Grain Boundary Phase Transitions in the Cu-Bi System

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Abstract. The grain boundary (GB) properties depend hardly on the GB phase transitions. The GB wetting phase transitions in the two-phase area of the bulk phase diagram control the penetration of a liquid phase along GBs. The GB prewetting and/or premelting phase transitions in the one-phase area of the bulk phase diagram where only the solid solution is in equilibrium lead to the formation of an equlibrium layer of a GB phase having a high diffusivity. The GB lines in the Cu–Bi bulk phase diagram are constructed both for GB arrays in polycrystals and individual GBs in bicrystals. The influence of temperature and Bi concentration on the GB segregation in symmetrical tilt <001> GBs, having misorientation angles of 33.2 and 36.5°, is determined. The presence of a quasi-liquid layer at GBs can explain the enhanced GB diffusivity in the Cu–Bi system, similar to that observed earlier in the Fe–Si–Zn system.

Introduction

Recently, it was shown that the grain boundary (GB) phase transitions can drastically change the properties of individual GBs and, as a result, the properties of polycrystals [1–13]. Particularly, the tie lines of the GB *wetting* phase transitions were experimentally constructed in the $S+L$ two-phase areas of several binary phase diagrams where the solid solution (S) and melt (L) are in equilibrium [5, 6, 12–16]. Later it was shown that in some cases GB layers of phases can occur which are thermodynamically stable in the GB but unstable in the bulk. Particularly, in case of *prewetting* or *premelting* the local melting at the GB can occur when only a solid solution is thermodynamically stable in the bulk [17]. Under premelting conditions the formation of a microscopically thin layer of a liquid phase with properties different from those of a bulk liquid is possible. Therefore, the term *quasi-liquid* is more appropriate in this case. The presence of quasi-liquid layer at GBs can drastically enhance the GB diffusivity [10–12], GB mobility [7] and GB segregation [3, 8]. The relationship between GB wetting/prewetting and GB segregation was first discovered by Kikuchi and Cahn [18]. They have shown that the GB core becomes more disordered (melted) and its width increases logarithmically with increasing temperature. Though the occupancy of each individual segregation site by the solute atoms decreases with increasing temperature, the value of the Gibbsian excess of impurity atoms increases because of the widening of the GB core. Recently, we studied the influence of the temperature and bulk concentration of Bi on the GB segregation in Cu(Bi) polycrystals [3, 8]. First of all, we have determined the solidus line of the Cu–Bi phase diagram with a high precision [19]. The availability of the Cu–Bi bulk phase diagram permitted us to properly discuss the results in terms of the stability of the bulk phases. The sudden changes of the GB Gibbsian excess of Bi were attributed as the result of a transition from the normal GB segregation to the quasi-liquid layer of the GB phase [3, 8].

Table 1. Orientations of the Cu bicrystals investigated.

<001> tilt angle Θ, deg	[310] twist angle Φ, deg	<013> tilt angle Ψ, deg
33.2±0.2	0.8±0.2	0.5±0.2
36.5±0.1	0.1±0.2	1.1±0.1

However, it is well known that the GB properties (particularly, the temperature of GB phase transitions) depend drastically on the crystallographic parameters of the GB. Therefore, the measurements on polycrystals deliver only an averaged information. The aim of this work is to study the influence of the temperature and bulk concentration of Bi on the GB segregation at individual GBs in Cu(Bi) bicrystals.

Experimental

The Cu bicrystals were grown in a pure graphite mould in high purity argon atmosphere by directional crystallization, using Cu single crystals of high purity (nominal 99.995%) Cu. It should be pointed out that the purity of the bicrystals used for the segregation measurements was higher than the nominal purity of the initial Cu material since the technique of growing bicrystals acts like a zone refinement of the Cu material. Bicrystals of 16 mm × 3 mm in cross-section and with lengths up to 200 mm were grown. The orientations of the grains of each bicrystal were determined by the Kossel technique. The advantage of this technique is that it can measure all three macroscopic parameters, describing the orientation of the adjacent grains with a very high precision. Table 1 contains the resulting tilt angles Θ with respect to the <001> axis, the twist angles Φ with respect to the <310> axis and the second tilt angles Ψ with respect to the <013> axis. The orientation of the GB plane was carefully adjusted during the bicrystal growth process but was not explicitly remeasured.

