INTERGRANULAR AND INTERPHASE BOUNDARIES IN MATERIALS

Radiotracer investigation of diffusion, segregation and wetting phenomena in grain boundaries

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Abstract The combination of so-called B- and C-type solute grain boundary (GB) diffusion measurements is a unique and reliable tool for the determination of the solute segregation factor for the true dilute limit conditions. A series of such measurements with different solutes in the same high purity Cu material gained comprehensive quantitative information on the solute segregation behaviour. Specially designed radiotracer experiments on bicrystals supplied valuable information on non-linear solute segregation and even a complete solute segregation isotherm could be determined. The strong solute segregation may invoke new effects. The GB wetting transition in the Bi–Cu system was investigated by radiotracer diffusion. A pronounced increase of GB diffusivity was observed in the two-phase (solid + liquid) region of the corresponding phase diagram, with the GB diffusivity of Cu being similar to the diffusion rate in a liquid. Such a GB diffusion enhancement exists even in the single phase (solid solution in Cu) region manifesting the existence of a pre-wetting GB phase transition in this system.

Introduction

The structure and chemistry of grain boundaries (GBs) could conventionally be studied by high-resolution transmission electron microscopy (HRTEM). Sigle et al. [1] studied recently the details of Al embrittlement by Ga on an atomistic level. The mechanism of embrittlement was examined by accurate analysis of changes in the GB structure associated with Ga segregation. Such a technique cannot be applied for the investigation of the atomistic characteristics of "arbitrary" GBs of a polycrystalline material, since the HRTEM studies require specific tilt boundaries with parallel low-index directions in the adjoining grains in order to visualize the atomic columns in both crystals. Alternatively, the total segregation level can conveniently be measured by TEM without atomistic resolution, see e.g. [2] or by Auger electron spectroscopy, which requires an intergranular fracture of the specimen [3]. Consequently, only brittle materials or solutes introducing embrittlement could be studied by the latter technique.

Strong solute segregation may introduce specific GB phase transitions [4]. It is a challenging task to reveal such phase transitions by a segregation study or even by an atom configuration analysis, since these phase transitions may correspond to small changes in atom positions. On the other hand, these changes of atom positions would result in corresponding changes of pertinent barriers for atom jumps (the migration energies). Since the diffusion rate depends exponentially on these energies, the experimental investigation of GB diffusion represents an appropriate and sensitive tool for the study of GB phase transitions. Moreover, only relatively pronounced solute concentrations can be studied by direct tools (such as HRTEM or Auger electron technique), whereas diffusion experiments deal with much smaller (radiotracer) solute concentrations.

The radiotracer method in combination with the serial sectioning is not a local technique and yields integrated information on the solute diffusivity in general high-angle GBs when being applied to a polycrystalline material. However, reliable systematics on the solute behaviour can be established using *the same* matrix material in

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experiments with different solutes. It is important to characterize the samples with respect to (critical) residual impurities. For example, already 1 ppm of S remarkably influences GB self- [5] and solute Ni [6, 7] diffusion in Cu.

GB segregation can be investigated by specially designed GB diffusion experiments combining measurements in Harrison's B and C kinetic regimes [8] on the same material. If the solute GB diffusion coefficient D_{gb} in the C regime and the so-called triple product $P = s \cdot \delta \cdot D_{gb}$ in the B regime are determined precisely, the GB segregation factor s can be evaluated as the ratio $P/(\delta \cdot D_{gb})$. Here δ is the GB diffusional width which is determined by the combination of the B and C regime measurements for GB *self-diffusion* (with the pertinent segregation factor $s = 1$). Experiments suggest that δ is almost temperature- and material independent resulting in $\delta \simeq 0.5$ nm [9–13]. This method implies that the GBs are homogeneous slabs of the thickness δ and a uniform diffusivity D_{gb}. Another important approximation is that δ is *the same* for self- and solute GB diffusion. Strictly speaking, this should not be the case and the matrix and solute atoms could use different paths for rapid movement along the GBs. However, the difference can hardly be of an order of magnitude and it introduces probably only a small uncertainty in the deduced s value. Note that δ is the *diffusional* GB width here and it should not be confused with the *structural* GB width.

