work well and showed that they can be significantly improved by accounting for each unique atomic site separately. In metallic alloys, segregation was shown to be strongly correlated with the interfacial stresses on an atomic site-by-site basis and that segregation greatly reduces the magnitude of the atomic level stresses and homogenizes the boundary. Comparison of segregation results in several binary alloy systems demonstrated that the difference in interfacial energies between the elements plays a more important role than atomic size in predicting the dominant segregant. These results were combined to examine the effect of segregation on interfacial cohesive energies/ideal fracture toughness in order to examine how tight existing theoretical bounds on these quantities are. Methods based upon small atomic clusters were used to determine average (over all orientations) surface properties and develop stereographic maps of surface energy, stress and segregation tendency for all surface orientations. These results were confirmed by calculating equilibrium Wulff plots (surface energy vs. misorientation) for both elemental metal and binary alloys. Segregation was found to significantly increase the order-disorder transformation temperatures at (001) surfaces in Ni-Pt and Cu-Pd alloys and steps on these surfaces resulted in transformation temperatures which were even higher (near the steps).

II. RESULTS FROM CURRENT DOE SPONSORED RESEARCH

This section outlines some of our results on our current DOE grant (DE-FG02-88ER45367) entitled "A Free Energy Simulation Method Based Study of Interfacial Segregation" which began on 9/1/91 and is scheduled to conclude on 8/31/94. Since this section is, by necessity, short, we encourage interested readers to consult the published papers which are listed at the end of this section. Our DOE sponsored research during this period had several goals: 1) to extend the free energy simulation method (which we developed on an earlier contract) to the case of alloys and interfacial segregation, 2) to explore how segregation to grain boundary and free surfaces in binary metallic alloys varied with the physical parameters (temperature, solute fraction, orientation/misorientation), 3) to explore the thermodynamics of interfacial segregation, 4) to examine the interplay between segregation and ordering at grain boundaries and surfaces, 5) to develop a method for determining average surface properties in pure metals and alloys (for a random polycrystal) and 5) to examine the effects of surface segregation on equilibrium Wulff plots and particle shapes.

Much of our work is based upon a simulation approach we call the free energy minimization method. This method is based upon the minimization of an approximate free energy functional with respect to the position of all of the atoms in the system and the local composition profile at constant chemical potential. The main approximations in this method are a point approximation for the configurational entropy (i.e., a Bragg-Williams model) and the local harmonic model of the vibrational contributions to the free energy, which approximates each atom as three Einstein Oscillators. We previously developed the local harmonic model under a previous grant. These approximations may be used with any type of description of atomic interactions. To date, we have successfully applied this method with pair potentials, EAM potentials (fcc metals), the Stillinger-Weber potential (for Si), the Tersoff potentials (for a variety of covalent materials), and shell models (of ionic solids). We have validated this approach by detailed comparison of perfect crystal thermodynamic properties (free energy, enthalpy, entropy, specific heat, thermal expansion, etc.) from other simulations and experiment, experimental binary alloy phase diagrams, phase diagrams determined from Monte Carlo simulations, and published Monte Carlo data on interfacial segregation. Our own results and those of Seidman suggest that this approach yields good segregation results as long as the size difference between solute and solvent atoms is not too large. One of the main advantages this new method enjoys over other methods such as Monte Carlo, is the efficiency with which the atomic structure of a defect, segregation **and** thermodynamic properties can be determined. The present method does not consider anharmonic atomic vibration effects, which may be important for defects such as vacancies, as recently noted by Foiles [Foiles]. However, Hairie and Sutton recently showed excellent correspondence between defect free energy determinations based upon harmonic models and those that included anharmonicity [Hairie].

