Grain Boundary Diffusion in Metals: Recent Developments

Christian Herzig and Sergiy V. Divinski

Institut für Materialphysik, Universität Münster, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany

An overview on recent progress in grain boundary (GB) diffusion study is presented with emphasis on physical phenomena encountered in GB diffusion experiments such as the linear and non-linear segregation effects. Systematic investigations on pure and alloyed poly- and bicrystals gave conclusive information on the solute segregation behavior and allowed to extract the segregation isotherm solely from GB diffusion studies. Recent progress in fundamental understanding of diffusion processes in two-scale materials with two types of short-circuit diffusion paths is discussed on the basis of GB self-diffusion experiments and Monte-Carlo simulations in powder sintered nanocrystalline material.

(Received August 28, 2002; Accepted October 10, 2002)

Keywords: grain boundary diffusion, grain boundary segregation, non-linear segregation, nanocrystalline material

1. Introduction

Knowledge of grain boundary (GB) diffusion characteristics of structural materials is important for many technological applications. For example, the durability of interconnections in microelectronics is often limited by electromigration of impurities along the GBs. GB segregation and/or co-segregation of solute atoms involved in solute GB diffusion are very important processes for understanding *e.g.* GB decohesion, Coble creep, and phenomena such as prewetting and wetting of GBs.¹⁾

The fundamentals of GB diffusion are at present well elaborated and were outlined *e.g.* in.¹⁾ The experimental results on GB diffusion existing in the literature up to the end of 80th were collected and critically reviewed in the handbook of Kaur, Gust, and Kozma.²⁾

Since the latest reviews on this subject,^{3,4)} some new and important results were obtained, both concerning experimental results and fundamental understanding of GB diffusion and linear and non-linear segregation. The present 'state of the art' in GB diffusion study was presented in a recent textbook⁵⁾ with an emphasize on the orientation dependence of the GB diffusivity P in bicrystals.

In the present review we put highlight into the segregation behavior and especially into the appearance of non-linear segregation of solutes derived and quantified by GB diffusion experiments. In Chapter 2 this problem will be analyzed for Ag GB diffusion in pure and alloyed Cu poly- and bicrystals. In Chapter 3 the fundamentals of GB diffusion in a two-scale material will be outlined on the grounds of new GB diffusion experiments and Monte-Carlo simulations in such material and a classification of possible diffusion regimes will be reviewed for the case of coexistence of differently fast diffusion paths.

2. GB Diffusion and Linear and Non-linear Segregation

Typically, GB diffusion experiments are performed in Harrison's B regime.⁶⁾ In this case the so-called triple product P can be determined from the experimental solute penetration profiles, $P = s \cdot \delta \cdot D_{gb}$. Here s is the solute segregation factor, δ the GB width, and D_{gb} the GB diffusivity. This

determination of P from GB diffusion penetration profiles assumes that the segregation factor s , which is defined as the ratio of the solute concentration in the GB c_{gb} and in the bulk $c_v(0)$ just near the GB,

$$s = \frac{c_{gb}}{c_v(0)}, \quad (1)$$

does not change along the corresponding (deepest) part of the penetration profile. This means that in the case of solute GB diffusion in a pure metal the tracer concentrations c_{gb} and $c_v(0)$ have to be sufficiently small to satisfy the dilute limit conditions. In Ref. 7) the absolute concentrations of the Ag tracer atoms in GBs of polycrystalline Cu, c_{gb} , were calculated from the measured specific radiotracer activity of the layer sections along the GB diffusion profiles. It was shown that $c_{gb} \ll 1$ at the penetration profile depths where the GB diffusivity P was evaluated.

The value of the GB width δ seems to be well-defined and existing estimates indicate that δ can be approximated as $\delta \simeq 5 \cdot 10^{-10}$ m in FCC metals, *e.g.* Ag.^{8,9)} Therefore, the measurements in the B regime kinetics yield the product $s \cdot D_{gb}$ (supposing that δ is known) but not these values separately. Since the segregation factor s varies remarkably with temperature and can be very large (see below), one can conclude practically nothing about the GB diffusivity D_{gb} itself from the measurements of the P values. In Fig. 1 the data on P in Cu and Ag matrices are collected for the solutes, for which s and D_{gb} were determined separately (see below). Excluding Te and Se in Ag, other solutes show P values similar to those for self-diffusion in Ag or Cu. Thus, it is of fundamental importance to determine separately s and D_{gb} in thermodynamical equilibrium conditions.