The degree of information is considerably enlarged when the GB diffusion measurements are performed using a radiotracer with a well-known specific activity. In such experiments, the *absolute* solute concentrations in both, the GB and the bulk can be determined in situ even at a very low level. As a result, the segregation can be studied quantitatively including non-linear effects. In the present article, the radiotracer technique is used for the experimental investigation of segregation phenomena in poly- and bi-crystalline copper and Cu–Bi alloys.

Experimental details

GB diffusion experiments with different solutes were performed on the same polycrystalline copper material with the nominal purity 5N8. The non-special bicrystals of a similar purity with the tilt angle $\theta = 36.0°$ were prepared by Dr. S. Prokofjev in the group of Prof. L. Shvindlerman (Institute of Solid State Physics, Chernogolovka, Russia). The Cu–Bi polycrystals of different selected compositions were produced and chemically analysed in the group of Dr. B. Baretzky (Max Planck Institute for Metals Research, Stuttgart, Germany).

Cylindrical specimens of about 10 mm in diameter and 3 mm in height were cut by spark erosion. One face of the

specimen was polished by standard metallographic procedures to a mirror-like quality. The samples were sealed in silica tubes and firstly annealed at 1,273 K for 2 days to remove the introduced near-surface stresses and then secondly at the temperature and at least for the double duration of the intended diffusion anneal in order to achieve an equilibrium GB segregation of all spurious impurity elements inherent in the material and to minimise grain growth during the subsequent solute tracer diffusion experiments.

An appropriate tracer solution (^{63}Ni, ^{110m}Ag or ^{207}Bi) was dropped on the prepared sample surface and dried. After the diffusion anneals in silica tubes filled by purified (5N) Ar, the samples were reduced in diameter (by at least 2 mm) to remove the effect of lateral and surface diffusion. The penetration profiles were determined by parallel mechanical sectioning by means of a microtome and weighing the sections using a microbalance. The radioactivity of each section i.e. the relative solute concentration was measured by a liquid-scintillation counter TRI CARB 2500 TR.

Solute segregation in high-purity Cu

GB diffusion measurements are typically carried out in Harrison's B kinetic regime [8]. In this case, the bulk diffusion length, $\sqrt{D_v t}$, is larger than the GB width δ (but still significantly smaller than the grain size). Here D_v is the volume diffusion coefficient and t the diffusion time. Formally, the parameter α,

$$\alpha = \frac{s\delta}{2\sqrt{D_v t}}, \tag{1}$$

has to be smaller than 0.1. In the case of self-diffusion ($s = 1$), the GB diffusion regime can unambiguously be established by an appropriate choice of the annealing time t at the given temperature T (i.e. for the given value of the bulk diffusion coefficient D_v). The analysis of the kinetic regime is much more involved in the case of solute diffusion due to an influence of the unknown segregation factor s. However, a self-consisted iterative procedure can be applied, if the C type measurements are also performed.

According to Suzuoka's exact solution of the GB diffusion problem [14], only the value of the triple product $P = s \cdot \delta \cdot D_{gb}$ can be determined from the corresponding penetration profiles measured under the B type kinetics. The experimentally obtained P values for Ni, Ag and Bi GB diffusion in high-purity Cu are presented in Fig. 1 as a function of the inverse temperature (solid symbols). The data suggest that the measured P values follow Arrhenius type temperature dependencies. The corresponding parameters are listed in Table 1. The good agreement of
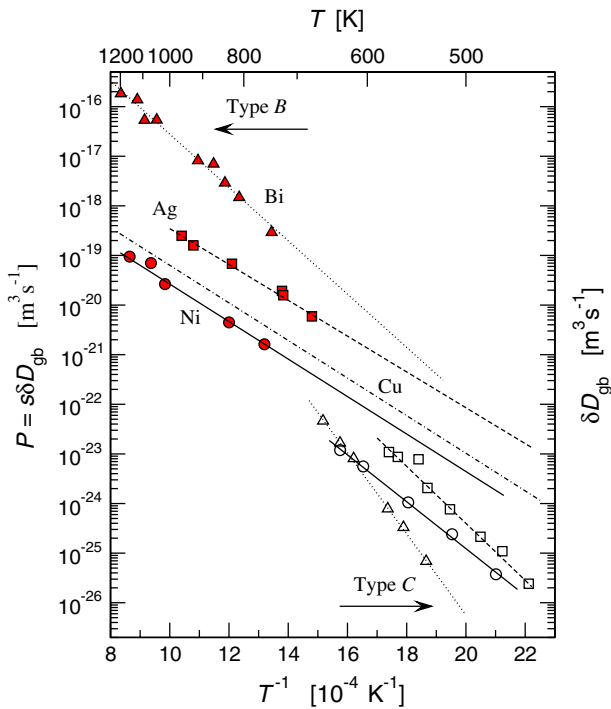
Fig. 1 Arrhenius diagram for GB diffusion of Ni [7] (circles, solid lines), Ag [15] (squares, dashed lines) and Bi [16] (triangles, dotted lines) in Cu in the type B (the P values, left ordinate, filled symbols) and in the type C kinetics (the product δD_{gb}, right ordinate, open symbols). The temperature dependence of Cu self-diffusion $P = \delta D_{gb}$ [5] is shown for comparison (the dotted-dashed line)

