Sergiy V. Divinski[a], Maik Lohmann[a], Sergej I. Prokofjev[b], Christian Herzig[a]

[a] Institut für Materialphysik, Universität Münster, Münster, Germany
[b] Institute of Solid State Physics, Chernogolovka, Russia

Quantitative experiments on the transition between linear to non-linear segregation of Ag in Cu bicrystals studied by radiotracer grain boundary diffusion

Dedicated to Professor Dr. Lasar Shvindlerman on the occasion of his 70th birthday

Non-linear segregation of Ag in Cu grain boundaries (GB) was quantitatively studied by radiotracer GB diffusion measurements on Cu bicrystals with non-special near $\Sigma 5$ symmetrical [001] tilt boundaries. Bicrystals were used to guarantee a stable GB during the annealing avoiding in this way disturbing effects like GB motion etc. on the measured diffusion penetration profile. The ^{110m}Ag radioisotope with a well-defined specific activity was applied. This allowed to determine quantitatively the amount of Ag solute atoms in a section as a function of the penetration depth. The controlled variation of the total amount of diffusing Ag atoms along the Cu GB resulted in a fundamental change of the GB penetration profile shape from almost linear to strongly curved. The curvature of the penetration profiles was unambiguously shown to be caused by non-linear segregation of Ag in Cu GB. The full Ag segregation isotherm was calculated from the corresponding GB diffusion penetration profile.

Keywords: Grain boundary diffusion of Ag in Cu; Solute segregation; Non-linear solute segregation

1. Introduction

Most technologically important materials are usually used in a polycrystalline form. Segregation of solute and residual atoms at internal interfaces represents an important phenomenon which may be both advantageous (activated sintering, ductilization of intermetallics by boron addition, etc.) as well as disadvantageous (segregation-induced embrittlement, grain boundary corrosion, etc.). The knowledge of the solute segregation characteristics at the interfaces is decisive for the design of materials by interfacial engineering [1] – a modern branch in material development.

So far Auger electron spectroscopy (AES) presents the most common approach to study solute segregation at grain boundaries (GB) in a quantitative manner [2–4]. However the AES technique can only be applied to inherently brittle materials or in the case of solute-induced embrittlement. In such cases the sample can be broken along a grain boundary and the segregation level can be examined. Since the samples most probably brake along interfaces with an increased solute concentration, such a method can suffer from inadequate statistics of solute distribution in the sample. Moreover, a significant interface coverage by a solute is required to detect reliably the Auger signal of solute atoms.

Analytical high-resolution TEM represents a promising approach to study locally the solute segregation [5–7]. Such measurements may also be carried out for ductile materials like Cu. Since this method is very local, it demands extended sampling to produce statistically reliable data. Again, a significant amount of solute atoms in a GB is necessary for solute detection with confidence.

On the other hand, the GB solute segregation can be studied by radiotracer GB diffusion. The key point here is the combination of GB diffusion measurements in the so-called types B and C kinetic regimes [8]. Whereas only the triple product $P = s \cdot \delta \cdot D_{\mathrm{gb}}$ can be determined in the B kinetic regime at somewhat higher temperatures, the GB diffusivity D_{gb} can directly be measured at lower temperatures in the C kinetic regime. Here δ is the GB width and s the segregation factor, which is defined as a ratio of the GB solute concentration, c_{gb}, to the solute concentration in the bulk just near the GB, $c_{\mathrm{v}}(0)$:

$$s = c_{\mathrm{gb}}/c_{\mathrm{v}}(0) \tag{1}$$

The experiments on GB self-diffusion (with the pertinent segregation factor being simply unity) demonstrated that $\delta \approx 0.5$ nm for the diffusional GB width in FCC metals and alloys [9, 10]. Then, combining the data on P and D_{gb} the solute segregation factor can be determined as $s = P/\delta D_{\mathrm{gb}}$. This approach has been already applied for several solutes in copper and silver, see e. g. recent overviews in Refs. [11, 12].

Since a tiny (tracer) amount of radioactive solute atoms is typically applied and are reliably detected by the radioisotope techniques, the solute segregation corresponding to true dilute conditions can thoroughly be studied.