The segregation characteristics can be determined from the direct Auger measurements.^{14,15)} In this case the sample has to be fractured *in situ* along a GB. This procedure limits the application of the method only to brittle materials, as *e.g.* to Fe or Fe alloys.^{16,17)} No such data exist for ductile materials *e.g.* Cu. Furthermore the sensitivity of the Auger technique is limited and a considerable fraction of a monolayer of segregated solute is required for detection.

On the other hand, the equilibrium segregation factor s , eq. (1), can be determined by specially designed GB diffusion experiments.

Fig. 1 Arrhenius plot of the product P of self-^{9,10)} and solute diffusion in Ag (Ni,¹¹⁾ Te,¹²⁾ and Se,¹¹⁾ dashed lines) and Cu of two purity levels, 5N (Au,¹³⁾ dotted lines) and 5N8 (Ag,⁷⁾ solid lines). Self-diffusion data (superindex 'sd') are presented by thick lines.

Fig. 2 Solute segregation factors s of Ag⁷⁾ and Au¹³⁾ in Cu (solid lines) and of Ni,¹¹⁾ Te,¹²⁾ and Se¹¹⁾ in Ag (dashed lines) determined by the radiotracer GB diffusion measurements.

2.1 Essence of B - C type diffusion measurements

Investigation of solute GB diffusion presents an elegant way to determine equilibrium segregation characteristics in the dilute limit by applying the Harrison⁶⁾ B and C regime GB diffusion measurements in the same material.¹⁾ This approach has already been successfully applied to several Cu- and Ag-based systems, see *e.g.*^{7,11-13)} The GB diffusivity D_{gb} can be directly determined in C regime conditions, when the tracer is exclusively allocated in GBs. The type C measurements require extremely high sensitivity of the counting facilities and the use of radiotracer with a high specific activity. Then, measuring also the triple product $P = s \cdot \delta \cdot D_{gb}$ in the B regime and taking $\delta \approx 5 \cdot 10^{-10}$ m,⁹⁾ the segregation factor s can be determined as

$$s = \frac{P}{\delta \cdot D_{gb}}, \quad (2)$$

usually by extrapolating the P values to low temperatures of the C -type measurements of D_{gb} .¹²⁾ Consequently the segregation enthalpy H_s therefore is obtained as the difference of the activation enthalpies of the B and C regime data: $H_s = Q_{gb} - H_{gb}$.

The results on solute segregation and directly measured GB diffusivities D_{gb} in Cu and Ag matrices are presented in Figs. 2 and 3, respectively. In dependence on the solute and the matrix the segregation factors varying from about 2 to 10^5 were measured, Fig. 2. Although the triple products P of solute diffusion are generally larger than those of self-diffusion, Fig. 1, smaller D_{gb} values are typically observed in comparison with self-diffusion, Fig. 3. The most pronounced retardation in solute diffusivity was observed for Ni GB

Fig. 3 Arrhenius plot of directly measured GB diffusivities D_{gb} of Ag⁷⁾ in 5N8 Cu (solid lines), Au¹³⁾ in 5N Cu (dotted line) and of Ni,¹¹⁾ Te,¹²⁾ and Se¹¹⁾ in Ag (dashed lines). The self-diffusivities of the corresponding matrices (superindex 'sd') are also presented by the thick lines.

diffusion in Ag, which was explained by the segregation of Ni atoms not directly in the GB core, but to the adjacent lattice plane(s).^{11,18)} While analyzing Figs. 1 and 3 one has to take into account that Cu matrices of two different purity levels were investigated in 7) and 13) and that the content of residual sulfur impurity influences remarkably GB self-diffusion in high-purity Cu.¹⁰⁾

2.2 C-type measurements of Ag GB diffusion in Cu

Recently the Hwang-Balluffi method was successfully applied to study Ag GB diffusion in Cu in the *C* regime conditions.¹⁹⁾ This permeation method does not yield the GB diffusivity D_{gb} but the product $\omega' = s \cdot \delta \cdot D_{gb} / s_s \cdot \delta_s$, where δ_s is the width of the segregated layer and s_s is the surface segregation factor.¹⁹⁾ The comparison with the results of the *B*-type measurements of $P = s \cdot \delta \cdot D_{gb}$ yielded the *surface* segregation enthalpy of about -34 kJ/mol.¹⁹⁾ Unfortunately, one cannot extract the GB segregation factor and the corresponding segregation enthalpy from such measurements.