the Arrhenius lines with the individual experimental points over several decades proves the reliability of the derived Arrhenius parameters. This is very important for the subsequent calculation of the segregation factor s, since an extrapolation of the P values to lower temperatures is necessary.

GB diffusion measurements in the C regime (when $\alpha > 1$) are experimentally more demanding since the small amount of solute atoms inside the GBs has to be detected. However, in this case the GB diffusion coefficients D_{gb} can directly be determined from the corresponding penetration profiles.

The temperature dependencies of the measured diffusion coefficients D_{gb} of Ni, Ag and Bi are presented in Fig. 1 (open symbols). For a convenient comparison with the P values, the GB diffusion coefficients D_{gb} multiplied by the GB width are presented in Fig. 1 taking the diffusional GB width as $\delta \cong 5 \times 10^{-10}$ m. Good linear Arrhenius dependencies are observed in the temperature intervals under consideration. The corresponding Arrhenius parameters are listed in Table 1.

Figure 1 demonstrates the importance of the C-type measurements. Large P values of the solutes are not necessarily related to large GB diffusivities, D_{gb}. Among the investigated solutes, for example, Bi is the fastest element under the B regime conditions, whereas the corresponding GB diffusion coefficient, D_{gb}^{Bi}, is the smallest at lower temperatures of the C regime measurements. On the other hand, Ag is faster than Ni in both regimes within the temperature interval from 400 to 1,200 K (Fig. 1).

After measuring D_{gb} and $P = s \cdot \delta \cdot D_{gb}$, the segregation factor s can be evaluated. When extrapolating the P values to the lower temperatures of the measurements in the C regime, it becomes obvious that the products $\delta \cdot D_{gb}$ are substantially smaller than P which means that the solute atoms under investigation (Ni, Ag or Bi) do segregate to the GBs in Cu resulting in corresponding values of $s > 1$ (Fig. 1).

Figure 2 presents the temperature dependence of the segregation factors for different solutes in Cu GBs studied so far. The factors vary between several units (for Au) to several ten thousands (for Bi or Se). The segregation increases with decreasing temperature by linear Arrhenius relations. For example, Bi strongly segregates in Cu GBs with a segregation enthalpy of about -53 kJ/mol. The absolute value of the Bi segregation enthalpy is the largest among all solutes in Cu studied so far by GB diffusion measurements. Note that the same high purity copper material was used in all these investigations except that for Au in Cu where the slightly less pure 5N Cu material was studied [17]. Therefore, the segregation factors can directly be compared, which makes this series of studies particularly valuable.

Table 1 Arrhenius parameters of solute and self-GB diffusion and segregation in high-purity Cu

