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The effect of bismuth on microstructure evolution of ultrafine grained copper

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ABSTRACT

The effect of bismuth on the microstructure evolution of ultrafine grained copper at elevated temperatures has been studied. Ultrafine grained copper polycrystals were produced employing the High-Pressure Torsion technique. Bismuth had little effect on kinetics of recrystallization and grain growth of as-processed copper. Bi-rich intergranular films at the grain boundaries were observed in the samples annealed between 700 and 900 °C. Complete wetting of the grain boundary triple junctions by the Bi-rich liquid phase was observed at the temperatures below the onset of complete grain boundary wetting. We attributed the fact that Bi does not affect the kinetics of grain growth to the abundance of twin boundaries not affected by Bi segregation.

1. Introduction

Due to its high thermal and electrical conductivity, pure copper is a material of choice for many applications in microelectronics and heat management. The mechanical properties of pure copper can be significantly improved by severe plastic deformation (SPD), which is widely used for producing bulk ultrafine-grained metallic materials [1]. Moreover, the diluted copper alloys served as model materials for the fundamental studies of impurity segregation to the grain boundaries (GBs) and triple junctions (TJs) [2,3]. In particular, the GB prewetting transition and the presence of quasi-liquid GB and dislocation pipe phases (sometimes referred to as "complexion" [4]) have been observed in the diluted Cu-Bi alloys [5–9]. Such disordered GB phases greatly affect the GB mobility and grain growth [10], the kinetics of GB diffusion and sintering [11], and the mechanical properties of material [12]. Very few studies have addressed the problem of the effect of disordered GB phases on recrystallization and grain growth in metallic alloys. Whereas it is well-known that the impurities segregating at the GBs impede their motion by the solute drag mechanism [13], the situation with the disordered GB phases is less clear. For example, a significant acceleration of GB mobility by the addition of Ga to pure Al was interpreted in terms of the presence of disordered Ga-rich phase at the GB [14]. A quantitative analysis of the phenomenon was proposed, in which the solute drag effect was combined with the impurity-dependent acceleration of the GB diffusion within the GB core [15].

The aim of the present work was studying the effect of Bi and of the Bi-rich GB phases (complexions) on the grain growth of pure Cu. We have selected the High-Pressure Torsion (HPT) technique to produce initial ultrafine grain microstructure of the pure Cu, with the aim of covering the widest possible range of grain sizes. The HPT processing results in high strength and homogeneous refined structure of the processed material, with the initial grain size in the range of few hundreds of nanometers [16].

2. Experimental

The discs of high purity (99.9995 wt.%) copper, of 10 mm in diameter and 0.7 mm in thickness, were processed by HPT at room temperature. The HPT processing (5 anvil rotations at a rotation rate of 1 rpm) was carried out under compressive pressure of 5 GPa in a Bridgman anvil-type unit using a custom-built computer controlled HPT device (W. Klement GmbH, Lang, Austria). As-deformed samples were subjected to isochronal (1 h) annealings in evacuated quartz ampoules (residual pressure 10^{-4} Pa) with

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and without a source of Bi (particle of pure Bi) in the temperature range of 500–900 °C. The particle of pure Bi was placed at some distance from the Cu specimen, so that the Bi atoms were supplied to the Cu specimen via the vapor phase.

For the microstructure characterization, we used high-resolution scanning electron microscopy (HRSEM, Zeiss Ultra Plus), high-resolution transmission electron microscopy (HRTEM; FEI Titan 80–300 keV S/TEM), and electron backscatter diffraction (EBSD; Bruker) in the HRSEM. The presence of Bi-phase in Cu polycrystals was qualified by energy dispersive X-ray spectroscopy (EDS) used in combination with HRSEM and HRTEM. TEM-samples were prepared by the lift-out method in a dual-beam focused ion beam (FIB; FEI Helios NanoLab DualBeam G3 UC). Cross-section views were prepared by the conventional technique of sample cutting and fine polishing followed by ion milling. The near-surface layer of about 50 µm in thickness from each side was polished in the process of cross-sectional samples preparation. The final polishing step was accomplished by using 50 nm Al_2O_3 suspension. Fine scratches were removed by Ar^+ ion milling using IV8 Gentle Mill (Technoorg Linda Ltd., Hungary) at 300 eV ion energy. The angle of beam incidence was 15° for the first 20 min and 10° for the next 20 min. For visualization of structural defects containing Bi phase, we used selective etching in RCA solution in ultrasonic bath for 9 min with the following immersion of the sample into ethanol in ultrasonic bath for 3 min.

