DOE/OBES

# Microstructural Evolution Based on Fundamental Interfacial Properties

**Final Report**
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*Background and Significance*:

The main objective of the project was to link the understanding of interfaces and impurity effects in particular to mesostructural models of the processes of microstructural evolution of interest to this project, namely solidification, grain growth and phase transformation. In addition, opportunities to connect the various unit processes together were made, as, for example, in models of solidification followed by grain growth. The phase-field method, for example, offers one obvious route towards doing this. In addition to this broader goal, we addressed the critical role of solute in controlling the anisotropy (and magnitude) of boundary mobility and energy. Verification against appropriate experiments was emphasized as a critically important activity for the project. For example, three-dimensional simulations of microstructural evolution with fully anisotropic interfacial properties were performed. During the period of the work, new methods for characterizing microstructures in 3D and in real time using synchrotron x-ray diffraction were being developed by the Risø National Laboratory (Denmark), ORNL, APS, CMU and others. The CMSN interacted with these efforts in order to develop direct comparisons of experiments and simulations, again with the objective of verifying the importance of anisotropy in interfacial properties.

The ultimate goal of any engineering science is the "reduction to practice" of an idea or concept. The end users of the products of this program are materials engineers and other designers concerned with microstructure dependent properties. The key concept embodied in our work was that of prediction of microstructural evolution based on fundamental interfacial properties. The path to relevance is therefore one that takes the results of atomic scale calculations of boundary properties and places those properties in codes for microstructural evolution (phase field, Monte Carlo etc.): this was embedded in the program. Further abstraction of the dependence of microstructural evolution on processing parameters then allows incorporation into macroscopic models of components and structures (e.g., finite element). In certain cases the evolution codes may retain the full physically based descriptions of boundaries and be used in a coupled mode with finite element models (as practiced at ORNL and SNL). Some examples of the latter approach exist for both deformation and annealing processes, in which grain size and texture are critical parameters and also for solidification for which the scale of the dendritic structure with its associated solute segregation patterns is critical information.

*Report:*

**Summary**

This first CMSN project has been operating since the summer of 1999. *The main achievement of the project was to bring together a community of materials scientists, physicists and mathematicians who share a common interest in the properties of interfaces and the impact of those properties on microstructural evolution.* Six full workshops were held at Carnegie Mellon (CMU), Northwestern (NWU), Santa Fe, Northeastern University (NEU), National Institute for Standards and Technology (NIST), Ames Laboratory, and at the University of California in San Diego (UCSD) respectively. Substantial scientific results were obtained through the sustained contact between the members of the project. A recent issue of Interface Science (volume 10, issue 2/3, July 2002) was dedicated to the output of the project. The results include: the development of methods for extracting anisotropic boundary energy and mobility from molecular dynamics simulations of solid/liquid interfaces in nickel; the extraction of anisotropic energies and mobilities in aluminum from similar MD simulations; the application of parallel computation to the calculation of interfacial properties; the development of a method to extract interfacial properties from the fluctuations in interface position through consideration of interfacial stiffness; the use of anisotropic interface properties in studies of abnormal grain growth; the discovery of abnormal grain growth from random distributions of orientation in subgrain networks; the direct comparison at the scale of individual grains between experimentally observed grain growth and simulations, which confirmed the importance of including anisotropic interfacial properties in the simulations; the classification of a rich variety of dendritic morphologies based on slight variations in the anisotropy of the solid-liquid interface; development of phase field methods that permit both solidification and grain growth to be simulated within the same framework.

At the outset of the project, we stated that "*Our goals are, therefore, to perform state-of-the-art atomistic calculations of interfacial properties and to couple these results directly into mesoscale models of microstructural evolution. The present proposal focuses on two closely related areas of microstructural evolution – solidification microstructures (dendrites and eutectics) and heterogeneous coarsening (grain growth and recrystallization).*" The fact that we have indeed accomplished these goals answers the question "*Why support the CMSN*?" Without this network, it is highly unlikely that this group of researchers would have assembled to tackle a scientific challenge of this nature and size because it required us as a group to choose a particular material (aluminum) and set of problems to work on.

This CMSN project was very successful in initiating new collaborations that have lead to major advances in computational models of microstructural evolution at the scale of atoms and microstructures. Please note that although CMSN funding contributed in various ways to this work, the majority of support was derived from other sources, including sources other than OBES. Numerous publications in leading scientific journals (3 Phys. Rev. Lett. articles, and entire issue of Interface Science devoted to the group activity, and several other publications listed below in this section) testify to the high productivity of these collaborations. Space does not permit to present a full explanation of all the results that have been obtained to date. A summary list with brief descriptions of accomplishments follows and for a few selected topics an expanded description follows this summary.