On the other hand the Ag GB diffusivity D_{gb} in Cu was directly measured in Ref. 7). The activation enthalpy H_s of Ag GB segregation in Cu was deduced to be -39.5 kJ/mol. The results of the two investigations are compared in Fig. 4. It is obvious that the values of $\delta\omega'$ are systematically smaller than δD_{gb} by about two orders of magnitude, although the corresponding activation enthalpies are very similar.

Fig. 4 Arrhenius plot of GB diffusion parameters measured in the *B* ($P = s\delta D_{gb}$ (circles)⁷⁾ and (dotted line)²⁰⁾) and *C* ($P = \delta D_{gb}$ (squares)⁷⁾ and $P = \delta\omega'$ (triangles)¹⁹⁾) regimes.

2.3 Additional interfering effects in the *B*-type measurements

It is common practice to consider the most deep tails of the GB diffusion penetration profiles for deducing P or D_{gb} values. Very often however the penetration profiles measured in the *B* regime conditions turn out to be remarkably curved, see *e.g.* the penetration profiles of Ag GB diffusion in polycrystalline Cu, Fig. 5. A variety of different factors may affect the profile shape. For example, if the GB concentration of the solute is increased above the dilute limit level and c_{gb} approaches a saturation level, non-linear solute segregation behavior has to be taken into account.²¹⁾ The effect of non-linear segregation on the GB diffusion profile shape has already been analyzed.^{22,23)} Moreover, motion of a fraction of GBs during the diffusion anneal²⁴⁾ and/or the existence of a spectrum of GBs with different diffusional characteristics,^{25,26)} may result in a curvature of the penetration profiles.

To establish reliably the physical nature of the processes coming into play in given experimental conditions, supplementary experiments are required, which involve the investigations of the temperature dependence of the profile curvature, effects of alloying on GB diffusion and segregation, and specially designed experiments on bicrystals. Especially the experiments on pure and alloyed bicrystals will provide an decisive answer in some situations, as will be shown below.

Fig. 5 Penetration profiles of Ag GB diffusion in high-purity polycrystalline Cu in the *B* regime.⁷⁾ The dashed lines represent hypothetical ideal *B*-type profiles.

2.4 Influence of moving boundaries on GB diffusion

The effect of moving boundaries was systematically studied using different tracers in Cu matrices of different purities.²⁷⁾ If a fraction $f^{(\text{mov})} \neq 0$ of GBs moves during the diffusion anneal, the GB diffusion-related part of the penetration profile can be presented by a sum of two exponentials:²⁴⁾

$$\bar{c}(y, t) = q_1 \exp\{-q_2 y\} + q_3 \exp\{-q_4 y^{6/5}\}. \quad (3)$$

The first term with the parameters q_1 and q_2 describes the contribution of the moving GBs, whereas the second term represents diffusion in stationary GBs in type *B* conditions (q_3 and q_4). Using the fitted values of the parameters q_i , the average GB velocity V and the fraction of the moving GBs $f^{(\text{mov})}$ can be evaluated as²⁴⁾

$$V = P \cdot q_2^2 \quad (4)$$

and

$$f^{(\text{mov})} = \frac{1}{1 + 0.3205 \frac{q_3}{q_1} \left(\frac{Vt}{\sqrt{D_v t}} \right)^{3/2}}, \quad (5)$$

respectively. Here, P is the GB diffusivity calculated from q_4 . The quantities V and f are the matrix related properties and should be mostly independent of the nature of the solute tracer in the dilute limit.

Our quantitative analysis of a larger series of type *B* diffusion profiles in Cu indeed yields reproducible results for a strongly segregating solute, like Ag, a slightly segregating solute, *e.g.* Au, and for GB self-diffusion experiments in polycrystalline Cu, Fig. 6. We conclude that it is GB motion that dominantly influenced the penetration profiles in Ref. 7). Therefore, non-linear segregation plays no distinct role in our experiments on polycrystalline Cu,⁷⁾ since the absolute tracer concentrations definitely range within the dilute limit in these experiments.

