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LOSS OF GRAIN BOUNDARY SEGREGANT DURING ION MILLING

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Bismuth segregates to grain boundaries in copper at intermediate temperatures (400-800°C).[1] Currently, x-ray microanalysis is being used to measure the degree of equilibrium segregation as a function of boundary character. As part of that study, transmission electron microscopy specimens were prepared by several techniques in order to select that method which produced optimum specimens. Electropolishing produced specimens of marginal quality because of preferential grain boundary attack. On the other hand, ion-milling produced good, thin specimens with little or no boundary attack. However, x-ray microanalysis on specimens ion-milled at room temperature indicated no bismuth segregation, whereas analysis on electropolished specimens indicated bismuth segregation. A loss of bismuth from the ion-milled specimens was proposed to result from the high vapor pressure of bismuth at slightly elevated temperatures. The use of a liquid nitrogen cold stage during ion-milling minimizes the loss of bismuth. It is likely that beam heating during ion-milling is a contributing factor in this process and must be controlled.

Experimental

A copper-bismuth alloy was prepared by a method similar to that used by Michael and Williams.[1] Bismuth was evaporated to ~0.15 μm thickness on both sides of high-purity copper sheet of 0.25 mm thickness. The sheet was annealed in evacuated quartz capsules at 400°C for 16 days in order to homogenize the material. Scanning electron microscopy (SEM) was used to determine the redistribution of bismuth on the scale of the grain size, ~30 μm. Specimens for analytical electron microscopy (AEM) were initially prepared by electropolishing. However, preferential etching occurred at the grain boundaries, producing marginal specimens. On the

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other hand, ion-milling with 6 kV Ar^+ ions in a Gatan ion miller produced good, thin specimens with little or no boundary attack. Both standard and liquid nitrogen cooled specimen stages were used for ion-milling.

A Philips EM400T-FEG microscope equipped with an EDAX 9100 analyzer provided high spatial resolution AEM capability. X-ray microanalysis was performed in the scanning transmission electron microscopy mode with a ~2-nm-diam. probe on boundaries oriented parallel to the electron beam. Since the Philips EM400T permits direct imaging of the probe, it was possible to avoid aberrated probes and also to measure the probe size and current density by scanning the magnified image of the probe over a 100 μm entrance aperture to a Gatan 607 electron energy loss spectrometer. Care was taken to minimize the influence of such experimental conditions as hole count[2], coherent bremsstrahlung radiation[3,4], and electron channeling[5], which can have detrimental effects on quantitative analysis. A Gatan liquid-nitrogen-cooled specimen holder was used to minimize contamination under the fine probe, with only a small increase in specimen drift rate. However, the probe could be easily maintained on boundaries by adjustments made on the basis of monitoring the intensities of two reflections in the diffraction pattern, one from each grain. The composition of the excited volume was calculated from the measured Cu Kα and Bi Lα intensities with the standardless thin foil approach developed by Zaluzec.[6]

Results

Scanning electron microscopy of the region ~1 μm below but parallel to the original surface indicated a nearly continuous film of bismuth ~0.4 μm thick at the grain boundaries [Figure 1(a)]. This film is obviously not equilibrium segregation, but the formation of a second phase, presumably from liquid bismuth attack of grain boundaries during the anneal. However, backscattered electron images from a transverse section of the sheet showed that the continuous film does not extend into the interior of the material, from which specimens for the AEM studies are prepared. Isolated precipitates of essentially pure bismuth were observed at grain boundary triple points throughout the thickness of the sheet [Figure 1(b)]. Their presence indicates that bismuth has penetrated the entire thickness along the grain boundaries.

Initial x-ray microanalysis performed on the specimens of marginal quality produced by electropolishing indicated bismuth segregation to high-angle grain boundaries and incoherent twin boundaries. No bismuth was detected by x-ray microanalysis of the matrix. No second phase was detected by either imaging or diffraction. Therefore, the bismuth enrichment at boundaries is associated with equilibrium segregation. On the other hand, no segregation was indicated by similar analyses on boundaries in ion-milled specimens nominally prepared at room temperature [Figure 2(a)]. No significant Bi M or L peaks were detected from the matrix or at grain boundaries in such specimens. At first, this inability to detect bismuth segregation was attributed to the variability of segregation with boundary character. However, after a multitude of boundaries were checked, without any indication of bismuth segregation, it was suspected that the bismuth was being lost from the boundaries during specimen preparation. In order to test this hypothesis specimens were ion-milled while at cryogenic temperatures. X-ray microanalysis of these specimens indicated the presence of bismuth at various high-angle grain and incoherent twin boundaries. A typical example is given in Figure 2(b), where the excited volume contains ~2.8 at. % Bi. Since the bismuth is concentrated at the grain boundary the actual bismuth composition at the boundary is significantly higher. Simpson et al[7] have shown that a false indication of boundary segregation can result from the preferential collection of one element at surface grooves associated with a boundary. However, x-ray microanalysis of boundaries tilted away from edge-on configuration has shown that the segregation detected was associated with the boundary plane and not with the intersection of the boundary with the foil surfaces. The measured bismuth segregation was genuine and not a specimen preparation artifact. Therefore, the absence of detectable bismuth segregation in the specimens ion-milled at nominally room temperature must be associated with the loss of bismuth during specimen preparation. Bismuth has a relatively high vapor pressure and may simply be lost by evaporation.