If the amount of solute atoms in a GB becomes larger, non-linear solute segregation effects become important [13]. The non-linear segregation may considerably affect the penetration profiles in the GB diffusion experiments by provoking a significant curvature of the otherwise linear penetration profiles, when plotting in adequate coordinates, e. g. $\ln \bar{c}$ vs. $y^{6/5}$ [14, 15], see also below. Here $\bar{c}$ is the layer tracer concentration (which is proportional to the experimentally determined specific activity of the section) and y is the penetration depth. In polycrystalline materials this effect may be overshadowed by probable GB motion [16, 17] or the co-existence of different GBs (e. g. low-angle and high-angle boundaries [18] and/or different high-angle boundaries [19]) with different diffusivities.

In order to study reliably the non-linear solute segregation at internal interfaces, samples with one stable GB are required. Therefore, a radiotracer investigation of GB diffusion of a solute along a single GB in a bicrystal is very promising, since the contributions of the above-mentioned disturbing factors into the penetration profile curvature may be either fully excluded or at least clearly separated. Furthermore, in a radiotracer experiment, the solute concentration in a GB can be easily manipulated in the desired manner by changing the applied amount of the tracer material with known specific activity.

The present paper reports on GB radiotracer diffusion of Ag in a Cu bicrystal with non-special near $\Sigma 5$ a symmetrical [001] tilt GB. The tilt angle $\theta = 36.0°$ was chosen. Extended variation of the initial amount of applied tracer material allows quantitative control of the solute concentrations in the GB during the diffusion annealing and thus the study of non-linear GB segregation of Ag in Cu in well-defined conditions.

2. Experimental procedures

2.1. Sample preparation

The present study was performed on Cu bicrystalline samples which originated from the series of specimens already used in our previous investigation of Au and Cu GB diffusion in Cu bicrystals with near $\Sigma = 5$ (310)[001] symmetrical tilt GBs [20, 21]. When comparing the Cu diffusivity in the bicrystals [21] with that measured in high-purity polycrystalline Cu [22], one can see that the bicrystals with about 1° deviation from the perfect $\Sigma 5$ (the tilt angle $\theta = 36.9°$) misorientation exhibit a similar GB diffusivity as measured in general high-angle boundaries of polycrystalline material. This is the reason why we have chosen on purpose non-special bicrystals with the tilt angle $\theta = 36.0°$ for the present investigation.

The bicrystals were prepared by Dr. S. Prokofjev in the group of Prof. L. Shvindlerman (Institute of Solid State Physics, Chernogolovka, Russia). The Cu bicrystals were grown in a high-purity graphite mould in Ar atmosphere by directional crystallization. Cu material of nominal 99.995 wt.% purity was used. Due to a zone refining effect in the bicrystal growing technique, the purity of the bicrystals was even better and can be compared with the purity of the Cu material used in our previous studies of solute GB diffusion [22–24]. Details of the bicrystal growth technique are described in Ref. [21].

Samples of 2 to 3 mm in height were cut by spark erosion. One face of the specimen was polished to mirror-like quality by standard metallographic procedure. After polishing the samples were sealed under argon atmosphere in silica tubes and annealed at 1273 K for 2 days to remove introduced near-surface stresses.

2.2. Radiotracer measurements

The radiotracer [110m]Ag (half-life 252 d, initial specific activity 78.9 MBq/mg) was produced from the isotope [109]Ag by irradiation with a well-defined neutron flux at the research reactor in Geesthacht (Germany). The tracer was used in form of a nitrate solution and deposited onto the polished face of the specimens by evaporation in a high-vacuum chamber. The samples were sealed in silica tubes under Ar atmosphere and subjected to diffusion annealing at $T = 723$ K. The temperature was measured and controlled by Ni–NiCr thermocouples to an accuracy of ± 1 K. After the diffusion anneals the samples were reduced in diameter (at least 1 mm) to remove effects of lateral and surface diffusion.

The penetration profiles were measured by the serial sectioning technique using a microtome. The activity of each section was determined by measuring the intensity of the β-radiation of the [110m]Ag tracer in a liquid scintillation counter of a very low background. The penetration depth was determined by weighing each section on a microbalance. The penetration profiles represent the plot of specific activity (activity per section mass) against the penetration depth.

3. Results and discussion

The present GB diffusion experiments in bicrystals were performed in Harrison's B kinetic regime [25]. The tracer distribution is mainly a result of fast diffusion along the GB and subsequent outdiffusion into crystal bulk. The GB diffusion-related part of the penetration profiles is linear in the coordinates of $\ln \bar{c}$ vs. $y^{6/5}$ [26].