2.5 GB diffusion in alloys (Ag in Cu)

To provoke non-linear segregation effects one can alloy inactive solute element to the matrix. Subsequent solute radiotracer GB diffusion experiments will proceed under the boundary condition that the segregation factor in the alloy,

$$s^{\text{alloy}} = \frac{c_{\text{gb}}^{\text{alloy}}}{c_{\text{v}}^{\text{alloy}}}, \quad (6)$$

is not changed along the GB penetration profile, $s^{\text{alloy}} = \text{const}$ for the given conditions and depends on the total concentration of the solute in the matrix.^{28,29)} Equation (6) can be applied, since the *isotope equilibrium* with respect to radiotracer and inactive solute atoms is expected to be maintained between the GB and the adjacent lattice at any depth.²⁹⁾

Generally, when changing the volume concentration of a solute, a non-linear dependence of c_{gb} on c_{v} is expected³⁰⁾ and s^{alloy} will differ from the corresponding segregation factor s^{pure} measured in pure metal ($s^{\text{alloy}} \leq s^{\text{pure}}$).

Bernardini *et al.*²⁰⁾ used eq. (6) to determine the segregation behavior of Ag in an Cu(Ag) alloy. As a result they measured the enrichment factor b appearing in the McLean

Fig. 6 The temperature dependence of the product VT (GB velocity times temperature) determined from the GB diffusion measurements of Ag in 5N8 Cu (circles and full line), Cu in 5N8 Cu (squares and dashed line), Cu in 5N Cu (triangles down), and Au in 5N Cu (triangles up and dotted line).²⁷⁾

isotherm³⁰⁾ (for the difference between b and the segregation factor s see Ref. 7)). Measurements only performed in the *B* kinetic regime were required in that approach. The segregation enthalpy was found to be -37 kJ/mol ²⁰⁾ in agreement with the *B-C* type GB diffusion measurements.⁷⁾

A closer inspection of the profiles measured for the Cu–0.09 at%Ag alloy²⁰⁾ however reveals that they are partly curved (especially at the two highest temperatures). These features were not analyzed so far. Moreover, no direct measurements of D_{gb} in an alloy existed until very recently.

2.5.1 C regime GB diffusion measurements in an alloy

GB diffusion measurements in the Cu–0.2 at%Ag alloy in the *C* regime were carried out for the first time in Ref. 31). In Fig. 7, the results of Ag GB diffusion in the Cu–0.2 at%Ag alloy are plotted together with the previous data on Ag GB diffusivity D_{gb} ⁷⁾ in high-purity Cu. Both data sets are almost identical. The following Arrhenius dependence is established for Ag GB diffusion in the Cu(Ag) alloy:

$$D_{\text{gb}}^{\text{alloy}} = 2.5 \cdot 10^{-4} \cdot \exp\left(-\frac{108.8 \text{ kJ/mol}}{RT}\right) \text{ m}^2/\text{s}. \quad (7)$$

Very similar values of the pre-exponential factor $D_0^{\text{pure}} = 1.73 \cdot 10^{-4} \text{ m}^2/\text{s}$ and the activation enthalpy $Q_{\text{gb}}^{\text{pure}} = 108.6 \text{ kJ/mol}$ were found for Ag GB diffusion in pure Cu.⁷⁾ Thus, *direct* measurements show that the Ag GB diffusivity in pure Cu and in the Cu–0.2 at%Ag alloy is the same within the limits of the experimental errors.

Fig. 7 Temperature dependence of Ag GB diffusion in the Cu-0.2 at% Ag alloy (filled circles, dashed line) in comparison with the Ag GB diffusivity in high-purity Cu⁽⁷⁾ (open circles, solid line). All data were measured under C regime conditions.

2.5.2 B regime measurements in an alloy

The penetration profiles measured for Ag GB diffusion in the Cu-0.2 at% Ag alloy turned out to be remarkably curved, Fig. 8, and this curvature does not monotonically depend on the temperature: at low and high temperatures the profiles are almost perfectly linear (e.g. at $T = 970$ and 668 K, Fig. 8), whereas the curvature is well pronounced at intermediate temperatures (e.g. at $T = 710$, 762 , and 892 K, Fig. 8).

The profile curvature cannot be explained by direct bulk diffusion since the volume penetration depths amount to only a few micrometers. As it was already mentioned, several factors can potentially give rise to the curvature of penetration profiles: e.g. (i) GB motion;⁽²⁴⁾ (ii) existence of a wide spectrum of GBs with different diffusivities;^(25,26) (iii) non-linear segregation of solute atoms.^(21,22)

Careful analysis proved that a hypothetically assumed motion of GBs does not dominate the curvature of penetration profiles in the Cu-Ag alloy, since the corresponding fractions of moving GBs would *increase* with decreasing temperature, a result which is physically unreasonable.

