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Scripta Materialia 50 (2004) 565–569
Scripta MATERIALIA
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Anisotropic phenomena at interfaces in bismuth–saturated copper

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Received 15 October 2003; received in revised form 15 October 2003; accepted 25 November 2003

Abstract

Anisotropic Bi segregation, at surfaces of a Cu polycrystal saturated with Bi at 1223 K, changes the Cu equilibrium shape from a faceted spheroid displaying all orientations to an almost polyhedral shape with missing orientations. Surface cleaning, followed by annealing at ~573 K, leads to Bi readsorption from some grain boundary sources.

Keywords: Copper; Bismuth; Grain boundaries; Surfaces

1. Introduction

The present study stems from our interests in the anisotropies of surface and grain boundary (GB) energies, and the manner in which adsorption at those interfaces might modify their anisotropies. Surface adsorption, topography and orientation can be easily measured by combining surface analytic methods with scanning probe microscopies, and orientation imaging microcopy (OIM). The same type of information on GB's requires more indirect or laborious methods [1], since the description of GB character requires 5 crystallographic parameters (instead of 2 for surfaces), and because of the difficulty of investigating buried interfaces.

The copper–bismuth (Cu–Bi) system, which is the subject of the present investigation, has been widely studied because it displays both GB embrittlement due Bi segregation [2], as well as liquid metal embrittlement [3,4].

Several studies have been performed on Cu equilibrated in Bi vapor. TEM experiments on Cu–Bi bicrystals have shown that GB's become faceted at high Bi adsorption [5,6], and it has been established that Bi segregation depends on GB misorientation [7,8]. The quantity of Bi at segregated GB's has been found to vary from a few tenths to 2 or 3 monolayers [2,7,9].

This note presents qualitative experimental results on the faceting of copper surfaces produced by Bi adsorption. It also describes a method for identifying segregated GB's through the observation of Bi re-equilibration at surfaces in a scanning Auger microprobe (SAM) equipped with a heating stage.

2. Experiments

A 99.995% pure copper sample [2] in the form of a $14\times9\times2$ mm platelet was purified by annealing for 18 h at 1223 K under a flow of pure hydrogen. The resulting Cu surface was studied by OIM, in a scanning electron microscope equipped with a field emission electron gun (FEG–SEM), and in an atomic force microscope (AFM).

After removal of the GB grooves resulting from the initial hydrogen anneal, by light polishing with 1 μm Al_2O_3 and 0.02 μm SiO_2, the sample was re-annealed for 16 h at the same temperature and atmosphere in the presence of a Bi drop saturated with copper (located in the annealing furnace on another nearby copper platelet). During annealing, the pure copper sample undergoes Bi-saturation by vapor phase transport, without

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[2] Containing 7 ppm (by weight) O, 6 ppm S, <0.5 ppm Ag, <2 ppm P, 6 ppm Te, 5 ppm Fe, 3 ppm Sb, 4 ppm Sn, 4 ppm Ni, and 13 ppm of additional elements with less than threshold levels.

1359-6462/$ - see front matter
doi:10.1016/j.scriptamat.2003.11.058

direct contact with the liquid. The solubility of bismuth in solid copper has a maximum value (due to retrograde solubility) of about 10^{-4} at 1223 K [10]. Following equilibration in Bi vapor, this sample was quenched, and examined first by FEG–SEM, and then by SAM. This sample will be referred as sample #1.

A second sample (sample #2) was equilibrated in the presence of a Cu-saturated Bi drop, in flowing hydrogen, for 16 h at 1223 K. This sample was fractured so as to examine the GB's on the fracture surface.

