Grain-boundary melting phase transition in the Cu-Bi system

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Copper embrittlement by Bi atoms is a typical example of a severe detrimental phenomenon in materials science. It has recently been proposed that the strong Bi segregation in Cu can cause a liquidlike film at the grain boundaries (GBs), when the alloy is in the single-phase (solid solution) region of the equilibrium phase diagram [L.-S. Chang, E. Rabkin, B. B. Straumal, B. Baretzky, and W. Gust, Acta Mater. **47**, 4041 (1999)]. However, a direct experimental confirmation of a liquidlike state of GBs in such a case is missing. If a liquidlike GB phase is indeed formed, the GB diffusivity should dramatically be enhanced. Radiotracer GB diffusion of ^{64}Cu and ^{207}Bi radioisotopes were measured in a set of well-characterized Cu-Bi alloys in the single-phase (solid solution) region of the equilibrium phase diagram as well as in the two-phase (solid +liquid) region. An abrupt increase of the GB diffusivities of both Cu and Bi by about two orders of magnitude was observed at certain Bi contents which are unequivocally in the single-phase region and are definitely less than that associated with the bulk solidus concentration. This critical Bi concentration was the same for self- and solute GB diffusion. With further increase of the Bi content and after exceeding the bulk solidus concentration, only marginal changes in the diffusivities of Cu as well as Bi were observed. The present results convincingly showed the occurrence of the premelting phase transition in GBs of the Cu-Bi system.

I. INTRODUCTION

Phase transitions in grain boundaries (GBs) are of continuously growing interest, especially since nanocrystalline materials become more and more available and find broad application. The formation of thermodynamically stable layers of a second phase in GBs can be both advantageous (e.g., materials produced by liquid-phase sintering) and disadvantageous (e.g., GB corrosion and GB brittleness). Bismuth-containing alloys become progressively important for solder applications in chip technology (e.g., the recently proposed Pb-free Sn-Bi or Sn-Ag-Bi soldering alloys). In such applications both the wetting phenomena at the GBs and the Bi-induced embrittlement of copper metallization can significantly influence the use of solder materials.[1,2]

The segregation of Bi in Cu was intensively studied by transmission electron microscopy (TEM) (Refs. 3–7) and Auger electron spectroscopy (AES).[8] The bulk solubility of Bi in Cu was carefully determined (Fig. 1). The AES measurements of as-quenched samples revealed a discontinuous jump of the segregation level of Bi at a certain Bi content in the single-phase region of the bulk phase diagram (dashed line in Fig. 1), and this was interpreted in terms of a premelting (prewetting) phase transition in the Cu-Bi system. Under the bulk phase diagram, bulk lines, bulk diffusion, etc., we introduce the parameters for perfect crystalline matrix only, not influenced by surfaces, interfaces, and other defects. A liquidlike film was proposed to cover the GBs of alloys already in the single-phase region of the phase diagram and the term "GB solidus" was introduced.[8]

In their pioneering work, Kikuchi and Cahn predicted theoretically the occurrence of a GB melting transition in a two-dimensional lattice-gas model.[9,10] They have shown that

the GB core becomes progressively more disordered (melted) with increasing temperature and the GB width diverges logarithmically at the melting point.

According to the prewetting model,[8] two thin quasiliquid layers surround the GB core in the Bi-rich GB phase. This model describes adequately the GB solidus and is in reasonable agreement with AES data.[8]
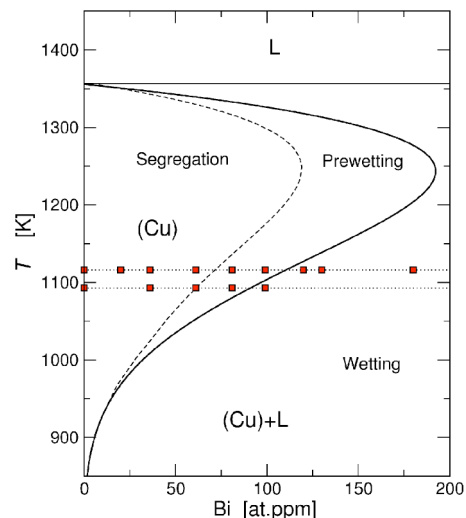

FIG. 1. Cu-rich side of the Cu-Bi phase diagram after Chang *et al.* (Ref. 8). The solid curve is the (retrograde) bulk solidus line. The dashed curve is the GB solidus line obtained for Cu-Bi polycrystals. The annealing temperatures (1116 and 1093 K) and the Bi concentration of the samples (0, 20, 36, 61, 81, 99, 120, 130, and 180 at. ppm Bi) are indicated. *L*=liquid; (Cu)=Cu-rich solid solution.

