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Segregation of Bismuth to Triple Junctions in Copper

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Abstract: Bismuth segregation in copper has been studied using energy-dispersive X-ray spectrometry (EDX) in a JEOL 2010F transmission electron microscope. In addition to the expected solute enrichment at grain boundaries, we have observed extremely high concentrations of bismuth at certain triple junctions, with significantly greater enrichment factors than in the adjacent grain boundaries. It is shown here that the triple junction segregation is a function of the parameters of the grain boundaries at the triple line, and existence of this type of segregation implies that the affected triple junctions embody excess free energy. At least one of the observed triple junctions may not obey the usual Σ-product rule, as a result of deviations from the exact coincidence misorientations.

Key words: segregation, microanalysis, grain boundaries, triple junctions, copper, bismuth

Introduction

The segregation of bismuth to grain boundaries in copper has been widely known and studied for many years (e.g., Spencer et al., 1957; Powell and Mykura, 1973; Baumann and Williams, 1981; Michael and Williams, 1984; Ference and Balluffi, 1988; Menyhard et al., 1989). This alloy system arguably represents the classic example of grain boundary solute segregation and is widely used as a model system for experimental studies regarding interfacial embrittlement, grain boundary structure, or experimental techniques.

Triple junctions are the lines where three grain boundaries meet, and they are essential features of the microstructure of polycrystalline material. Nevertheless, only a few studies of triple junction behavior have been reported, in contrast with the profusion of studies of grain boundaries. Recently, interest in triple junctions has grown for a number of reasons. Triple junctions are preferential sites for chemical attack (Palumbo and Aust, 1989), they are implicated in the formation of electromigration damage in thin conductor lines (Schreiber, 1986; Huang and Yang, 1989), and they can represent a large fraction of the material volume in nanocrystalline materials (Palumbo et al., 1990). In this preliminary paper, we report a finding of segregation to triple junctions that varies strongly from junction to junction and can exceed the segregation at grain boundaries by a large factor.

This type of segregation has not previously been reported, to the best of our knowledge. It may have important technological consequences.

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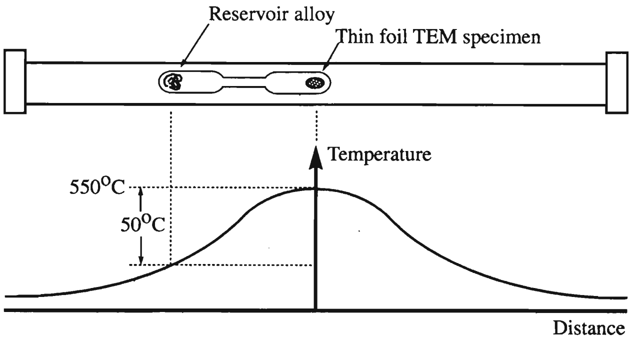

Figure 1. Experimental setup for bismuth doping.

Materials and Methods

Thin polycrystalline films of copper were prepared by evaporating copper onto freshly cleaved (001) rocksalt substrates in a background vacuum of approximately 10^{-7} torr (13 μPa). The substrate temperature was 250°C. The thickness of copper film was estimated to be 100 nm from the deposition rate, and the rocksalt was removed by dissolving it away in distilled water. Bismuth was doped into the grain boundaries of copper using the conditions suggested by the work of Ference and Balluffi (1988). The copper films were annealed with a copper-bismuth reservoir alloy (0.5 at.% Bi) encapsulated within a quartz tube in a vacuum of 10^{-7} torr, as depicted schematically in Figure 1. The copper film and reservoir alloy were separated by 20 cm. The furnace temperature was adjusted so that the copper polycrystal film was kept at a temperature of 550°C, while the reservoir alloy was at 500°C, for 24 h. The difference in temperature ensures that bismuth diffusion out of the reservoir alloy is the rate-limiting step in the doping process, and surface accumulation of bismuth on the copper specimens is avoided. Using this treatment, the diffusion distance for bismuth in the grain boundaries of the copper specimen is estimated to be a thousand times the foil thickness, so the concentration in the grain boundaries should be fully equilibrated through the film thickness. Bismuth-doped specimens were observed in a JEOL 2010F field-emission-gun transmission electron microscope (FEG TEM) equipped with an energy-dispersive X-ray detector and Gatan image filter (GIF). By virtue of its high brightness, the microscope is capable of producing a probe size of less than 1 nm with good beam current.