We have recently tested the free energy minimization method's ability to predict thermodynamic data by comparison with an empirical thermodynamic technique which is fit to equilibrium thermodynamic data (CALPHAD) and experiment. The test was to determine the enthalpies of formation of metastable Ag-Cu alloys as a function of composition. The experimental enthalpy of formation data was obtained by our collaborators E. Ma and M. Atzmon by ball milling elemental powders and examining them via Differential Scanning Calorimetry (DSC). The free energy minimization determination of the equilibrium Ag-Cu phase diagram and the enthalpy of formation and lattice parameters of the metastable solid solutions were shown to be in good agreement with the experimental measurements. CALPHAD calculations made in the same metastable regime, however, significantly overestimate the enthalpy of formation. The free energy minimization method was also found to be superior to empirical techniques such as CALPHAD because it produces an atomic model, which can be interrogated to determine additional data not typically available through CALPHAD approaches, such as the temperature and composition dependence of the lattice parameter.

As a first application of this method, we performed atomistic simulations of segregation to [001] $\Sigma 5$ twist boundary in Ni-Cu alloys over a wide range of temperature and compositions within

the solid solution region of the phase diagram. In addition to the grain boundary segregation profile, grain boundary structures, free energies, enthalpies, and entropies were determined. We found that for all alloy bulk compositions ($0.05 \cup C \cup 0.95$) and temperatures ($400 \cup T\ (K) \cup 1000$) examined, Cu segregates strongly to the grain boundary. The width of the segregation profile was limited to approximately two atomic planes on each side. Classical segregation theories were shown to yield a poor representation of the resultant segregation profiles. This was shown to result from the oversimplification of the interfacial structure within the classical theories. The grain boundary thermodynamic properties were found to depend sensitively on the magnitude of the grain boundary segregation. The free energy, enthalpy, entropy of segregation and the change in grain boundary excess volume were shown to be linearly proportional to the magnitude of the grain boundary segregation.

Next, we examined segregation to (100) free surface in Ni-Cu alloys. In addition to the surface segregation profile, surface structures, free energies, enthalpies, and entropies were determined. As in the $\Sigma 5$ grain boundary case, Cu segregates strongly to the (100) surface. But unlike in the $\Sigma 5$ boundary case, Ni was shown to segregate to the plane immediately below the surface. The width of the segregation profile is limited to approximately three atomic planes. The resultant segregation profiles are shown to be in good agreement with an empirical segregation theory. The agreement in this case is attributed to the much simpler structure of the (100) surface as compared with the $\Sigma 5$ boundary. A simpler method for determining the equilibrium segregation in terms of the properties of unrelaxed pure Ni and pure Cu surface data was proposed and shown to be more accurate than existing empirical segregation theories. As for the $\Sigma 5$ boundary, the surface thermodynamic properties depend sensitively on the magnitude of the surface segregation and the enthalpy and entropy of segregation, and the change in the interlayer spacing adjacent to the surface were shown to vary linearly with the magnitude of the surface segregation.

After examining the variation of the interfacial segregation properties for a single grain boundary and single surface, we undertook a systematic investigation of the dependence of the segregation properties on a structural variable - namely, grain boundary misorientation. The segregation, thermodynamic, and structural properties of [001] twist boundaries in Cu-Ni alloys were examined over a wide range of misorientations ($15^o \cup \theta \cup 45^o$) and temperatures ($600\ K \cup T \cup 1100\ K$) at a bulk composition of 6% Cu. The results show that Cu always segregates to the boundary. The average concentration of the first atomic layer adjacent to the boundary increases monotonically with misorientation and no obvious cusps were observed. All the other thermodynamic properties vary smoothly with the misorientation, with the exception of the vibrational entropy of the boundaries without segregation. The vibrational entropy of the unsegregated boundary is quite distinct; it shows a large peak at the misorientation corresponding to the $\Sigma 17$ boundary and two minima near the $\Sigma 13$ and $\Sigma 5$ boundary misorientations. These peaks disappear upon segregation. The concentration distribution within the plane of the grain boundaries exhibits a pattern which can be described by the same structural unit model established for the structures of the [001] twist boundaries in pure materials. However, the structural unit model was shown to provide a much more accurate description of grain boundary structure than it does for the segregant description. Regions of large tensile stress showed greater segregation than do regions of compressive stress. Regions of large shear stress tended to show reduced segregation compared with regions of small shear stress. After segregation, the maximum hydrostatic stress is dramatically reduced such that the magnitude of the hydrostatic stress varies only slightly between atomic sites. The site-to-site variation in the shear stress is not significantly reduced by segregation. This demonstrated the important effect of atomic size mismatch in determining segregation behavior and how the atomic size mismatch relaxed the grain boundary structure.