3. Results and discussion

3.1. Pure copper

An OIM investigation of the surface orientations of all grains in sample #1 showed that they were essentially uniformly distributed. Images obtained by FEG–SEM and AFM showed that the surfaces of the grains were free of micro-facets. An absence of micro-facets is consistent with the known equilibrium crystal shape (ECS) of pure copper at 1253 K [11]. The copper ECS displays {1 1 1}, {1 0 0}, {1 1 0}, and possibly small {1 1 3} facets, separated by rounded surfaces. These rounded surfaces connect tangentially to the facets, so that all orientations are present on the ECS. Thus, pure Cu does not display any unstable surface orientations susceptible to faceting. The absence of micro-facets on the sample also demonstrated that the hydrogen annealing treatment successfully eliminated surface-active impurities, such as O and S, which are known to produce significant ranges of unstable surface orientations in copper [12,13].

3.2. Copper–bismuth alloy

3.2.1. Anisotropy of surface energy

After Bi-saturation, sample #1 was re-examined by FEG–SEM. This showed that the GB network had undergone only minor changes as a result of the Bi saturation treatment at 1223 K, but that the surfaces of all grains now displayed micro-facets. Fig. 1 is an SEM image of a typical micro-faceted surface region. Some surfaces consist of three facets (triangular pyramids) and others of two facets (long steps) on a scale of the order of 100 nm. From these results, one can conclude that, in comparison with the ECS of pure copper at similar temperatures, Bi adsorption at 1223 K leads to angular connections between facets and surrounding surfaces (i.e. produces unstable surface orientations), and possibly produces new cusps in the γ-plot (i.e. the polar plot of the surface energy as a function of crystallographic orientation).

Additional information on the ECS of Bi-covered Cu surfaces was obtained by fracturing sample #2. Examination of the intergranular fracture surface by FEG–SEM revealed the presence of micro-cavities on several GB's. The cavities, which represent "negative" crystals of the Bi-covered Cu surface, are highly faceted, as shown in Fig. 2(a). The faceted cavity shape is compared in Fig. 2(b) with a hypothetical ECS constructed by means of the Wulffman software [14] for assumed values of the anisotropy. This comparison shows that the ECS of the Bi-covered Cu surface consists of large {1 1 1}, {1 0 0} and {3 2 0} facets, and possibly small {1 1 0} facets. The images of the cavities do not allow a clear determination of whether the facets are connected by curved surfaces. However, the observations of the general faceting of grain surfaces, described above, ensures that most surface orientations are missing from the Cu–Bi γ-plot. The relative values of the surface energies of the faceted orientations used to produce Fig. 2(b) are $\gamma_{\{1\,1\,1\}} = 1$, $\gamma_{\{1\,0\,0\}} = 1.07$, $\gamma_{\{3\,2\,0\}} = 1.06$, $\gamma_{\{1\,1\,0\}} \geqslant 1.08$.

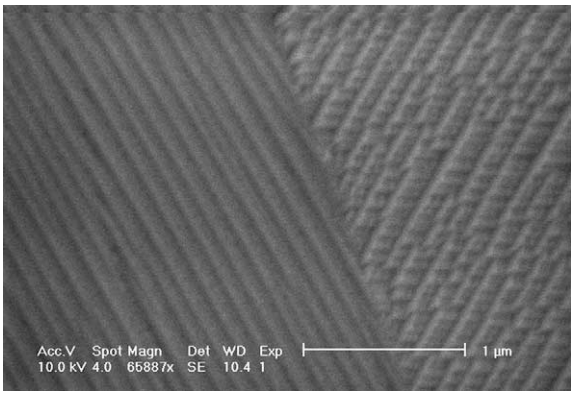

Fig. 1. SEM micrograph of a Cu surface equilibrated with Bi at 1223 K showing typical "pyramidal" and "stepped" micro-facets on two surfaces separated by a twin boundary.

The development of new facet orientations, as well as the disappearance of some stable surface orientations, as a result of adsorption in Cu–Bi is qualitatively analogous to the faceting of Pb by metallic adsorbates (Bi + Ni) [15]. Whereas it is generally accepted that non-metallic surface-active impurities (O, S, etc.) increase the surface energy anisotropy of metals, the present results provide evidence for the possibility that surface-active metallic impurities can be equally potent in increasing that anisotropy.