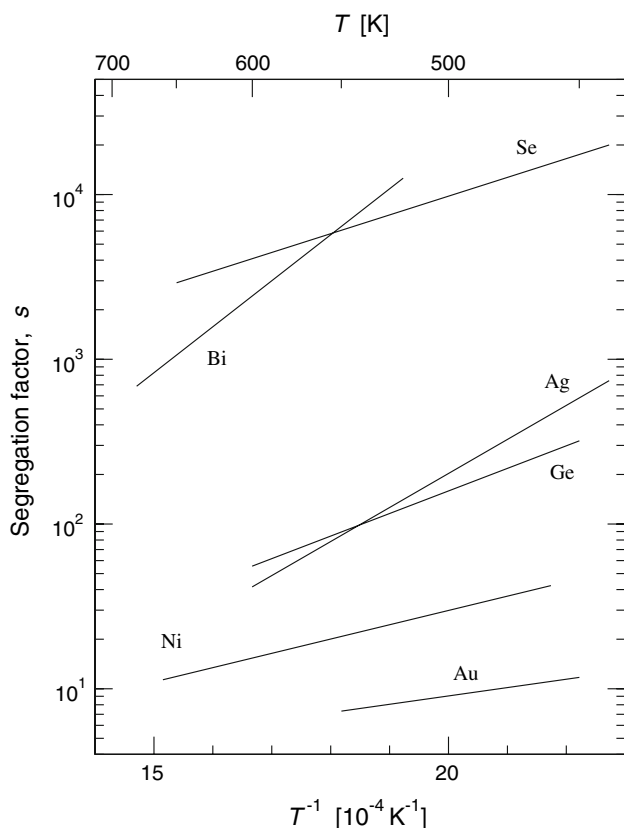| Tracer	P_0 (m³/s)	Q_{gb} (kJ/mol)	D_0 (m²/s)	H_{gb} (kJ/mol)	s_0	$-H_s$ (kJ/mol)	Reference
Cu	3.9×10^{-16}	72.5	7.8×10^{-7}	72.5	–	–	[5]
Au	2.1×10^{-15}	81.2	4.9×10^{-6}	91.0	0.90	9.8	[17]
Se	6.6×10^{-15}	52.8	2.6×10^{-7}	74.6	52	21.8	[18]
Ag	1.4×10^{-15}	69.1	1.7×10^{-4}	108.6	0.016	39.5	[15]
Ge	4.0×10^{-16}	58.6	2.8×10^{-6}	84.8	0.29	26.2	[19]
Bi	6.6×10^{-12}	102.8	2.4×10^{-1}	156.2	0.054	53.4	[19]
Ni	1.9×10^{-16}	73.8	6.9×10^{-7}	90.4	0.60	16.6	[7]

Fig. 2 Temperature dependence of the segregation factor s for different solute elements in Cu: Ni [7], Ag [15], Au [17], Se [18], Ge [19] and Bi [16]
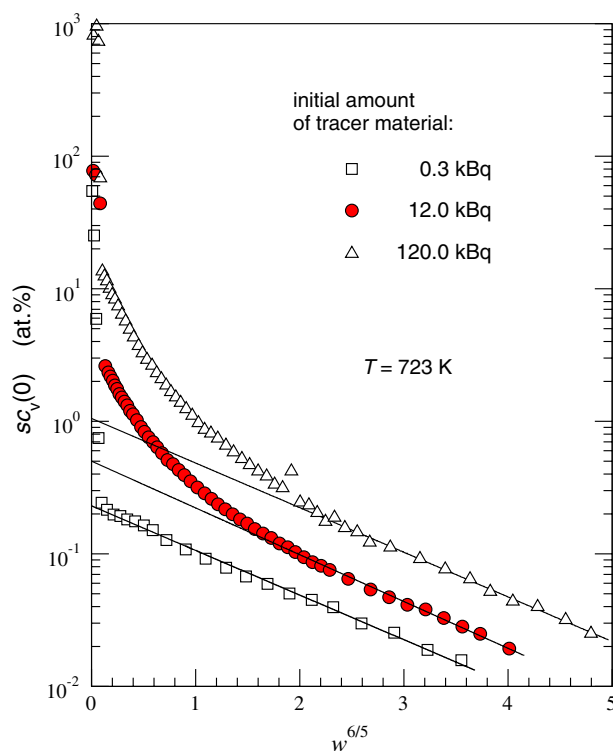

Fig. 3 Penetration profiles of Ag bulk diffusion in non-special near $\Sigma5$ Cu bicrystal after applying different amounts (radioactivities) of initial tracer material onto the polished surface: 0.3 kBq (squares), 12 kBq (circles) and 120 kBq (triangles). $w = y/\sqrt{\beta D_v t}$ is the reduced penetration depth, where $\beta = P/2D_v\sqrt{D_v t}$

Non-linear segregation of Ag in Cu Σ5 GBs

The amount of solute in a typical GB diffusion experiment on a polycrystalline material is quite small both in the GBs and in the bulk. This fact was demonstrated by using the ^{110m}Ag radiotracer with well-known specific activity [15]. Therefore, the results in Fig. 2 refer to the true dilute limit of solute segregation. Non-linear solute segregation could be invoked in experiments on bicrystals [20].