In order to develop a more general understanding of the effects of atomic parameters (such as atomic size) on segregation behavior, we performed a comparative study of segregation to (001) surfaces and $\Sigma 5$ [001] twist boundaries in three distinct binary systems: Ag-Au, Au-Pd and Cu-Ni. These three systems were chosen because they represent cases where the atomic size mismatch and sublimation energies vary over an appreciable range. On the (001) surface, Ag segregated to the surface layer in the Ag-Au system, Au segregated in the Au-Pd system and Cu segregated in the

Cu-Ni system. The degree of segregation was, in most cases, higher for Cu-Ni than for the other two systems, although the biggest atomic size mismatch occurred in the Au-Pd system. In all cases, there was a slight increase in the concentration of the atomic species that did not segregate to the surface layer either one or two (002) planes below the surface. Analysis of the data showed that the tendency for segregation scales better with the difference of the surface free energies of the two atomic species than with the atomic size mismatch or the sublimation energy. This may be because the variation in atomic size was not very large from system to system. In the $\Sigma 5$ [001] twist boundary case, Au always segregated to the boundary plane in the Au-Pd system and Cu always segregated in Cu-Ni alloys. However, in the Ag-Au alloy system, Au segregated in Au-rich alloys and Ag segregated in the Ag-rich alloys, although the segregation was very weak across the whole range of Ag-Au alloy composition examined (5% to 95% Ag). This effect can be understood by consideration of the Gibbs adsorption isotherm, which shows that the sign of the segregation depends on the slope of the grain boundary free energy versus concentration curve. This slope changes sign only in the Ag-Au system and does so near the 50-50 composition, which is where the simulation results suggest that the dominant boundary segregant changes. Rather poor agreement between the Langmuir-McLean adsorption isotherm and the present results were shown to be a direct consequence of the fact that there are more than one symmetry distinct sites in the $\Sigma 5$ boundary. If a heat of segregation term is included in the Langmuir-McLean analysis for each non-equivalent site, then this approach will lead to reasonable agreement with the simulation. This reasonable agreement with the Langmuir isotherm obtained for the (001) surface is attributable to the fact that it has only one symmetry distinct site.

We examined the thermodynamics of a series of surfaces as a function of orientation, with and without segregation, in order to understand the effect of segregation on the equilibrium Wulff plot and, hence, equilibrium particle shapes. We examined pure Pd, Au, Ag, and Cu surfaces and surfaces in binary alloys consisting of the same elements. By examining the structure and thermodynamics as a function of step spacing, we have been able to predict the variation of surface thermodynamic properties as a function of surface orientation. The angles corresponding to cusps on the Wulff plots were determined and the depths of the cusps (and hence the size of the facets on crystallites) for the elemental metals were shown to vary with temperature. This data was analyzed to determine the enthalpy and entropy of the surfaces as a function of misorientation. The variation in cusp depths with temperature was shown to be related to the relative entropies of the surfaces at cusp and off-cusp orientations. To our knowledge, this is the first study of Wulff plots using realistic descriptions of atomic interactions and as a function of temperature. The above calculations on surface properties versus step spacing or surface orientation were repeated in the following binary alloy systems: Pd-Au, Pd-Ag, and Pd-Cu. The degree of segregation was found to vary from site to site (between ledge and terrace) and a well-defined terrace segregation and ledge segregation could be identified. For orientations far from a cusp, this could be used to predict the form of the Wulff plot and its variation with composition. We found that the depth of the cusps on the Wulff plot varies with the degree of segregation and hence with the bulk composition and temperature. However, we did not find, in any of these systems, that this variation led to a large qualitative change in the Wulff plot. For example, we did not observe the formation of or loss of any cusps that would lead to the appearance or disappearance of a facet on a crystallite. This was primarily due to the similarity between the solute and solvent elements examined. Nonetheless, we believe that such transitions will be observable in other systems, some of which we are now investigating.