The occurrence of the premelting GB phase transition in the Cu-Bi system was indirectly verified by electrical resistivity measurements.[11] The discontinuity of the first derivative of the dependence of the GB energy on the bulk Bi concentration at the GB solidus reveals that the GB premelting transition is of first order.[12] The occurrence of a GB Bi-rich layer between the GB and bulk solidus lines has been observed with the aid of high-resolution electron microscopy.[3–5] The quantitative compositional mapping of Bi segregation to Cu GBs revealed a large anisotropy in the segregation levels and a strong Bi effect in GB fragmentation.[6] The computer modeling suggests that specific interfacial phases are formed in the Cu-Bi system.[3,4,13]

However, a direct experimental prove of the GB premelting transition (i.e., the appearence of a liquidlike GB layer) is still missing. If a GB premelting phase transition does occur in the Cu-Bi system, it can be studied very sensitively *in situ* by specially designed radiotracer GB diffusion measurements. The GB phase transformation and changes in the nature of the GB phases (especially if formation of a liquidlike layer is involved) manifest themselves in strong changes of the GB diffusivities, which can be studied with a high sensitivity, since the diffusivity depends exponentially on the corresponding changes in the interatomic interactions. For this reason, diffusion studies are superior to other relevant techniques such as AES and TEM applied for detecting a GB phase transition. In a GB diffusion experiment, the tracer distribution is formed around many GBs in a polycrystalline material during the pertinent diffusion anneal and quenching effects play no role. Note that quenching to room temperature may significantly disturb the results of an AES study, if solute bulk diffusion is appreciably fast.[14] Moreover, the annealing times in a GB diffusion experiment typically are long enough to approach equilibrium segregation of the diffusing solute atoms.

In this article, the results of direct radiotracer measurements of GB self- (^{64}Cu tracer) and solute (^{207}Bi tracer) diffusion in Cu-Bi alloys across the bulk and so far hypothetical GB solidus lines are reported. Measurements with both of the two tracers are decisive to verify independently the results and, most importantly, to conclusively separate the segregational and structural changes in the GBs of the alloys.

In order to establish the effect of the phase transformation on GB diffusion it is necessary to perform the GB diffusion study at relatively high temperatures, where the GB and bulk solidus lines are well separated, see Fig. 1. In a previous study of Bi radiotracer GB diffusion in pure Cu we confirmed already the reliability of such measurements if special care is taken.[15]

II. EXPERIMENT

A. Sample preparation

Cylindrical Cu-Bi polycrystals containing 0, 20, 36, 61, 81, 99, 120, 130, 180, and 450 at. ppm Bi were produced from Cu and Bi of 99.999 wt. % purity by casting in vacuum. All samples were homogenized for 24 h at 1273 K in evacuated (5×10^{-4} Pa) silica ampoules. After homogenization, the Bi content in the specimens was measured by atomic absorption spectroscopy in a Perkin-Elmer spectrometer. The details of the heat treatment are given in Ref. 16.

The samples (8 mm in diameter and 3-mm thick) were cut by spark erosion from the ingots. The average grain size was measured to be about 100 μm. The specimens were preannealed at the temperatures and for the time of intended diffusion anneals in order to stabilize the microstructure and to ensure equilibrium segregation of all spurious residual impurities. The anneals were performed in silica ampoules under Ar atmosphere (about 10^1 Pa).

B. Radiotracer measurements

The radiotracer ^{207}Bi (half-life 38 a) was purchased from the Los Alamos National Laboratory in the form of a nitrate solution. The original solution was diluted with double-distilled water.

The radiotracer ^{64}Cu (half-life 12.7 h) was produced by neutron irradiation of high-purity copper (natural content of the mother isotope ^{63}Cu is 69.17%) at the research reactor in Geesthacht, Germany. Its specific activity was about 500 MBq/mg. The activated chip was in few hours delivered to our lab in Münster, dissolved in nitric acid, and then diluted with double-distilled water.

The tracer (^{207}Bi or ^{64}Cu) was dropped on the polished sample surface and dried. The applied total activity of the Bi tracer was about 10 kBq per sample, whereas about 100 kBq of ^{64}Cu had to be initially applied to the samples due to its short lifetime. The samples were sealed in silica tubes in a purified (5 N) Ar atmosphere and subjected to the given diffusion anneals. The temperatures were measured and controlled with a Ni-NiCr thermocouple with an accuracy of about ± 1 K. After the diffusion anneals the samples were reduced in diameter (by at least 1 mm) to remove the effect of radial diffusion. The penetration profiles were then determined by parallel mechanical sectioning on a microtome.

The activity of each section was determined by measuring the intensity of the radioactive decays of ^{207}Bi (or correspondingly ^{64}Cu) in a liquid-scintillation counter TRI CARB 2500 TR. To perform these measurements the sections were dissolved in 90 μl of diluted (50%) nitric acid. The counting time was chosen to result in a statistical error of the counting rate of less than 2%. The penetration profiles present the relative specific activity (counting rate per section mass) plotted against the depth and allow the determination of the GB diffusivity, which is much larger in a liquidlike material than in a solid under comparable experimental conditions.

III. RESULTS

The GB diffusion experiments were performed in Harrison's *B*-kinetic regime.[17] This regime is characterized by fast tracer diffusion along the GBs with subsequent leakage of the tracer atoms into grain interior via bulk diffusion. It is important that the bulk diffusion length is much larger than the GB width δ, but still smaller than the grain size d (the bulk diffusion fluxes originating from different GBs should not overlap). Formally, the following conditions should be fulfilled:

$$\alpha = \frac{s\delta}{2\sqrt{D_v t}} < 0.1 \qquad (1)$$

and

$$\beta = \frac{P}{2D_v^{3/2}t^{1/2}} > 10. \qquad (2)$$

Here s is the solute segregation factor (for self-diffusion $s=1$), t is the diffusion time, D_v is the bulk diffusion coefficient, P is the so-called triple product $P = s\delta D_{GB}$, where δ and D_{GB} are the GB width and GB diffusivity, respectively.