The GB diffusion experiments in bicrystals were performed in Harrison's B kinetic regime. Thus, the GB diffusion-related part of the penetration profiles has to be linear in the coordinates of $\ln \bar{c}$ versus $y^{6/5}$ [14]. Here $\bar{c}$ is the layer concentration of the solute (which is proportional to the relative specific activity measured experimentally) and y is the penetration depth.

The equilibrium GB segregation factor s of Ag in Cu is $s \approx 12$ at $T = 723$ K [15]. This value of s corresponds to the dilute limit of solute segregation of Ag in general high-angle Cu GBs [15]. We assume that nearly the same value of the segregation factor corresponds to segregation of Ag in the Cu bicrystal with non-special symmetrical near $\Sigma = 5\,[001]$ tilt ($\theta = 36.0°$) GB under investigation [20].

After applying a typical amount of the tracer material onto the polished sample surface (about 12 kBq) and annealing, a strongly curved penetration profile was measured (Fig. 3, circles). In Fig. 3 the Ag solute concentration in the crystal bulk just near the GB, $c_v(0)$, multiplied by the equilibrium segregation factor, s, is plotted against the reduced penetration depth, $w^{6/5}$, $w = y(4D_v/P^2t)^{0.25}$. The amount of Ag atoms in the GB and the adjacent bulk crystal was calculated as described in Ref. [15].

The product $s \cdot c_v(0)$, which is plotted in Fig. 3, is equal to the GB solute concentration, c_{gb}, if the segregation behaviour corresponds to the dilute limit. If $c_v(0)$ and c_{gb} exceed the concentration level corresponding to the dilute limit conditions, the linear relation between them is no longer valid. For example, the McLean isotherm [21] may describe non-linear segregation in some particular cases:

$$\frac{c_{gb}}{c_{gb}^0 - c_{gb}} = b\frac{c_v}{1 - c_v}. \tag{2}$$

Here c_{gb}^0 is the solute concentration corresponding to the GB saturation and b is the enrichment factor. All concentrations are in mole fractions. By accounting for the solute–solute interactions [22] or applying a multilayer segregation approach, see e.g. [23, 24], far more complicated

cases can be analysed. Such detailed analysis requires a separate study and is out of the scope of the present article. Here, we focus on the fundamental possibility to investigate the transition from linear to non-linear isotherm by the radiotracer method.

The non-linear dependence of c_{gb} on c_v affects the shape of the penetration profiles of GB solute diffusion resulting in an upward deviation from the otherwise linear shape [25, 26]. However, in a general case of GB diffusion in a polycrystalline material, it is an involved task to relate unambiguously the curvature of the penetration profile to the non-linear solute segregation. The situation is much simpler in the present case of GB diffusion of Ag in the Cu bicrystal. The analysis has shown that neither GB motion nor GB multiplicity caused this curvature. Moreover, almost perfect (linear) B-type penetration profiles were measured for GB diffusion of Au in the same Cu bicrystals [27]. Since Au segregates only very moderately at Cu GBs [16] (Fig. 2), we suggested that it is the non-linear segregation of Ag to Cu GB which results in the pronounced curvature of the penetration profile. Two additional GB diffusion experiments prove the existence of the non-linear segregation in the present case.

By applying a smaller amount of the initial tracer material about 300 Bq, an almost linear penetration profile is measured (Fig. 3). By increasing the amount of the initial tracer material to about 120 kBq, a pronounced curvature is again observed (Fig. 3).

The deepest linear parts of all three penetration profiles are almost parallel in the reduced coordinates and very similar values of the triple products are thus derived. If a sufficiently small amount of tracer material is applied, a fully linear penetration profile is measured (Fig. 3, squares). Therefore, a linear relation between c_{gb} and $c_v(0)$ holds along the GB in such a case. All disturbing factors, which could potentially produce a curvature of a GB diffusion penetration profile and which are not directly related to the solute amount in the GB, are thus absent in the present measurements on bicrystals.

If a certain level of the solute concentration in the sample is approached, there occurs a fundamental change in the shape of the penetration profiles—they reveal a significant curvature. The further increase of the initial tracer amount (i.e. of the resulting solute concentration in the GB and in the adjacent crystal) results in a parallel shift of the deepest part of the profile to higher concentrations and in a stronger deviation from the linearity in the near-surface region.