Furthermore it was hypothetically supposed⁽³¹⁾ that the curvature of the penetration profiles in Fig. 8 originates from the presence of GBs with very different diffusivities P in the Cu(Ag) alloy. Although the GB diffusivities P may form a continuous spectrum, for simplicity the profiles were fitted by a sum of two Suzuoka solutions:⁽³²⁾

$$\bar{c}(y, t) \cong A \exp\{-q \cdot y^{6/5}\} + A_{\text{fast}} \exp\{-q_{\text{fast}} \cdot y^{6/5}\}. \quad (8)$$

In this approximation it is assumed that only two classes of GBs with different diffusivities dominate the GB diffusion penetration, with “regular” (A and q) and fast (A_{fast} and q_{fast})

Fig. 8 Penetration profiles of Ag GB diffusion in the Cu-0.2 at% Ag alloy in the B regime. k is a scaling factor and y is the penetration depth. The lines present a four-parameter fit according to eq. (8).

diffusivities. The parameters q and q_{fast} determine the triple products P_{alloy} and $P_{\text{fast}}^{\text{alloy}}$, respectively, whereas the fraction f of the GBs with a regular diffusivity can be calculated as

$$f = \frac{1}{1 + \frac{A_{\text{fast}}}{A} \sqrt{\frac{P_{\text{fast}}^{\text{alloy}}}{P_{\text{alloy}}}}}. \quad (9)$$

The temperature dependencies of P_{alloy} and $P_{\text{fast}}^{\text{alloy}}$ are plotted in Fig. 9. It is seen that in spite of the crude approximation introduced by eq. (8), P_{alloy} and $P_{\text{fast}}^{\text{alloy}}$ vary systematically with temperature and the following Arrhenius dependencies can be established:

$$P_{\text{alloy}} = 3.24 \cdot 10^{-15} \cdot \exp\left(-\frac{82.4 \text{ kJ/mol}}{RT}\right) \text{ m}^3/\text{s} \quad (10)$$

and

$$P_{\text{fast}}^{\text{alloy}} = 1.31 \cdot 10^{-15} \cdot \exp\left(-\frac{67.1 \text{ kJ/mol}}{RT}\right) \text{ m}^3/\text{s}. \quad (11)$$

The difference between P_{alloy} and $P_{\text{fast}}^{\text{alloy}}$ may result from the difference in the respective s and/or $D_{\text{gb}}^{\text{alloy}}$ values, since it is reasonable to assume that δ is almost constant.

In Ref. 25) the curvature of the penetration profiles of Zn GB diffusion in Al was explained by the presence of large-angle GBs with remarkably different diffusivities D_{gb} . This effect is not relevant in the present case, since the fraction of GBs showing different diffusivities does not remain independent on temperature but changes regularly with temperature. The key arguments which lead to the conclusion that the variations in P are due to variations in s however come from GB diffusion experiments on Cu bicrystals.

Fig. 9 Temperature dependence of Ag GB diffusivities P_{fast}^{alloy} (open circles) and P^{alloy} (filled circles) in the polycrystalline Cu–0.2 at%Ag alloy and Ag GB diffusivity P in pure Cu (dashed line). The solid lines represent the Arrhenius fits. For comparison, the GB diffusivities P^{pbi} (open squares) and P_{slow}^{pbi} (filled squares) measured in a Cu near $\Sigma 5(310)[001]$ bicrystal are shown. The GB diffusivity P^{abi} of pre-alloyed Cu bicrystal is also presented (triangle).

