MICROSTRUCTURAL EVOLUTION AND INTERFACIAL MOTION IN SYSTEMS WITH DIFFUSION BARRIERS

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1 Research Results During Funded Period

1.1 Research Goals

This research program was designed to model and simulate phase transformations in systems containing diffusion barriers. The modeling work included mass flow, phase formation, and microstructural evolution in interdiffusing systems. Simulation work was done by developing Cahn-Hilliard and phase field equations governing both the temporal and spatial evolution of the composition and deformation fields and other important phase variables.

In the original work one-dimensional analytical solutions were developed to test methods and to gain insight as to phase evolution in interdiffusing systems. This scope was expanded to include research related to systems with diffusion barriers. Two projects were successfully completed. The first involved microstructure evolution in thin film systems, while the second involved reacting systems under high electrical currents (electromigration). The latter project was based on experimental results in lead free solder systems.

Most of these research topics were initiated and performed in conjunction with co-PI Professor W.C. Johnson at the University of Virginia. This was accomplished by working visits by PHL to the University of Virginia over the course of the grant, and at conferences in those years. WCJ and PHL also had regular phone discussions.

1.2 One-Dimensional Phase Evolution in Alloys

We used Cahn-Hilliard type equations to model the evolution of microstructure in bulk alloys. This work emphasized the role of compositional strains and elastic effects on spinodal decomposition and coarsening. We found that elastic effects can favor nonequilibrium phases, can significantly alter kinetic paths, and can generate unexpected sequences of phase formation.

1.3 Phase Transformations in Thin Films

Just as in bulk systems, elastic stresses in solid thin films affect their mechanical and electrical properties. For example, stresses may lead to mechanical failure, such as fracture due to tensile stresses, and wrinkling and local loss of adhesion at the film-substrate interface [M. Ohring, *Materials science of thin films*, 2nd ed., Academic Press, San Diego, 2002]. Elastic stress can also be used in appropriate ways to improve the performance of certain electronic devices.

In order to examine these issues, as well as to develop a general tool to study phase evolution in the presence of diffusion barriers, we expanded the one-dimensional phase field model described above to study composition and phase evolution in two or three spatial dimensions. As a necessary step to make these methods computationally efficient, we developed new analytical results to calculate the elastic field owing to compositional strains in two and three dimensions, computationally a very time consuming step. These results give the elastic fields arising from compositional strains for an arbitrary composition field $c(x, y, z)$ in a thin film on a compliant substrate. Using these analytical solutions, the performance of the 'semi-analytic' elasticity solver used in the simulations was significantly improved.

These phase field model and the elasticity solver were used to study phase evolution in isotropic and anisotropic (cubic) films, where the film is either free-standing or attached to a substrate. Stresses in the film arise owing to both compositional self-stress and, in the film-substrate case, misfit between the film and substrate. Numerical simulations in both two- and three-dimensions were performed for the composition evolution. Results show that elastic strength, epitaxial misfit, elastic anisotropy, external mechanical loading and film-substrate geometry affect both the kinetics of evolution and the long-time metastable configurations of the evolution. In particular, we observe phenomena such as forming of columnar structure, switching of layers, and phase alignment in preferred directions.

1.4 Phase Transformations with Electrical Currents

Electromigration arises when an electric current is applied to a metal. It is caused by the interaction between the applied electric field and the positive ions, and the subsequent scattering of these ions and the conduction electrons (wind force). There is also a Coulomb force acting on the ions acts in the opposite direction to the wind force. Electromigration is believed to be the main cause of failure of integrated circuits and microelectronic devices. For example, in metallic interconnects (made of Al or Cu) the order of magnitude of electric current densities— 10^6 A/cm^2 —and the range of temperature at which the device operates— 100 ^{o}C or higher —drives electromigration flux large enough to cause void nucleation and growth that ultimately leads to a opening in the interconnect [K.N. Tu, *J. Appl. Phys.* 94, 2003]. Electromigration is also important in solder joints, even though the average current densities carried are two orders of magnitude lower than in interconnects. Electromigration in solder joints lead to excess growth of intermetallic compound that can cause microcracks to initiate [L.E. Felton et al., *Appl. Phys. Lett.* 54, 1989].