The Cu bicrystals were cut into pieces of 3 mm × 3 mm × 15 mm. The GB was perpendicular to the long axis and was positioned in the middle of the sample. The method of vapour transfer was used to obtain Cu samples containing Bi. The samples were etched in an aqueous solution of 50% HNO_3 in order to remove the oxidized film. Each sample was then sealed separately in a silica tube with a Bi vapour source. Differing from the pure Bi source used by Li and Zhang [20], the Cu–Bi alloys were prepared as Bi vapour sources. The compositions of these alloys were Cu–4.5 at.% Bi for temperatures lower than 850°C and Cu–0.3 at.% Bi for the higher temperatures. Alloys of these compositions are in the two-phase region at the annealing temperature so that the formation of a liquid phase in the Cu single crystal could not occur during annealing. A pure liquid Bi source even in a small amount can induce the formation of a liquid phase on a Cu target. The silica tubes were positioned in the furnace in such a way that the Cu crystals were kept at the desired temperature while the temperature of the Cu–Bi alloy was about 5°C higher. Different annealing times for a vapour transfer were chosen in order to produce samples with different Bi content (2×10^4, 1.8×10^5 and 6.2×10^5 s for 37, 61 and 100 at. ppm Bi, respectively). All samples were homogenized at 850 °C for 168 h in evacuated (5×10^4 Pa) silica ampoules without a Bi source. After homogenization, the Bi content in the specimens was measured by atom absorption spectroscopy in a Perkin-Elmer spectrometer (model 5000) with the extreme relative accuracy of 10^{-9}g/g. The specimens were then annealed at temperatures between 600 and 1000 °C for various times estimated from the Bi diffusion coefficient of Bi in Cu [21]. After annealing the specimens were quenched *ex situ* and then fractured *in situ* in the ultra high vacuum chamber of a PHI 600 Scanning Auger Multiprobe at the temperature of liquid nitrogen. The Bi concentration was measured by means of Auger electron spectroscopy (AES) at 20-30 sites on the fracture surface. The standard methods of the Auger signal processing have been used [21]. In this work we express the Bi concentration at the GBs in monolayers (ML) of Bi. One ML of pure Bi contains 9.3 atoms/nm^2.
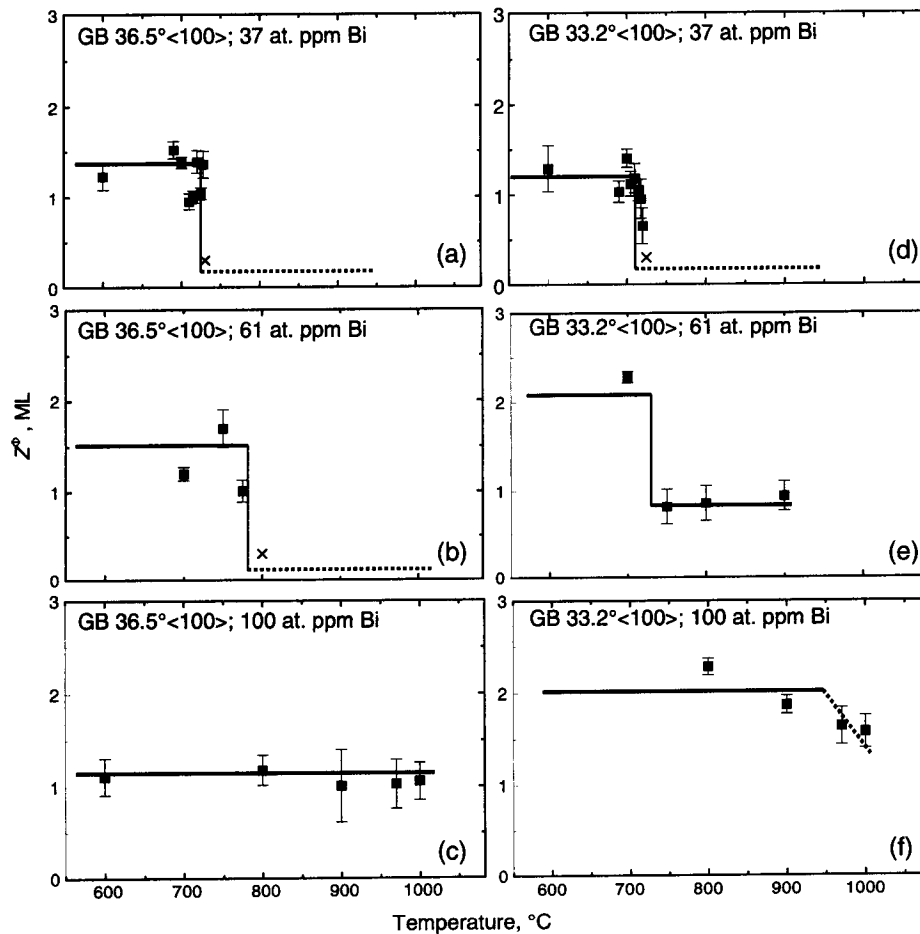
Fig. 1. Temperature dependence of the GB concentration of Bi in Cu(Bi) bicrystals for two different tilt GBs and three different bulk concentrations of Bi. The lines are guides for the eye.

