NASA-CR-201857

IN-26-CR
OCIT
67553

Final Report

NASA Grant NAG8-944

Principal Investigators:

Kenneth A. Jackson and Brian J. J. Zelinski

University of Arizona

This is a final report on the theoretical and experimental work performed under NASA Grant NAGA-944. The goal of this research was to develop an understanding of phase transformations in alloys that occur under conditions which are far from equilibrium.

Our lack of understanding of non-equilibrium phase transformations in alloys or mixtures is viewed as the most important and challenging outstanding basic problem in materials science today. Before about 15 years ago it was not appreciated that the equilibrium phase diagram does not describe phase transformations under conditions which are far from equilibrium. Since then there have been many experimental studies designed specifically to explore this regime, but there has not been an understanding of the phenomena based on sound physical principles. There has been no basis for making predictions to guide experiment. All that has been available is an ad hoc expression which has been used to fit experimental data. Our computer modeling has now changed this. Our Monte Carlo simulations based the simple Kossel-Stranski model (as applied to alloys) reproduces the experimental observations. The origin of these effects is still not completely clear but the computer simulations have given us significant new insights to help us to understand the experiments. Other 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 for example, the microstructure of rapidly solidified small droplets, and the distribution of the component elements resulting from nucleation and growth in containerless processing. Our simulations provide a new framework for the interpretation of these experiments.

Our Monte Carlo computer simulations have reproduced in detail experimental observations of the strong dependence of the distribution coefficient on growth rate, and have been used to predict its dependence on a variety of other growth parameters. The simulations also predict changes in the effective equilibrium temperature for various growth conditions. These simulations are based on the input of the equilibrium thermodynamic properties of the alloy system, and reproduce the usual behavior near equilibrium. The results of these simulations for conditions far from equilibrium are not predicted by any standard quasi-equilibrium thermodynamic model for growth. Our computer modeling efforts have been directed towards mapping out the general features of non-equilibrium growth phenomena, and although we have concentrated on the details of the atomic scale interactions at the interface, it is capable of modeling cellular and dendritic growth directly.

Experimentally, we have pursued three efforts to explore these non-equilibrium phenomena. We

have observed a jump in the growth rate of dendrites in ammonium chloride-water mixtures which reproduces earlier experimental results on both tin and nickel alloy dendrites, but with the major advantage that the growth morphology can be observed *in situ* in ammonium chloride-water mixtures, and the growth rate can be measured readily. We have begun experiments on oscillations in the growth produced by the rapid motion of a laser across a surface. These oscillations have been observed in silver and aluminum alloys, and we are studying them in tin alloys in order to correlate the results with earlier experiments on dendritic growth of tin alloys. A Bridgman apparatus has been constructed to measure the growth rate and orientation dependence of the **k**-value in InSb, making use of spreading resistance measurements to determine concentrations, and Peltier pulsing to determine growth rates.

These ground-based experiments are subject to uncertainties due to convection, even more so than experiments measuring dendritic growth rates in pure materials. Experiments conducted in a convection free, reduced gravity environment would be of great value, and we plan to submit a proposal for flight experiments after we have explored these systems with ground-based experiments.

Our computer model is based on the Monte Carlo scheme which has been so successful in modeling the growth of pure materials, and which has played a major role in the development of our present understanding of crystal growth processes. It incorporates automatically the surface roughening transition, the effects of step density and surface configuration on growth, and so on. We have modified the Monte Carlo model used for the growth of pure materials only by the introduction of two species of atom in order to model the growth of alloys. The assumptions about the interactions between the atoms is the same except that input data for both species are needed, and these are based on the equilibrium thermodynamic properties of the alloy to be modeled. Although these assumptions are quite simple, the predictions are quite complex, and not readily amenable to analytical analysis. We have also been working with some success to develop a descriptive analytical model using the results of the simulations as a guide.

We have reported [see appended paper 1] simulations for a "diffusionless" transformation, where the transformation takes place by the motion of the interface, but the atoms do not move: their position is fixed on lattice sites. These simulations correspond to a "shear" or martensite-type transformation where the interface moves very rapidly, at rates approaching the speed of sound, so that the atoms do not have sufficient time to diffuse as the transformation front passes. The growth rate in these simulations was found to be zero on the $\mathbf{T_0}$ line for the alloy. On this line, the free energy of the solid alloy is equal to the free energy of the liquid alloy with the same composition. This is clearly the expected behavior for a diffusionless transformation. The kinetics of a diffusionless transformation should depend on the difference between the free energies of the two phases, rather than on the difference between the chemical potentials in the two phases of the species present. For the diffusionless case, "freezing" or "melting" should be reversible at $\mathbf{T_0}$, depending on which phase has the lower free energy. These results provided the first clear-cut confirmation of this expectation.

We have also successfully modeled [see appended paper 2] the dopant distribution following laser melting of ion-implanted bismuth in silicon. After implantation, the sample was surface melted with a laser to a depth of about 1 micron. The liquid layer then re-solidified quickly, resulting in a bismuth distribution which was determined by Rutherford backscattering to be quite different than that predicted using the equilibrium distribution coefficient, 7×10^{-4}. The actual distribution coefficient in this experiment was determined to be 0.1 This experiment and many other similar experiments unequivocally established that the **k**-value is strongly dependent on growth rate. Our

computer simulations have reproduced this result without any special assumptions.

Data from simulations have been accumulated for a variety of different growth temperatures and with various diffusion coefficients. The thermodynamic properties of bismuth in silicon have been used as a model system for many of these simulations since bismuth is a typical dopant in silicon and these alloys have been studied extensively experimentally. For the simulations, a growth temperature is chosen and a normalized growth rate is calculated from the net number of atoms added to the crystal during the simulation. The distribution coefficient in the simulations can be fitted with $\mathbf{k} = (\mathbf{k_e} + \mathbf{A}v^2/\mathbf{D})/(1+\mathbf{A}v^2/\mathbf{D})$ where $\mathbf{k_e}$ the equilibrium value of the distribution coefficient, **A** is a constant, **v** is the growth rate, and **D** is the diffusion coefficient. The simulation results compare well with experiment [see appended paper 3].

There is a significant dependence the **k**-value on the orientation of the growth front [see appended paper 4]. For example, the incorporation of the dopants is greater for growth on the faceted (111) plane of silicon than on other orientations. Similar results have been reported for many semiconductor crystals, where this is known as the "facet effect". Our simulations reproduce these results without the introduction of any new parameters, but merely by changing the crystallographic orientation of the growth front in the computer. We have carried out extensive simulations to test the suggestion that it is the step velocity which determines the incorporation of dopants into the growing crystal [to be published].

In summary, we have developed Monte Carlo computer simulation programs based on the standard model for crystal growth, making use of standard thermodynamic values for input, and we have explored the consequences of this model in the regime which is far from equilibrium. We have obtained results which are not anticipated by standard thermodynamic models, and which provide significant agreement with experimental observations.