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Identification of a bilayer grain boundary complexion in Bi-doped Cu

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Using aberration-corrected scanning transmission electron microscopy, we have directly observed a bilayer grain boundary complexion in Bi-doped Cu, akin to that observed in Ni–Bi [Science, 333: 1730 (2011)]. In comparison with the Ni–Bi bilayer, the Cu–Bi bilayer appears to exist in a much narrower chemical potential window attributable to the fact that Cu–Bi and Ni–Bi have different pair-interaction potentials. Furthermore, these bilayers often form in conjunction with nanoscale faceting. This study demonstrates that direct imaging of the atom columns provides a more accurate understanding of the structure, chemistry and distribution of the adsorbates in a grain boundary and their role in embrittlement.

Keywords: Grain boundary segregation; Embrittlement; Complexion; Aberration-corrected STEM; Adsorption

Grain boundary (GB) adsorption and its role in embrittlement are classical problems in metallurgy that are still puzzling the materials research community today. Bi-doped Cu is one of the most extensively studied model systems for GB adsorption (segregation) and embrittlement. In 2004, two articles published in *Nature* [1] and *Nature Materials* [2], respectively, debated whether the embrittlement in Cu–Bi is caused by a size or an electronic effect; both studies were based on the assumption that Bi forms monolayer (submonolayer) adsorption at Cu GBs, and the foundation of such embrittlement studies would be modified if this monolayer adsorption assumption is not always true. In fact, an earlier Auger electron spectroscopy (AES) study by Chang et al. [3] suggested the occurrence of a GB "prewetting" transition (i.e. a GB adsorption transition analogous to that in Cahn's critical-point wetting model for binary liquids [4]) and the prewetted GBs are represented by ~2 monolayers of Bi adsorption as estimated by AES; a further study suggested that the prewetting transition occurs in conjunction with a "premelting" structural transition that increases GB diffusivity discontinuously [5]. However, subsequent AES studies using annular detectors (with better quantification capabilities) estimated the Bi adsorption levels (for Cu specimens annealed in contact with Bi liquid) to be ~1–4 nm thick Bi layer in 2001 [6]; this result was then revised to be <1 monolayer in 2008 [7]. On the other hand, Keast et al. used scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDXS) to quantify the GB excesses of Bi and determined it to vary from 0 to 2 monolayers in different GBs; consequently, they concluded AES was less accurate in quantification [8,9]. In this study, we used an aberration-corrected (AC) STEM and high-angle annular dark-field (HAADF) imaging to directly reveal the existence of bilayer adsorption in Cu–Bi, and we further suggest that the nanoscale faceting could complicate the interpretation of the measured GB adsorption levels by AES or EXDS.

There has been growing awareness emerging from experimental results (especially AC-STEM), as well as theoretical and computational predictions, that these grain boundary adsorbents can be treated as true equilibrium thermodynamic states of matter, stabilized by the abutting grains [10–12]. These grain boundary interfacial states have been referred to variously as interphases, intergranular films, pre-wetting films, quasi-liquid

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layers or complexions. For consistency we will refer to them as complexions in order to avoid any risk of confusing them with bulk phases. AC-STEM HAADF studies have revealed the existence of a series of discrete complexions including (nominally) "clean" GB's, monolayers/submonolayers, bilayers, trilayers, nanoscale films of equilibrium thickness, and wetting films of arbitrary thickness in oxides [10–13], metals [14] and semiconductors [15]. Of particular relevance here is the fact that the bilayer segregation was found to form ubiquitously in Ni–Bi [12], a system that exhibits embrittlement behavior similar to that of Cu–Bi. Accordingly, this motivated us to examine Cu–Bi using AC-STEM HAADF imaging in the present study. To prepare the samples, high-purity Cu foils (99.9999%; average grain size ~200 μm) were annealed at 700 or 953 °C for 5 h in a reducing atmosphere (flowing Ar/5% H_2) in contact with Bi–Cu liquids of the equilibrium compositions on the liquidus line (i.e. 22 at.% Cu at 700 °C and 80 at.% Cu at 953 °C) and water quenched. The cross-sections were examined by scanning electron microscopy (SEM) utilizing a Hitachi SU6600 field-emission microscope equipped with an EDXS analyzer. Transmission electron microscopy (TEM) specimens were extracted at regular intervals along the GBs of interest by a focused ion beam (FIB) instrument (FEI Strata DB 235). The specimens were characterized utilizing a JEOL 2200FS AC-STEM equipped with an EDXS analyzer and a HAADF detector.

