Computational Investigations of Solid-Liquid Interfaces

Final Report

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Table of Contents

1. Project Overview	2
2. Project Accomplishments	3
2.1 Crystal-Melt Interface Properties in Alloys.....	3
2.2 Faceted Solid-Liquid Interfaces.....	4
2.3 Non-Equilibrium Kinetic Processes at Alloy Crystal-Melt Interfaces	6
2.4 Grain Boundaries at High Homologous Temperatures.....	6
3. List of Publications	7

1. Project Overview

In a variety of materials synthesis and processing contexts, atomistic processes at heterophase interfaces play a critical role governing defect formation, growth morphologies, and microstructure evolution. Accurate knowledge of interfacial structure, free energies, mobilities and segregation coefficients are critical for predictive modeling of microstructure evolution, yet direct experimental measurement of these fundamental interfacial properties remains elusive in many cases. In this project first-principles calculations were combined with molecular-dynamics (MD) and Monte-Carlo (MC) simulations, to investigate the atomic-scale structural and dynamical properties of heterophase interfaces, and the relationship between these properties and the calculated thermodynamic and kinetic parameters that influence the evolution of phase transformation structures at nanometer to micron length scales. The topics investigated in this project were motivated primarily by phenomena associated with solidification processing of metals and alloys, and the main focus of the work was thus on solid-liquid interfaces and high-temperature grain boundaries. Additional efforts involved first-principles calculations of coherent solid-solid heterophase interfaces, where a close collaboration with researchers at the National Center for Electron Microscopy was undertaken to understand the evolution of novel core-shell precipitate microstructures in aluminum alloys. The next section reviews the main accomplishments under this project.

2. Project Accomplishments

2.1 Crystal-Melt Interface Properties in Alloys: In the development of the modern theoretical framework for understanding dendrite growth, attention focused initially almost exclusively on the relationship between the steady-state tip radius and velocity of a growing dendrite. An issue of equal fundamental and practical importance, that received considerably less attention until recently, is the question of the crystalline orientation selected by the growing dendrite tip. This orientation selection affects the overall symmetry of the growing dendrite and is an important factor governing the morphology and growth rate of solidification microstructures. In most materials dendrite tips choose high-symmetry growth directions, leading to six-fold symmetry for dendrites growing in the basal planes of hexagonal snow crystals and many hcp metals, and four-fold symmetry for most cubic metals growing along $\langle 100 \rangle$ directions. However, a growing number of observations have been reported where alloying has been found to induce dramatic changes in solidification morphologies, leading to highly complex growth shapes that remain incompletely understood. In the most detailed study of this phenomenon to date, Haxhimali et al.¹ showed that over a range of Zn compositions, the dendrite growth direction, in commercially relevant Al-Zn alloys, changes smoothly from $\langle 100 \rangle$ to $\langle 110 \rangle$. To interpret the experimental results the authors performed phase-field simulations of dendrite growth where both the four-fold and six-fold parameters characterizing the anisotropy in the crystal-melt interfacial free energy (γ) were varied. The modeling study showed that in the space of these two anisotropy parameters there exist regions where $\langle 100 \rangle$ and $\langle 110 \rangle$ growth are preferred, as well as an intermediate “hyperbranched” region where the misorientation angle, as measured from the $\langle 100 \rangle$ growth direction, varies smoothly from 0 to $\pi/4$. A key assumption in this theoretical interpretation is

¹ T. Haxhimali, A. Karma, F. Gonzales and M. Rappaz, “Orientation selection in dendritic evolution,” *Nature Mat.* 5, 660-664 (2006).

that alloying can lead to changes in the anisotropies of γ strong enough to induce changes in dendrite growth direction. Prior to the efforts under this project there was no direct evidence either from experiment or simulation that this was the case. Work completed in this project [2,13] yielded new insights into the nature of alloying effects on the free energies of crystal-melt interfaces, and demonstrated that indeed composition-induced variations in γ anisotropies can be significant on the scale required to induce changes in dendrite growth directions, even in an alloy system with fairly ideal solution-thermodynamic properties.

Figure 1: Results of atomistic calculations of equilibrium solid-liquid phase boundaries (a) and crystal-melt interfacial free energy anisotropy parameters (b). Results are from work recently submitted to Physical Review Letters [6], and are described in further detail in the text.