3.2.2. Anisotropy of surface segregation

Sample #1 was then transferred to the SAM, where Auger analysis of the surface revealed the presence of Bi, O and C. The latter two elements represent normal contamination of the surface resulting from exposure of the sample to laboratory air and the SEM environment. After light sputtering in the SAM to clean the surface of the effects of exposure to air (a process which also removed surface Bi) the sample was annealed at 623 K in order to re-equilibrate the copper surface with Bi. The kinetics of this process are sufficiently rapid to generate a

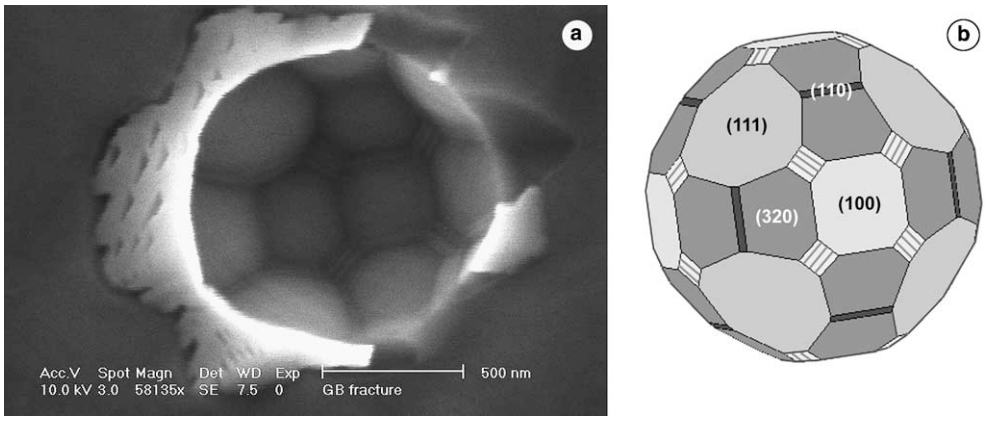

Fig. 2. (a) A GB pore in the shape of a truncated negative crystal of Bi-saturated copper equilibrated for 18 h at 1223 K. The regions between the {3 2 0} facets consist of a series of steps, as do those between {3 2 0} and {1 0 0}. (b) Half of the the equilibrium crystal shape corresponding to the previous image, calculated using the Wulffman software with the relative surface energy values given in the text [14].

Bi-covered surface in ~4 h. A chemical map of the sample surface using the Auger Bi-peak, taken at the end of the equilibration period, is displayed in Fig. 3. This shows that Bi adsorption is anisotropic. Although Bi segregates to all grain surfaces, the Bi-coverage differs by about 25% between maximum and minimum coverages. Such anisotropy of equilibrium surface coverage has previously been observed in other alloy systems (e.g. [15]).

3.2.3. Anisotropy of surface diffusion

The regenerated Bi-covered surface was sputtered clean one last time, and sample #1 was reheated to 533 K. The kinetics at this temperature were slow enough to allow many areas to be monitored periodically by Auger Bi mapping so as to determine several features of the re-equilibration process.

During the course of the anneal, the surface composition of a group of grains was monitored by acquiring periodic Auger spectra. These measurements showed that the surface slowly regains adsorbed Bi, without the appearance of detectable traces of either S or O, confirming that the observed micro-faceting after equilibration with Bi resulted from Bi adsorption, rather than the segregation of other common surface-active Cu contaminants.

Evidence of surface diffusion anisotropy was found. This is illustrated in Fig. 4, which shows Bi spreading from a small Bi source to form an elliptical halo over the surface of a single grain of orientation (1 1 2). The fastest diffusion direction is [−1 1 0]. In fcc materials, anisotropy of surface diffusion is to be expected on all but {1 1 1} and {1 0 0} surfaces. Circular Bi diffusion halos growing around Bi particles have been observed, for example, on the Cu(1 1 1) [16].