According to the Suzuoka solution [26], the triple product $P = s \cdot \delta \cdot D_{gb}$ can be determined from the slope of the GB diffusion-related part of the penetration profile:

$$P = 1.308 \sqrt{\frac{D_v}{t}} \left(-\frac{\partial \ln \bar{c}}{\partial y^{6/5}} \right)^{-5/3} \tag{2}$$

Here t is the diffusion time and D_v is the bulk diffusion coefficient. The bulk diffusivity of Ag in Cu was taken from the investigation of Barreau et al. [27]:

$$D_v = 0.61 \cdot 10^{-4} \cdot \exp\left(-\frac{194.4 \, \text{kJ} \cdot \text{mol}^{-1}}{RT} \right) \, \text{m}^2 \text{s}^{-1} \tag{3}$$

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

Equation (2) can be applied if the parameter $\beta = s\delta D_{gb}/2D_v\sqrt{D_v t} > 10^4$ [26]. This condition was found to hold in the present case, see Table 1. Additionally, the bulk diffusion length has to be much larger than the GB width δ in the B kinetic regime, i. e. the parameter α,

$$\alpha = s\delta/2 \sqrt{D_v t} \tag{4}$$

has to be reasonably small, $\alpha < 0.1$. The equilibrium GB segregation factor s of Ag in Cu was taken from our pre-

Table 1. The parameters of Ag GB diffusion in Cu symmetrical near $\Sigma 5$ [001] tilt ($\theta = 36.0°$) bicrystal at $T = 723$ K. P is the GB diffusivity determined.

Amount of tracer material (kBq)	t (s)	P (m^3/s)	$\alpha = \dfrac{s\delta}{2\sqrt{D_v t}}$	$\beta = \dfrac{s\delta D_{gb}}{2D_v\sqrt{D_v t}}$
0.3	244 500	3.83×10^{-20}	7.8×10^{-3}	9.5×10^{4}
12	2 673 300	4.22×10^{-20}	2.4×10^{-3}	3.2×10^{4}
120	2 673 300	4.51×10^{-20}	2.4×10^{-3}	3.4×10^{4}

vious study of Ag GB diffusion in both the type-B and type-C kinetic regimes in polycrystalline copper, where the temperature dependencies of the triple product P and the GB diffusivity D_{gb} were separately determined [23]. As a result,

$$s = 0.016 \exp\left\{-\frac{-39.5\,\text{kJ} \cdot \text{mol}^{-1}}{RT}\right\} \qquad (5)$$

was obtained, which means $s \approx 12$ at $T = 723$ K. This value of s corresponds to the dilute limit of segregation of Ag in general high-angle Cu GBs [23]. 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. Hoffman et al. investigated the orientation dependence of GB solute segregation (C, P, and Si) in symmetrical Fe-3.5 at.% Si tilt GBs [28]. The smallest value of the segregation enthalpy was found for symmetrical GBs of high coincidence. As the tilt angle deviates from a high coincidence orientation, the segregation enthalpy increases and attains its maximum value for general high-angle boundaries. Therefore, our assumption about the segregation level in the bicrystal under consideration seems to be plausible.

Taking $\delta = 0.5$ nm, the parameter α can now be calculated from Eq. (4) and its value satisfies the B regime conditions, see Table 1.

When applying a typical amount of the tracer material to the polished sample surface (about 12 kBq) and performing the GB diffusion annealing, a strongly curved penetration profile was measured (Fig. 1, circles). In Fig. 1 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, $w^{6/5}$, $w = y/(\beta D_v t)^{0.5}$. The distribution of Ag atoms in the GB and the adjacent bulk crystal is governed by GB diffusion of Ag in the Cu bicrystals. Then the amount of Ag atoms inside of the bulk crystals far from the external sample surface ($y \gg \sqrt{D_v t}$) is determined by their leakage from the GBs, Fig. 2. In a sectioning experiment, one determines the specific activity of the radiotracer in the given section of the thickness Δy. Generally, this specific activity is proportional to the solute layer concentration $\bar{c}$. Since the Ag radioisotope with a well-known specific activity, $A = A_0 \exp(-t_{exp}/\tau)$, was used ($A_0$ and τ are the initial activity and the decay constant, respectively), the bulk solute concentration in a section, $\bar{c}$, can be determined from the measured activity of the section [23]:

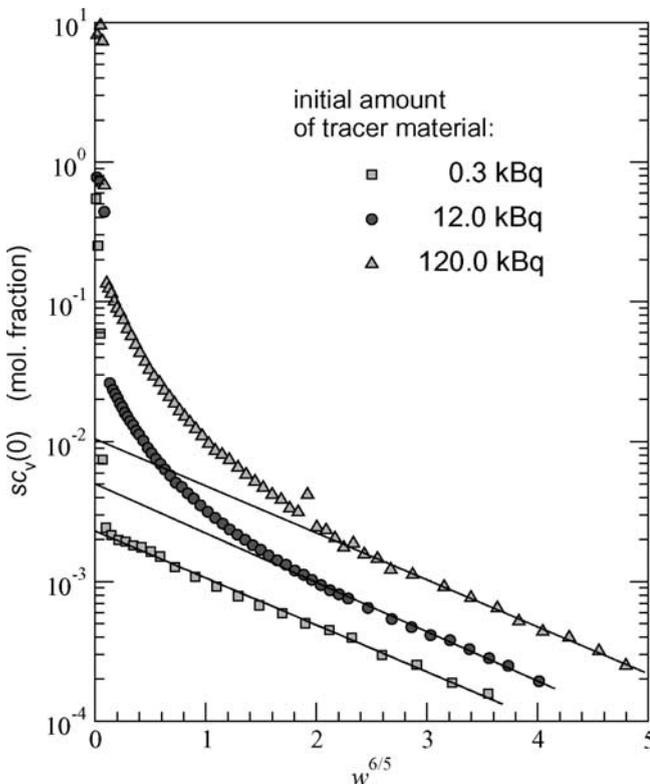$$\bar{c} = \frac{A_{exp}}{A}\frac{W_{Cu}}{W_{Ag}}\frac{1}{\gamma_{eff}} \qquad (6)$$

Fig. 1. Penetration profiles of Ag bulk diffusion in Cu near $\Sigma 5$ bicrystal after applying different amounts 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.
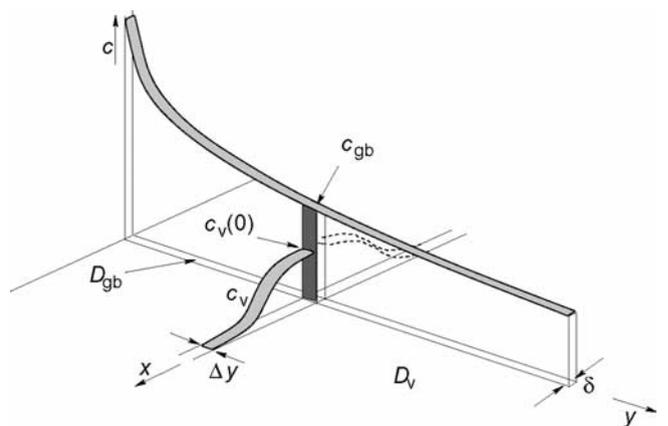

Fig. 2. Schematic representation of the solute atom distribution in a bicrystal after a diffusion anneal (thick lines). The solute concentration in the GB, c_{gb}, and the solute concentration in the bulk crystal in a section Δy, c_v, are plotted. y is the penetration depth and x is the coordinate perpendicular to the GB of the thickness δ. c_v as a function of x describes the solute leakage from the GB into bulk crystal by bulk diffusion with the diffusivity D_v. The ratio of the GB solute concentration, c_{gb}, and the bulk solute concentration just near GB, $c_v(0)$, determines the segregation factor s, Eq. (1).

Here A_{exp} is the measured specific activity (counting rate per section mass) in a section, W_{Cu} (W_{Ag}) is the molar mass of Cu (Ag), and γ_{eff} is the known efficiency of our counting system. The solute concentration, $\bar{c}$, is given in molar fractions. Then, having applied the Fisher model of GB diffusion [29], the bulk solute concentration at the GB, $c_{\text{v}}(0)$, can be calculated from the layer concentration $\bar{c}$ [23]:

$$c_{\text{v}}(0) = \frac{d}{4} \sqrt{\frac{\pi}{D_{\text{v}}t}} \bar{c} \tag{7}$$

Here d is the bicrystal diameter.