1) The development of new capillary fluctuation methods (CFM) to compute accurately both the magnitude and the weak anisotropy of the solid-liquid interfacial free-energy, $\gamma$ (Hoyt, Asta et al. 2001). This approach exploits (i) the inverse relationship between the mean-square-amplitude of equilibrium capillary fluctuations and the interface stiffness ($\gamma+\gamma''$), and (ii) the fact that the interface stiffness ($\gamma+\gamma''$) is one order of magnitude more anisotropic than $\gamma$ itself, which makes this method uniquely capable of resolving for the first time the very weak anisotropy of $\gamma$ that strongly influences dendritic evolution.
2) The extension of the CFM to compute the solid-liquid interface kinetic coefficient $\mu$ and its anisotropy (Hoyt, Asta et al. 2002) by use of the statistical relationship between the nonequilibrium response of the interface to a small driving force and its dynamic fluctuation properties (fluctuation-dissipation theorem).
3) The application of CFM methods to compute the magnitude and the anisotropy of both $\gamma$ and $\mu$ for several elemental metallic systems including Ni, Cu and Al (Hoyt, Asta et al. 2001; Hoyt, Asta et al. 2002; Morris 2002; Morris, Lu et al. 2002). Also the first computation of $\gamma$ for a binary alloy system Ni-Cu using CFM (Asta, Hoyt et al. 2002).
4) The first fully quantitative phase-field simulations of dendritic solidification in a metallic system (deeply undercooled Ni) with input parameters (anisotropy and magnitude of both $\gamma$ and $\mu$) computed from atomistic simulations (Bragard, Karma et al. 2002). The simulation results for the dendrite growth velocity versus undercooling were found to be in good quantitative agreement with experiment data.
5) A (potentially major) new insight into dendritic evolution has been obtained from both atomistic simulations with the CFM and analytical sharp-interface calculations (solvability theory). Namely, at least two anisotropy parameters (Hoyt, Asta et al. 2001; Morris 2002; Morris, Lu et al. 2002), rather than a single one traditionally considered, are necessary to fully represent the entire solid-liquid $\gamma$-plot surface and to explain a vast range of experimentally observed dendrite growth morphologies (<100> , <110> , <112>, <320>...).
6) The development of a new quantitative phase-field model of alloy solidification (Karma 2001). This model yields a much less stringent restriction on the choice of the diffuse interface thickness in the phase-field model that makes modeling alloy solidification on experimentally relevant length and time scales computationally feasible for the first time.
7) The extension of solidification phase-field models to polycrystalline materials (Warren, Kobayashi et al. 2003).
8) Atomistic simulations demonstrating that the low mobility of the solid-liquid interface for the <111> orientation is not due to the formation of stacking faults, but, more likely, to the higher density of atoms in planes perpendicular to this orientation.
9) Microstructural and texture evolution demonstrated to be dependent on grain boundary properties during grain growth (Demirel, Kuprat et al. 2003). This comparison of experimental and simulated coarsening was performed for the same aluminum foil for which anisotropic properties had previously been determined (experimentally) (Yang, Rollett et al.

2001). The notable contribution of this work was a detailed quantitative comparison of experimentally evolved microstructures and the corresponding simulated evolution at the scale of individual grains.
10) A new approach to constructing statistically representative 3D microstructures based on 2D plane sections (electron back-scatter diffraction scans) shows promise for providing realistic input to mesostructural simulation codes (Saylor, Fridy et al. 2004). The power of this Voronoi-tesselation based approach lies in the ability to take pixel-based data sets from experimental characterization and convert them directly to voxel-based input data sets for Monte Carlo simulations. This statistical reconstruction method can be contrasted with the serial section reconstruction approach that has been developed by Voorhees and others that relies on destructive characterization of small volumes of material. Data sets from the method should also be easily adaptable to the requirements of mesh generators for finite element codes. Please note that the first paper written on this method was awarded the Henry Marion Howe Prize for the Best Paper in Metallurgical and Materials Transactions in 2004.
11) New applications of phase field modeling to the simulation of eutectic growth in three dimensions have been developed. These simulations permit the details of lamellar spacing versus growth rate to be explored along with the microstructural details of how the lamellar spacing adapts to changes in growth rate.
12) Fully three-dimensional models of grain boundaries moving under curvature driving forces in molecular dynamics (MD) simulations have been run for a wide range of boundary types to obtain both energy and mobility information. More information on grain boundary mobility is emerging that addresses temperature dependence (Upmanyu, Srolovitz et al. 1999). A similar compensation temperature effect is found as in experimental studies. A compensation effect means that there is a temperature at which the mobilities of different boundary types coincide. It is generally found only for a series of closely related boundaries such as pure <111> tilt boundaries.
13) Insertion of anisotropic grain boundary properties into models of grain growth and analysis of coarsening kinetics has been performed (Upmanyu, Hassold et al. 2002). The results of simulations of grain growth with anisotropic boundary properties comparing the Monte Carlo (Potts) model and the phase field model show excellent agreement.
14) A detailed analysis of abnormal grain growth kinetics has been performed using the Potts grain growth model (Radhakrishnan, Sarma et al. 2001). In one work, we showed good agreement for the kinetics of abnormal growth between the Potts model and the existing theory for abnormal grain growth. In another work, the Potts model was again used to show that the known properties of low angle grain boundaries can be inserted into a model of subgrain coarsening and abnormal coarsening studied. The behavior of such a system was generalized into a theory for the nucleation rate in recrystallization based on subgrain coarsening, also known as recovery (Holm, Miodownik et al. 2003). This represents the first analytical description of nucleation of recrystallization based on actual microstructural information.
15) The first advances in our understanding of solute drag on moving interfaces in more than 30 years (Mendelev and Srolovitz 2001). It has been found, for example, that the effect of solute drag is not symmetric and that solutes that are attracted to boundaries have a different effect compared to solute that are rejected from boundaries. A predictive theory for the effects of solute concentration, temperature, and multiple solutes on grain boundary migration has been developed.
16) An analysis of the liquid film equilibrium thickness between two solid grains in the phase-field model and the existence of a wet-dry transition resulting from bistability of two different microscopic thicknesses, a one nanometer scale "wet" one and an Angstrom scale "dry" one.