3. Results and discussion

3.1. Microstructure characterization

The mean grain size was determined from the SEM-images and from the EBSD-measurements. We employed the EBSD technique to obtain both sizes and orientations of grains. The average grain size in Cu samples before HPT processing was about 300 µm. Cross-section views of as-deformed Cu samples showed a bimodal microstructure, which implies the presence of ultrafine grains with an average grain size of about 300 nm formed in the process of grain refinement during HPT, and larger grains of about 1 µm in diameter, which formed as a result of dynamic recrystallization during HPT processing. Such dynamic recrystallization during SPD is not uncommon in ultra-high purity metals [17,18]. Annealing-induced recrystallization and grain growth in HPT-processed Cu and Cu-Bi samples result in increasing grain size with the annealing temperature. Fig. 1 shows the Inverse Pole Figure (IPF) maps of Cu-Bi samples (cross-section views) subjected to post-deformation annealings at 500 °C (Fig. 1a) and 900 °C (Fig. 1b). The grains are colored according to their transverse in-plane orientation coded in the stereographic triangle shown in the insert. Black pixels refer to Bi inclusions or to zero solutions. The phase contrast provided by EBSD measurements can be used in principle for the detection of Bi inclusions. However, this method cannot provide a reliable confirmation of Bi location in cross-sectional samples due to the possibility of removing of Bi atom from their sites during polishing procedure. IPF maps illustrate a significant textural heterogeneity in the samples. The annealed samples exhibit a high number of twin boundaries, which suggests that twinning plays an important role during recrystallization and grain growth. The large recrystallized grains exhibit a higher number of twin boundaries and a lower spread of orientations due to sharpening of the texture upon annealing.

The microstructures formed due to recrystallization and grain growth processes at a given temperature in the pure Cu and Cu-Bi polycrystals are similar. In other words, no apparent influence of Bi on the microstructure evolution of Cu polycrystals is revealed. Post-deformation annealing results in the grain growth from an