Results and discussion

The tilt GBs chosen by us in this work belong to a set of Cu bicrystals with tilt GBs grown for the investigation of diffusion near the coincidence misorientation $\Sigma 5$ (Σ being the inverce density of coincidence sites) [22]. The bicrystals in this set have very small misorientation steps (17 samples in the Θ range 33.2°-39.3°). The investigation of tracer diffusion of Cu and Au in these GBs characterized a very strong influence of Θ on the GB kinetic propeties[22]. The transition from special to general boundary near the coincidence misorientation $\Sigma 5$ was also observed in this set of samples [23, 24]. As a result, we have chosen (1) a GB having Θ = 36.5° most close to the coincidence misorientation $\Sigma 5$ and (2) a GB with Θ = 33.2° which is outside of the $\Sigma 5$ special misorintation range.

In Fig. 1 the temperature dependence of the GB Gibbsian excess Z^{Φ} of Bi in Cu(Bi) bicrystals is shown. At low concentration (37 at. ppm Bi, Figs. 1a and 1d) the step-like discontinuous decrease of the Z^{Φ} value can be clearly seen. The cross in Figs. 1a, b and d is used for the samples which
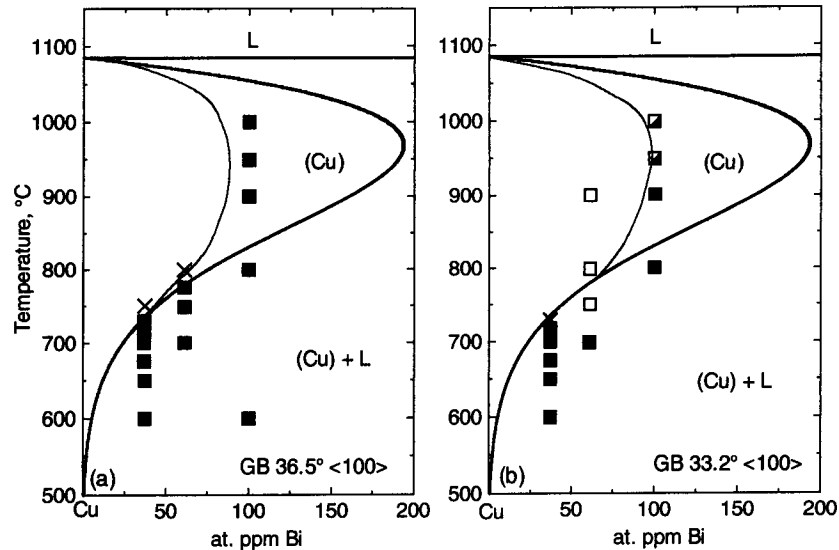
Fig. 2. The GB segregation data from Fig. 1 for the GB 36.5° <001> (a) and the GB 33.2° <001> (b) presented in the bulk Cu–Bi phase diagram. The bulk solidus line was obtained experimentally [19]. The GB solidus lines (thin solid lines) are also shown.

exhibited a ductile fracture and on which, therefore, it was impossible to perform the AES measurements. The behaviour of the Z^Φ (T) plots in Figs. 1a and d is similar to that of polycrystals with a low concentration of Bi (1 and 13 at. ppm). In these samples the transition from brittle to ductile failure also appears after the drop of Z^Φ, and the low-concentration branch of Z^Φ (T) is very short [3].

At a higher concentration (61 at. ppm Bi, Figs. 1b and e) the step-like discontinuous decrease of the Z^Φ value is more pronounced and appears at a higher temperature. These plots are similar to the Z^Φ (T) curves for polycrystals with 25 and 50 at. ppm Bi. We supposed that a layer of the quasi-liquid phase appears in the GBs [3]. The discontinuity in the temperature dependence marks the GB phase transition from the GB quasi-liquid layer to the usual GB segregation. At temperatures below the jump, the Gibbsian excess Z^Φ in polycrystals is constant and rather high exceeding 2 ML. In bicrystals the Z^Φ value at the high-concentration branch is slightly lower than 2 ML. At temperatures above the Z^Φ jump, the usual GB segregation was observed in polycrystals, the Z^Φ value was about 1 ML and decreased with increasing temperature.

The plots for Cu–100 at. ppm Bi (Figs. 1c and 1f) are similar to those for polycrystals with 75, 87, 102 and 150 at. ppm Bi; namely, the Z^Φ value for the 36.5° <001> GB is nearly constant at all temperatures studied (like in polycrystals with 150 at. ppm Bi). The Z^Φ value for the 33.2° <001> GB decreases slightly with increasing temperature similar to the Z^Φ (T) curve for polycrystals with 75, 87 and 102 at. ppm Bi). Therefore, the GBs with different crystallography, structure and properties reveal also differences in the segregation behaviour.