The results of the modeling work [2,13] are summarized in Figure 1. In this work, which represents the first detailed calculation of the composition dependence of crystal-melt interfacial free energies in an alloy, we considered a model Lennard-Jones alloy system featuring zero size-mismatch and fairly ideal solution thermodynamics. This system provided an important benchmark, the results for which isolate the effects on crystal-melt interface properties arising from solute partitioning and the associated composition and density profiles across the solid-liquid interface, without introducing complicating factors associated with size mismatch. The phase diagram for the system considered in this work featured a “lens” type solid-liquid phase diagram, shown in Fig. 1 (a), where the temperature is expressed in reduced Lennard-Jones units. The capillary-fluctuation method was employed to compute excess free energies between coexisting crystal and melt phases, with composition given by the corresponding solidus/liquidus boundaries. In Figure 1 (b) results of the calculations are plotted for the four-fold and six-fold anisotropy parameters, ϵ_1 and ϵ_2 , respectively. These parameters, which characterize the dependence of γ on interface normal, determine dendrite growth orientations in the limit of low undercoolings, as shown by the solid-lines representing results of the previous phase-field modeling by Haxhimali et al.. For large positive values of ϵ_1 and relatively small values of ϵ_2 , dendrite growth along $\langle 100 \rangle$ is preferred, as observed in most cubic materials. However, for small values of ϵ_1 and relatively large negative values of ϵ_2 , dendrite growth along $\langle 110 \rangle$ is

avored, as observed in some Al alloy systems. The central question addressed in the atomistic work was whether the composition induced variations in these anisotropy parameters can be strong enough to lead to changes in growth orientation.

The results for Lennard-Jones alloys, plotted with red symbols in Fig. 1(b) suggested that this is indeed the case. While the pure element anisotropy parameters (indicated by $T=0.4639$ and 0.6185) fall firmly inside the $\langle 100 \rangle$ domain, the effect of alloying is seen to amplify the magnitude of the six-fold anisotropy parameter, increasing tendencies toward $\langle 110 \rangle$ growth. For elemental metals such as Al, where the anisotropies have been predicted to lie close to the boundary between $\langle 100 \rangle$ and hyperbranched growth [13], these variations in anisotropy parameters arising from compositional changes are seen to be strong enough to induce changes in growth orientation.

2.2 Faceted Solid-Liquid Interfaces: In solution growth, and growth of ionic or covalent solids from their melts or liquid catalysts, faceted interface morphologies are commonly observed. In these contexts crystal growth rates and morphologies are sensitively affected by the thermodynamic and kinetic properties of steps present on vicinal interfaces. In this project we applied MD simulations in detailed studies of crystal-melt interface steps, employing the Stillinger-Weber (SW) model of Si as a model system [6,9,16].

Figure 2: Snapshot of a simulation cell (a) showing steps at a faceted crystal-melt interface in Si. Results of non-equilibrium MD simulations are plotted in (b) showing calculated step mobilities as a function of step spacing (l).

Non-equilibrium molecular-dynamics (NEMD) methods were applied to investigate crystal growth at interfaces with orientations vicinal to the faceted $[111]$ plane. Steps at this interface were found to have a double-height structure and are characterized as being highly diffuse structurally. In the NEMD simulations, a step-flow growth mode was verified and found to be stable up to undercoolings on the order of 30 K. Step mobilities were calculated from simulations featuring a wide range of step spacings, from roughly 0.8 to 4.6 nm. In this nanometer-scale range the step mobilities were found to display a pronounced dependence on step spacing, as shown in Figure 2. It is observed that relatively strong step-step interactions give rise to a decrease in step roughness with decreasing step spacing, correlating with an associated decrease in step mobility. The magnitudes of the calculated step mobilities are found to be roughly an order of magnitude larger than the predictions of classical theories which assume that step motion is governed by the attachment of “adatoms” from the liquid to the solid at well-defined kink sites. In contrast to the classical picture, the simulations for SW-Si crystal-melt interfaces suggest that steps advance by rearrangements of the atoms on the layer above the crystal terrace that are already highly ordered relative to the liquid phase. Atoms in this

interfacial layer are expected to be more easily able to rearrange themselves to form crystalline order (and thus advance the step forward), thus requiring a lower driving force than that assumed in the classical model to advance the step forward.

The tools developed in the work on SW-Si models were extended in simulation studies of size effects on nucleation kinetics in model systems crystallizing in confined geometries [16]. The work was motivated in the context of catalyst-mediated nanowire growth, where kinetic processes at the growth interface can play an important role in governing wire compositions, morphologies, and growth rates. Simulated growth rates displayed a dependence on nanowire diameter consistent with a size dependent barrier for facet nucleation. A theory for the interface mobility was developed, establishing a source for size-dependent growth rates that is an intrinsic feature of systems possessing growth interfaces with faceted and rough orientations.

Figure 3: MD snapshots illustrating the interface structure for liquid Pb (gold spheres) against solid Cu (blue). The panel on the left shows a side view highlighting the layers of the liquid Pb against solid Cu. The right panel shows the lateral order within the first two Pb interfacial layers: gold circles are the first-layer atoms and the black holes are the positions of the second layer atoms; blue denotes the Cu interfacial layer. The first-layer Pb atoms are seen to display a high degree of order, with a well-defined orientation relationship relative to the Cu (111) planes.