While most surface science studies and much of the available data on surfaces focuses on high symmetry, low index surfaces, we find that our knowledge of high index, low symmetry surfaces is very poor. In addition, very little information is known on average surface properties - such as average thermodynamic properties of a polycrystalline surface, even though most of the crystalline materials in widespread use are polycrystalline. To address this shortcoming, we have been investigating methods for obtaining average surface properties and approximate surface properties of all surfaces. We have been doing this by performing atomistic simulations of nearly spherical, crystalline (fcc) clusters of Ag, Au, Cu and Pt as a function of temperature and cluster size. The rationale for this is that the surface of a sphere contains all possible surfaces and a

average of a physical property over the surface of a sphere is equivalent to evaluating the property on a surface of a random polycrystalline solid. Atomic clusters with radii greater than approximately four lattice parameters (a_0) yield cluster average surface energies and surface stresses that are within a few percent of those obtained from very large clusters. The variation of the cluster average surface properties with cluster size is dominated by a geometrical effect associated with the discrete spacing between atomic planes. This effect must be normalized out before extrapolating the results to infinite cluster size (i.e., the bulk thermodynamic limit). This size effect is almost entirely associated with the structure of the cluster and is independent of the type of element within the same bulk crystal structure. Comparison of the cluster average surface free energy with those of the more commonly studied high symmetry flat {100}, {110}, and the {111} surfaces suggest two useful approximations. For an fcc metal crystal, the average surface free energy is nearly identical with that of a {110} surface. A linear, least squares fit suggests that this estimate can be further improved by employing a linear relationship incorporating the {100}, {110}, and the {111} surface free energies. The validity of our determination of average surface properties was confirmed in the case of surface stresses. The average diagonal surface stress is the mean surface tension. Since continuum elastic analyses show that the pressure inside a sphere is twice the surface tension divided by the sphere radius, we measured the pressure at the center of the spherical clusters (at several cluster sizes) and demonstrated that it yields the same surface tension that we calculated directly. Additionally, we confirmed that the surface energies obtained as averages over the spherical clusters agreed with that obtained from the Wulff plots in the limit of large cluster size.

We have also examined how segregation affects average surface properties. This was done by performing atomistic simulations of spherical clusters as a function of temperature and average composition. The resultant segregation isotherms were not well fit by the standard Langmuir isotherm, presumably because the surface of these clusters contain many non-equivalent sites, each with a distinct heat of segregation. The surface segregation data obtained from the clusters can be represented in a surface segregation map. This segregation map is a contour map of the surface segregation projected into two dimension as a stereographic projection. A similar map was constructed for the surface energy and surface tension. These maps can be used to determine the properties of a surface of arbitrary orientation. The accuracy of this approach is limited, by the discreteness of finite size clusters, since the surface area of a particular surface {hkl} on the cluster may not be sufficiently large to incorporate even a single period. This problem can be alleviated somewhat by performing the calculations at several sizes and extrapolating to infinite size. This too is somewhat problematic since many properties were found not to vary monotonically with cluster size. Nonetheless, we believe that this is a promising, approximate method.