In order to design the GB diffusion measurements in the B-kinetic regime the solute segregation factor s has to be known. In a previous work,[15] the GB segregation factor of Bi in pure Cu was determined by a special set of GB diffusion measurements in both the B- and C-kinetic regimes. The triple product $P = s\delta D_{GB}$ and the GB diffusion coefficient D_{GB} were separately determined in the B and C regimes, respectively. Since the average GB width is a well-defined quantity for GB diffusion in pure metals [$\delta \approx 0.5$ nm (Ref. 18)], the pertinent segregation factor s was determined as a function of temperature for true dilute concentration conditions. Here one has to remember that only a tiny amount of tracer material is applied in a typical radiotracer diffusion experiment.

Bismuth was found to segregate very strongly at GBs in Cu. The segregation factor s and the directly measured GB diffusion coefficients D_{GB} of Bi in pure Cu follow the relations[15]

$$s = 5.4 \times 10^{-2} \exp\left\{ -\frac{53.4 \text{ kJ mol}^{-1}}{RT} \right\} \qquad (3)$$

and

$$D_{GB} = 0.24 \exp\left\{ -\frac{156.2 \text{ kJ mol}^{-1}}{RT} \right\} \text{m}^2/\text{s}, \qquad (4)$$

where R is the gas constant and T is the absolute temperature.

At the temperatures of the present GB diffusion measurements, which are abnormally high for typical GB diffusion experiments (about $0.85T_m$, where T_m is the melting point of Cu), it is an experimentally involved task to keep $\beta > 10$, Eq. (2). However, a weaker condition than Eq. (2), namely, $\beta > 1$, was shown[15] to provide reliable results, if the penetration profiles are followed several orders in decrease of the tracer concentration.

In order to calculate the diffusion parameters α and β and the triple product P [see Eq. (7) below] the bulk diffusion coefficients D_v of Bi and Cu diffusion in Cu have to be known. For Bi diffusion, the data of Gorbachev *et al.*,[19] measured in the temperature range 1074–1348 K, were used in the present work

$$D_v^{Bi} = 7.66 \times 10^{-5} \exp(-178.1 \text{ kJ mol}^{-1}/RT) \text{m}^2/\text{s}. \qquad (5)$$

For Cu diffusion, the data of Maier[20] were used:

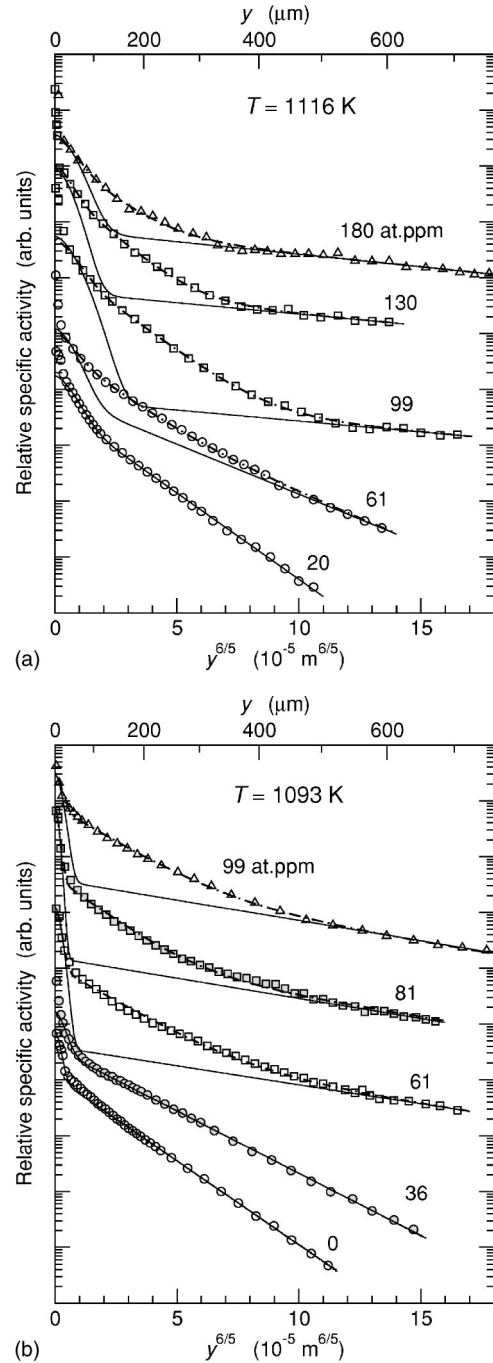$$D_v^{Cu} = 1.0 \times 10^{-5} \exp(-196.8 \text{ kJ mol}^{-1}/RT) \text{m}^2/\text{s}. \qquad (6)$$

FIG. 2. Radiotracer penetration profiles of Bi GB diffusion in a set of Cu-Bi alloys with the given Bi content at $T=1116$ K (a) and 1093 K (b). y is the penetration depth. The contributions of two kinds of short-circuit paths in addition to direct bulk diffusion can be recognized for the diffusion of Bi at Bi contents $\leqslant 61$ at. ppm (the corresponding fits are drawn by dashed lines). The solid lines represent the contribution of the GBs with the highest diffusivity plus the direct bulk diffusion flux.

