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Investigation of the Embrittlement of Bi Doped Cu Bicrystals by Aberration-Corrected Scanning Transmission Electron Microscopy

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The embrittlement of Cu grain boundaries (GBs) with Bi is a well-known and studied phenomenon most commonly observed as intergranular fracture.[1] Due to the propensity for Bi embrittled Cu to fail catastrophically during processing expensive and time consuming purification steps must be taken to ensure the integrity of the Cu. Though frequently observed, the mechanisms that promote such embrittlement in Cu-Bi systems are poorly understood. The segregation of Bi to the Cu grain boundaries is thought to embrittle the boundaries either by a size effect phenomenon or by changing the electronic structure of the Cu at the boundaries.[2, 3] The orientation of the Cu boundaries also appears to have an effect on the severity of the embrittlement observed.[4] A clearer picture of what is happening at the boundary on an atomic scale is needed to differentiate between the two proposed mechanisms and identify the dominant interaction. The ability to accurately study the nature of this embrittlement requires sub-nanometer imaging and analysis techniques as the changes in composition occur only at the boundary, a distance often less than a nanometer. More recent developments in microscopy, aberration-corrected scanning transmission electron microscopy (AC-STEM) in particular, make studies of local changes in structure and composition across such small distances possible. To ensure the identification of the embirttlement mechanism the investigation and analysis of the Bi doped Cu GBs must be paired with *in-situ* mechanical measurements of the same boundaries.

To systematically study the nature of Bi embrittlement of Cu, Cu bicrystals with specific orientations displaying a full range of embrittling behavior have been selected. Twist boundaries with orientations of 45, 33, 13.5, and 6 degrees were used in this study.[4] These Cu bicrystals were doped with Bi by being placed in contact with Bi shot and held at a temperature of 600°C for 3 days in a tube furnace. Electron transparent specimens were prepared using an FEI DB-235 Focused ion beam (FIB) instrument. FIB damage was removed and the specimens were then further thinned using a Fischione Model 1040 NanoMill. Figure 1 (a) shows a bright field image of a thinned 33° bicrystal specimen displaying a sharp contrast change across the GB. Convergent beam diffraction analysis for accurately determining misorientation between the two grains and boundary plane analysis was performed in a JEOL JEM-2000FX. High resolution transmission electron imaging (HRTEM), high-angle annular dark-field imaging (HAADF), and X-ray energy dispersive spectroscopy (XEDS) of the boundary were performed on JEOL JEM-2200FS and JEOL JEM-ARM200CF analytical electron microscopes. Figure 1 (b) and (c) show HRTEM and HAADF images of a 33° GB with the lower side aligned to a [110] type zone axis. Figure 2 shows a spatial difference of X-ray spectra on and off the GB from a 33° Bi doped bicrystal displaying the presence of Bi at the GB. In addition to TEM specimens, larger mechanical testing samples were prepared on the FIB instrument. These samples, along with a microelectromechanical system (MEMS) device allow for *in-situ* mechanical testing of the same GBs used in the TEM investigation. Combination of the TEM analysis results with the mechanical testing results has allowed the composition and electronic structure of embrittled boundaries to be directly compared to boundaries displaying no embrittlement.