We studied the role of electic current on interdiffusion and phase formation in model solder joints. The solder joint and metallization contact are not in thermodynamic equilibrium and interdiffusion is likely to occur during use. Interdiffusion can lead to intermediate phase formation, the growth kinetics of which are directly affected by the electric current and electromigration [e.g., C.M. Chen and S.W. Chen, Acta mater., 2461 (2002)]. Together with W.C. Johnson and his group, we developed an analytic expression for the thickness of an intermediate phase as a function of time in the presence of an electric current. We neglected elasticity but considered that the phases can have different electrical conductivities. Results agree with the experimental work of Chen and Chen, who describe and measure the the growth rate of intermediate phases in Sn/Ag and Sn/Ni systems at different temperatures as a function of the applied current.

Chen and Chen's micrographs also show that one of the interfaces between the metal and the intermetallic is slightly corrugated, reminiscent of morphological instabilities at planar two-phase interfaces. This motivated us to perform a morphological stability analysis of growth in electromigrating systems. We considered small perturbations of the planar interfaces between the intermediate phase and the surrounding metals, and analyzed how the applied current will affect their morphological stability.

We found that that the primary factors that determine whether electric current can destabilize an interface are the direction of the electric current and the ratio of the conductivities across the interface of interest. Instability can only occur if these parameters are in specific ranges; for example, an interface can only be unstable if current enhances diffusion *and* the conductivity increases across the interface (in the direction of current). These are necessary but not sufficient conditions, as the detailed conditions for instability–e.g. the precise magnitude of the current required to destabilize an interface– depend on the thickness of the intermediate phase as well as other system parameters.

Based on these results, we conclude that electromigration driven instabilities in the systems considered by Chen and Chen are very unlikely. We continue to search for experimental cases in which electromigration driven instabilities are observed. We are also comparing our analytic results with W.C. Johnson's work using phase field modeling for electromigrating systems.

2 Personnel

- Perry Leo is Professor and Associate Head in the Department of Aerospace Engineering and Mechanics at the University of Minnesota.

- Yubao Zhen completed his PhD in February 2005. He is currently a Professor of Solid Mechanics at the Harbin Institute of Technology, Harbin, China
- Ana Rasetti completed her MS in Spring 2006. She is currently teaching high school.

3 Publications

The following publication have resulted from research supported entirely by grant DE-FG02-99ER45770. Ana Rasetti's work on interdiffusion and morphological stability is ongoing and papers from this work are in various stages of preparation.

1. P.H. Leo and M.H. Schwartz, The energy of semicoherent interfaces, *Journal of the Mechanics and Physics of Solids* 48, pp. 2539 – 2557, 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 *Modeling the Performance of Engineering Structural Materials II*, (TMS-AIME) pp. 203-214, 2001.
5. W.C. Johnson and P.H. Leo, Sequences of phase formation in multiphase stressed plates, *Metallurgical and Materials Transactions* 33A, pp. 1901-1911, 2002.
6. X. Li, J. Lowengrub, Q. Nie, V. Cristini and P. Leo, Microstructure Evolution in Three-Dimensional Inhomogeneous Elastic Media, *Metallurgical and Materials Transactions* 34A, pp. 1421-1431, 2003. DOE acknowledged for Leo's contribution.
7. Yubao Zhen and P.H. Leo, Three-dimensional compositional elastic fields in solid films on a compliant substrate, *Journal of Elasticity* 81, pp. 21 –50, 2005.
8. Yubao Zhen and P.H. Leo, Diffusional phase transformations in self-stressed solid films, *Thin Solid Films* 513, pp. 223 – 234, 2006.

4 Invited and Contributed Talks

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

1. Department of Theoretical and Applied Mechanics, Cornell University, April, 2007.
2. Department of Mathematics, University of California at Irvine, February, 2006.
3. TMS Anuual Meeting, San Antonio, TX, Spring 2005
4. TMS Anuual Meeting, San Francisco, CA, Spring 2005
5. Department of Materials Science and Engineering, Johns Hopkins University, March 2004.
6. TMS Anuual Meeting, Charlotte, NC, Spring 2004.

7. TMS Annual Meeting, San Diego, CA, Spring 2003.
8. TMS Annual Meeting, Seattle, WA, Spring 2002.
9. Department of Mathematics, Illinois Institute of Technology, Spring 2002.
10. Department of Engineering Science, University of Wisconsin, December 2001.
11. Gordon Conference on Thin Films, Summer 2000
12. SIAM meeting on Mathematics and Materials, Philadelphia PA, May 2000.