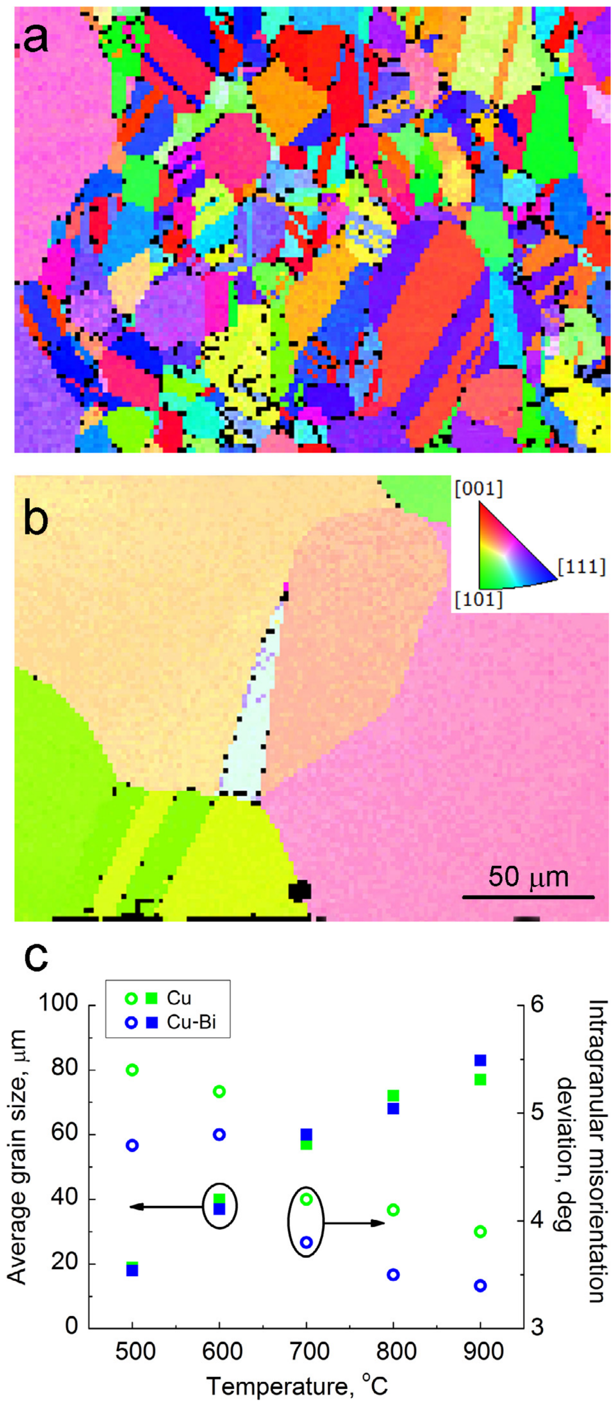

Fig. 1. The IPF maps (in-plane transverse direction) of Cu-Bi samples annealed at 500 °C (a) and 900 °C (b). The pixel size is 1.8 µm. A grain tolerance angle of 2° was used for pixel grouping. (c) Dependence of the average grain size (left vertical axis, blue and green solid squares) and intragranular misorientation deviation (right vertical axis, blue and green open circles) on the annealing temperature.

average value of 300 nm in the as-deformed samples to about 80 µm in the samples annealed at 900 °C, irrespective of the presence of Bi (Fig. 1c, left axis). We used the value of intragranular misorientation deviation (IMD) as a measure of strain within individual grains. This parameter is defined as an average of all misorientation differences between the pairs of pixels in a grain. Fig. 1c (right axis) shows the maximum IMD values, evaluated at a condition of the lower misorientation threshold of 2°. For both pure Cu and Cu-Bi samples the IMD value decreases with increasing annealing temperature, which indicates a diminution of intergranular strain in the samples as a consequence of recrystallization and grains growth.

3.2. Wetting of structural defects

We observed that heat treatment of Cu polycrystals in the temperature range 500–600 °C results in partial wetting of the near-surface GBs by liquid Bi. The estimation of the penetration depth of Bi based on the radiotracer diffusion coefficient of Bi along the GBs in pure Cu measured in Ref. [19] yields the value of 150 μm at the temperature of 500 °C. At higher annealing temperatures the penetration depth exceeds the thickness of HPT-processed sample. The temperature raise to 700 °C leads to the appearance of pseudopartially wetted GBs within the Cu-Bi samples. Copper grains are separated from each other by intergranular films of