The product $s \cdot c_{\text{v}}(0)$, which is plotted in Fig. 1, is equal to the GB solute concentration, c_{gb}, if the segregation behavior corresponds to the dilute limit, see Eq. (1). If $c_{\text{v}}(0)$ and c_{gb} exceed the concentration level corresponding to the dilute limit conditions, the linear relation between them, Eq. (1), is no longer valid. Non-linear solute segregation has to be considered instead. In an ideal case, the simple McLean isotherm may describe the non-linear segregation [30]:

$$\frac{c_{\text{gb}}}{c_{\text{gb}}^0 - c_{\text{gb}}} = b \frac{c_{\text{v}}}{1 - c_{\text{v}}} \tag{8}$$

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. More elaborate approaches include simultaneous segregation to several monolayers [31] and/or solute–solute interactions [32].

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 [13–15]. However, in a general case it is an involved task to relate unambiguously the penetration profile curvature to a non-linear solute segregation. As it was mentioned in the Introduction, such factors as motion of a part of GBs during the diffusion anneal [16, 17], the co-existence of small- and high-angle boundaries in the material [18], and/or the existence of several types of high-angle GBs with very different diffusivities [19] may cause a curvature of the penetration profiles in a polycrystalline material. A comprehensive analysis is then required to separate these possible contributions, as it was done e.g. for GB diffusion of Ag in polycrystalline Cu [23]. In that investigation it was convincingly shown that the profile curvature was a result of GB motion during diffusion anneal [23]. The investigations with different radiotracers (Ag, Au, Cu) in the same Cu material gave similar results for both the absolute values as well as for the activation enthalpy of motion of arbitrary large-angle boundaries [33]. The segregation of Ag in Cu remained to be linear along the corresponding profiles in that case, since the GB concentration of Ag atoms in polycrystalline Cu was estimated to be less than 10^{-3} (in mole fractions) [23]. Such a small value satisfies reasonably the dilute limit conditions.

The situation is fundamentally different in the present case of GB diffusion of Ag in the Cu bicrystal. The following salient features were established by optical microscopy after diffusion experiments:

• no GB motion occurred; the GB was perpendicular to the outer surface before and after the diffusion annealing;

• no GB multiplicity with a length scale of about 100 μm was observed. Such a GB multiplicity could hypothetically cause a curvature of the GB diffusion penetration profiles, as it was found for GB diffusion of Au along the incoherent twin boundary in a diffusion-bonded Cu bicrystals [34];

• almost perfect (linear) B-type penetration profiles were measured for GB diffusion of Au in the same Cu bicrystals [21]. Note that Au segregates only very moderately at Cu GBs [35], whereas Ag shows a strong GB segregation [23], Eq. (5).

If the profile curvature in Fig. 1 is the result of non-linear segregation of Ag at Cu GB, a strong variation of the amount of the in-diffused Ag solute in the GB has to produce profound changes in the shape of the penetration profiles.

We performed two additional GB diffusion experiments to prove the transition from linear to non-linear segregation:

1. By applying a smaller amount of the initial tracer material e.g. about 300 Bq. As a result the initial amount of Ag atoms at the outer surface was less than in the above-described experiment by a factor of 40;

2. By increasing the amount of the initial tracer material to about e.g. 120 kBq that corresponds to 10 times the Ag amount at the outer surface before diffusion anneal.

The resulting penetration profiles are additionally presented in Fig. 1. The following salient features are observed:

1. The most deep linear parts of all three penetration profiles are almost parallel in the reduced coordinates and very similar values of the triple products are derived, Table 1. This confirms the consistency of the present measurements.

2. If a sufficiently small amount of tracer material is applied, a fully linear penetration profile is measured (Fig. 1, squares). Therefore, a linear relation between c_{gb} and $c_{\text{v}}(0)$ holds along the GB in such a case. All disturbing factors, which potentially could 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.

3. 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. These are features which were theoretically observed in the analysis of the GB diffusion problem in the presence of non-linear segregation [15].

4. The deviation from the linearity starts at almost the same value of the GB and bulk concentrations, $c_{\text{gb}} = s \cdot c_{\text{v}}(0) \approx 2 \times 10^{-3}$ (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.