The GB segregation data are depicted together with the bulk solidus line (thick solid line) of the Cu–Bi system in Fig. 2. The thin solid line is plotted through the points, at which the discontinuous change of the GB Gibbsian excess of Bi occurs. This line represents, therefore, the GB phase transformation in the phase diagram in the coordinates "temperature – bulk concentration of Bi".
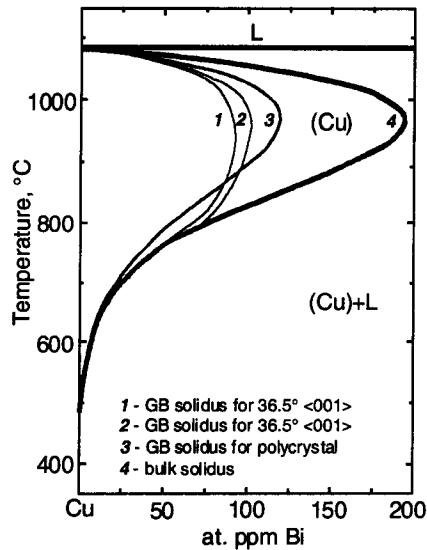
Fig. 3. Cu–Bi phase diagram: GB solidus lines obtained for the GBs 36.5° <001> (*1*) and 33.2° <001> (*2*); the GB solidus line for polycrystals (*3*) and the bulk solidus and liquidus lines are also shown. For simplicity, the experimental points are omitted. The GB solidus line for polycrystals was calculated using the model for the GB prewetting phase transition [3].
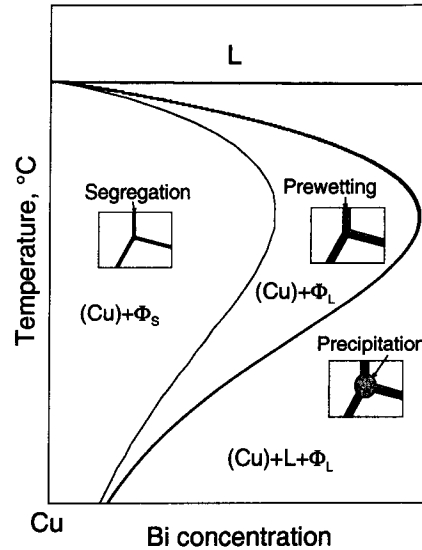
Fig. 4. Scheme of the microstructure in various fields of the Cu–Bi phase diagram. (Cu)+Φ_S :solid solution in the bulk and segregation in the GBs. (Cu)+Φ_L: solid solution in the bulk and a quasi-liquid layer in the GBs. (Cu)+L+Φ_L: solid solution and melt phases in the bulk and a quasi-liquid layer in the GBs.

Because of the similarity of the GB phase transformation line with the bulk solidus line (both lines have a characteristic retrograde shape), we call the former the *GB solidus line*. The curves for the GBs 36.5° <001> and 33.2° <001> have a similar form, but the GB solidus for the GB 36.5° <100> is shifted to lower concentrations of Bi.

The bulk solidus *4*, the GB solidus obtained for polycrystals *3* [3] and the GB solidus lines *1* and *2* for both individual GBs are shown together in Fig. 3. For simplicity, all experimental points are omitted. Neither line *1* nor line *2* coincide with the solidus line obtained for polycrystals. The most remarkable feature is that the solidus lines for individual GBs intersect the line obtained for polycrystals. In polycrystals we cannot control the path of the brittle intergranular failure. During the brittle fracture, the crack path chooses the weakest GBs in the polycrystal. Obviously, the form of the GB solidus measured in a polycrystal is defined by the condition of the easiest failure. The data in Fig. 3 reveal that this condition selects different GBs at different temperatures. As can be seen from Fig. 3, the GB phase transformation lines lie almost entirely in the single-phase area of the bulk phase diagram. Therefore, we are dealing with the true GB phase transformation induced by a segregation process, and not with the precipitation of a second phase at the GB.

In the prewetting model of GB segregation we assume that the quasi-liquid layer Φ_L at the GB is thin but inhomogeneous. The Bi-rich core region still has a structure similar to the structure of the

untransformed GB core, but being surrounded by two thin layers of the quasi-liquid phase (Fig. 4) [3]. The presence of the quasi-liquid layer Φ_L at the GBs can explain the enhanced GB diffusivity in the Cu–Bi system [25, 26], similar to that observed earlier in the Fe–Si–Zn system [9–11]. At higher concentrations of Bi, after intersection of the bulk solidus line the bulk liquid L appears in the material together with solid solution (Cu) and a quasi-liquid phase Φ_L at the GBs. At lower concentrations of Bi, after intersection of the GB solidus line only the solid solution (Cu) is present in the material, containing GBs with a usual segegation layer Φ_S.

Acknowledgements

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