During the annealing, the Bi-based liquids penetrated into the Cu GBs. The average liquid penetration lengths (for the micrometer-scale "Bi penetration tips" such as that shown in Fig. 1b) were measured to be 23 ± 5 μm at 700 °C and 80 ± 17 μm at 953 °C, respectively, based on SEM images for specimens annealed for 5 h. In a specimen annealed at 953 °C (Fig. 1), STEM characterization revealed a sub-100 nm thick intergranular film that is >100 μm long in front of the micrometer-scale tip with a gradually tapering thickness (Fig. 1b). As shown in Figure 1, the thickness of the nanoscale film tapered from ~75 to ~55 nm thick over a distance of ~100 μm, which gives a tapering dihedral angle of ~0.03°; in contrast, the apparent dihedral angle (projected on the cross-sectional plane) on the micrometer-scale shown in the SEM image in Figure 1b is ~15°. STEM and EDXS characterization showed that this tapering film is nanocrystalline Bi (Fig. 1c); it is likely that this film formed during the quenching as Cu precipitated out to adjacent Cu grains (noting that the equilibrium liquid at the annealing temperature of 953 °C contained ~80 at.% Cu). On the other hand, a "clean" GB without any observable Bi atoms in HAADF imaging was observed at a distance of ~280 μm from the micrometer scale tip (Fig. 1f and g).

Figure 2 shows a nanofaceted GB that was observed in a FIB specimen lifted at a distance of ~253 μm from the micrometer-scale tip (as schematically shown Fig. 1a), between the sub-100 nm thick tapering film (Fig. 1c) and the "clean" GB (Fig. 1d). The facets appeared as parallelograms as elucidated by the guidelines in Figure 2b. One set of facets was close to an edge-on orientation, for which adsorption of Bi was clearly observed. Upon careful tilting of the near-edge-on faceted GBs to an edge-on condition, bilayer adsorption of Bi atoms was clearly evident (Fig. 2c). The possibility of substantial adsorption of Bi on the other set of facets that was not edge-on cannot be ruled out, but it cannot be confirmed either.

A similar segregation behavior was observed in a faceted GB segment in a Cu–Bi sample annealed at 700 °C (Fig. 3). In this case the GB was aligned edge-on and two rows of Bi atom columns can be clearly distinguished in Figure 3c by virtue of their contrast in the HAADF images. EDXS analysis confirmed that these bilayers are Bi-enriched. A set of through-focus images was obtained to confirm that the segregation is truly a bilayer, not a result of the projection of atomic steps with monolayer adsorption of Bi in the GB.

Although the possible existence of bilayers was suggested by an AES study by Chang et al. [3,16,17], to the best of our knowledge this is the first direct TEM observation of such bilayers at Cu GBs. The only other

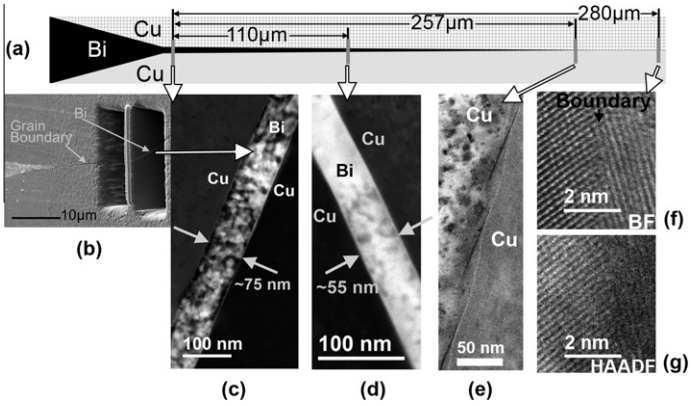

Figure 1. (a) Schematic illustration of wetting and adsorption of Bi at the grain boundaries in a Cu specimen annealed in contact with an equilibrium Bi–Cu liquid at 953 °C for 5 h. (b) SEM micrograph of the micrometer-scale Bi penetration tip, along with the GB after FIB sectioning. (c) A STEM HAADF micrograph of the same boundary indicates a Bi layer of ~75 nm thick. (d) HAADF-STEM micrograph of a grain boundary cross-section extracted at a distance of ~110 μm from the Bi tip; a ~55 nm thick intergranular Bi layer can be easily identified. (e) Bright-field (BF)-STEM image of a nanofaceted grain boundary segment. (f) BF-STEM micrograph of a "clean" grain boundary segment at a distance of ~280 μm from the micrometer scale Bi tip and (g) corresponding HAADF-STEM micrograph indicating a clean boundary.

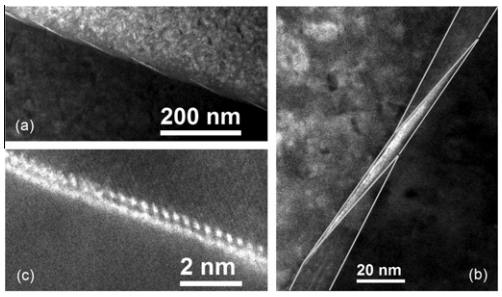

Figure 2. STEM HAADF micrographs of (a) a nanoscale faceted GB that was found ~257 μm from the micrometer-scale Bi penetration tip in the specimen shown in Fig. 1; (b) an enlarged view of a nanofaceted segment of the GB, in which the white acute parallelogram represents the facet close to an edge-on condition; and (c) the GB facet under an edge-on condition showing a bilayer complexion.