A. Bi GB diffusion

Bi GB diffusion experiments were performed at $T=1093$ and 1116 K in selected Cu-Bi alloys. Due to the low solubility of Bi in pure Cu the constant source initial conditions were expected. According to Whipple's exact solution,[21] the
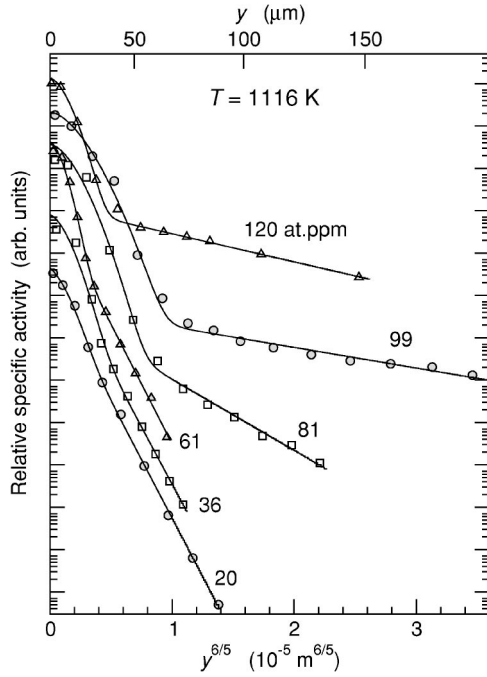
FIG. 3. Penetration profiles of Cu GB diffusion in Cu-Bi alloys with the given Bi content at $T=1116$ K. The solid lines represent the fits involving bulk and GB diffusion.

TABLE I. Experimental parameters of [207]Bi radiotracer GB diffusion experiments in Cu-Bi alloys. The values P^{slow} and P^{fast} refer to the GB diffusivities calculated from a general six-parameter fit of the penetration profiles (dashed lines in Fig. 2).

Bi content (at. ppm)	t (ks)	$\sqrt{D_v t}$ (μm)	P^{fast} (m^3/s)	P^{slow} (m^3/s)	β
			$T=1116$ K		
0			1.0×10^{-16}		
20	2.58	30	1.1×10^{-16}		5
36	2.64	31	3.0×10^{-16}	1.3×10^{-16}	43
61	2.64	31	2.8×10^{-16}	1.3×10^{-16}	43
81	2.58	30	4.0×10^{-15}	1.4×10^{-16}	199
99	2.28	28	4.0×10^{-15}	1.1×10^{-16}	201
130	2.04	27	3.1×10^{-15}	1.0×10^{-16}	332
180	1.56	24	3.9×10^{-15}	1.1×10^{-16}	260
450	1.56	24	1.1×10^{-14}		650
			$T=1093$ K		
0	8.04	44	5.3×10^{-17}		3
36	8.04	44	8.9×10^{-17}		4
61	3.66	29	1.5×10^{-15}	8.9×10^{-17}	111
81	3.48	29	1.3×10^{-15}	8.9×10^{-17}	94
99	8.04	44	1.2×10^{-15}	8.9×10^{-17}	64

GB-related tail of the penetration profile has to be linear in the coordinates of $\ln \bar{c}$ vs $y^{6/5}$ ($\bar{c}$ is the layer concentration and y the penetration depth).

The penetration profiles for [207]Bi diffusion in the Cu-Bi alloys are shown in Fig. 2. Whereas the Bi penetration profiles in pure Cu[15] and in the Cu-Bi alloys with a low Bi content (<20 at. ppm) can be well described by a superposition of bulk and GB diffusion, an additional short-circuit contribution is detected in the Cu-Bi alloys with Bi contents larger than 36 at. ppm (compare solid and dashed lines in Fig. 2). After a very short near-surface part of the penetration profiles, which is related to direct bulk diffusion, at least two short-circuit-related contributions can be distinguished in the profiles. We will mainly focus on the deepest part of the concentration profiles, which represent the contribution of the GBs with the highest diffusivity. This contribution (together with the contribution of direct bulk diffusion) is shown in Fig. 2 by solid lines.

The deepest parts of the penetration profiles are well linear in the corresponding coordinates and the pertinent slope $\partial \ln \bar{c}/\partial y^{6/5}$ allows us to calculate the value of the triple product $P=s\delta D_{GB}$ according to the Whipple solution[21]

$$P = 1.322\sqrt{D_v/t}[-\partial \ln \bar{c}/\partial y^{6/5}]^{-5/3}, \qquad (7)$$

if $\beta>10$. In the case of $1<\beta<10$, the results of the Le Claire analysis[22] of Whipple's solution were used. For example, at $\beta=4$ the numerical factor of $2(0.75)^{5/3}\approx 1.238$ is used instead of 1.322 in Eq. (7) taking into account the normalized penetration depths assessed in our experiments.

The calculated diffusivity values along with other related parameters of the GB diffusion experiments are listed in Table I. Note that whereas Bi GB diffusion at $T=1093$ K

was directly measured in pure Cu (Bi content=0), the corresponding values at $T=1116$ K were calculated from the Arrhenius parameters established in Ref. 15. The values of the diffusion parameters α (about 2×10^{-4}) and β (see Table I) satisfy the inequalities in Eqs. (1) and (2). This fact confirms that the present measurements were performed in the true type-B kinetic regime.

In order to calculate the P^{slow} and P^{fast} values in Table I the radiotracer penetration profiles were fitted by a sum of two Whipple solutions (plus direct bulk diffusion contribution). Therefore, a six-parameter fit was performed (dashed lines in Fig. 2).