**Capillary Fluctuation Method**

Items 1 through 6 above point to the impact of the development of a new *capillary fluctuation method* (CFM) aimed at accurate computation of the magnitude and anisotropy of both the solid-liquid interface free-energy and the kinetic coefficient. This method is described in what follows.

In materials with atomically rough solid-liquid interfaces, which include most metals and alloys, the anisotropy of the interfacial free energy is very small, on the order of 1 per cent. Nevertheless, the anisotropy strongly influences the growth rate and morphology of

dendrites. We have developed a technique (Hoyt, Asta et al. 2001), known as the capillary fluctuation method (CFM), that can accurately compute the weak anisotropy by monitoring interfacial fluctuations during equilibrium molecular dynamics simulations. A result from capillary theory states that the Fourier amplitudes of the interfacial fluctuations are governed not by the interfacial free energy $\gamma$, but by the stiffness $\gamma+\gamma''$, where $\gamma''$ is the second derivative of the interfacial energy as a function of the angle of the local interface normal relative to its average orientation. The power of the CFM stems from the fact that the stiffness is typically an order of magnitude more anisotropic than $\gamma$. Figure 1 is a snapshot from an MD simulation of pure Ni modeled using interatomic potentials of the embedded atom type. Atoms of the solid (shown in red) are distinguished from those of the liquid (green) through the calculation of a crystalline order parameter and the interface profile, depicted as the heavy solid line, is found from the positions normal to the interface plane where the order parameter changes rapidly. By repeating MD simulations for several interface orientations the complete dependence of $\gamma$ on orientation can be extracted. It was found in the original work on Ni and all subsequent CFM studies that $\gamma$ as a function of $\hat{n}$ can be accurately represented using the fourth- and sixth- order terms of a cubic harmonic expansion, i.e., linear combinations of spherical harmonics that obey the cubic crystalline symmetry. As described in below the higher order $\gamma$ expansion may be important in understanding the complex dendrite growth morphologies observed in many Al alloys. The CFM has emerged as a highly useful technique for resolving the small anisotropy associated with rough interfaces, having been applied to date for the pure metals Al, Ag, Au, Cu, Ni and Pb, (Hoyt and Asta 2002; Morris 2002; Morris, Lu et al. 2002; Sun, Hoyt et al. 2004) as well as the binary alloy Cu-Ni (see below) (Asta, Hoyt et al. 2002).

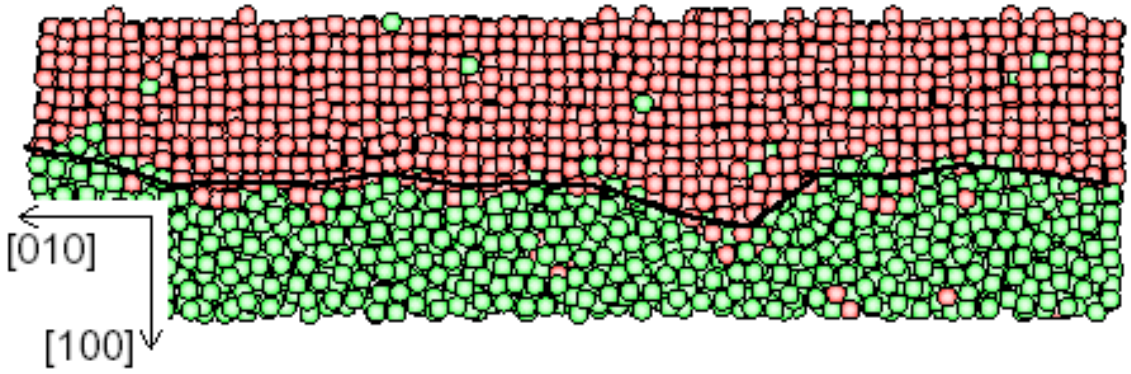


Fig. 1: Snapshot taken from an equilibrium molecular-dynamics simulation of solid-liquid interfaces in Ni. The interface is oriented with a [100] interface normal with the [010] direction aligned along the quasi-2D solid-liquid boundary. Atoms of the solid (shown in red) are distinguished from those of the liquid (green) through the calculation of a crystalline order parameter and the interface profile, depicted as the heavy solid line, is found from the positions normal to the interface plane where the order parameter changes rapidly.