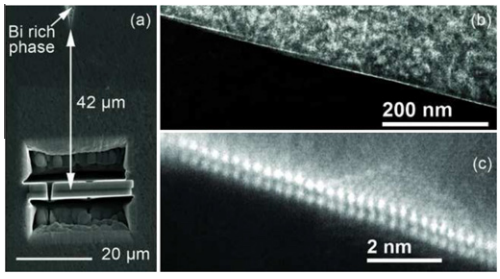

Figure 3. (a) SEM micrograph of a FIB specimen sectioned ~42 μm from the micrometer-scale Bi penetration tip in a specimen quenched from 700 °C. STEM HAADF micrographs showing (b) that this GB is faceted and (c) that bilayer adsorption of Bi atoms is evident at a facet in an edge-on condition.

direct observation of adsorption of Bi in Cu has been made on a special symmetric 36.87° [0 0 1] tilt GB in a bicrystal, where a monolayer (submonolayer) adsorption (without any drastic atomic rearrangement of the surrounding lattice) was observed [2]. In contrast, the GBs examined in this work were most likely general GBs that were randomly picked in the polycrystalline samples. This study further suggested that the nanoscale faceting (as shown in Figs. 2a and 3b) can make the adsorption levels measured by AES (or EDXS) more difficult to interpret. This is consistent with Keast et al.'s reports [8,9], in which measurements of GB excesses of Bi for more than 50 GBs in polycrystalline Cu samples with STEM-EDXS showed that segregation levels vary greatly in the general range of 0–2 monolayer equivalents; the authors also noted that special (especially Σ3) GBs are largely free of Bi adsorption. Similarly, a prior study also showed that a special GB in Ni–Bi was free of bilayer adsorption [12].

A point to be noted here is that the "monolayer equivalent" was calculated based on the density of a bulk Bi phase for most of the prior analytical studies. The structure and density of the adsorbed Bi atoms at GBs (such as those shown in Figs. 2c and 3c) are expected to be different from those in a bulk pure Bi phase, and entropy-driven mixing is inevitable at high temperatures. The nanoscale faceting shown in Figures 2a and 3b will complicate the situation further. Thus, great care should be exercised when interpreting the calculated "monolayer equivalent" numbers based on AES or EDXS measurements; the latter is at least more accurate in terms of the number of adsorbed atoms per unit area. In contrast, direct imaging of the atom columns may provide a more accurate measure of the structure and distribution of the adsorbates in the GB in many cases.

A prior study suggested the following mechanism of stabilizing a bilayer in Ni–Bi [12]. As Bi atoms penetrate along a general GB, they are adsorbed on Ni grain surfaces. Because Bi atoms bond more strongly to Ni grain surfaces than to themselves, the adsorption of Bi will "separate" a general GB into two grain surfaces, each with a coherently adsorbed "monolayer" of Bi; then, the two adsorbed Bi monolayers bond weakly and incoherently to each other. In such a mechanism, a bilayer complexion can be stable in a binary A–B system if: (i) B is a strong segregant (Bi segregates strongly in both Ni and Cu due to the large size misfit); (ii) B–B bonds are weak (Bi–Bi bonds are in fact very weak); and (iii) A–B bonds are relatively strong, i.e. the pair-interaction parameter is negative or slightly positive. The pair-interaction (regular-solution) parameters of Ni–Bi and Cu–Bi are estimated by the Miedema model to be -14.8 and $+14.2\ \mathrm{kJ\,mol^{-1}}$, respectively. This may explain the fact that bilayers are ubiquitously present in Ni–Bi but only observed in Cu–Bi in a narrow chemical potential window (between the sub-100 nm thick tapering Bi film and the "clean" GB as shown in Fig. 1). If this hypothesis is correct, the Bi-based bilayer should be completely unstable in metals where the pair-interaction parameter is large and positive. Experiments are currently in progress to verify this prediction.

Faceting of Cu GBs in presence of a minute amount of Bi is well documented in the literature [18–21]. In particular, Ference and Balluffi [18] demonstrated reversible faceting–defaceting transitions upon removal of Bi adsorption (via heating the specimen in vacuum) and reintroduction of Bi adsorption. The faceting in the present samples was observed in conjunction with bilayer formation on at least one set of facets (Figs. 2 and 3). We hypothesize that the bilayer formation is the root cause of the nanoscale faceting. According to the Gibbs isotherm, more adsorption will reduce GB energy more significantly. Thus, certain orientations of grain surfaces (facets) that have high numbers of adsorption sites will be stabilized upon adsorption of Bi and formation of a bilayer (recalling that each monolayer of the bilayer is coherently adsorbed on the adjacent grain surface). This will promote the faceting of a general GB.

In conclusion, a bilayer complexion was observed in faceted segments of random GBs in polycrystalline Cu samples annealed at 700 and 953 °C. In comparison with Ni–Bi where bilayers form ubiquitously, these bilayers in Cu–Bi appear to exist in narrower chemical potential windows. This difference can be explained by the difference in the pair-interaction parameters of the two systems in a preliminary thermodynamic model. These bilayers often form in conjunction with nanoscale faceting, and we hypothesize that the formation of bilayers is the root cause of this faceting. The observed bilayer and nanoscale faceting may play important roles in GB and liquid metal embrittlement, which have not been fully recognized in prior theoretical and modeling studies.

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