These features unambiguously prove that the non-linear segregation of Ag is definitely the reason of the curvature of the penetration profiles observed.

3.1. Evaluation of the segregation isotherm for Ag in Cu

If the segregation isotherm is known, one can predict the shape of penetration profile by using e. g. the approach developed by Mishin and Herzig [15]. An important and still unresolved subject is the solution of the inverse problem: the determination of the segregation isotherm from a curved penetration profile. This problem was considered in [36]. However, that approach includes the important but experimentally unrealistic assumption that the tracer concentration at the very first point of the penetration profile has to correspond to the bulk solubility limit and the "GB solubility limit" simultaneously [36]. Since tracer evaporation, surface oxidation, improper specimen adjustment for parallel sectioning, and other phenomena may strongly affect the activity measured experimentally in a near-surface region, another approach is required.

In the present case, the situation is profoundly different from that considered by authors of Ref. [36]. Fortunately, we have extra information on the tracer distribution and segregation behavior, which is not easy to obtain in a general case: (i) the absolute bulk solute concentration just near the GB, $c_v(0)$, is known as a function of the penetration depth y (Eq. (7) and Fig. 1); (ii) the equilibrium segregation factor, s, was independently determined for the dilute limit conditions [23], Eq. (5); and (iii) the GB solute concentration, c_{gb}, can be calculated as a function of y for the deepest part of the penetration profile from known $c_v(0)$ by applying Eq. (1).

Applying Gibbs extention [37] of the standard Fisher model of GB diffusion [29], the following expressions can be written down for the bulk and GB solute concentrations for the deepest (linear) parts of the penetration profiles:

$$c_v(0) = c_v^0 \exp\left\{-\frac{y}{L\sqrt{s}}\right\}, \quad y > y_0 \tag{9}$$

and

$$c_{gb} = sc_v^0 \exp\left\{-\frac{y}{L\sqrt{s}}\right\}, \quad y > y_0 \tag{10}$$

Here $L = \sqrt{\delta D_{gb}}\left(\frac{\pi t}{4D_v}\right)^{1/4}$ is the reduced depth and y_0 is the penetration depth after which the linear penetration profiles (corresponding to linear solute segregation) are measured. Generally the bulk and GB concentrations may be decomposed as

$$c_v(0) = \Delta_v + c_v^0 \exp\left\{-\frac{y}{L\sqrt{s}}\right\} \tag{11}$$

and

$$c_{gb} = \Delta_{gb} + sc_v^0 \exp\left\{-\frac{y}{L\sqrt{s}}\right\} \tag{12}$$

respectively. The terms $\Delta_v(y)$ and $\Delta_{gb}(y)$ represent the deviations of the measured tracer concentrations at the depth y from the solution of GB diffusion problem in the presence of only linear segregation. The total tracer distribution obeys the standard equation of GB diffusion [29]:

$$\frac{\partial^2 c_{gb}}{\partial y^2} = L^{-2} c_v(0) \tag{13}$$

with the boundary condition $c_v(0) \to 0$ and $c_{gb} \to 0$ as $y \to \infty$. Combining Eqs. (11)–(13), the following equation is obtained,

$$\frac{\partial^2 \Delta_{gb}}{\partial y^2} = L^{-2}\Delta_v \tag{14}$$

with a more appropriate boundary condition $\Delta_v = \Delta_{gb} = 0$ as $y \geq y_0$. This is a simple second-order differential equation which can be solved by double integration. As a result the GB solute concentration will be found as a function of the penetration depth, y:

$$c_{gb}(y) = sc_v^0 \exp\left\{\frac{-y}{L\sqrt{s}}\right\} + L^{-2}\int_{y_0}^{y}d\tau\int_{y_0}^{\tau}\Delta_v(u)\,du \tag{15}$$

Since $c_v(0)$ is measured as a function of the penetration depth y, Eq. (15) implicitly determines the segregation isotherm $c_{gb}[c_v(0)]$.