The kinetic coefficient, $\mu$, is the constant of proportionality between the velocity of a planar solid-liquid boundary and the interface undercooling. $\mu$ and its anisotropy are essential input parameters in phase field modeling of dendrite growth in highly undercooled melts. Using EAM Ni as a test system, we have investigated three separate MD techniques for computing $\mu$ (Sun, Hoyt et al. 2004): a free solidification method, an imposed pressure technique and the kinetic extension of the CFM. Within numerical uncertainty it was found that all three methods yield equivalent results. In addition, the free solidification scheme was used to extract $\mu$ in several pure metal systems, including Au and Ag (Hoyt and Asta 2002). Two important results have emerged from the MD studies. The {100} vs. {110} anisotropy in $\mu$ is quite high, on the order of 15%, and the magnitude of the kinetic coefficient is a factor of 4-5 less than the upper velocity limit predicted from entropic considerations. The values of $\mu$ obtained from simulation have been used to test various theories of crystal growth rates, including the rate theory approach of (Broughton, Gilmer et al. 1982) and the model of (Mikheev and Chernov 1991) based on density functional theory.

**First quantitative phase-field simulations of dendritic solidification in a metallic system with input anisotropy parameters computed from MD simulations (item 4):**

This project was the first direct attempt to combine atomic-scale and mesoscale methods to obtain parameter-free predictions of microstructural evolution during solidification. The anisotropic interfacial energy and kinetic coefficient calculated using the CFM and free-solidification methods described above were used as input parameters in fully three-dimensional phase-field simulations of the crystallization of deeply undercooled Ni melts (Bragard, Karma et al. 2002). The results of these simulations are summarized in Figs. 2a-c.

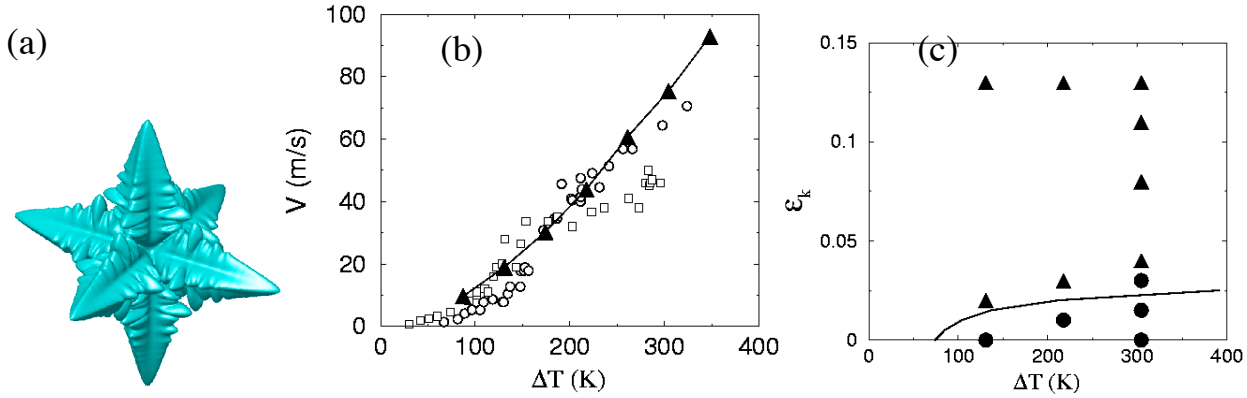


Fig. 2: (a) Snapshot of solid-liquid interface in mesoscale phase-field simulations of the solidification of pure Ni undercooled by 87 K (Bragard *et al.* 2003). These simulations use input parameters for the anisotropic solid-liquid interface kinetic coefficient and free-energy obtained from atom-scale simulations (Hoyt *et al.*, 1999 and 2001). (b) Comparison of dendrite velocity vs. undercooling ΔT in simulations (filled triangles and solid line) and two sets of experiments by Lum *et al.* (1996) (open squares) and Willnecker *et al.* (1989) (open circles). (c) Growth morphology diagram showing the region of existence of dendrites (filled triangles) and tip-splitting morphology (filled circles) in the plane of kinetic anisotropy $\varepsilon_k=(\mu_{100}-\mu_{110})/(\mu_{100}+\mu_{110})$ and undercooling.

The results of the simulations are compared quantitatively to experiments in Fig. 2b. This comparison shows that the phase-field model predictions are in remarkably good quantitative agreement with the measured solidification rates (Willnecker, Herlach et al. 1989; Lum, Matson et al. 1996) for the anisotropy parameters obtained from the MD simulations. In order to gain insight into the role of anisotropy, additional simulations were carrier out by varying independently the magnitude of the capillary and kinetic anisotropy. Varying the magnitude of the capillary anisotropy was found to have very little influence on the results. In contrast, we found that the growth morphology depends sensitively on the magnitude of the kinetic anisotropy as illustrated in Fig. 2c.

These results are important because solidification models to date have mainly considered the role of the magnitude of the kinetic coefficient, but not its anisotropy. The main effect of decreasing the magnitude of $\mu$ (i.e. of making the interface kinetics more sluggish) is to increase the interface kinetic undercooling, $V/\mu$, which in turn reduces the thermodynamic driving force for solidification and hence the solidification rate. The results of Fig. 2c stress the importance of also incorporating the magnitude of the anisotropy of the kinetic coefficient to accurately model dendritic evolution at large solidification rates. In particular, a smaller kinetic anisotropy leads to a smaller dendrite growth rate and dendrites cease to exist all together if the kinetic anisotropy falls below some critical value of the order of a few percent that depends on undercooling. Below this critical anisotropy, dendrite growth is replaced by a tip splitting growth morphology with a smooth macroscopic envelope of the solidification front, as opposed to an angular envelope for dendrite growth above this critical anisotropy.