If a crack propagates along a grain boundary, the boundary is destroyed and two surfaces are created. The difference between the free energies of the grain boundary and the two surfaces is, thermodynamically, the energy needed to propagate a crack and is known as the Griffith energy or the cohesive energy of the grain boundary (it is equal to the critical strain energy release rate for intergranular fracture in a perfectly brittle material). We have employed the data described above to estimate this quantity in several different limits. Rice and Wang demonstrated that the true cohesive energy must lie between the cohesive energy corresponding to creating the two surfaces from the grain boundary with equilibrium segregation at both surface and grain boundary (i.e., slow fracture) and the cohesive energy corresponding to only the grain boundary having equilibrium segregation and the surfaces having the composition inherited from the boundary (i.e., fast fracture) [Rice]. These two limiting cases are rigorous bounds on the true cohesive energy in fracture. For all Ni-Cu alloy bulk compositions ($0.05 \leq C \leq 0.95$) and temperatures ($400 \leq T(K) \leq 1000$) examined, Cu segregates strongly to both the grain boundary and the free surface. The difference between the fast and slow fracture cohesive energies is very small. Therefore, these results demonstrate that, at least in the Ni-Cu system, the theoretical bounds on the cohesive energy are very tight. This study represents the first unambiguous validation of these important theoretical results.

In addition to studying segregation to interfaces in solid solution alloys, we have recently been focusing our attention on grain boundaries in ordered alloys and surfaces. Specifically, we

examined the $\Sigma 5$ and $\Sigma 13$ (001) twist and $\Sigma 5$ (310)/[001] tilt grain boundaries in ordered $Ni_{3-x}Al_{1+x}$ as a function of alloy composition x (for $x<<1$) and temperature. This alloy was chosen for the study since the effect of B on the ductility of $Ni_{3-x}Al_{1+x}$ is known to be a sensitive function of composition. In the temperature range studied (300 - 900K), we find that there is almost no segregation, strong Al segregation, and weak Ni segregation to the grain boundary for the stoichiometric, Al-rich, and Ni-rich bulk compositions, respectively. For all boundaries examined in the Al-rich bulk alloys, we found that the Al segregation substantially lowers the grain boundary free energy. However, small variations in the bulk composition in Ni-rich alloys, leads to only very small changes in the grain boundary cohesive energy. Nonetheless, segregation may play an important structural role. The Al segregation to the $\Sigma 5$ (310)/[001] tilt grain boundary in the Al-rich alloys leads to the formation of a very thin layer of ordered NiAl (B2 crystal structure) at the grain boundary. This region is a well defined phase, whose width grows with decreasing temperature. This result suggests that the segregation induced change in crystal structure may be responsible for the abruptness of the B ductility effect, with respect to bulk composition.

Our observation of a phase transition at a grain boundary is not without parallel on free surfaces. We have recently investigated order-disorder transitions on the (001) surfaces of Ni-Pt alloys. On the Ni-rich side of the phase diagram, we observed a second order, order-disorder transition at temperatures well above the bulk phase transition temperature. At the transition temperature, the first (002) atomic plane changed from a disordered plane to an ordered one with the c(2x2) pattern. The second (002) plane changed from a disordered plane to a nearly pure Ni plane. Subsequent planes retain their essentially bulk-like, disordered structure. On the Pt-rich side of the phase diagram, an order-disorder surface transition also occurred substantially at temperatures substantially above the bulk transition temperature. However, on this side of the phase diagram, the transition was shown to be first order. At the (bulk composition dependent) transition temperatures, the first and third (002) planes became nearly pure Pt and the second plane became nearly pure Ni. The ordering surface transition upon cooling the Ni-rich sample was found to be primarily enthalpically driven. The variation of the transition temperature with bulk concentration was understood in terms of the sign of the segregation (which element segregated) and whether the segregation pushed the surface composition toward a region of higher or lower T_c in the bulk phase diagram. Similar effects are observed on the (001) surface of Cu-rich Cu-Pd alloys. We also found that the presence of a regular array of [001]/[010] steps on a (01n) vicinal surface (i.e., a surface slightly miscut relative to (001)), increases the surface transition temperature. In this case, however, the ordered region occurs primarily adjacent to the step on the lower (001) terrace and extends several interatomic spacings along the step and into the bulk.