3.2.4. Anisotropy of GB segregation

An Auger Bi-map taken early during the 533 K anneal is displayed in Fig. 5. This shows that certain,

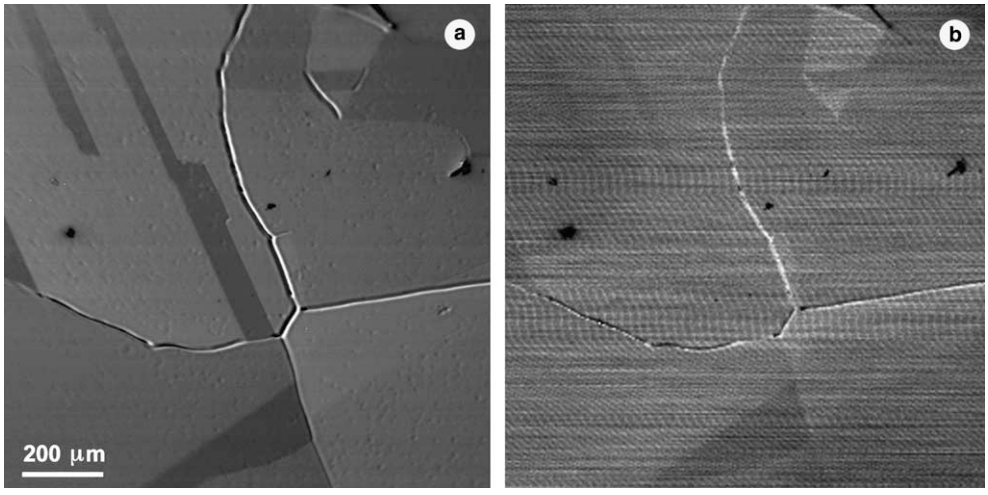

Fig. 3. Anisotropy of Bi segregation on Cu at 623 K: (a) SEM micrograph showing grooved GBs and twin boundaries; (b) Corresponding Bi Auger map: brighter regions have higher Bi adsorption.

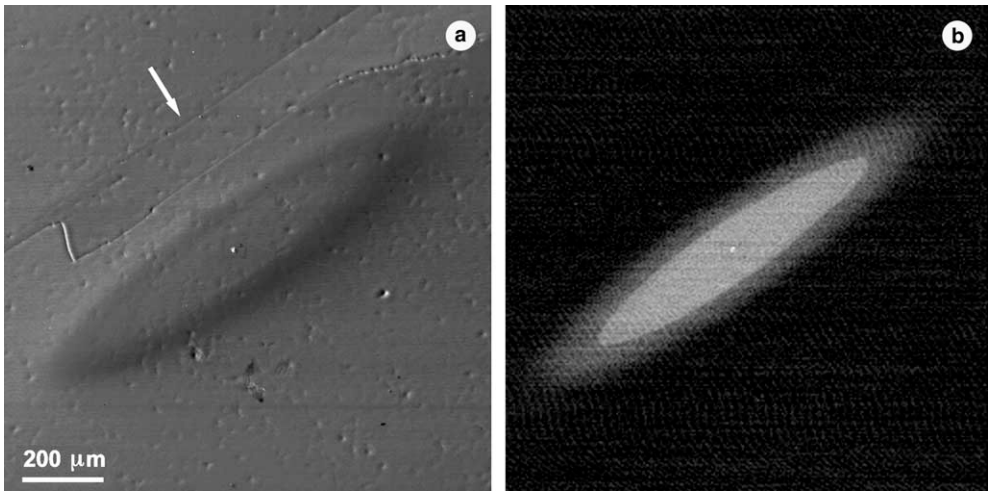

Fig. 4. Anisotropy of Bi diffusion over copper at 533 K: (a) SEM map at 3 keV showing an elliptical Bi halo close to a twin boundary (arrow); (b) Corresponding Auger Bi map.