**Modeling of grain growth with anisotropic grain boundary properties (Item 13)**

Recently, the diffuse-interface phase field model of grain growth has been generalized to account for anisotropy in grain boundary properties such as energy and mobility (Kazaryan, Wang et al. 2000). The model allows for quantitative characterization of the kinetics and morphological evolution of grain growth with both inclination and misorientation dependence

of grain boundary mobility and energy (Kazaryan, Wang et al. 2001; Kazaryan, Wang et al. 2002). An analytical treatment of grain growth in systems of anisotropic boundary mobility was also developed (Kazaryan, Patton et al. 2002).

Through CMSN collaborations anisotropic grain boundary properties obtained from atomistic simulations have been incorporated directly into the phase field and Monte Carlo models (Upmanyu, Hassold et al. 2002). While the atomistic simulations demonstrate strong anisotropies in both boundary energy and mobility, phase field simulations of microstructural evolution demonstrate that anisotropy in boundary mobility plays little role in the stochastic evolution of the microstructure. On the other hand, anisotropy in the grain boundary energy strongly modifies both the topology of the polycrystalline microstructure and the kinetic law that describes the temporal evolution of the mean grain size.

Also through CMSN collaborations, the generalized phase field model has been applied to study abnormal grain growth and the results are compared with concurrent Monte Carlo simulations and existing analytical treatments based on mean field approximation (Radhakrishnan, Sarma et al. 2001). It is found that there are significant differences between the predictions obtained using the two simulation techniques, and the analytical predictions do not agree with either phase field or Monte Carlo simulations. More detailed investigations are underway to understand the fundamental differences between these approaches for predicting the extent of abnormal grain growth.

**Segregation Transition and Drag Force at Grain Boundary**

The CMSN collaborations prompted the group to work on "dirty" boundaries. We investigated solute segregation at grain boundaries and the corresponding drag effect on grain boundary migration. A continuum model of grain boundary segregation based on kinetic Monte Carlo (Mendelev and Srolovitz 2001a, 2001b, 2001d, 2002b, 2002c), gradient thermodynamics and its discrete counterpart (discrete lattice model) have been developed (Ma, Dregia et al. 2003) and analytical theory (Mendelev and Srolovitz 2000, 2001b). The models variously include heat of segregation, intrinsic boundary mobility, solute diffusivity, co-segregation, solute thermodynamics, concentration gradients, spatial variation of gradient-energy coefficients, and the spatial variation of atomic volume and concentration dependence of solute – grain boundary interactions. The applications of the model to a nominally planar grain boundary in ideal and regular solutions under various conditions provide considerable insight into the contributions of these terms to the equilibrium and steady-state solute concentration profiles across the grain boundary, the segregation transition temperature and the corresponding drag forces. There remains some debate as to the role of the gradient terms in a regular solution model. The incorporation of more than simply ideal solution thermodynamics into impurity drag theories were found to be particularly important in accurately predicting the role of impurity drag

While the continuum, 1-d theories predict a sharp transition of grain boundary mobility as a function of temperature (related to the sharp transition of solute concentration of grain boundary as a function of temperature), discrete models in higher dimension show no such sharp jump or hysteresis. We are currently trying to understand the difference between one and higher dimensions (and continuum vs. discrete effects) within a self-assembling, dynamical systems framework.. This framework shows under what conditions hysteresis should be observed experimentally and why it is most commonly not seen.

The results of these microscopic models for impurity drag effects in boundary migration can be used directly in models for microstructural evolution. This is done either directly through phase field models or by using the microscopic models to produce equations of motion for the boundaries that incorporate the drag effects directly.

**Publications from the Project**

Many of the contributions are appearing in print and an exhaustive list is difficult to compile because of the distributed nature of the project. Selected papers are listed below. As an example, Karma and co-workers have recently published a paper in Phys. Rev. Letters (2001) on their work on extracting properties from measurement of interfacial stiffness in MD simulations of solid-liquid systems (listed above). A group of papers from the collaboration has been assembled and has been published in Interface Science with Rollett, Karma and Srolovitz as guest editors. The list of titles is given in the table below. A special issue of JOM appeared in 2004. This set of articles emphasized broader overviews of the activities in the group in an effort to reach the wider materials community, as opposed to detailed

technical progress. Other articles published by the members of the project: {Umantsev, 2001 #2159; Umantsev, 2001 #2160; Umantsev, 2001 #2162; Umantsev, 2002 #2161; Karma, 2001 #2153; Lobkovsky, 2002 #2155; Kinderlehrer, 2002 #1941; Kinderlehrer, 2001 #2068; Kinderlehrer, 1999 #2154; Mendelev, 2002 #2156; Mendelev, 2001 #2140; Mendelev, 2001 #2141; Mendelev, 2001 #2142; Mendelev, 2002 #2144; Mendelev, 2002 #2148; Asta, 2001 #2149; Asta, 2001 #2150; Asta, 2001 #2151; Hoyt, 1999 #2227; Rollett, 2002 #2048; Rollett, 2001 #1942; Rollett, 2002 #2014; Takashima, 2000 #1858; Upmanyu, 2002 #2157; Upmanyu, 1999 #1979; Upmanyu, 1999 #2158; Upmanyu, 2002 #2045}.