Results

We have examined many low- and high-angle boundaries in our polycrystal films; however, none of them exhibited the faceting behavior observed by Ference and Balluffi (1988). The general structure of the polycrystal copper film after bismuth doping is shown in Figure 2. Figure 2 is a broad view of seven grain boundaries and three triple junctions in a bismuth-doped specimen. The misorientations of the grain boundaries in this image were determined by computer-aided Kikuchi-line analysis (Chen and King, 1987) and their characterization in terms of the coincidence-site lattice model is indicated in Table 1. The Σ-value for each of the boundaries is identified by the application of Brandon's criterion (Brandon, 1966) for the maximum al-

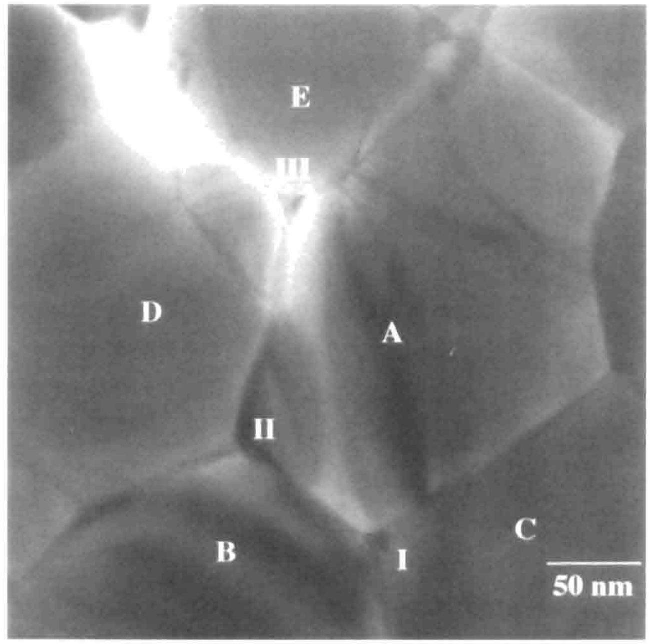

Figure 2. A broad view of seven grain boundaries and three triple junctions in a bismuth-doped specimen.

Table 1. Misorientation Data for Observed Boundaries

Boundary designator	Rotation axis	Misorientation angle	Σ-value
AB	[−0.9785, 0.1987, 0.0240]	106.8°	21
BC	[0.8874, −0.3293, −0.3233]	95.9°	5
AC	[0.9010, −0.4187, −0.0851]	160.68°	105
BD	[−0.9984, −0.0528, −0.0200]	134.5°	29
AE	[0.9853, −0.1460, −0.1003]	162.6°	21
DE	[0.9980, −0.0530, −0.0210]	169.2°	25
AD	[−0.9008, −0.2076, −0.3822]	31.45°	random

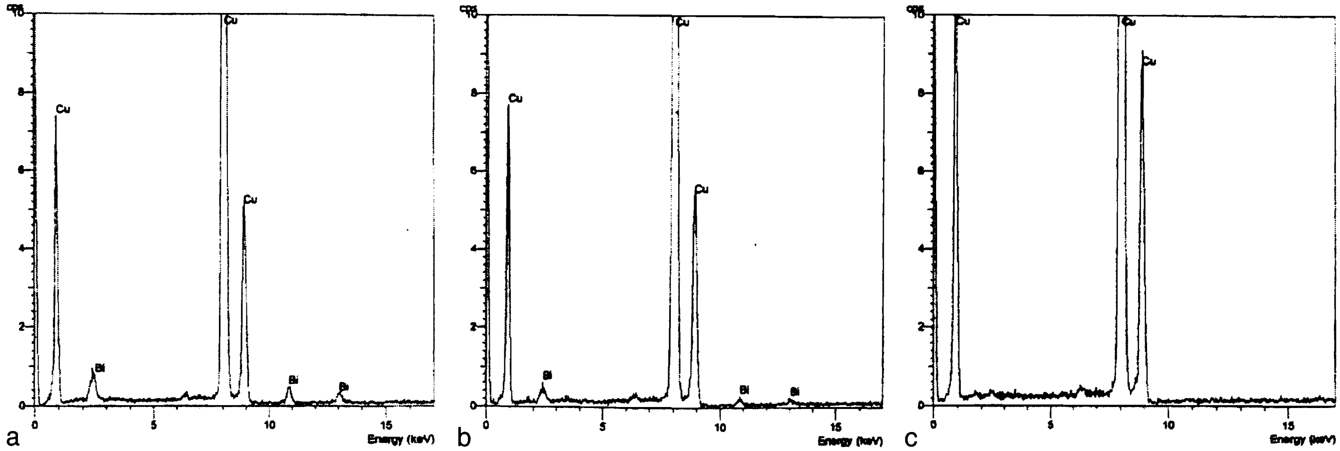

Figure 3. Typical EDX spectra, obtained from a triple junction TJI (**a**), grain boundary AB (**b**), and the interior of grain A (matrix, **c**).