More details pertaining to the individual research studies referred to above may be found in the publications listed below. Also included is a list of research talks presented based upon the research results generated through the DOE grant.

PERSONNEL

The current DOE project was conducted by three graduate students and the three co-PI's: Professor David J. Srolovitz and Dr. Reza Najafabadi of the Department of Materials Science and Engineering of the University of Michigan and Dr. Richard LeSar of Los Alamos National Laboratory. Dr. LeSar received no funding from this grant. Dr. Hongying Wang was a graduate student on this project who completed his Ph.D. in August, 1992. He is currently a post-doc at the Los Alamos National Laboratory. The other two graduate students are Mr. Sriram Swaminarayan and Mr. Yang Cha. Mr. Swaminarayan is a Materials Science and Engineering graduate student and Mr. Cha is a Physics graduate student. Both students have already completed their Masters degree. Mr. Cha replaced Dr. Wang when he graduated.

PUBLICATIONS

These publications based upon DOE sponsored research have either appeared, have been submitted or are in preparation from the beginning of the current contract until the present (9/91-1/94).

1. R. Najafabadi, H. Y. Wang, D. J. Srolovitz, and R. LeSar, "The Effects of Segregation on Grain Boundary Cohesive Energies in $Ni_{3-x}Al_{1+x}$", Scripta Metallurgica et Materialia **25**, 2497-2502 (1991).

2. R. Najafabadi, H. Y. Wang, D. J. Srolovitz, and R. LeSar, "A New Method for the Simulation of Alloys: Application to Interfacial Segregation", Acta Metallurgica et Materialia, **39**, 3071-3082 (1991).

3. R. Najafabadi, H. Y. Wang, D. J. Srolovitz and R. LeSar, "Free Energy Simulation of Grain Boundary Segregation and Thermodynamics in $Ni_{3-x}Al_x$", in *High Temperature Ordered Intermetallic Alloys*, eds. L. Johnson, D. P. Pope, and J. O. Stiegler, Materials Research Society Symposium Proceedings, **213**, 51-56 (1991).

4. H. Y. Wang, R. Najafabadi, D. J. Srolovitz and R. LeSar, "The Free Energy Simulation Approach to Grain Boundary Segregation in Cu-Ni," *Defects in Materials*, ed. P. D. Bristowe, J. E. Epperson, J. E. Griffith, and Z. Liliental-Weber, Materials Research Society Symposium Proceedings **209**, 219-224 (1991).

5. H. Y. Wang, R. Najafabadi, D. J. Srolovitz and R. LeSar, "Segregation to Σ5 [001] Twist Grain Boundaries in Ni-Cu Alloys", Philosophical Magazine A **65**, 625-655 (1992).

6. H. Y. Wang, R. Najafabadi, D. J. Srolovitz, and R. LeSar, "Segregation Effects on the Fracture of Grain Boundaries in Ni-Cu Alloys: An Atomistic Simulation Study of Ni-Cu Alloys", Met. Trans. **23A**, 3105-3113 (1992).

7. H. Y. Wang, R. Najafabadi, D. J. Srolovitz, and R. LeSar, "(100) Surface Segregation in Cu-Ni Alloys", Phys. Rev. B **45**, 12,028-12,042 (1992).

8. D. J. Srolovitz, W. H. Yang, R. Najafabadi, H. Y. Wang, and R. LeSar, "Microstructural and Segregation Effects in the Fracture of Polycrystals", in *Atomic-Level Properties of Interface Materials*, ed. D. Wolf and S. Yip (Chapman and Hall, London, 1992), pg. 691-702.