This method was applied to the two curved penetration profiles measured for GB diffusion of Ag in the Cu bicrystal, see Fig. 1. The results, i. e. c_{gb} as function of $c_v(0)$, are presented in Fig. 3. The resulting segregation isotherms derived from the two independent GB diffusion experiments are consistent. One realizes that using very sensitive radiotracer GB diffusion measurements on bicrystals with a suitable tracer 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. 3 by the McLean isotherm, Eq. (8). Since the McLean isotherm should reduce to the Henry type isotherm in the dilute limit, the relation

$$s^{Henry} = b \cdot c_{gb}^0 \tag{16}$$

can be derived from Eq. (8). Since s^{Henry} has already been measured in our previous independent investigation [23],
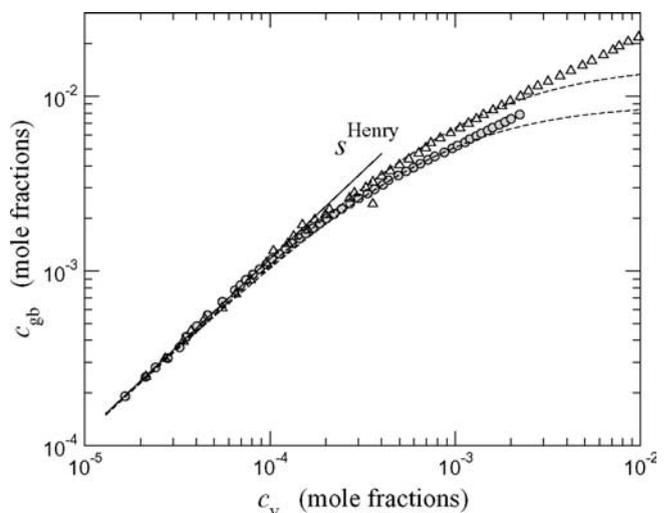

Fig. 3. Segregation isotherms of Ag in Cu at $T = 723$ K derived from the experimental profiles in Fig. 1. A hypothetical linear segregation isotherm, $c_{gb} = s^{Henry} \cdot c_v$, is shown by the solid line and the McLean isotherms, $c_{gb} = bc_{gb}^0 c_v/(1 - c_v + bc_v)$, Eq. (8), are represented by the dashed lines.

we have only one fitting parameter, c_{gb}^0. The least-squares fits yield the somewhat unexpected results, namely $c_{gb}^0 \approx 0.01$ (in mole fractions). This suggests that already one per cent of Ag solute atoms causes the "saturation" of Cu GBs. One has to emphasize that this is not a saturation in the strict sense. The Cu GB can incorporate indeed more than one per cent of Ag atoms. The value $c_{gb}^0 \approx 0.01$ corresponds to the amount of Ag atoms which may segregate in a Cu GB with the given segregation enthalpy of $H_s = -39.5$ kJ/mol. This value was measured for the equilibrium segregation of Ag in Cu GBs in the true dilute limit, Eq. (5) [23]. Segregation above this level demands that Ag atoms have to be positioned at other places with a smaller segregation enthalpy. Our previous measurements of Ag GB diffusion in the Cu-0.2 at.% Ag alloy in the B and C kinetic regimes [38] resulted in a segregation enthalpy of −25.7 kJ/mol, which may correspond to a further type of sites available for segregation in the GB. Note that the segregation energies of −40.2 and −22.4 kJ/mol were calculated for the most probable sites of segregation of Ag atoms in a Cu Σ5 (210)[001] tilt GB [39].

4. Summary and conclusions

GB diffusion of Ag in Cu bicrystals was studied by the radiotracer technique using the [110m]Ag radioisotope with a well-defined specific activity. Applying very different amounts of initial tracer material to the outer surface, one can control the solute concentration in the GB in order to switch from linear to non-linear segregation behavior. To our knowledge this is the first unambiguous experimental verification of non-linear segregation in a GB diffusion experiment. As a result, the full segregation isotherm of Ag at a symmetrical near Σ5 (310)[001] tilt Cu GB is determined.

The purpose of the present paper was to investigate quantitatively the transition from linear to non-linear segregation of Ag atoms in a non-special Cu GB in well-defined conditions. A further but a quite involving task would be to measure the orientation dependence of the segregation characteristics by this method spanning the concentrations from very dilute to large amounts of solute in both the bulk crystal and the GB.

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Correspondence address

Dr. Sergiy Divinski
Institut für Materialphysik, Universität Münster
Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany
Tel.: +49 251 83 39030
Fax: +49 251 83 38346
E-mail: divin@uni-muenster.de