Our most recent work related to the properties of faceted crystal-melt interfaces has involved molecular-dynamics studies of chemically heterogeneous interfaces. The systems investigated in this work are Pb/Cu [25] and Pb/Al. The work on these materials was motivated by experimental studies in the group of Uli Dahmen at the National Center for Electron Microscopy, in which *in-situ* electron microscopy studies of the Brownian motion of small embedded Pb liquid particles yield unique insights into the thermodynamic properties and kinetic processes governing the motion of faceted solid-liquid interfaces. Our work led to the identification of a novel pre-freezing layer in (111) oriented Pb/Cu interfaces [25], Figure 3, that is absent for other crystalline orientations. Compared to Pb/Cu, our results for Pb/Al show less ordering of the liquid at the interface, but a more pronounced degree of alloying in the interfacial layers. The Al/Pb results have also been generalized in the first study of the structure and dynamics of steps at faceted, chemically-heterogeneous solid-liquid interfaces. A manuscript related to this work is currently under preparation.

2.3 Non-Equilibrium Kinetic Processes at Alloy Crystal-Melt Interfaces: Under the non-equilibrium conditions characteristic of rapid solidification, solute effects on solidification microstructures arise due to their influence on interface mobilities, and the closely-related phenomenon of solute trapping. In this project we developed a non-equilibrium MD methodology for the study of such properties. A major technical issue that has been addressed in this work is related to the large thermal gradients induced in rapid growth simulations, due to the release of latent heat [18,22,23]. The methods that have been developed in this work were applied to a model Lennard-Jones alloy system featuring large solute partitioning between solid and liquid phases, and the Ni-Cu alloy system modeled by embedded-atom-method potentials [26]. The relationships between the interface velocity, thermodynamic driving force, and solute partition coefficient were computed and analyzed within the framework of kinetic theories accounting for solute trapping and solute drag. The results show a transition to complete solute trapping at high growth velocities, establish appreciable solute drag at low growth velocities, and provide insights into the nature of crystalline anisotropies and solute effects on interface mobilities. Specifically, we demonstrated anisotropy in the crystal-melt interface mobility comparable to that obtained for elemental fcc-forming systems, while showing a tendency for reduced values of the mobility in alloys relative to corresponding pure element systems. The MD data also indicated the presence of appreciable solute drag for the systems considered.

2.4 Grain Boundaries at High Homologous Temperatures: Surface premelting – the formation of thin, liquid-like films on solid surfaces at temperatures below the melting point – is a well established phenomenon with important consequences for many natural processes. Premelting at grain boundaries – the formation of nanometer-scale films with liquid-like properties confined between misoriented grains – can have similarly important consequences in the context of materials processing and service, by dramatically altering the properties of polycrystals at high temperatures. To understand outstanding interfacial phase-transition aspects underlying this phenomenon, we have undertaken collaborative research under the Computational Materials Science Network program that led to the developed of new computational methods for quantitative studies of grain boundary premelting. This effort led to fundamental new insights into the nature of the “disjoining forces” that energetically favor the formation of premelted films by effectively pushing apart crystal-liquid interfaces. [12,20,21,24,28].

Molecular dynamics simulations were applied in a comparative study of (i) a $\Sigma 9 \langle 115 \rangle 120^\circ$ twist and (ii) a $\Sigma 9 \langle 110 \rangle \{411\}$ symmetric tilt boundary in a classical embedded-atom model of elemental Ni. Although both boundaries feature highly disordered structures near the melting point, the nature of the temperature dependence of the width of the disordered regions in these boundaries is qualitatively different, as illustrated in Figure 4 (a). The former boundary displays behavior consistent with a logarithmically diverging premelted layer thickness as the melting temperature is approached from below, while the latter displays behavior featuring a finite grain-boundary width at the melting point. It was demonstrated that both types of behavior can be quantitatively described within a sharp-interface thermodynamic formalism involving a width-dependent interfacial free energy, referred to as the disjoining potential. The disjoining potential for boundary (i) is calculated to display a monotonic exponential dependence on width, while that of boundary (ii) features a weak attractive minimum. Boundary (ii) is found to feature a structure at high homologous temperatures characterized by localized regions of disorder, separated by highly ordered “solid bridges,” as illustrated in Figure 4 (b).

Figure 4: The figure on the left (a) displays MD snapshots and equilibrium grain-boundary width histograms for three boundaries displaying qualitatively distinct structures at high homologous temperatures. The $\Sigma 11$ tilt boundary remains highly ordered while the $\Sigma 9$ twist boundary displays a large premelted layer. The $\Sigma 9$ tilt boundary shows intermediate behavior, illustrated in (b), characterized by the formation of localized regions of disorder separated by ordered “solid bridges”.

In similar studies for bcc metals, we reported the finding of a novel grain-boundary structural phase transition in both molecular-dynamics and phase-field-crystal simulations of classical models of Fe [24]. This transition is characterized by pairing of individual dislocations with mixed screw and edge components. It was found that this type of transition is driven by a combination of factors including elastic softening, core interaction, and core disordering. At high homologous temperatures the occurrence of this transition is shown to prevent premelting at misorientation angles where it would otherwise be expected.

3. List of Publications

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