9. H. Y. Wang, R. Najafabadi, D. J. Srolovitz and R. LeSar, "Interfacial Segregation in Ag-Au, Au-Pd, and Cu-Ni Alloys: I. (001) Surfaces", Interface Science **1**, 7-30 (1993).

10. H. Y. Wang, R. Najafabadi, D. J. Srolovitz and R. LeSar, "Interfacial Segregation in Ag-Au, Au-Pd, and Cu-Ni Alloys: II. [001] Σ5 Twist Grain Boundaries", Interface Science **1**, 31-47 (1993).

11. R. Najafabadi and D. J. Srolovitz, "Order-Disorder Transitions at and Segregation to (001) Ni-Pt Surfaces", Surface Science **286**, 104-115 (1993).

12. H. Y. Wang, R. Najafabadi, D. J. Srolovitz and R. LeSar, "Segregation To and Structure Of [001] Twist Grain Boundaries in Cu-Ni Alloys", Acta Met. Mat. **41**, 2533 (1993).

13. R. Najafabadi, D. J. Srolovitz, E. Ma, and M. Atzmon, "Thermodynamic Properties of Metastable Ag-Cu Alloys: Atomistic Simulation, CALPHAD Calculations, and Experiment", J. Appl. Phys. **74**, 3144 (1993).

14. R. Najafabadi and D. J. Srolovitz, "Segregation to Tilt Grain Boundaries in $Ni_{3+x}Al_{1-x}$ Alloys: A Free Energy Minimization Study", ed. I. Baker, R. Darolis, J. D. Wittenberger and M. H. Yoo, Materials Research Society Symposium Proceedings **288**, 189 (1993).

15. S. Swaminarayan, R. Najafabadi, and D.J. Srolovitz, "Polycrystalline Surface Properties from Spherical Crystallites: Ag, Au, Cu, and Pt", Surface Science, in press.

16. S. Swaminarayan, R. Najafabadi, and D.J. Srolovitz, "Enhanced Second Layer Ni Segregation in Cu-Ni Clusters", in preparation.

17. R. Najafabadi and D. J. Srolovitz, "Equilibrium Crystallite Shape of EAM fcc Metals, in preparation.

18. R. Najafabadi and D. J. Srolovitz, "Surface Segregation Effects on the Equilibrium Crystallite Shape in Binary EAM Metals", in preparation.

19. R. Najafabadi and D. J. Srolovitz, "Step Enhanced Ordering on (001) Surfaces of in Cu-Pd", in preparation.

RESEARCH TALKS

These talks are based upon our DOE sponsored research and were presented from the beginning of the current contract until the present (9/91-1/94).