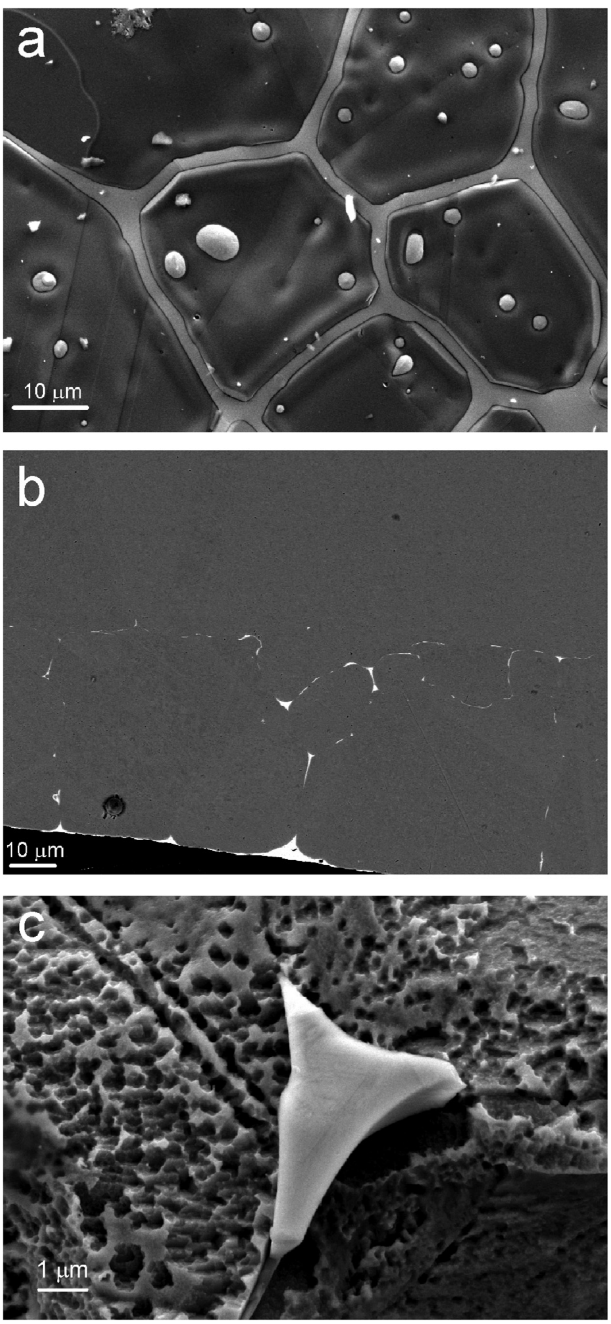

Fig. 2. SEM images of Cu-Bi sample annealed at 800 °C: surface after annealing (a), cross-section view (b). The edge of the cross-section sample is seen in the lower part of the image. Triple junction etched on the sample surface (c).