2.6 GB diffusion in bicrystals (Ag in Cu)

Cu bicrystals with orientations close to the $\Sigma = 5(310)[001]$ GB were used.³¹⁾ The tilt angle $\theta = 36.0^\circ$ is reasonably far away from the exact $\Sigma 5$ misorientation ($\theta \cong 36.9^\circ$) to result in a GB diffusivity being similar to that of random large-angle grain boundaries in polycrystalline Cu.³³⁾

An Ag penetration profile measured on the bicrystal at $T = 723$ K is shown in Fig. 10. From the Ag concentration in a layer section — known from the specific radiotracer activity — the absolute Ag concentration in the bulk adjacent to the GB, $c_v(0)$, was deduced.³¹⁾ Multiplying this value by the known segregation factor s for the dilute limit (determined in⁷⁾), an upper estimation of the Ag tracer concentration within the GB was obtained as $s \cdot c_v(0)$, Fig. 10. (The real Ag GB concentration can be smaller than $s \cdot c_v(0)$ in the case of non-linear segregation.) The amount of Ag tracer in the single boundary of the bicrystal was found to be remarkably higher than that in high-purity polycrystalline Cu when applying the same initial surface activity. This fact was explained³¹⁾ by surface diffusion which drives a significant amount of tracer atoms to the single GB in case of a bicrystal versus a distribution over a large number of GBs in a polycrystal. As a result, the penetration profile in the bicrystal is substantially curved, a circumstance which becomes especially pronounced due to the large depth of profile detection (up to $700 \mu\text{m}$). If the profile in Fig. 10 is processed according to eq. (8), the values of the GB

Fig. 10 Penetration profiles of Ag (circles, left ordinate) and Au (squares, right ordinate) GB diffusion in a Cu near $\Sigma = 5(310)[001]$ bicrystal. The Ag concentration is given in mole fractions, s and $c_v(0)$ are the segregation factor and the concentration in the volume adjacent to the GB, respectively. The solid line presents the four-parameter fit according to eq. (8), from which P^{pbi} and P_{slow}^{pbi} were calculated.

diffusivity P_{slow}^{pbi} and P^{pbi} (corresponding to the slow and fast diffusivity parts, respectively) can be determined. These values are shown in Fig. 9 by filled (P_{slow}^{pbi}) and open (P^{pbi}) squares. Good agreement is observed with the data measured in the polycrystalline Cu–Ag alloy and in the pure Cu bicrystal, which indicates that the origin of the complex profiles in the Cu–Ag alloy and in the pure Cu bicrystals is the same. Measurements at other temperatures and in pre-alloyed Cu bicrystal supported this conclusion, Fig. 9.

This common cause cannot be due to a multiplicity of GB structures, because Au GB diffusion in the same Cu near $\Sigma 5$ bicrystal³³⁾ produces a nearly perfect type B penetration profile (Fig. 10). The profile curvature for Ag diffusion therefore originates from the much larger segregation factor for Ag in Cu than for Au in Cu (Fig. 2).

Thus, the curvature in the Ag penetration profile in Fig. 10 results from non-linear segregation.

2.7 Segregation isotherm of Ag in Cu

Having measured the Ag penetration profile of the quality given in Fig. 10, one can determine the segregation isotherm for Ag in Cu at $T = 723$ K from the GB diffusion measurements only. This has been done in the following steps:

1. The segregation factor for the deepest part of the profile (representing Henry type conditions) was calculated from the Arrhenius dependence established in pure Cu.⁷⁾
2. Since the specific activity of the tracer was fairly precisely known, the absolute bulk concentration of the Ag tracer adjacent to the GB, $c_v(y)$, was estimated as function of the depth y .

3. Because $D_{\text{gb}}^{\text{alloy}} \cong D_{\text{gb}}^{\text{pure}}$ for Ag GB diffusion (Fig. 7) and because there exists no variation of P along the Au penetration profile in the same bicrystal (Fig. 10), it is reasonable to assume that $D_{\text{gb}} \cong \text{const}$ along the Ag penetration profile.
4. When applying the Fisher model³⁴⁾ and introducing the segregation isotherm $c_{\text{gb}} = g(c_v)$, the GB concentration of the Ag tracer follows the equation:

$$\frac{\partial^2 c_{\text{gb}}}{\partial y^2} = L^{-2} \cdot c_v = L^{-2} \cdot g^{-1}(c_{\text{gb}}). \quad (12)$$

Here L is the reduced depth, $L = \sqrt{\delta D_{\text{gb}} (\frac{\pi t}{4D_v})}^{1/4}$.

5. Since the solution of eq. (12) is known at large depths in terms of the Fisher model, $c_v(y) = c_v^0 \cdot \exp(-y/Ls^{1/2})$ and $c_{\text{gb}}(y) = s \cdot c_v(y)$, one can integrate eq. (12) and the relation

$$c_{\text{gb}}(y) = L^{-2} \int_{\infty}^y dv \int_{\infty}^v c_v(u) du \quad (13)$$

yields the segregation isotherm (with v and u being the integration variables).