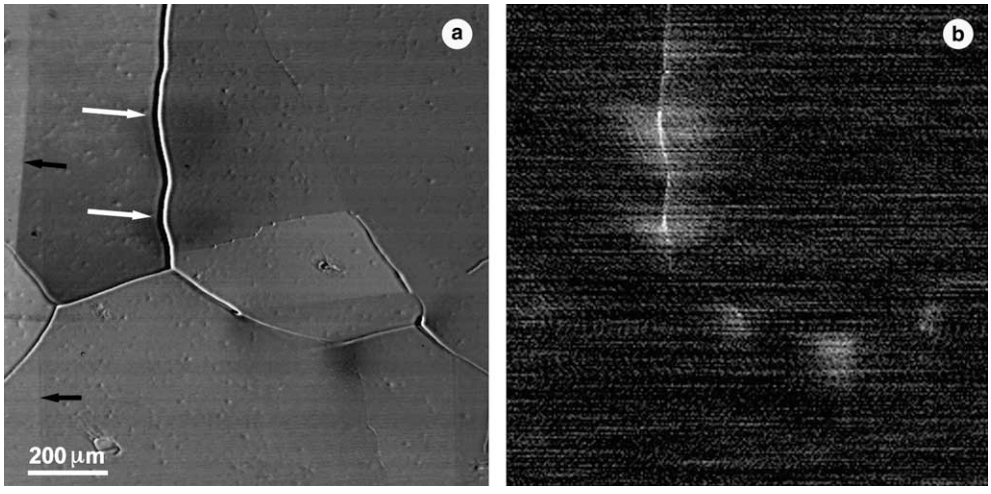

Fig. 5. Anisotropic GB sources of Bi at 533 K: (a) SEM micrograph; (b) corresponding Bi Auger map.

though not all, GB segments and triple points act as the sources of Bi for surface coverage restoration. The fact that certain GB's emit Bi only from some segments demonstrates that the strength of a source can depend on GB inclination. In particular, two regions which emit Bi strongly (indicated by white arrows in Fig. 5) are both located on left-pointing GB bumps, indicating locations of similar inclination. Other related observations may be summarized as follows:

(a) Twin boundaries do not act as Bi sources (black arrows in Fig. 5).
(b) Certain GB's appear to sweat out Bi along their whole length, even though they are curved (indicating that some GB's act as sources, independently of local inclination).
(c) Other GB's do not emit any Bi, indicating an anisotropy in the quantity of Bi adsorbed at GB's.

Point (c) above is consistent with previous observations of Bi segregation on Cu–Bi fracture surfaces, mentioned earlier, that indicate the existence of a distribution in the strength of GB segregation, ranging from a few tenths to a 2 or 3 monolayers [2,7,9].

The fact that the re-equilibration of the surface with Bi occurs by the regurgitation of Bi from GB's is interesting. The bulk concentration of Bi at the original equilibration temperature of 1223 K is only of the order of 10^{-4}, and restoration of the Bi surface concentration of about one monolayer would require segregation to the surface of all the Bi contained in some 10^4 bulk atom layers of the Cu–Bi alloy, by the slow process of volume diffusion. Thus, Bi is more readily supplied by GB's, since many of them contain much higher than bulk concentrations of Bi, and since GB diffusivity is much greater than volume diffusivity. Since GB diffusivity is also anisotropic, it is reasonable to assume that those

GB's (with high free volume) that are able to accommodate high concentrations of Bi, are most likely those which also display high diffusivity.

3.2.5. Usefulness of experimental approach

As far as we are aware, the experimental approach of loading GB's with segregant, and then observing the re-equilibration of the cleaned surface, so as to infer the strength of GB segregation on different GB's, is quite new. A few years ago, Ma and Balluffi [17] studied GB diffusivity by monitoring the rate of arrival of a diffusing species on one side of a thin foil that had been coated with diffusing species on the other side. However, both the purpose and implementation of that approach were quite different. The experimental approach developed here is viewed as potentially valuable in our ongoing efforts to establish a relationship between GB segregation and GB character (as described by the five macroscopic degrees of freedom of a GB in orientation space).

Acknowledgements

This work was supported by the MRSEC program of the National Science Foundation under Award Number DMR-0079996. DC would also like to acknowledge support by the European Community through a TECLA grant #FIKW-CT00092-2000.

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