The deviation from the linearity starts at almost the same value of the GB and bulk concentrations of Ag, $c_{gb} = s \cdot c_v(0) \approx 2 \times 10^{-3}$ (in mole fractions). The linearity of the penetration profiles below this value suggests that the Ag GB concentration is directly proportional to

that in the adjacent crystal and the proportionality factor is the equilibrium segregation factor s.

Applying Gibbs extension [28] of the standard Fisher model of GB diffusion [29], the segregation isotherm was calculated [20]. The results, i.e. c_{gb} as function of $c_v(0)$, are presented in Fig. 4. The resulting segregation isotherms derived from the two independent GB diffusion experiments are consistent. One realizes that using very sensitive radiotracer GB diffusion measurements with a suitable tracer on bicrystals one can reliably determine the segregation isotherm already starting from very small GB concentrations. Regarding this feature, the presented radiotracer method is superior to other experimental techniques so far applied for treating the segregation phenomena.

We fitted the experimental results in Fig. 4 by a single McLean-type isotherm, Eq. 2. Since the McLean isotherm should reduce to the Henry type isotherm in the dilute limit, the relation

$$s^{Henry} = b \cdot c_{gb}^0 \tag{3}$$

can be derived from Eq. 2. Since s^{Henry} has already been measured in our previous investigation [15], we have only one fitting parameter, c_{gb}^0. The least-squares fit yields a somewhat unexpected result, namely $c_{gb}^0 \approx 0.01$ (in mole fractions). This suggests that already 1% of Ag solute atoms causes the "saturation" of Cu GBs. This is not a saturation in a strict sense. The Cu GB can incorporate indeed more than 1% of Ag atoms. The value of $c_{gb}^0 \approx 0.01$ has been determined in three independent experimental investigations: (i) GB diffusion of Ag in high-purity polycrystalline copper in the B and C kinetic regimes [15];
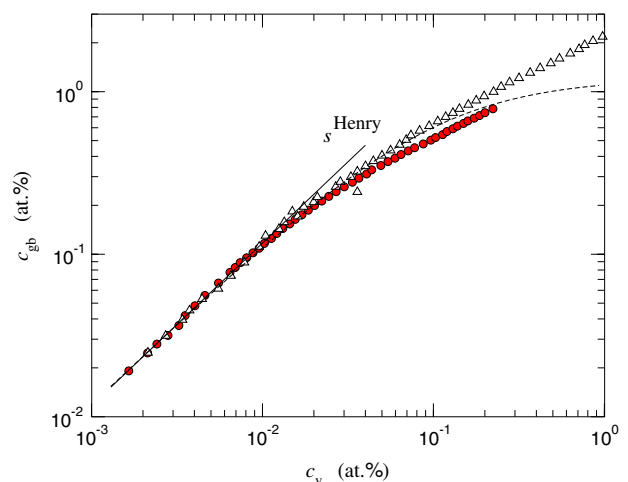

Fig. 4 Segregation isotherms of Ag in Cu at $T = 723$ K derived from the experimental profiles in Fig. 3. A hypothetical linear segregation isotherm, $c_{gb} = s^{Henry} \cdot c_v$, is shown by the solid line and the McLean isotherm, $c_{gb} = bc_{gb}^0 c_v/(1 - c_v + bc_v)$, Eq. 2, is represented by the dashed line

(ii) GB diffusion of Ag in polycrystalline Cu–0.2 at.% Ag alloy [30]; and (iii) GB diffusion of Ag in pure Cu bicrystals [20]. Therefore, we strongly believe that c_{gb}^0 is indeed so small for the Ag segregation in Cu. The reasons of such a small value of c_{gb}^0 requires further studies. From our point of view, the most reliable explanation is that the value $c_{gb}^0 \approx 0.01$ corresponds to the amount of Ag atoms which segregates with the given segregation enthalpy of $H_s = -39.5$ kJ/mol in a Cu GB. This is the value that has been measured for the equilibrium segregation of Ag in Cu GBs in the true dilute limit [15]. Segregation above this level demands that Ag atoms have to be positioned at other places with a smaller segregation enthalpy. Figure 4 demonstrates that the amount of the segregated Ag atoms increases continuously over the value of $c_{gb}^0 \approx 0.01$. Thus, the true segregation isotherm is not of the McLean type in the present case. Note that the observed behaviour does not contradict to the existence of a specific interfacial phase transition (multilayer phase transition) predicted for the Ag segregation in Cu [23] at larger interfacial coverages.