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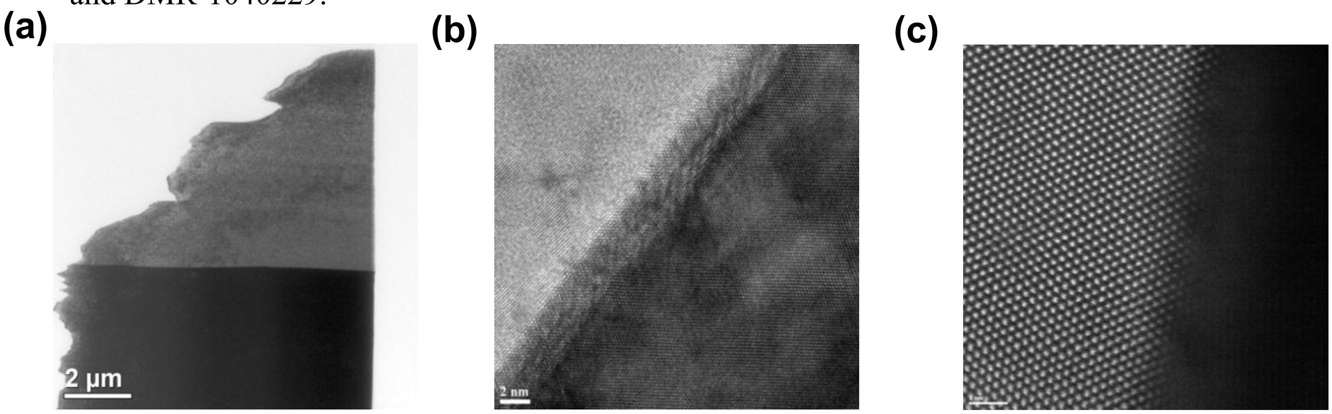

Fig. 1 33° Cu bicrystal prepared by FIB oriented with one side of bicrystal at [110] zone axis viewed with a) low-mag TEM, b) HRTEM, and c) HAADF-STEM

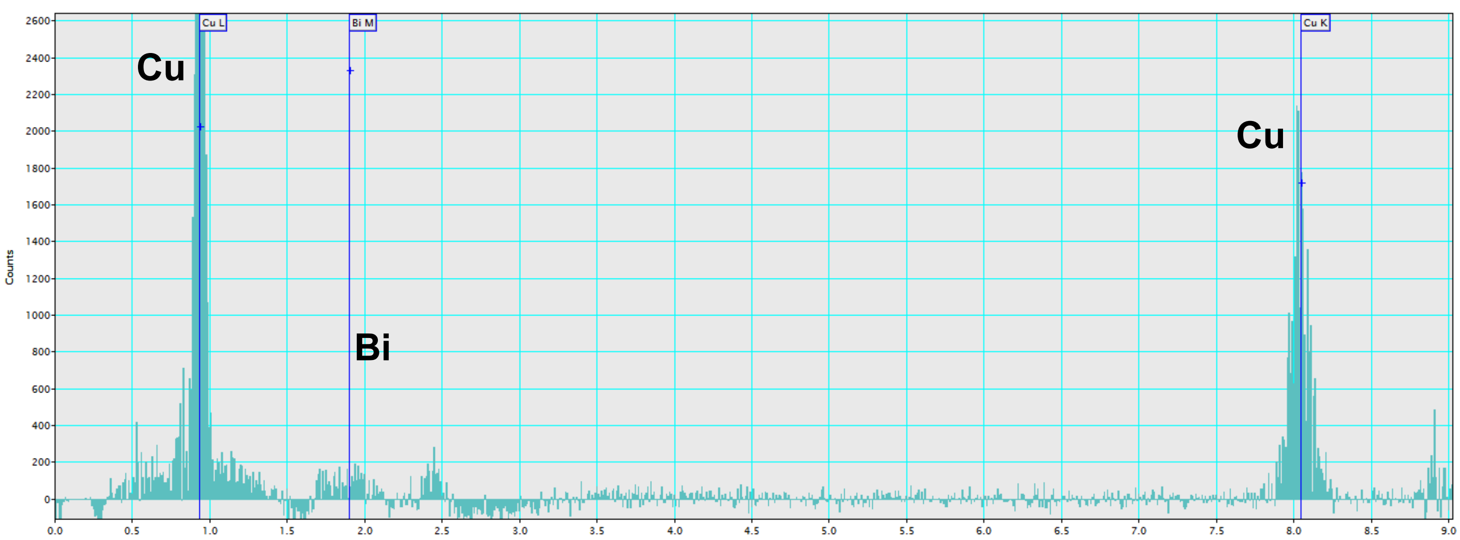

Fig. 2 XEDS spatial difference spectrum of Bi doped 33° Cu bicrystal prepared by FIB showing Bi segregation to GB

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