lowable deviation from the exact coincidence misorientation. The copper film obtained in our expeiment was a [100] textured columnar polycrystalline film. The rotation axes for grain boundaries AB, AC, BD, AE, DE, and AD are within 10° of [100]. The misorientations of grain boundaries AB, BC, AC, BD, AE, DE in Figure 1 are close to CSL systems of Σ21a, Σ5, Σ105, Σ29, Σ21a, Σ25. AD is designated a "random" boundary. While the misorientations of AB and AE are close to Σ21, grains B and E are rotated relative to each other about an axis near [100] by approximately 90°. Triple junction I (TJI) comprises a Σ5(BC), Σ21(AB), and a Σ105(AC) grain boundary. Joining triple junctions II (TJII) and III (TJIII) is a random boundary. Triple junction II (TJI) comprises a Σ21(AB), Σ29(BD), and a random boundary (AD), while TJIII comprises a Σ25(DE), Σ21 (AE), and a random grain boundary (AD). Dark contrast is visible at all of these triple junctions.

Figure 3 shows typical EDX spectra obtained from triple junction TJI, grain boundary AB, and the interior of grain A. The X-ray spectra were acquired with a beam diameter, d, less than 1 nm and acquisition times of 100 sec. Cu Kα peaks, corrected for background, would contain from 10,000 to 16,000 counts, while Bi Lα peaks from triple junction contained from 500 to 750 counts, and from the grain boundary region they contained 100 to 150 counts. Bismuth is undetectable in the spectra from the grain interiors. The spectrum taken from the triple junction clearly exhibits a larger bismuth peak whose height should be assessed in relation to the adjacent copper Lα peak, which forms a useful comparison.

The composition of bismuth in the grain boundaries and triple junctions was determined from X-ray spectra

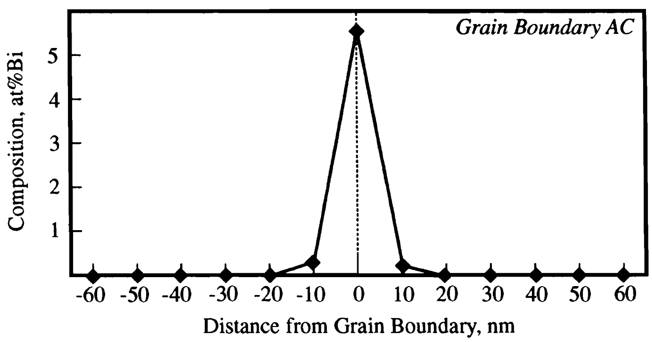

Figure 4. A typical composition profile across a grain boundary AC.

using the Cliff-Lorimer equation (as described in Goldstein et al., 1986) and a truncated cone model for the beam spreading (Doig and Flewitt, 1978; Baumann and Williams, 1981; Michael and Williams, 1984). The truncated cone model phenomenologically takes the beam-spreading effect on the sampling volume into account. The beam broadening, b, calculated using a single scattering algorithm (Williams and Carter, 1996), was about 30 nm for the specimen thickness of 100 nm. A grain boundary thickness of 1 nm is assumed and the total X-ray exciting volume is taken as a truncated cone with a top diameter equal to the spot size d and bottom diameter equal to square root of $d^2 + b^2$. A typical composition profile across a grain boundary (in this case, boundary AC) is shown in Figure 4. The enrichment at the boundary is very localized, and quite significant.

Concentration profiles along some of the grain boundaries adjacent to the triple junctions are shown in Figure 5. There is a marked enhancement of the bismuth content at the triple junctions and it declines, within a few tens of

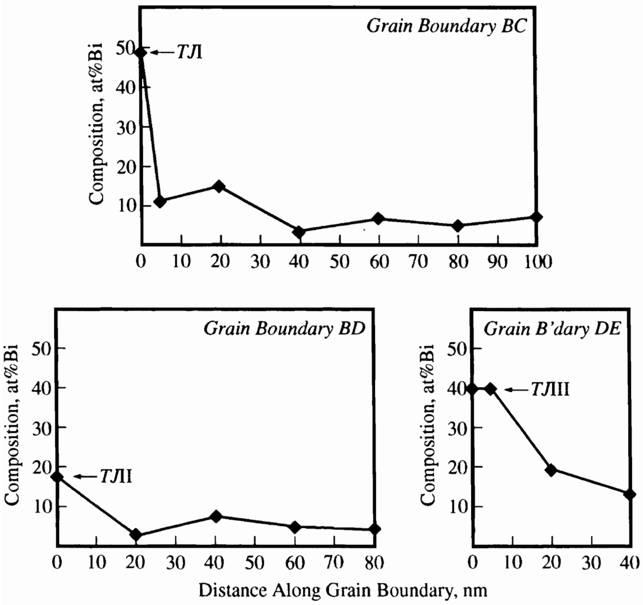

Figure 5. Concentration profiles along the grain boundaries BC, BD, and DE.