GB phase transition by solute wetting in the system Cu–Bi

Copper embrittlement by Bi atoms is a typical example of a severe detrimental phenomenon in materials science. It has been recently proposed that the strong Bi segregation in Cu can cause a liquid-like film at the grain boundaries, already when the alloy is still in the single-phase (solid solution) region of the equilibrium phase diagram [31]. The Cu-rich part of the Cu–Bi phase diagram is shown in Fig. 5. The regions of Bi segregation, pre-melting and melting states are indicated according to the observations of Chang et al. [31]. However, a direct experimental confirmation of a liquid-like state of GBs in such a case was missing. If a liquid-like GB phase is indeed formed, the GB diffusivity should dramatically be enhanced. We emphasise that the present radiotracer diffusion study differs basically from the experiments on liquid Bi penetration in copper [32].

We have measured both ^{207}Bi and ^{64}Cu GB radiotracer diffusion in Cu–Bi alloys as a function of Bi concentration [33]. The concentration dependence of the triple product P^{Bi} for diffusion of Bi in the Cu–Bi alloys at $T = 1{,}116$ K is shown in Fig. 6. For a better comparison with the GB self-diffusion data the enhancement of the GB diffusivity in the Cu–Bi alloys is plotted, i.e. the ratios of the corresponding GB diffusivities P in the given Cu–Bi alloy to the pertinent diffusivity in pure Cu, $P^{(Cu-Bi)}/P^{(Cu)}$. In the single-phase (Cu-rich solid solution) region, the value of P^{Bi} increases moderately up to the Bi content of 60 at.ppm. Between 60 and 80 at.ppm Bi, a conspicuous enhancement of the diffusivity by more than one order of the magnitude
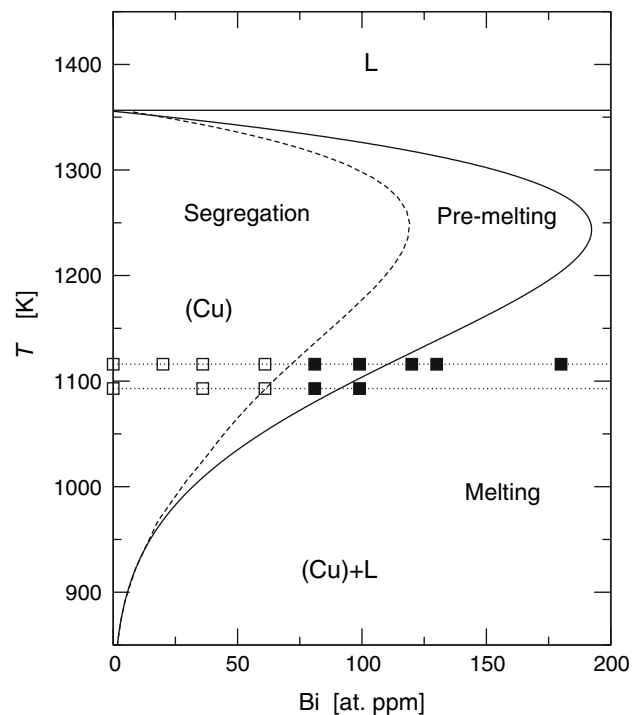

Fig. 5 Cu-rich side of the Cu–Bi phase diagram after Chang et al. [31]. The solid curve is the (retrograde) bulk solidus line. The dashed curve is the GB solidus line obtained for Cu–Bi polycrystals. The annealing temperatures (1,116 and 1,093 K) and the Bi concentration of the samples are indicated. The solid symbols indicate the samples in which fast diffusion paths were detected. L = liquid; (Cu) = Cu-rich solid solution
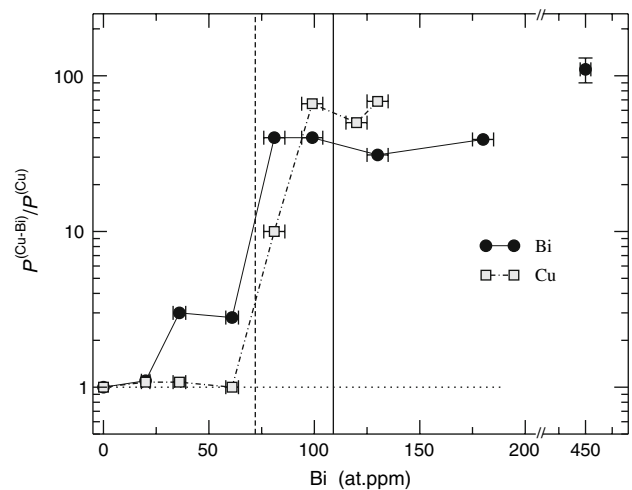

