FINAL REPORT

DOE GRANT DE-FG02-99ER45771

1 July 2003 - 30 June 2007

**Microstructural Evolution and Interfacial Motion
in Systems with Diffusion Barriers**

William C. Johnson
Department of Materials Science and Engineering
P.O. Box 400745
University of Virginia
Charlottesville, VA 22904-4745

Tel: (434) 982-4884
Fax: (434) 982-5799
e-mail: wcj2c@virginia.edu

1 Research Results During Funded Period

1.1 Research Goals

The initial goal of this research program was to model and to simulate phase transformations in systems containing diffusion barriers. The modeling work included the development and testing of code to describe mass flow, the kinetics of phase formation, elastic deformation, and subsequent microstructural evolution occurring during interdiffusion. The primary simulation tools to be used were a class of diffuse interface methods described by the Cahn-Hilliard and phase field equations for the temporal and spatial evolution of the composition and deformation fields and other relevant phase variables. One-dimensional analytical solutions were also to be developed both to test the numerical methods and to establish connections to physical systems.

During the early stages of the research program, two new areas of research related to systems with diffusion barriers were identified. The first area concerned phase formation and diffusional phase transformations in reacting systems subject to high electric current densities. Such high-current environments are common in lead-free solders, for example, and have important technological applications. The second area was an offshoot of the present work, and concerned theoretical modeling of phase evolution and cyclical amorphization of metallic alloys during ball milling.

Many aspects of this research were initiated and performed in conjunction with co-PI Perry Leo (PHL) at the University of Minnesota during working visits to WCJ at the University of Virginia in summers 2002-05, at professional conferences, and by regular phone discussions.

1.2 Phase Transformations with High-density Electrical Currents

One of the factors that contributes to the overall reliability of certain electronic devices is the reliability of solder joints in the device. Solder joints and metallization contacts are not in thermodynamic equilibrium and so interdiffusion can occur during use, leading to intermediate phase formation. One feature of such systems is that the growth kinetics of intermediate phases, the sequence of phase formation, and even the temporal power laws governing intermediate phase thickness can be affected by the electric current and electromigration [e.g., C.M. Chen and S.W. Chen, *Acta mater.*, 2461 (2002)].

As a guide to the simulation work, we derived an analytic expression for the intermediate phase thickness as a function of time in the presence of an electric current ignoring elastic effects and assuming the electrical conductivity of the phases is independent of composition. Asymptotic analysis of this equation yielded three different temporal power laws for the interphase thickness. When the electron flow aids the primary diffusing species, the intermediate phase thickens proportional to the square-root of time at short times while it is linearly proportional to time at longer times. Interestingly, this power-law behavior is opposite to that predicted and observed in the presence of interfacial kinetic barriers. When the electron flow hinders the diffusion of the primary diffusing species, a limiting thickness of the intermediate phase is predicted which is approached asymptotically with time. The results of this analysis are being prepared for publication.

The mechanism of electromigration is widely accepted to be the transfer of momentum from conducting electrons to diffusing ions on the lattice sites. The effect of electromigration on diffusion is described by the introduction of an effective charge into the driving force for diffusion; controversy surrounds whether the effective charge is a constant or whether it depends in some manner on the current density. We used a different approach based on classical electromagnetic theory and the conservation of energy and momentum in diffusing systems with electric current densities to show that the effective charge should depend linearly on the current density. We showed that the work done by the electric field can contribute both to the driving force and the activation energy for diffusion. We also derived an equation for the time to failure by electromigration that resembles Black's equation but which has an additional current

dependent exponential term. This work is being prepared for publication and generated much interest at PZ thesis defense. The results of this work is being prepared for publication.

A diffuse interface model accounting for mass diffusion, the formation of an intermediate phase, elastic deformation and high-density electric currents has been developed assuming cubic anisotropy in two dimensions. Elastic stress can arise from compositional strains and misfit strains between the phases; the elastic constants and the electric conductivity depend on both the local composition and phase.

The coupled governing equations for the composition field, phase field, elastic displacement and electric potential are solved simultaneously and numerically using a finite difference scheme and a Crank-Nicholson time-stepping method. The coupled Cahn-Hilliard and Allen-Cahn equations for the composition and phase fields are solved by non-linear multi-grid methods. The equations for elastic equilibrium and a quasi-stationary equation for the electric potential are solved using linear multi-grid methods. These techniques allow extension to additional phases and diffusing components.