B. Cu GB diffusion

The penetration profiles measured for ^{64}Cu radiotracer GB diffusion in Cu-Bi alloys are shown in Fig. 3. At Bi contents smaller than 80 ppm the concentration profiles are well described by a superposition of bulk and GB diffusion (solid lines in Fig. 3). At higher Bi content—similarly to Bi GB diffusion—a contribution of an additional short-circuit diffusion path may be indicated. However, due to the time limitations with handling of this short living ^{64}Cu radioisotope it was impossible to separate reliably this additional contribution. Consequently, we concentrate ourselves on the clearly observed contribution of the fastest short-circuit diffusion ways.

Suzuoka's instantaneous-source solution[23] was applied to analyze the Cu penetration profiles

$$P = \delta D_{GB} = 1.084 D_v^{0.469} t^{0.531}[-\partial \ln \bar{c}/\partial y^{6/5}]^{-5/3}, \qquad (8)$$

for $10<\beta<100$ and

TABLE II. Experimental parameters of ^{64}Cu radiotracer GB diffusion experiments in Cu-Bi alloys at $T = 1116$ K.

Bi content (at. ppm)	t (ks)	$\sqrt{D_v t}$ (μm)	P (m^3/s)	β
0			1.3×10^{-19}	
20	1.68	3.2	1.4×10^{-19}	4
36	1.68	3.2	1.4×10^{-19}	4
61	1.68	3.2	1.3×10^{-19}	3
81	1.68	3.2	1.3×10^{-18}	34
99	1.92	3.4	8.6×10^{-18}	204
120	1.68	3.2	6.5×10^{-18}	140
130	1.68	3.2	8.9×10^{-18}	226

$$P = \delta D_{GB} = 1.206 D_v^{0.492} t^{0.508} [-\partial \ln \bar{c}/\partial y^{6/5}]^{-5/3}, \quad (9)$$

for $10^2 < \beta < 10^4$.

The experimental parameters and derived diffusivities are summarized in Table II. The Cu GB self-diffusivities in pure Cu were calculated from the Arrhenius parameters established in Ref. 24.

IV. DISCUSSION

The concentration dependence of the triple product P^{Bi} for diffusion of Bi in the Cu-Bi alloys is shown in Fig. 4 for the two temperatures under investigation. In the single-phase (Cu-rich solid solution) region the value of P^{Bi} increases moderately up to the Bi content of 60 or 40 at. ppm at $T = 1116$ or 1093 K, respectively. Between 60 and 80 at. ppm Bi a conspicuous enhancement of the diffusivity by more than one order of the magnitude is observed at $T = 1116$ K, see Fig. 4(a). At the lower temperature of 1093 K such an increase occurs between 40 and 60 at. ppm Bi [Fig. 4(b)]. These concentration intervals lie definitely below the bulk solidus, which corresponds to about 109 and 88 at. ppm Bi at $T = 1116$ or 1093 K.[8] The position of bulk solidus is represented by the vertical solid lines in Figs. 4(a) and 4(b). With further increase of the Bi content (>80 at. ppm) and even after exceeding the bulk solidus concentrations no significant change in the diffusivity is observed within the limits of experimental uncertainties (see Fig. 4).

The Cu self-diffusivity P^{Cu} in the Cu-Bi alloys as a function of the Bi content is shown in Fig. 5. In the case of ^{64}Cu tracer the diffusion parameter P^{Cu} is reduced to the double product δD_{GB}, and segregation is not involved in the values determined experimentally. Thus, the variation of δD_{GB} with Bi concentration in the Cu-Bi alloys can mainly be related to the corresponding changes in the D_{GB} values. The experiments at $T = 1116$ K yielded nearly constant values up to some critical Bi concentration (about 60 at. ppm), followed by an almost abrupt increase in the diffusivity in the concentration range 70–90 at. ppm Bi. With further increase of the Bi content above about 90 at. ppm, nearly the same diffusivities are observed in both the single-phase and the two-phase regions of the phase diagram (Fig. 5). The experimental results [Figs. 4(a) and 5] show that the critical Bi concentration
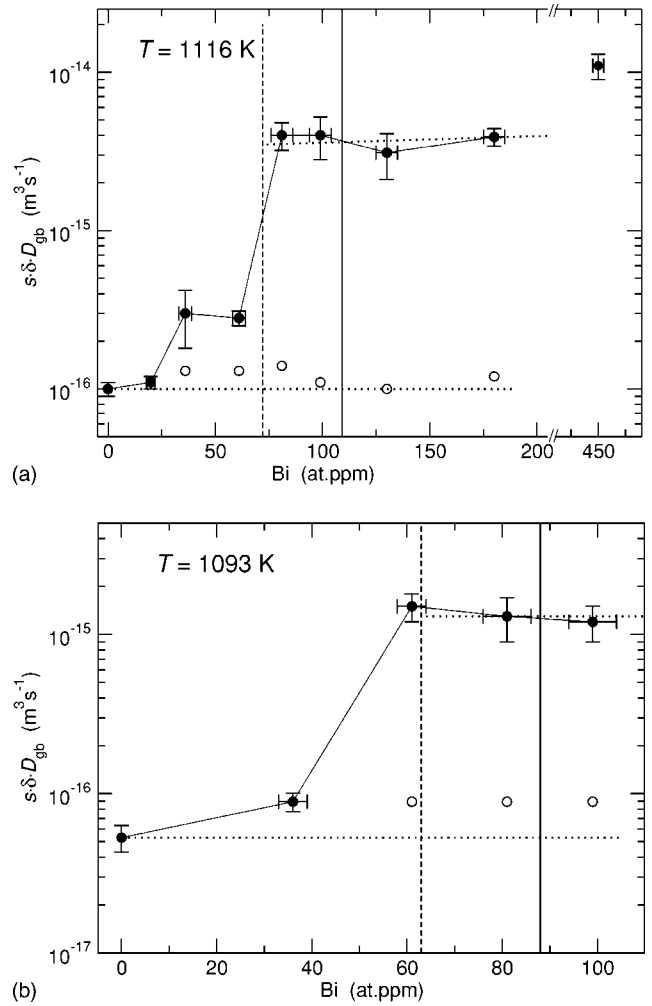

