Non-Equilibrium Phase Transformations

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Objectives

The goal of this research is to develop an understanding of the structure and properties of multi-component materials produced by phase transformations which occur under conditions which are far from equilibrium. The development of a sound physical understanding of non-equilibrium phase transformations in alloys is perhaps the most important and challenging outstanding basic problem in materials science today. There have been many experimental studies designed specifically to explore this regime, but the underlying physical processes have not been properly understood. *Ad hoc* equations have been used to fit experimental data and these have remained essentially unchanged for the past decade. We are using Monte Carlo modeling based on the Ising model, which played a major role in developing our understanding of the atomic level processes in the crystallization of pure materials, to study crystallization processes in alloys. The computer modeling provides a powerful tool to help us to understand the experimental results, to develop a detailed understanding of the processes involved, and as a predictive tool for guiding experiment.

Microgravity

Projects supported by NASA are making major experimental contributions to our understanding of nucleation and crystallization in the regime where these effects are important, including the microstructure of rapidly solidified small droplets, the growth rate discontinuities observed during dendritic solidification of alloys, the extended solid solubility ranges observed due to rapid solidification, and the distribution of the component elements resulting from nucleation and growth in containerless processing. Our simulations and modeling provide a new framework for the interpretation of these experiments.

Significant Results

Monte Carlo modeling using a Spin-1 kinetic Ising model has been used to simulate non-equilibrium binary alloy solidification. Simulations have been carried out for various growth temperatures, growth rates, surface roughnesses, liquid diffusivities, equilibrium segregation coefficients, entropies of fusion, and compositions of the liquid. The non-equilibrium segregation coefficient, k (the ratio of the solid composition to the liquid composition at the interface), decreases with liquid diffusivity and surface roughness, and increases with growth velocity. Overall, the Monte Carlo results are consistent with experiment. The non-equilibrium segregation coefficient was also found to increase with concentration of the liquid, but the effect is small at low concentrations.

For simulations of the growth of pure silicon, the bonding structure was based on the diamond cubic crystal structure, and roughening transition was scaled to correspond to the experimental

roughening transition. The growth on the (111) face at small undercoolings depended on the rate of nucleation of new layers, as expected on a faceted interface. This growth rate was fitted to a poly-nuclear growth model, using a specific step free energy which was about 10% of the specific surface free energy. Extrapolation to Czochralski growth rates gave an undercooling of about 5 degrees for the (111) facet, which agrees well with estimates based on experiment.

The non-equilibrium distribution coefficient was investigated as a function of orientation for various growth rates using simulations. The thermodynamic properties and crystal structure were chosen to correspond to bismuth-doped silicon, with an equilibrium *k*-value of 7×10^{-4}. Values for *k* were obtained for several orientations of the solid/liquid interface along the zone axis between [111] and [100]. For the same growth rate, *k* was found to be greatest for solid/liquid interfaces parallel to the (111) plane, as is found experimentally. The orientation dependence of the *k*-value in the simulations compares well with the experimental orientation dependence reported by Aziz *et al.*, although there is a discrepancy in the growth rate dependence. The kink site density at the interface was determined and found to depend on orientation in the simulations, and on undercooling for the (111) face. The net growth rate at the kink sites was found to vary linearly with undercooling, as expected. The overall growth rate was found to be the product of the step density and kink-site velocity, as expected. The orientation dependence of the *k*-value arises because the step density at the interface depends on orientation, which results in an orientation dependence of the kink site velocity for given overall growth rate.

A novel analytical model for the non-equilibrium incorporation of dopants during crystallization has been developed. The model relies heavily on insights gained from the Monte Carlo computer simulations. It is based on a physical picture of the ability of the interface to transfer, between species, the chemical potential required for crystallization. This happens when a dopant atom cannot move fast enough to escape the advancing interface. The model has three parts:

(1) The first is a pair (for a binary alloy) of equations, one for the rate of crystallization of each component of the alloy, which incorporate the possibility of the transfer of the "chemical potential for crystallization" between the species at the interface. These equations are based on the standard expression for the growth rate of a pure material, and they reduce to the usual thermodynamic description of the alloy system at equilibrium.

(2) The second component is the relationship between the crystallization time for a fluctuating interface and the diffusional jump time, which sets the relative time scale for a dopant atom to escape from the advancing interface. The same relationship had been found earlier by Temkin in his analyses of alloy crystallization.

(3) The third component of the model depends on the motion of dopant atoms at the interface within the time allowed by the advancing interface. This depends on the details of the interface configurations, and, although the general features of this relationship are clear, its detailed functional form can apparently vary somewhat.

This model predicts a non-equilibrium *k*-value which compares well with Monte Carlo computer simulations and with experimental results. The model seems to have significant predictive capabilities, and can be used to predict velocity-dependent "kinetic" phase diagrams, which define the range of extended solid solubilities found during rapid crystallization.