Two-dimensional simulations of the intermediate phase growth were performed for systems with non-planar interfaces both in the presence and absence of a diffusion barrier. The temporal power laws obtained from the one-dimensional asymptotic analysis were observed in the simulations, with the phase thickness proportional to the square-root of time at early times and linearly proportional to time at later times. A limiting phase thickness was also observed when the electron flow was in the opposite direction to the primary diffusion flux. Growth rates were found to be strongly influenced by the relative electrical conductivities of the phases. The conductivity also was found to influence the morphological stability of a perturbation in the interface. For example, when the perturbed region had a higher conductivity than the phase into which it protrudes, a channeling effect of the electrons led to a thinner and pointed interface when the electron flow assists diffusion, but to a thicker and blunter interface when the electron flow hinders diffusion. In agreement with recent experiments, simulations also displayed a polarity effect for which the growth rate of an intermediate phase can be enhanced by changing the direction of electron flow. These simulation results are being sorted out for publications.

1.3 Gradient Energy Coefficient

We developed a new approach to calculate Cahn-Hilliard gradient energy coefficients from bulk thermodynamic data available through such commercial software as CALPHAD databases. Our approach permits the composition and temperature dependence of the gradient energy coefficient to be estimated for FCC and III-V type binary and ternary alloys. This approach will allow us to connect more realistically our model with experiment. The work on binary systems has been published and a second paper on ternary systems is planned.

1.4 Cyclic Amorphization during Ball Milling

In September 2003, WCJ and Dr. Harriet Kung discussed the possibility of using some excess DOE funds at UVa to initiate a combined experimental and theoretical study examining phase formation during ball milling. This work was then implemented as a joint project with Prof. J.K. Lee at Michigan Technological University and Prof. G.J. Shiflet at UVa. In 2004 a graduate student was employed at UVa to continue the experimental work on the ball milling of Co-Ti alloys. Unfortunately, he was unable to complete the research after several months of effort. Nevertheless, we were able to complete some initial experiments which permitted us to quantify physical parameters necessary to include in our theoretical development of driven systems during ball milling.

In the theoretical work, we used a system of thermodynamic balance equations to describe the time evolution of a two-phase, crystal-amorphous element of material undergoing ball milling. The thermodynamic state of the microstructure was assumed to depend on the phase fraction, the deformation state

of each phase, and the homogeneous temperature. Constitutive laws for the time rate-of-change of the deformation state of each phase and the phase fraction were developed. The constitutive laws for the deformation account for energy storage due to defect creation and for recovery processes that decrease the stored energy of the system. Three steady-state solutions were found for a variety of assumed constitutive laws; a state of crystalline phase only, a state of amorphous phase only, and a two-phase system consisting of a mixture of crystalline and amorphous phases.

The linear stability of each steady-state solution was analyzed and the results were displayed in bifurcation diagrams where the steady-state phase fraction was plotted as a function of the input power. For the simple analysis presented, a system comprised only of the amorphous phase was linearly unstable for all input power; the system comprised only of crystalline phase was linearly stable for small input powers but unstable for larger powers; and the two-phase system was stable for all physical solutions. For certain derived combinations of materials parameters and rate constants, the two-phase, steady-state system exhibits oscillatory behavior in which the phase fraction of the amorphous phase oscillates about the steady-state value (asymptotically stable spiral point). It was also shown how the effective power supplied to the milled material and the dissipation coefficient can be determined by monitoring the system temperature as a function of time. This thermodynamic approach can be extended to more complex driven systems and provides predictive capability.

2 Personnel

W. C. Johnson is Professor of Materials Science and Engineering at the University of Virginia. He received the UVA School of Applied Science and Engineering's Distinguished Faculty Award in 2005.

Peng Zhou is a graduate student majoring in Engineering Physics who successfully defended his Ph.D. thesis in July 2007. His thesis work was rated as outstanding by his examining committee. Peng will begin working in August 2007 as a visiting Assistant Professor of Applied Mathematics in the research group of Prof. John Lowengrub at UC-Irvine.

Hongbo Cong began working on the ball milling project after completing his M.S. degree. Unfortunately, he was unable to continue on the project.

3 Publications

The following publication have resulted from research supported entirely by grant DE-FG02-99ER45771. Several others stemming from Peng Zhou's thesis work are in various stages of preparation.