1. TMS Fall Meeting, Chicago, 10/92 - "Thermodynamic and Structural Properties of [001] Twist Grain Boundaries in Gold", presented by R. Najafabadi.
2. Mid-West Solid State Theory Conference, East Lansing, MI, 10/91 - "New Atomistic Methods for Free Energy Determination", presented by D. J. Srolovitz - **Invited**.
3. University of Michigan, Physics Department 11/92 - "Statistical Mechanics Extensions to Atomistic Simulation of Defects", presented by D. J. Srolovitz - **Invited**.
4. MRS Fall Meeting, Boston, 12/91 - "Segregation to $\Sigma 5$ (001) Twist Boundaries in Au-Ag, Au-Pd, and Ni-Cu Alloys", presented by H. Y. Wang.
5. MRS Fall Meeting, Boston, 12/91 - "Segregation Effects on Grain Boundary Fracture in Ni-Cu Alloys", presented by D. J. Srolovitz.
6. MRS Fall Meeting, Boston 12/91 - "Segregation to twist grain boundaries in $Ni_{3-x}Al_x$", presented by R. Najafabadi.
7. Carnegie-Mellon University 2/4/92 - "Interfacial Segregation", presented by D. J. Srolovitz - **Invited**.
8. APS March Meeting 3/17/92 - "Order-Disorder Transition at (100) surfaces of a Pt-Ni model: A Free Energy minimization Study", presented by R. Najafabadi.
9. Princeton University 4/3/92 - "Statistical Mechanics Extensions to Atomistic Simulation of Defects", presented by D. J. Srolovitz - **Invited**.
10. MRS Spring Meeting, San Francisco 4/27/92 -"Approximate Atomistic Methods for Determining Defect Thermodynamics", presented by D. J. Srolovitz - **Invited**.
11. MRS Spring Meeting, San Francisco 4/27/92 - "Segregation to (n10) Surface in Pd-Cu, Pd-Au, and Pd-Ag: A Free Energy Minimization Study", presented by R. Najafabadi.
12. Virginia Technical University, Blacksburgh, VA, 5/92 - "Application of the Local Harmonic Method to Interfacial Segregation in Binary Alloys", presented by H. Y. Wang.
13. 6th International Conference on Intergranular and Interphase Boundaries in Materials 6/25/92 - "Simulating Equilibrium Grain Boundary Segregation", presented by D. J. Srolovitz - **Invited**.
14. University of Groningen, The Netherlands 7/2/92 - "Surface and Grain Boundary Segregation in Metallic Alloys", presented by D. J. Srolovitz - **Invited**.

15. 6th International Conference on Intergranular and Interphase Boundaries in Materials, University of Groningen, The Netherlands 7/2/92 - "Surface and Grain Boundary Segregation in Metallic Alloys", presented by D. J. Srolovitz - **Invited**.
16. MSE Department Colloquium, UM, Ann Arbor, MI 9/92 - "Recent Advances in Atomistic Simulation: Is it time to lock up the lab?", presented by D. J. Srolovitz - **Invited**
17. TMS Fall Meeting, Chicago, 10/92 - "Segregation to High Index Surfaces in Pd-Au and Pd-Cu Binary Systems", presented by R. Najafabadi.
18. General Electric Research Laboratory, Schenectady, NY, 11/92 - "Free Energy Methods for Atomistic Simulation", presented by D. J. Srolovitz.
19. TMS Fall Meeting, Chicago, IL, 11/92 - "Interfacial Segregation", presented by H. Y. Wang - **Invited.**
20. MRS Fall Meeting, Boston, 12/92 - "The Effect of Segregation on the Cohesive Energy of Grain Boundaries in $Ni_{3-x}Al_x$", presented by R. Najafabadi.
21. American Physical Society, March Meeting, Seattle, WA, 3/93 - "Surface Order-Disorder Transitions", presented by D. J. Srolovitz - **Invited**.
22. American Physical Society Match Meeting, Seattle, WA, 4/93 - "Surface Energy and Stress of Large Spherical Metallic Clusters", presented by S. Swaminarayan.
23. University of Washington, Seattle, WA, 4/93 - "Interfacial Phase Transitions", presented by D. J. Srolovitz - **Invited**.
24. MRS Spring Meeting, San Francisco, 5/93 - "Interactions Between Steps on the (001) Surface of Pd", presented by R. Najafabadi.
25. MRS Fall Meeting, Boston, 12/93 - "The Effect of Biaxial Strain on the (001) Surface Order-Disorder Transition in a Cu-rich Cu-Pd Alloy", presented by R. Najafabadi.
26. Turkish Technical University, Istanbul, Turkey, 1/94 - "Interfacial Segregation: Grain Boundaries and Free Surfaces", presented by D. J. Srolovitz - **Invited**.
27. Weizmann Institute, Rehovot, Israel, 1/94 - "Segregation Induced Interfacial Phase Transitions", presented by D. J. Srolovitz - **Invited**.
28. Int. Conf. on Advances in Physical Metallurgy (ICPM-94), Bombay, India, 3/94 - "Ordering at Interfaces", presented by D. J. Srolovitz - **Invited**.

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