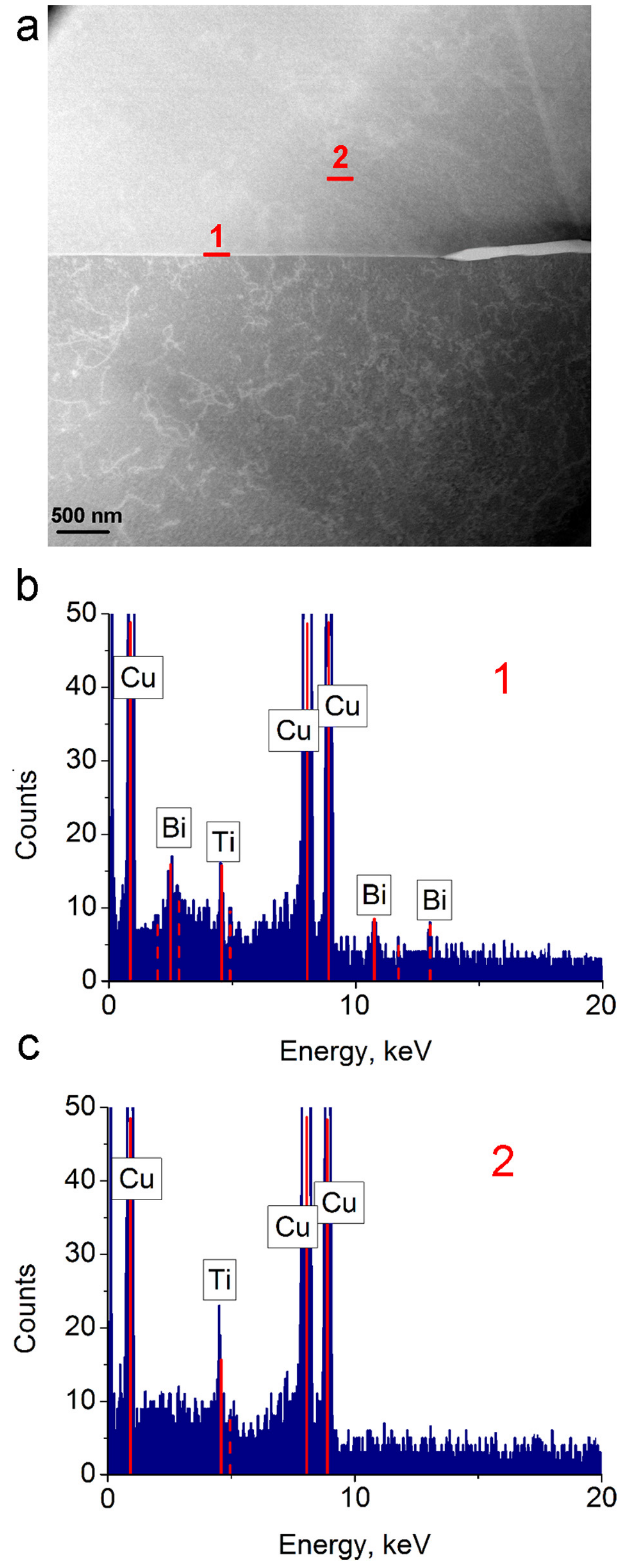

Fig. 3. HAADF-STEM image of the Bi-rich intergranular film at the GB (a); chemical composition of the thin intergranular film at the GB (1) and of the Cu grain interior (2) measured by EDS in TEM (b, c). TEM specimen was extracted from the Cu-Bi sample annealed at 800 °C at the randomly selected GB. TEM specimen was mounted on a Ti-grid, which explains the appearance of a Ti peak in the spectra.

Bi-rich phase with the thickness of several nanometers [20]. Still a number of GBs remain free of any intergranular phases. The transition from incomplete to complete GB wetting begins above the temperature of 700 °C. Complete wetting of the grain boundary TJs by the Bi-rich liquid phase takes place at the temperatures below the onset of complete grain boundary wetting, as in Ref. [21]. The Bi-rich liquid phase delineates the GB grooves on the sample surface creating an impression of complete GB wetting (Fig. 2a), yet the cross-sectional micrographs demonstrate that in most cases the contact angle between the Bi-rich melt and the GB is non-zero, i.e. the GB wetting is partial. Pseudopartial GB wetting characterized by the presence of thin Bi-rich intergranular films of several nanometers in thickness are also observed inside the samples (Fig. 2b). A large number of GBs contacting the liquid phase exhibit the contact angle below 60 deg, so that the solid/liquid interface at the TJs is concave (Fig. 2c). Most of the TJs throughout the sample thickness are completely wetted by the Bi-rich phase.

The existence of Bi-rich thin intergranular film of 2–4 nm in thickness is confirmed by STEM (Fig. 3a). This film is contacting the micrometer-thick intergranular Bi-rich layer. The contact angle between the tip of the micrometer-thick layer at the GB and the nanometer-thick Bi-rich film is non-zero, indicating a pseudo-partial GB wetting. The analysis of chemical composition (Fig. 3b) of the GB (the EDS spectrum acquired from rectangular area 1 denoted in Fig. 3a) shows the presence of a small amount of Bi, unlike the case of Cu grain interior (spectrum acquired from rectangular area 2) since the bulk solubility of Bi in Cu is extremely low [22]. No Bi was detected inside the twin boundaries. This confirms a known fact about very low segregation level of Bi in $\sum 3$ GBs [23]. Thus, the following hierarchy of the penetrating liquid phase was established above 700 °C: completely wetted 1D defects (TJs) [21], the mixed population of completely and pseudopartially wetted GBs (2D defects), and the partially wetted and non-wetted GBs (mainly coherent twin boundaries).

4. Conclusions

The presence of intergranular Bi-rich liquid like phase (complexion) at the GBs, as well as complete wetting of the TJs and GBs by the liquid phase have little effect on recrystallization and grain growth in the samples of ultra-pure Cu processed by HPT. In this respect, the present results are different from the results of Harmer and co-workers who found significant changes in the kinetics of grain growth in ceramic materials containing nanometer-thick layers of intergranular phases [10]. It is unlikely that the solute drag and accelerated diffusion effects [15] perfectly cancel each other, resulting in similar GB mobilities in the samples of pure Cu and of the Cu-Bi alloy. In our opinion, the results of the present study indicate that the GBs not affected by Bi serve as a kinetic bottleneck of the recrystallization and grain growth processes in the Cu-Bi alloys. The coherent twin boundaries abundantly present in both the pure Cu and Cu-Bi samples may play a role of such kinetic bottlenecks. Indeed, it is known that these GBs in the Cu-Bi alloys are not affected by Bi segregation [22], and exhibit decreased mobility and diffusivity [24,25].

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