1. W. C. Johnson, "Superficial stress and strain at coherent interfaces", *Acta mater.* **48**, pp. 433-444, 2000.
2. W.C. Johnson and P.H. Leo, "Coarsening of self-stressed plates," *Scripta materialia* 43, pp. 1027-1032, 2000.
3. P.H. Leo and W.C. Johnson, "Spinodal decomposition and coarsening of stressed thin films on compliant substrates," *Acta materialia* 49, pp. 1771-1787, 2001.
4. W.C. Johnson, P.H. Leo, Y. Zhen, and S.M. Wise, "Spinodal decomposition in thin plates subjected to a temperature gradient," in *Modelling the Performance of Engineering Structural Materials II*, (TMS-AIME) pp. 203-214, 2001.
5. B.R. Hinderliter and W. C. Johnson, "Numerical method for the evolution of multiphase systems with non-equilibrium, stressed planar interfaces," *Mater. Sci. Engr.* B88, pp 1-8, 2002.

6. W.C. Johnson and P.H. Leo, "Sequences of phase formation in multiphase stressed plates," *Metal. Mater. Trans.* 33A, pp 1901-1911, 2002.
7. P.W. Voorhees and W.C. Johnson, "The thermodynamics of elastically stressed crystals," of over 200 pages for *Solid State Physics* - Invited review, Vol. 59, pp 1-201, 2004. DOE and NSF acknowledged.
8. J.K. Lee and W.C. Johnson, "On cyclical phase transformations in driven alloy systems: Thermodynamics," ICCES, 2005.
9. E.A. Lass, W.C. Johnson, and G.J. Shiflet, "Correlation between CALPHAD data and the Cahn-Hilliard gradient energy coefficient κ and exploration into its composition dependence," CALPHAD, 30, pp. 42-52, 2005.
10. E.A. Lass, P. Zhou, W.C. Johnson, G.J. Shiflet, "A method for the correlation of the Cahn-Hilliard gradient energy coefficient with bulk thermodynamic data," *Proceedings of International Conference on Solid-to-solid Phase Transformations*, Eds. J.M. Howe et al., TMS-AIME, pp. 87-92, 2005.
11. W.C. Johnson, J.K. Lee, and G.J. Shiflet, "Thermodynamic treatment of cyclic amorphization during ball milling," *Acta Mater.* 54, pp. 5123-33, 2006.
12. J.K. Lee and W.C. Johnson, "On cyclical phase transformations in driven alloy systems: A mass-action kinetics approach," *Materials Science Forum* 539-43, pp. 3207-12, 2007.
13. P. Zhou, W.C. Johnson, A. Lucente, J.R. Scully, "Solute-lean composition profiles around spherical nanocrystals in an amorphous matrix: Implications for corrosion resistance." Submitted. (DOE acknowledged by PZ.)

4 Invited and Contributed Talks

The following talks dealt with some or all of our DOE supported research:

1. Diffusion Conference, Zakopane, Poland, September 15, 1999: Effect of Interfacial Kinetic Barriers on Interface Motion. (Invited)
2. Pennsylvania State University, November 8, 1999: On the Sequence of Phase Formation in Coherent Solids. (Invited)
3. NIST, January 13, 2000: Sequence and Kinetics of Phase Formation in Coherently Stressed Thin Plates. (Invited)
4. SIAM meeting on Mathematics and Materials, Philadelphia PA, Spring 2000 (poster presentation on phase formation in thin films, with P.H. Leo and Steven Wise).
5. TMS Fall Meeting, October 10, 2000: Stress Induced Metastability in Thin Films. (Invited)
6. Computational Mechanics Meeting, August 2, 2001: Sequences of Phase Formation in Thin Films on Compliant Substrates. (Invited)
7. TMS Fall Meeting, November 6, 2001: Spinodal Decomposition in Thin Plates Subjected to a Temperature Gradient.
8. TMS Fall Meeting, November 6, 2001: Competitive Phase Growth in Stressed Thin Films (S. Wise presenter).

9. Michigan Technological University, August 9, 2002: Phase decomposition in stressed plates (Invited)
10. TMS Annual Meeting, Seattle WA Spring 2002: (Invited)
11. Korea University; Seoul, Korea; October 24, 2002: Diffusional phase transformations in small systems (Invited)
12. TMS Spring Meeting, Charlotte, NC, March 15, 2004: Cyclical Amorphization during Ball Milling (Invited)