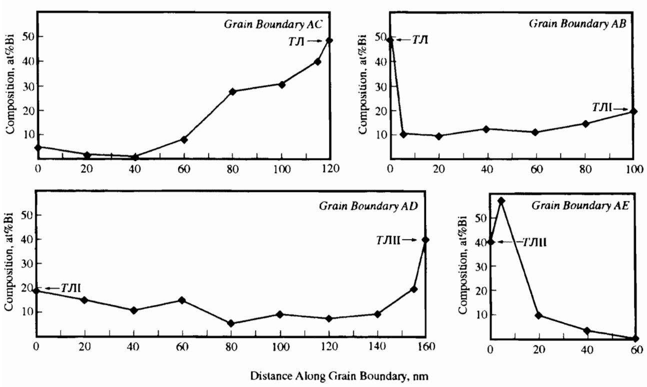

Figure 6. Concentration profiles along the grain boundaries AC, AB, AD, and AE.

nanometers, to a more normal grain boundary concentration. There was less significant enhancement of the bismuth concentration, relative to the adjacent grain boundaries, at TJII, as illustrated in Figures 5 and 6. There was a concentration peak associated with TJIII, as shown in Figures 5 and 6, but in this case it appears to have been displaced from the actual location of the triple junction. Concentration maxima are observed in the grain boundaries DE and AE, at a location about 20 nm from triple junction TJIII itself, and there is no maximum associated with triple junction TJIII in boundary AD. No evidence was found for the formation of second-phase precipitates or new grains at any of the triple junctions, either by imaging or microdiffraction.

Discussion

One of our triple junctions (TJI) is formed by the intersection of coincidence-site lattice (CSL) grain boundaries, and the other two each comprise two CSL boundaries and a "general boundary." The intersections of exact CSL boundaries are governed by the Σ-product rule, which requires that the Σ-value of one boundary must be the product of the Σ-values of the other two. This rule is obeyed for TJI, but it generates a paradox in interpreting the Σ-value for the boundary between TJII and TJIII. The Σ-rule would predict that boundary AD should be $\Sigma 609$, on the basis of TJII, and $\Sigma 525$, on the basis of TJIII. Since the deduced Σ-values of boundary AD are both high, it would normally be considered not to have significant structure, and thus to be "random." More formally, it might be considered that the slightly deviated misorientations of the low-Σ boundaries generate a third (high-Σ) boundary for which the deviation exceeds the Brandon limit for the predicted CSL, or even produces a misorientation that falls within the Brandon limit for a different CSL. Such failures of the Σ-product rule could be a general problem for triple junctions between boundaries with moderate deviations from exact CSL misorientaions. Dislocation continuity at such triple junctions is potentially a very interesting issue. It must be the case that the primary dislocation content of the boundaries is continuous at the triple junction, but the secondary dislocation content appears not to be. This is a paradox that requires further investigation.

Quantitation of our EDX data, even within the very simple model that we have used, is a little more complicated than is usual for a grain boundary segregation analysis, and some care is needed in interpreting the results. A small difference between the EDX spectra from a grain boundary and an identically segregated triple junction might be expected as a result of the finite probe size of the electron microscope. The recorded spectrum is essentially averaged over the sampling volume and this includes some interfacial material and some of the grain interiors. At the triple junction, the sampling volume includes more grain boundary material and correspondingly, less matrix, as indicated schematically in Figure 7. This effect, however, produces no enhancement of the signal if the probe is contained entirely

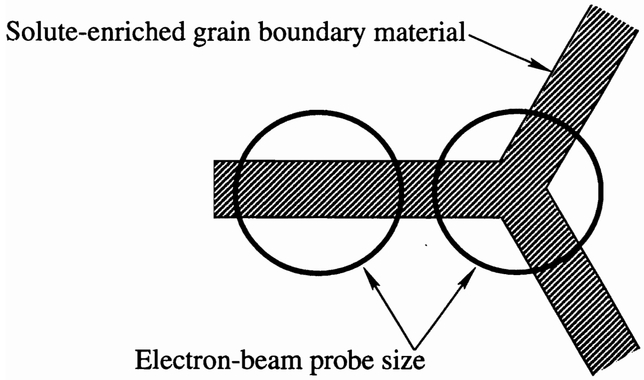

Figure 7. Schematic illustration of the EDX sampling volume at a triple junction and a grain boundary. Note that more solute-enriched material is sampled at the triple junction.

within the boundary width, and a 50% increase in the bismuth signal relative to that of copper in the limit of a very large probe size. Experimental cases will fall between these two limits. The massive enrichment factors shown in Figures 3 and 5 and the smooth variation of the enrichment in the vicinity of the triple junction clearly indicate that the observed effect is real and not an instrumental artifact caused by the finite sampling volume.