***Listing of Papers Appearing in Volume 10, Issue 2-3, of Interface Science (July 2002)***

| *Paper* | *First Author, affiliation* | *Title* | *Pages* |
|---|---|---|---|
| 1 | J. Bragard, A. Karma, Y.H. Lee and M. Plapp | Linking Phase-Field and Atomistic Simulations to Model Dendritic Solidification in Highly Undercooled Melts | 121-136 |
| 2 | M. Demirel, Andrew P. Kuprat, Denise C. George, Galen K. Straub, and Anthony D. Rollett | Linking Experimental Characterization and Computational Modeling of Grain Growth in Al-Foil | 137-141 |
| 3 | J. Morris Z.Y. Lu, Y.Y. Ye and K.M. Ho | The Anisotropic Free Energy of the Solid-Liquid Phase Boundary in Al | 143-148 |
| 4 | H. Ramalingam, M. Asta, A. van de Walle, and J. J. Hoyt | Atomic-Scale Simulation Study of Equilibrium Solute Adsorption at Alloy Solid-Liquid Interfaces | 149-158 |
| 5 | K.A. Jackson | The Interface Kinetics of Crystal Growth Processes | 159-169 |
| 6 | B. Radhakrishnan and T. Zacharia | The Effect of Lattice Temperature on Abnormal Subgrain Growth Simulations using a Monte Carlo Technique | 171-180 |
| 7 | J. J. Hoyt., M. Asta and Alain Karma | Atomistic Simulation Methods for Computing the Kinetic Coefficient in Solid-Liquid Systems | 181-189 |
| 8 | M. Mendelev, and D.J. Srolovitz | Co-segregation effects on Boundary Migration | 191-199 |
| 9 | M. Upmanyu,., G. N. Hassold, A. Kazaryan, E. A. Holm, Y. Wang, B. Patton and D. J. Srolovitz | Boundary Mobility and Energy Anisotropy.... | 201-216 |
| 10 | R. Napolitano, Shan Liu, and R. Trivedi, | Experimental Measurement of Anisotropy in Crystal-Melt Interfacial Energy | 217-232 |
| 11 | D. Kinderlehrer, S. Ta'asan, Irene Livshits and Darren E. Mason | The Surface Energy of MgO: Multiscale Reconstruction from Thermal Groove Geometry | 233-242 |
| 12 | M. Mendelev, and D.J Srolovitz | Domain Wall Migration in 3-d in the Presence of Diffusing Impurities | 243-250 |

**Postdocs and Students Supported, 1999-2003**

**Jean Bragard**, Northeastern Univ., worked with Alain Karma on phase field modeling of dendrite growth through August 2001.

**Alex Lobkovsky**, Northeastern Univ., worked primarily with Alain Karma on phase field modeling of dendrite growth and on fundamental issues related to the uniqueness of grain boundary mobility under different driving forces in direct collaboration with Srolovitz and Mendelev.

**Zhong-Yi Lu**, Ames National Laboratory, primarily working with Jamie Morris on the extraction of energy and mobility from molecular dynamics simulations of the solid-liquid interface.

**Irine Livshits**, Carnegie Mellon University, worked primarily with David Kinderlehrer and Anthony D. Rollett on the development of the mathematics of grain growth. She is now an Assistant Professor at the University of Central Arkansas.
**Mikhail Mendelev**, Princeton Univ., working primarily with David Srolovitz on the interaction of solutes with moving boundaries via simulation and theory; also empirical interatomic potential development. He is now a staff member at the Ames Laboratory.
**Soonwuk Cheong**, Carnegie Mellon Univ., primarily worked with Prof. A.D. Rollett on the translation of experimental data sets from automated electron back-scatter diffraction (EBSD) system to Monte Carlo grain growth simulations. He completed his PhD in May 2002 and is now a staff member at the Alcoa Technical Center where he continues to use the simulation tools that he became familiar with during his association with the CMSN project.
**Tomorr Haxhimali,** Northeastern Univ., who recently started his PhD thesis under the supervision of Prof Karma at NEU and who his expected to work primarily on solidification projects related to the proposed work over the next 2-3 years. Tomorr attended the last CMSN meeting and is expected to work in close collaborations with postdocs and other members of the CMSN collaboration.
In general, each of these individuals was supported at the 50% level by the CMSN project.