FIG. 4. Concentration dependence of the Bi GB diffusivity P^{Bi} in Cu-Bi alloys at $T = 1116$ K (a) and 1093 K (b). The full and open symbols correspond to the P^{fast} and P^{slow} values, respectively. The solid and dashed vertical lines represent the bulk and GB solidus concentrations after Chang *et al.* (Ref. 8), respectively. The dotted lines represent the Bi diffusivities in pure Cu and in two-phase (solid+liquid) Cu-Bi alloys.

is nearly the same for both solute (Bi) and self- (Cu) diffusion, i.e., about 70 at. ppm at $T = 1116$ K. These observations allow convincing conclusions on the existence of a premelting (prewetting) GB phase transition and, therefore, of liquidlike GB layers between the bulk and GB solidus lines in this system.

In the following discussion we adopt the reasonable assumption that any variation in the diffusional GB width δ is moderate and can be neglected with respect to changes in the s and/or D_{GB} values. By comparing the GB diffusion data of Cu and Bi, a set of similar, but in some cases, different features are to be observed. The diffusivity of Bi in pure Cu is almost three orders of magnitude faster than the Cu self-diffusivity at the same temperature [compare Figs. 4(a) and 5]. This difference cannot exclusively be attributed to the pertinent GB segregation factor for Bi, since s is only about 17 at $T = 1116$ K according to Eq. (3). At this temperature, the GB diffusion coefficient, Eq. (4), is higher by about two
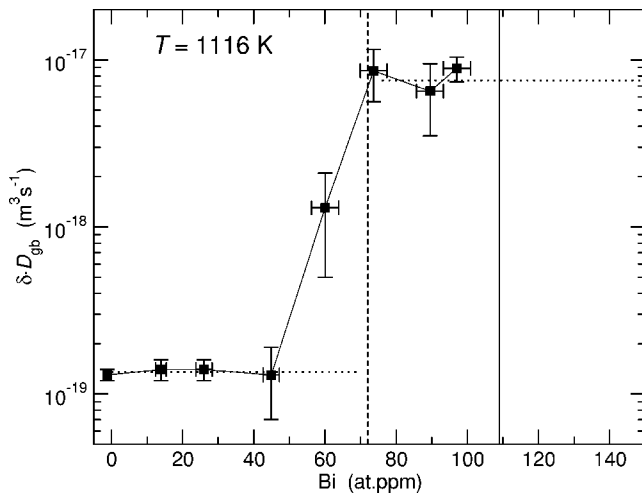
FIG. 5. Concentration dependence of the Cu GB diffusivity P^{Cu} in Cu-Bi alloys at $T=1116$ K. The dotted lines represent the Cu diffusivities in pure Cu and in two-phase (solid+liquid) Cu-Bi alloys.

orders of magnitude than the GB self-diffusion coefficient of Cu in pure Cu.

The concentration dependencies of Cu and Bi diffusion in Cu-Bi alloys can conveniently be compared starting at high Bi concentrations, which definitely lie in the two-phase region of the equilibrium phase diagram. Relative to the corresponding values in pure Cu, both the GB diffusivities of Cu and Bi are considerably enhanced in the two-phase (solid+liquid) region and are almost independent on the Bi concentration. This high GB diffusivity is preserved even at Bi contents which are distinctly smaller than the bulk solidus concentration and thus are within the single-phase region. With subsequent decrease of the Bi content, the GB diffusivity of Cu drops almost instantaneously to the self-diffusivity value in pure Cu, whereas the GB diffusivity of Bi decreases more gradually, see Figs. 4(a) and 5. Although the GB diffusivities of Bi and Cu in pure Cu are very different, the relative increases of both values are dramatic but similar when these values are measured in the two-phase (solid+liquid) region. This circumstance suggests a common origin of the observed phenomena.