The variation of the measured bismuth content near the enriched triple junction is particularly interesting. An apparently decaying bismuth concentration would result from a finite probe size, even if the triple junction embodies a step-function change in concentration. However, the observation of a peak at a small distance from the junction itself, as in the case of TJIII, and the long tail of the solute profile of TJI along boundary AC (Fig. 4) would seem to argue that other effects also occur in our specimens. A smoothly decaying concentration profile at a triple junction would indicate one of two things, depending on whether the material has been properly equilibrated. If the material is indeed at or near equilibrium, as we believe, given the length of our annealing treatment, then the enhanced segregation near the triple junction indicates that the triple junction has an effect on the properties of the grain boundaries that it joins, extending some distance from the junction itself. This might result from a strain field, decaying with distance (i.e., like that of a dislocation but not like that of a disclination, which produces a constant strain at all distances from its core). On the other hand, if equilibration has not been achieved, the solute distribution may result from diffusion of bismuth into the specimen via the triple junction, then leaking out into the grain boundaries. In this case, the solute distribution would represent a kinetic transient that would be expected to be removed after longer annealing times. The length of our diffusion anneal strongly favors the interpretation of the concentration profiles as equilibrium effects, but it remains to be determined whether they are real or else instrumental artefacts.

The variation of segregation factors from junction to junction indicates a strong variability of the behavior of the triple points with their structure, since the structure of a triple junction depends on the relative orientations of meeting grains and the inclination of boundary planes. In simple thermodynamic terms, segregation occurs when the collection of solute in a particular location reduces the free energy of the system. The fact that segregation occurs at triple junctions is therefore strongly suggestive of the existence of an excess free energy associated with those triple junctions in the unsegregated state. The variability of segregation from junction to junction also suggests that the triple junction energy is variable, depending on the misorientation and the boundary plane.

It is interesting that TJI exhibits marked segregation relative to its constituent grain boundaries whereas TJII does not. TJI comprises a $\Sigma 5$ grain boundary, while all of the boundaries at TJII have Σ-values in the range of 20–30. TJIII is a little different from TJI and TJII. Although it comprises two boundaries of the same misorientation (AE and AD) as those (AB and AD) in TJII, there is a large segregation peak associated with this junction; there is a much smaller one for TJII. This tends to argue against any simple interpretation of segregation variability based upon the coincidence indices of the boundaries meeting at a triple junction. The boundary plane must also play an important role, but it was not well determined in this preliminary experiment. The most notable feature of TJIII, however, is that the peak value of the concentration is located at a point slightly displaced from the triple junction itself. This might have resulted from grain boundary migration occurring after the segregation profile was created, pulling the triple junction away from its solute atmosphere. This suggests the possibility of pinning and unpinning events which, by competing with solute dragging by the triple junctions, may have important effects upon processes such as grain growth.

Segregation to triple junctions may be an important phenomenon in alloys like Al-Cu, which is used for interconnects in integrated circuits. It is known that the copper segregates to the grain boundaries in this material and it is believed to have a powerful effect in retarding grain boundary diffusion (Cemak, 1990). Segregation to triple junctions in nano-crystals may extend the apparent limits of solid solubility and also stabilize the microstructure of the materials through a solute drag effect on the triple junctions themselves. To investigate this possible effect, it might be interesting to conduct grain growth simulation experiments in which triple junctions motion is more strongly retarded than grain boundary motion.

Conclusions

Bismuth segregation to triple junctions in copper can far exceed the enrichment factors found at grain boundaries. The segregation to triple junctions is powerfully affected by the nature of the triple junctions themselves, as controlled by the misorientations and boundary plane of the constituent grain boundaries. To understand the segregation behavior completely and systematically, it is necessary to determine both misorientation and the crystallography of all of the boundaries intersecting a triple junction.

The Σ-product rule is found to be not strictly obeyed for triple junctions comprising near-coincidence boundaries with significant deviations from the exact coincidence misorientations. The Σ-product rule may produce errors in interpreting Σ-values for such cases.

Acknowledgments

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