MURI Progress Report

This report is a brief summary of the progress made to date and the near term plans for the ONR MURI project on "Tailoring of Atomic-Scale Interphase Complexions for Mechanism Informed Material Design" involving the following five participating institutions: Lehigh University (LU), Carnegie Mellon University (CMU), University of Illinois at Urbana Champaign (UIUC), Clemson University (CU) and Kutztown University (KU). A program kick-off meeting was held on June 23rd, 2011 at Lehigh University attended by the P.I.'s of the program and the ONR program review committee headed by Dr. David Shifler.

Work conducted on **metal systems** has focused on understanding the nature, stability and role of complexions in Ni-Bi and Cu-Bi alloys (where the host element is underlined). These systems are well known to undergo metal embrittlement but the mechanism has remained illusive. In the *Ni-Bi system* LU and CU have further characterized a significant number of random (high-energy low-symmetry) grain boundaries and confirmed that a bilayer interfacial phase of Bi occurs at all random boundaries. They have developed a thermodynamic model for the atomic mechanism for the formation and stability of the bilayer and its role in embrittlement. These results were published in Science on September 23, 2011. LU has been developing an atomistic model to describe the surface segregation/phase behavior of Bi on Ni, which will then be extended to grain boundaries. CMU has been developing mesoscale models of grain boundary behavior to apply to these systems and is also measuring the grain boundary orientation and energy distributions of the same samples used in the Science paper. CU/LU will conduct a kinetic study to determine whether Bi slows or accelerates the grain boundary mobility. This has important implications to the role of interphase complexions in stabilizing bulk nanograin structures in metal systems (discussed in the following sections).

In the *Cu-Bi system* LU has conducted a preliminary study of Bi segregation using aberration corrected scanning transmission electron microscopy (AC STEM) of samples prepared by CU and found a bilayer interfacial phase of Bi at the grain boundaries analogous to what was observed in the Ni-Bi system. UIUC has conducted a study of the grain boundary diffusion of gold into polycrystalline thin films of Cu, with and without Bi, using SIMS. The initial results have led to the result that Bi segregation at low temperatures *slows down* the grain boundary diffusion in Cu by about an order of magnitude. A thermally induced transition in boundary diffusivity, consistent with complexion theory, returns the diffusivity to values a slightly lower (~factor of 2) than pure copper. This is contrary to what has been observed in ceramic systems such as alumina in which the diffusion was *enhanced* in bilayer phases and higher order complexions. Work is in progress to measure the effect of Bi on grain growth and to measure the GB orientation and energy distributions (at CMU) on identical samples.

These interesting results of a potential thermally induced monolayer to bilayer transition of boundary diffusion in the Cu-Bi system opens up a new line of investigation into how atomic-scale interphases might be exploited to stabilize nanograin metallic structures. This transition is likely associated with a large change in grain boundary energy, which may account for an observed reduction in grain boundary mobility. Schuh's group at MIT has shown in some highly publicized work that nanograins in electrodeposited metal alloys such as Ni-W can be dramatically stabilized against coarsening by grain boundary segregants. They have explained the suppression of nanograin growth in terms of a segregation-induced lowering of the grain boundary energy (to zero in certain cases). The MURI team proposes to explore the role of grain boundary interphases in the stabilization mechanism and to uncouple the influences on energy vs. mobility. Initially, they will prepare nanograin Ni by electrodeposition, with and without Bi and other GB segregants. UIUC will use the SIMS technique to measure GB diffusion over a range of grain sizes and dopant concentrations in nanograin metallic structures. They will vary the relative amount and type of interphase present. This will be correlated with simultaneous observations of the grain boundary phases by AC STEM (at LU) and measurements of the GB orientation and energy distribution (at CMU) and GB mobility (at CU), as well as theoretical modeling (at CMU/LU and CU).

The MURI team has also established collaboration with the group of Dr. Alexis Lewis at the Naval Research Laboratory on Al-Mg alloys. CMU will conduct GB orientation and energy distribution measurements and LU will conduct in-situ hot stage AC STEM on samples supplied by Dr. Lewis.

In work conducted on producing metal-complexionized **ceramic systems** (MCC's) LU and UIUC have been exploring a variety of processing approaches for incorporating complexions of Cu in alumina (polycrystals and bicrystals). LU is modifying a high temperature furnace to be able to precisely control the oxygen partial pressure and process samples at extremely low oxygen partial pressures where stable Cu-Al interphase complexions are theorized to form. After establishing the optimum processing conditions for metal complexion formation the MURI team will send samples to CMU for GB orientation/energy distribution analysis and to UIUC for diffusion measurements. LU will study the mechanical properties of the complexion phases and UIUC will measure their thermal transport properties. An important goal of this program for future work is to explore the effects of reducing the grain size to increase the relative amount of the interphase and to observe how this affects the material properties. The MURI team is collaborating with Imperial College London (ICL) on various aspects of this work, where ICL will study the free surface complexions and the MURI team will study the GB complexions in samples processed under the identical conditions, exploring the existence of a grain boundary to surface complexion analogy. The theory groups at CMU and LU have made progress in developing atomistic models to simulate grain boundary structures in alumina with the ultimate goal of extending them to incorporate the formation of interphase complexions of metals.

CMU will provide LU with samples of WC-Co composites for AC STEM characterization of the grain boundaries to clarify the existence and nature of the interphase complexions in this classic high-toughness high-strength composite. CMU will measure the GB orientation/energy distributions of the same samples.

The CU team is also preparing yttria stabilized zirconia (YSZ) specimens and is studying study how dopants/impurities will affect GB impedance. After initial screening with hot-stage impedance measurements, specimens will be sent to be characterized by LU, UIUC and CMU.

Finally, the MURI program has initiated a *seed project* exploiting interphase complexions to explore the possibility of creating a *novel hybrid ceramic material possessing a unique combination of properties*. They have been synthesizing alumina (a transparent and highly electrically insulating material) containing a GB interphase of indium tin oxide (ITO) (a transparent and highly electrically conducting material) in an attempt to create a highly conducting transparent alumina.