**Exchange of personnel**
A feature of the project has been the exchange of personnel between institutions and a portion of the budget was explicitly reserved for this activity. The following provides a list of such exchanges and their purpose. Other exchanges certainly took place that were not supported with CMSN funds.
• A PhD student (Melik Demirel) from the Materials Science and Engineering Department at CMU made an extended visit to the Los Alamos National Laboratory in the summer of 2000 in order to learn how to use the Los Alamos finite element model for grain growth. He has completed his PhD (from CMU) at Los Alamos in which he made detailed comparisons of grain growth between experiments and simulations. His conclusion was that very good agreement can be obtained between experiment and simulation but only if the appropriate anisotropy is included. In the case of the subgrain structures studied, the anisotropy of mobility is the key feature. He completed a postdoc fellowship at Los Alamos and is now an Assistant Professor at the Pennsylvania State University (main campus) in the Materials Science Department.
• A PhD student from Princeton (Moneesh Upmanyu) was a post-doc at ORNL and is now an Assistant Professor at the Colorado School of Mines as of the summer of 2002.
• A member of the group from industry, Chris Wolverton (Ford Research) has continued the collaboration between Ford and Penn State University (Long-Qing Chen) to study the effect of interfacial properties on precipitation in the Al-Cu system. This collaboration is focused on the relative stability of the numerous different precipitates in the Al-Cu system such as 'theta-prime' ($Al_2Cu$) which is now thought to be more stable than the theta phase at low temperatures (<200°C) in contrast to the currently accepted ordering of thermodynamic stability of the series GP zones, θ", θ' and θ.
• Upmanyu (ORNL), Srolovitz (Princeton), Rollett (CMU), Holm (Sandia), and Wang (OSU) combined atomistic determination of boundary mobility and energy anisotropy with phase field and Monte Carlo models of anisotropic grain growth.
• Upmanyu (ORNL), Srolovitz (Princeton), Lobkovsky (Northeastern), and Warren (NIST) combined atomistic simulations and phase field models of coupled grain rotation and migration.
• Mendelev (Princeton), Srolovitz (Princeton), Karma (Northeastern) and Lobkovsky (Northeastern) performed Monte Carlo simulations and analytical theory on the anisotropy of interface migration.
• Rollett (CMU) and Srolovitz (Princeton) jointly analyzed the mobility of low angle grain boundaries.
• Mendelev (Princeton), Srolovitz (Princeton), Asta (Northwestern) and Morris (Ames) developed a series of interatomic potentials for modeling solid-solid and solid-liquid interfaces in a series of metallic systems.
• Asta (Northwestern Univ.), Hoyt (Sandia Labs.) and Karma (Northeastern), in conjunction with several postdocs and students, developed methods of analyzing the results of molecular

dynamics simulations of solid-liquid interfaces to extract anisotropic quantities (described elsewhere).

In summary, the group made progress towards realizing its vision of a comprehensive computational approach to calculating the anisotropy of interfaces and demonstrating the impact on microstructural evolution.

**The computational materials science challenge:**

This project brought together people with a broad experience in high performance computing, particularly in the areas of molecular dynamics simulations and phase-field modeling. The various researchers each had access to a number of computational resources, including various cluster computers at Ames, Princeton, Northeastern, and Sandia, and also through the Pittsburgh Supercomputing Center. Furthermore, the project was awarded significant resources from the Department of Energy's National Energy Research Scientific Computing Center (NERSC) at Lawrence Berkeley National Laboratory. In fiscal year 2002, we used 117,000 MPP hours at NERSC, and the allocation was 130,000 for FY2003. This usage included diverse members of the Network, including researchers from Northwestern, Carnegie-Mellon, Ohio State, and Ames Laboratory. In addition to using this time for production runs, development of new codes continued after this funded period, including a parallel grain-growth simulation code that we expect to make publicly available. We also made an effort to encourage the development of resources of publicly available codes, by inviting people from the high-performance computing centers and from people creating open-source software for scientific uses to our meetings.

Clearly, in this project, and in this network in general, the most critical computational materials science challenge is to determine the effect of impurities ("dirt") on interface mobility and its anisotropy and to make the connection between atomistic calculations and microstructural models. This will challenge the group to make innovations both in the existing codes and to generate new algorithms.

**Subcontract or Consortium Arrangements:**

The team for the new project (starting Fall 2003) comprised many of the same individuals and institutions as in the first project. Based on the new topic, however, there were some changes of participants. The participants in the new project are identified in the table below.

| Name | Institution |
|---|---|
| M. Baskes | Los Alamos National Laboratory |
| A. Kuprat[1] | Los Alamos National Laboratory |
| C. Battaile[1] | Sandia National Laboratories, Albuquerque |
| E.A. Holm[1] | Sandia National Laboratories, Albuquerque |
| *L.-Q. Chen[1] | Pennsylvania State University |
| *S. Foiles[1] | Sandia National Laboratories, Albuquerque |
| J. Hoyt[2] | Sandia National Laboratories, Albuquerque |
| J. Morris[2] | Ames Laboratory |
| R. Napolitano[2] | Ames Laboratory |
| R. Trivedi[2] | Ames Laboratory |
| B. Radhakrishnan[1] | Oak Ridge National Laboratory |
| A. D. Rollett[1] | Carnegie Mellon University |
| *S. Ta'asan[1] | Carnegie Mellon University |
| *D. Kinderlehrer[1] | Carnegie Mellon University |
| D. J. Srolovitz[1] | Princeton University |
| V. Vitek[1] | University of Pennsylvania |
| A. Karma[2] | Northeastern University |
| M. Asta[2] | Northwestern University |
| D. Seidman[1] | Northwestern University |
| J. Warren[1] | NIST |
| *D. Lewis[2] | NIST |
| *H. Frost[1] | Dartmouth College |
| M. Upmanyu[1] | Colorado School of Mines |
| *Y. Wang[1] | Ohio State University |
| *K. Jackson[3] | Arizona State University |
| *C. Maurice[4] | Ecole Polytechnique, St. Etienne, France |