One other test of this proposed loss mechanism was performed. A long, straight high-angle grain boundary was selected in a specimen ion-milled at low temperature. The bismuth level in the excited volume was ~1.9 at. % Bi for this boundary [Fig. 3(a)]. The same boundary was reexamined after a brief ion-milling at nominally room temperature under reduced milling conditions (300 s and 3 kV), which removed <0.5 μm of material. No bismuth segregation was detected [Fig. 3(b)]. As the segregation is expected be approximately constant along a given boundary, the proposed loss of bismuth from boundaries during nominal room temperature ion-milling was confirmed.

The question of beam heating during ion-milling is relevant to this problem. Beam heating of 100-150°C has been reported for specimens clamped during milling.[8] However, it has been shown that specimen temperatures as high as ~370°C can be realized for some specimens.[9] At 370°C, elemental bismuth would be liquid and its vapor pressure would be ~10^{-5} Pa (~10^{-7} torr). This would be sufficient for bismuth to evaporate from the free surface. However, a large portion of the segregated bismuth has been lost from boundaries in regions ~50 nm thick. Such loss indicates sufficient mobility of bismuth along boundaries to permit bismuth to diffuse to the free surfaces to be lost. Cooling during ion-milling prevents bismuth loss in two ways; it reduces the rate of evaporation at the free surface and reduces diffusion of segregant to the free surface.

Conclusions

The loss of bismuth segregated at high-angle grain and incoherent twin boundaries during nominal room temperature ion-milling has been demonstrated. The loss appears to be related to beam heating and the high vapor pressure of bismuth at slightly elevated temperatures. Such high vapor pressures are not uncommon for strong segregants in metallic systems (e.g. As, Cd, S, Sb, and Te). Therefore, care must be taken in specimen preparation for AEM measurement of such segregation. Similar problems may occur in ceramic systems, where greater beam heating is possible.

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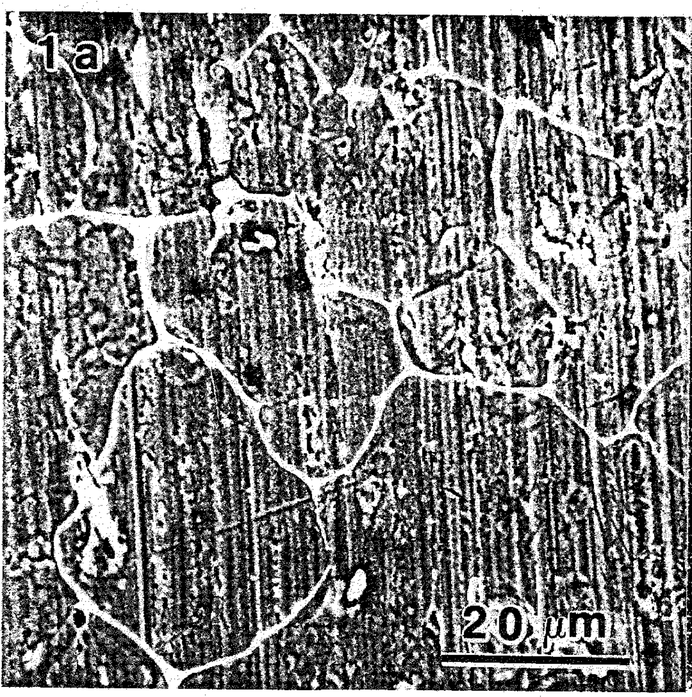
Figure captions

FIG. 1.--Scanning electron micrographs of Cu-Bi alloy. (a) Backscattered electron (BSE) image of region ~1 μm below coated surface prepared by mechanical grinding. Continuous film of bismuth ~0.4 μm thick revealed at grain boundaries. (b) BSE image of transverse section of sheet indicating isolated precipitates of bismuth at grain boundary triple points (arrowed) and absence of detectable continuous grain boundary film in bulk of specimen.

FIG. 2.--X-ray microanalysis of high-angle grain boundaries in Cu-Bi alloy. Note: Cu $K\alpha$ peaks are 4x full scale. (a) X-ray spectrum from boundary in specimen ion-milled at nominally room temperature. No significant bismuth peaks present. (b) X-ray spectrum from boundary in specimen ion-milled at low temperature. Bismuth content of excited volume ~2.8 at. % Bi.