The GB wetting phase transition is schematically illustrated in Fig. 6. In the two-phase region (solid α+liquid L) the GB is not completely wetted and the contact angle amounts to $\theta>0$, if the GB energy σ_{GB} is lower than the energy of two solid/liquid interfaces $2\sigma_{\alpha L}$, Fig. 6(d). If $\sigma_{GB}>2\sigma_{\alpha L}$, the GB is wetted completely by the liquid phase and $\theta=0$ [Fig. 6(b)]. The energies σ_{GB} and $\sigma_{\alpha L}$ depend on temperature and a temperature T_w may exist, at which the temperature dependencies $\sigma_{GB}(T)$ and $\sigma_{\alpha L}(T)$ intersect. This is the temperature of the GB wetting phase transition.[25] With increasing temperature, the contact angle θ decreases gradually with increasing temperature down to $\theta=0$ at T_w. Above T_w the contact angle remains $\theta=0$ [Fig. 6(b)]. Such a behavior defines a tie line of GB wetting phase transition at T_w in the two-phase region $(\alpha+L)$ of the bulk phase diagram (Fig. 6). Above this tie line, the GBs with an energy σ_{GB} cannot exist in equilibrium with the liquid phase; the liquid phase forms a layer separating the crystals.
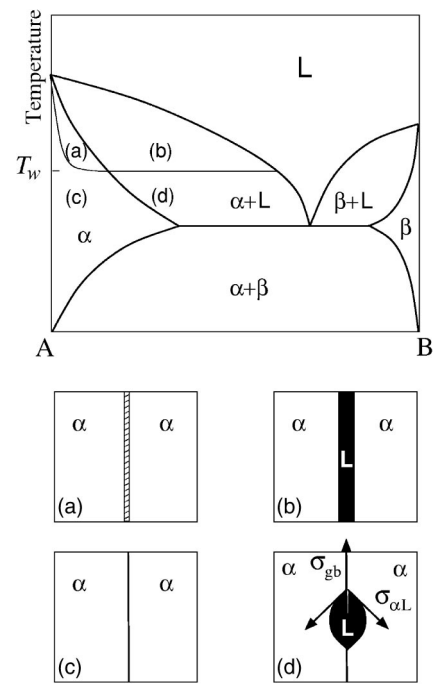

FIG. 6. An example of a bulk phase diagram with a tie line of GB wetting at T_w and its continuation as a GB solidus line (GB prewetting phase transition line). The schemes below illustrate the solute behavior at a GB in different regions of the phase diagram. Liquidlike layer (multilayer adsorption layer) in the one-phase (solid solution) region (a). Liquid phase L wets GB in the solid phase α in the two-phase region $\alpha+L$ (b). Conventional GB segregation at a GB in the one-phase region (c). Liquid phase L does not wet GB of the phase α in the two-phase region $\alpha+L$ (d).

The tie line of the GB wetting phase transition can be continued in the single-phase region of the bulk phase diagram where only solid solution is in equilibrium in the bulk.[26] Above the GB wetting tie line T_w in the two-phase solid+liquid $\alpha+L$ region $\sigma_{GB}>2\sigma_{\alpha L}$. If we intersect the bulk solidus at $T=$const and move a bit into the single-phase region α, the GB energy σ_{GB} will be still higher than the energy $2\sigma_{\alpha L}$ of two solid/liquid interphase boundaries. The GB can then be substituted by two solid/liquid interfaces with the energy gain $\Delta G=\sigma_{GB}-2\sigma_{\alpha L}$, which stabilizes the GB layer of the liquidlike phase [Fig. 6(a)]. On the other hand, the appearance of the liquidlike GB phase (otherwise unstable in the bulk) instead of the GB leads to the energy loss Δg per unit thickness and area. Equaling these energies the thickness l of the liquidlike GB phase is defined by the equation $\sigma_{GB}-2\sigma_{\alpha L}=l \cdot \Delta g$. The thickness l depends on the solute concentration and temperature and becomes $l=0$ at the line of GB premelting (or prewetting) phase transition. This line can be called the GB solidus, at which an abrupt transition from conventional GB segregation [Fig. 6(c)] to the formation of a liquidlike GB layer [Fig. 6(a)] occurs.

The temperature of about 820 K was established as the temperature T_w of the GB wetting phase transition in the Cu-Bi system.[27] The temperatures in the present investigation are considerably higher. Thus, the GBs had to be wetted by a liquid phase in the present measurements within the two-phase region.

In the present paper, GB tracer diffusion was consistently measured over the segregation, prewetting, and wetting regions of the Cu-Bi phase diagram at the same temperature (Fig. 1). In the segregation region, the GB diffusion of Cu is almost constant, whereas the GB diffusivity of Bi moderately increases following a change in the corresponding segregation factor. By exceeding the GB solidus concentration both diffusivities are abruptly enhanced revealing a structural transformation occurring at the GBs (the prewetting or premelting phase transition when a liquidlike layer appears at the GBs). Afterwards, the GB diffusivities of Cu and Bi remain almost constant (but different) for this temperature, although the Bi concentration continuously increases from the prewetting to the wetting region of the phase diagram, i.e., from the GB solidus line to the bulk solidus line. This finding indicates that no significant changes at the GBs are associated with exceeding the bulk solidus concentration and the appearance of a liquid phase in the Cu-Bi system. In the course of a wetting (melting) phase transition, the GBs of the solid phase in the solid+liquid region are replaced by a liquid phase. Taking into account the results of Chang *et al.*,[8] GBs in the Cu-Bi alloys with more than about 109 at. ppm Bi at $T = 1116$ K (i.e., in the two-phase region) should be covered by a liquid film. The present experimental data reveal that at such high Bi concentrations the relevant GB diffusivities of both Cu and Bi are enhanced by about two orders of magnitude in comparison with those in pure Cu at this temperature. Taking the GB width as 0.5 nm the Cu diffusivity D_{GB} in the Cu-Bi alloys with 100–140 at. ppm Bi (i.e., in the two-phase region of the phase diagram) can be estimated as 10^{-8} m^2 s^{-1}. This is a value which is typical for bulk diffusion in the liquid state. Such a very high GB diffusivity is also maintained after falling below the bulk solidus and entering the single-phase (solid solution) region to a certain Bi concentration. This behavior is a strong evidence that a liquidlike film still covers the GBs in the Cu-Bi alloys in the concentration range between the dashed and solid lines in Figs. 4 and 5, although such a liquid phase is unstable as a bulk phase. Such a behavior can directly be related to a prewetting (premelting) phase transition in the Cu-Bi system.