Notes: "1" indicates an investigator primarily interested in the effects of solutes on solid-solid interfaces; "2" indicates an investigator primarily interested in the effects of solutes on the solid-liquid interface; “3” indicates an investigator who will be invited to a subset of the meetings for discussion on specific topics; “4” indicates a corresponding foreign investigator who will be invited to attend if they are already in the US at the time of a meeting; "*" indicates an investigator who was not an original member of the current project.

**Appendix A: CMSN Workshops on Anisotropic Boundaries, Solidification and Grain Growth**

## Agenda for 6th Workshop on Anisotropic Boundaries, Solidification and Grain Growth, Ames Laboratory/Iowa State University, Oct. 15-16, 2002.

**Tuesday, Oct. 15**

| | |
|---|---|
| 8:30 | Opening Discussion |
| 10:00 | Mark Asta, Deyan Sun<br>"Solid-liquid-interface kinetic coefficient from atomic-scale simulation" |
| 11:00 | Christoph Beckermann<br>"Phase-field simulations of dendrites with theormosolutal transport and flow" |
| 11:30 | Break for lunch |
| 12:45 | Planning & Discussion |
| 2:15 | Alain Karma<br>"Anisotropic interface motion under different driving forces in the low-temperature Ising model" |
| 2:45 | Stephen Foiles<br>"Segregation to grain boundaries: From ideal towards general boundaries." |
| 3:15 | David Srolovitz "Generalized development of interatomic potentials for atomistic simulations of crystalline defects and the solid-liquid interface" |
| 4:00 | Virtual Reality Applications Center tour |
| 6:30 | Dinner |

**Wednesday, Oct. 16**

| | |
|---|---|
| 8:30 | Tony Rollett<br>"3D Potts Model Simulations of Grain growth with anisotropic grain boundary properties" |
| 9:00 | Priya Manohar<br>"An efficient, parallel Monte Carlo method for asynchronous simulation of grain growth: Preliminary Studies" |
| 9:30 | B. Radhakrishnan<br>"Deformation and recrystallization modeling of aluminum bicrsytals" |
| 10:00 | Break |
| 10:15 | Moneesh Upmanyu<br>"Grain boundary mobilities in Al: Dependence on driving force and misorientation axis" |
| 10:45 | Final discussion |
| 12:15 | Lunch |

**Agenda for 7th Workshop on**
**Anisotropic Boundaries, Solidification and Grain Growth,**
**UCSD, La Jolla, San Diego, March 6-7th, 2003**

Hosted by Professor Herbert Levine, Physics Department, UCSD

Rimac Building, 4th floor conference room

THURSDAY

12:30pm Ralph Napolitano, Ames Lab: "Solidification of Al-Si eutectics- current understanding and challenges"

1:00pm Jeff Hoyt, SNL and Mark Asta, NWU, "An Atomistic Study of Disorder Trapping in a Model Ni-Al Alloy".

1:30pm discussion

1:45pm Brian Laird, University of Kansas, "Structure and transport properties of crystal-melt interfaces for binary mixtures"

2:15pm Moneesh Upmanyu, Colorado School of Mines, "Extracting grain boundary entropy from MD simulations"

2:45pm discussion

3:00pm M.I. Mendelev, S. Han, D.J. Srolovitz and G.J. Ackland, Princeton Univ., "Development of a New Interatomic Potential for Iron Appropriate for Describing Point Defects and the Liquid – Solid Interface"

3:30pm Mark Asta, D. Sun, J. J. Hoyt, M. I. Mendelev and D. Srolovitz, NWU, "Solid-Liquid Interfaces in bcc-Fe."

4:00pm discussion (perhaps in separate S/L and S/S subgroups to discuss future directions, preparation for review etc.)

FRIDAY

8:00am Breakfast (provided)

8:45am Herbert Levine, UCSD, "Dynamic Fracture"

9:30am Corbett Battaile, SNL, "Simulating Recrystallization and Stress-Induced Interface Migration."

10:00am Long-Qing Chen, PSU, "Phase-field simulation of dislocation-solute interactions"

10:30am discussion

10:45am Jamie Morris, Ames, "Free energies of solids, liquids and interfaces"

11:15am Ira Livshits, Central Arkansas Univ.: Remarks on Mesoscale Modeling for

Anisotropic Grain Growth.

11:45am lunch (provided)

1:15pm Yunzhi Wang, OSU, “Texture Development in Systems of Anisotropic Energy and Mobility”

1:45pm Tony (A.D.) Rollett, Priya Manohar, CMU, “Development of a parallel Potts model for grain growth,” and, “Texture development during grain growth”

2:15pm B. Radhakrishnan, ORNL, “Hot Deformation and Recrystallization of Particle-Containing Aluminum Alloys.”

2:45pm discussion

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