FIG. 3.-- X-ray microanalysis of same high-angle grain boundary. Note: Cu $K\alpha$ peaks are 4x full scale. (a) X-ray spectrum of boundary in specimen prepared by low temperature ion-milling. Apparent bismuth content of excited volume ~1.9 at. % Bi. (b) X-ray spectrum from same boundary recorded after brief ion-milling under reduced conditions (300 s and 3 kV), at nominally room temperature. No bismuth segregation detected.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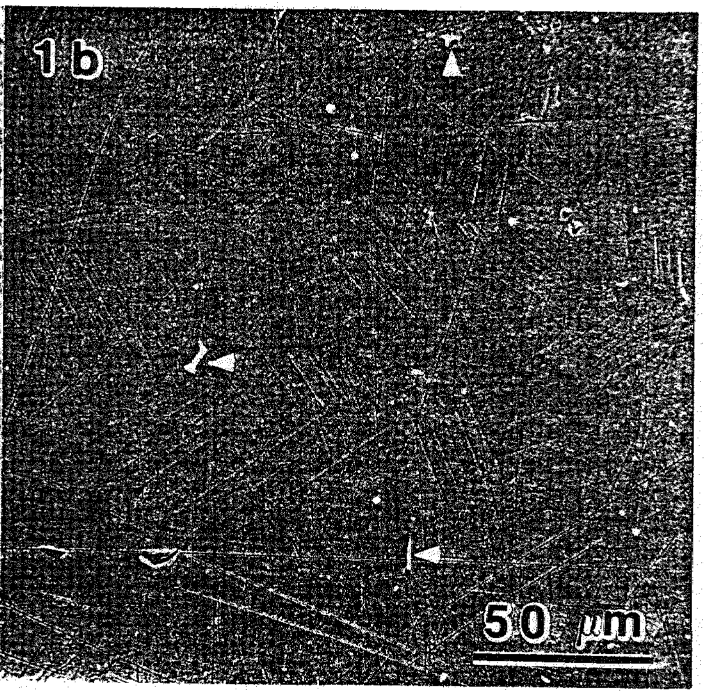
20 μm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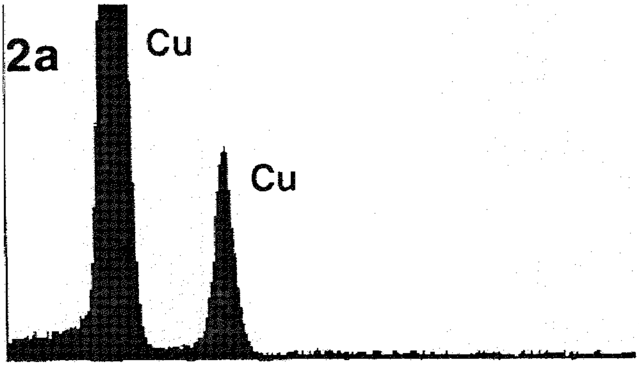
50 μm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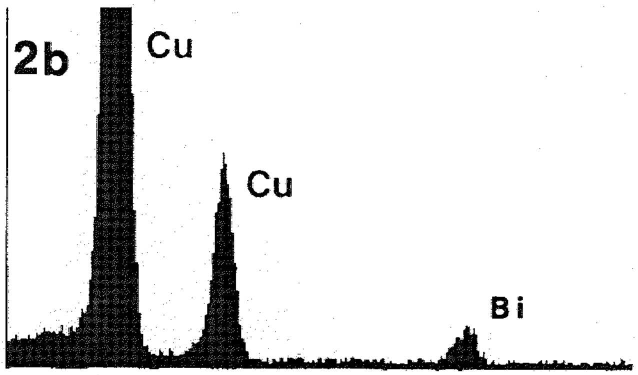
Cu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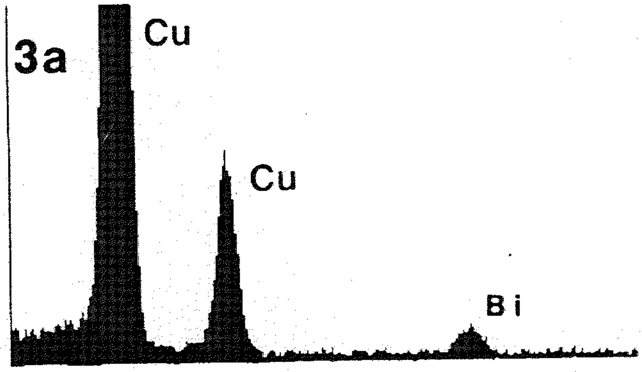
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Cu
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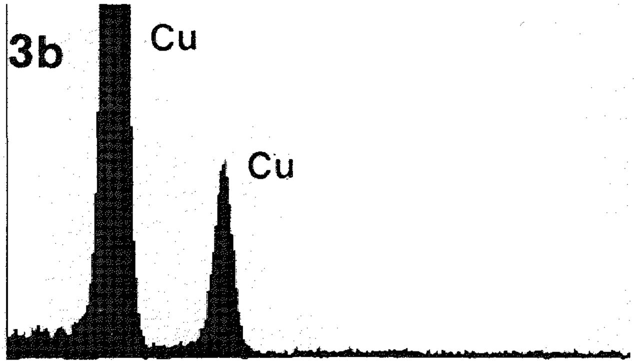
3b
Cu
Cu