The GB diffusion measurements yield integral (averaged) information on the GB diffusivities in the material ($s\delta D_{GB}^{Bi}$ for Bi and δD_{GB}^{Cu} for Cu). On the basis of the present results, we therefore cannot conclude whether melting (GB melting with increasing temperature[10]) or prewetting (formation of two liquidlike layers around GB core[8]) phase transition occurs particularly in the Cu-Bi system. However, a liquidlike state of the Cu GBs at certain Bi concentrations already in the one-phase (Cu-rich solid solution) region is unambiguously established.

The critical Bi concentrations, at which the atomic mobilities in the GBs exhibit a steplike change, correspond well with the position of the GB solidus line which was suggested by an AES study[8] (dashed lines in Figs. 4 and 5). The similar GB diffusivities of Cu observed in the two-phase (solid+liquid) region, where the GBs are covered by a liquid phase, and in the adjacent area of the single-phase region suggest similar (liquidlike) GB structures. Also the segregation factor of Bi is not changed by crossing of the bulk

solidus.[8] Therefore, we may conclude that the pertinent GB diffusion coefficients of Bi are also nearly the same in this specific range of Bi concentrations. The gradual decrease in the GB diffusivity of Bi in the single-phase region below the critical Bi concentration—as compared to an abrupt change in the GB diffusivity values of Cu—thus can directly be related to a corresponding change in the segregation factor of Bi.

In the present paper, we have focused on the GBs with the highest diffusivities in the Cu-Bi alloys. A conspicuous enhancement of GB diffusion was observed at a certain temperature-dependent Bi content. This enhancement is related to the premelting (prewetting) phase transition in the GBs of the Cu-Bi alloys. However, this transition is not homogeneous. Whereas the GBs which have undergone the phase transformation reveal an increased diffusivity, there exists a certain fraction of general high-angle GBs which are characterized by much smaller atomic mobilities. This fact was unambiguously established for the Bi tracer (Fig. 2), but can be anticipated for the Cu tracer, too. Considering the penetration profiles in Fig. 2 as a superposition of two contributions from "fast" (P^{fast}) and "slow" (P^{slow}) GBs, a perfect agreement with the experimental data is obtained. An important feature is that the P^{slow} values are almost the same and equal to the GB diffusivity P^{Bi} of Bi in pure Cu, Fig. 4. One may suppose that P^{slow} represents the contribution of high-angle GBs in the Cu-Bi alloys which either are not covered or only partially (noncontinuously) covered by a quasiliquid layer. The fraction of such boundaries decreases with increasing Bi content and approaches zero in the Cu-450 at. ppm Bi alloy.

The GB diffusivity of Bi of the Cu-450 at. ppm Bi alloy exceeds the corresponding values of the Cu-Bi alloys with Bi contents near the bulk solidus concentration by a factor of 2. This effect may be explained by a corresponding change in the segregation factor and (that is most important from our point of view) in the width of the GB layer due to the increasing oversaturation of the solid solution.

V. SUMMARY AND CONCLUSIONS

(1) Cu self- and Bi solute GB diffusion was measured in a set of well-characterized Cu-Bi alloys in both the single-phase (solid solution) and two-phase (solid+liquid) regions of the Cu-Bi phase diagram. An abrupt change in the diffusivity of Cu as well as that of Bi is observed distinctly below the bulk solidus line. The critical Bi concentration is almost the same for both diffusivities and depends on temperature.

(2) The Bi concentration corresponding to the jump in the GB diffusivities of Cu-Bi alloys nearly coincides with the concentrations at which the prewetting phase transition was proposed to occur from the results of previous AES studies[8] (the GB solidus line).

(3) With further increase of the Bi content and after exceeding the bulk solidus practically no changes in the GB diffusivities of both Cu and Bi are observed within the limits of the experimental uncertainties up to a Bi content of 180 at. ppm, although these measurements were performed in the two-phase (solid+liquid) area of the phase diagram

above the tie line of the GB wetting phase transition.

(4) The large enhancement of the GB diffusivity yields strong evidence for the existence of a liquidlike film (otherwise unstable in the bulk) along GBs in a certain region of the single-phase (solid solution) field and occurrence of a GB premelting (prewetting) phenomenon.

The experimental findings of the present paper put new insight into the intensively disputed topic of phase transitions at GBs in polycrystalline materials. The formation of a liquidlike GB film with a drastically enhanced diffusivity can dramatically influence the functional properties of technologically important materials resulting in both advantageous (e.g., activated sintering) as well as in detrimental (e.g., GB cracking or catastrophic electromigration) effects. The use of Bi for solder application may be hindered by the formation of a liquidlike GB phase which presumably accelerates the Cu interconnect degradation through enhanced electromigra- tion in microelectronic devices. Moreover, technologically pure Cu (especially that produced from recycled copper) mostly contains several ppm of residual Bi. Consequently, even such a small amount of Bi may be of concern for a safe use of Cu in the single-phase region of the bulk equilibrium phase diagram.

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