Fig. 6 Concentration dependence of the Bi (circles) and Cu (squares) GB diffusivities $P^{(Cu-Bi)}$ in Cu–Bi alloys at $T = 1{,}116$ K. The values are normalised on the respective diffusivities $P^{(Cu)}$ in high-purity Cu. The solid and dashed vertical lines represent the bulk and GB solidus concentrations after Chang et al. [31], respectively

is observed. This concentration interval lies definitely below the bulk solidus, which corresponds to about 109 at.ppm Bi at $T = 1{,}116$ K [31]. With a 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. 6).

The normalised Cu self-diffusivity P^{Cu} in the Cu–Bi alloys as a function of the Bi content is also shown in Fig. 6. The experiments at $T = 1,116$ K yielded nearly constant values up to the same critical Bi concentration (about 60 at.ppm), followed by a steep increase in the diffusivity values in the concentration range 70–90 at.ppm Bi. With a further increase of the Bi content above about 90 at.ppm, however, nearly the same diffusivity values are observed in both the single-phase and the two-phase regions of the phase diagram (Fig. 6). Although the GB diffusivities of Bi and Cu in pure Cu are very different, cf. Fig. 1, the relative increases of both values are pronounced 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 experimental results reveal unambiguously a remarkable enhancement of the GB diffusivities P^{Cu} and P^{Bi} in a vicinity of the solidus line at the given temperature. What is the nature of this phenomenon? 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, as this is the case for Bi GB diffusion. Hypothetically, the corresponding changes in both, the GB width δ and the GB diffusion coefficient D_{gb} could substantially contribute to the observed increase of the GB diffusivity.

According to Chang et al. [31], GBs in the Cu–Bi alloys with more than about 109 at.ppm Bi at $T = 1,116$ 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 to those in pure Cu at this temperature. Assuming that the GB width is about 0.5 nm and it is not changed significantly with the increased Bi content 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^{-9}–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 behaviour yields strong evidence that a liquid-like film indeed covers the GBs in the Cu–Bi alloys in the concentration range between the dashed and solid lines in Fig. 6, although such a liquid phase is unstable as a bulk phase. Such a behaviour can directly be related to a prewetting (premelting) phase transition in the Cu–Bi system.

Is the assumption of the constant value of $\delta \approx 0.5$ nm reasonable? The theory of wetting transition [34–36] predicts a logarithmic-like divergence of the thickness of the GB liquid layer. A thin liquid GB layer appears first at the GB prewetting phase transition in a close contact to the neighbouring crystals [37]. Therefore, one may expect a significant order in such a 2D-confined liquid film. As a result, the GB diffusivity cannot immediately be enhanced. As the Bi content increases, the liquid layer thickens and the corresponding GB diffusivity enhances remarkably. The experimental data at $T = 1,116$K (Fig.6) suggest that already in the Cu–90 ppm Bi alloy, the double product $\delta \cdot D_{gb}$ is enhanced by two orders of magnitude. Although a slight increase in δ can be expected according to the wetting transition theory near the prewetting line, we conclude that this diffusivity enhancement corresponds to the pertinent increase of D_{gb} validating the above estimates of the GB diffusion coefficients in the wetting region. With a further increase of the Bi content in the Cu–Bi alloys the Bi GB diffusivities increase from 4×10^{-15} (at 180 ppm Bi) to 1.1×10^{-14} m^2 s^{-1} (at 450 ppm Bi) at $T = 1,116$ K. This increase may be related to a corresponding thickening of the liquid layer, however a change in the pertinent segregation factor s^{Bi} cannot be ruled out.

Summary

The radiotracer GB diffusion measurements represent a unique and sensitive tool for studying quantitatively solute segregation phenomena in a broad interval of corresponding GB concentrations of the solute—from the true dilute limit to non-linear segregation. A complete segregation isotherm can be derived in special cases. The existence of the melting (wetting) GB phase transitions can be elucidated by measuring the kinetic properties of internal interfaces.

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