The result, *i.e.* c_{gb} as a function of c_v , is presented in Fig. 11. We note as important progress that one can determine the segregation isotherm already starting from very small GB concentrations by using very sensitive radiotracer GB diffusion measurements with a suitable tracer on bicrystals.

2.8 GB segregation of Ag in pure and alloyed Cu

In Fig. 9 the data on Ag GB diffusion in Cu–0.2 at% Ag alloy are compared with the results on Ag GB diffusion in high-purity Cu.⁷⁾ It is seen that the diffusivity $P_{\text{fast}}^{\text{alloy}} = s_{\text{fast}}^{\text{alloy}} \cdot \delta_{\text{alloy}} \cdot D_{\text{gb}}^{\text{alloy}}$ of the “fastest” GBs in the Cu–0.2 at% Ag alloy practically coincides with the data on $P^{\text{pure}} = s^{\text{pure}} \cdot \delta_{\text{pure}} \cdot D_{\text{gb}}^{\text{pure}}$ in high-purity Cu.⁷⁾ Since the direct (C regime) measurements of the GB diffusion coefficients in pure Cu and in the Cu–0.2 at% Ag alloy gave the same results, $D_{\text{gb}}^{\text{alloy}} \cong D_{\text{gb}}^{\text{pure}}$ (cf. Fig. 7), one can conclude that the segregation factors of Ag in pure Cu, s^{pure} , and in the fastest GBs of the Cu–0.2 at% Ag alloy, $s_{\text{fast}}^{\text{alloy}}$, are also similar since it is reasonable to assume that $\delta_{\text{alloy}} \cong \delta_{\text{pure}}$. The fact that $s_{\text{fast}}^{\text{alloy}} \cong s^{\text{pure}}$ indicates that in the studied temperature interval

and for the given alloy composition, the Ag GB concentration in a part of the GBs corresponds to the dilute limit of segregation and diffusivities of such GBs are the same as in pure Cu. Other GBs contain a relatively high concentration of Ag atoms, and these are those GBs that reveal the slower diffusivities P^{alloy} .

Since $D_{\text{gb}}^{\text{alloy}} \cong D_{\text{gb}}^{\text{pure}}$, the difference between $P_{\text{fast}}^{\text{alloy}}$ and P^{alloy} is mainly related to the difference in the corresponding segregation factors, meaning that $s^{\text{alloy}} < s_{\text{fast}}^{\text{alloy}}$ and thus $s^{\text{alloy}} < s^{\text{pure}}$.

It is not unusual that segregated atoms do not cover uniformly all GBs in a polycrystalline sample. In Ref. 35), a broad distribution of the amount of Bi atoms segregated at GBs in polycrystalline Cu was reported using high-resolution transmission electron microscopy. While part of the Cu GBs was covered by Bi atoms, it was impossible to detect Bi segregation in other GBs.³⁵⁾ Furthermore, in an Auger Electron Spectroscopy study a sample has to be fractured *in situ* along GBs to determine the segregation characteristics. The sample is more likely to break along GBs with a higher concentration of segregated atoms (which usually induce GB brittleness), while less segregated GBs cannot be studied.

Having determined the Cu(Ag) alloy diffusivity in the C kinetics, $D_{\text{gb}}^{\text{alloy}}$, and in the B kinetics, P^{alloy} , it is possible to calculate the segregation factor in the alloy, s^{alloy} , as a function of temperature using eq. (2). According to the Cu–Ag phase diagram,³⁶⁾ 0.2 at% of Ag in Cu corresponds to the solid solubility limit at $T \sim 550$ K. This means that the B regime measurements³¹⁾ were completely performed in the interval of Ag solid solution in Cu.

In order to determine s one cannot, as usual, extrapolate the P values to low temperatures, since the bulk solubility limit would be approached and the precipitation enthalpy may become involved. Thus, the $D_{\text{gb}}^{\text{alloy}}$ values were extrapolated to higher temperatures having in mind that $D_{\text{gb}}^{\text{alloy}}$ corresponds to the solid solution of Ag in Cu (Fig. 12). The segregation of Ag in Cu–0.2 at% Ag alloy can be presented by the following Arrhenius dependence:

$$s^{\text{alloy}} = (3.4_{-1.9}^{+4.5}) \cdot 10^{-2} \cdot \exp\left(-\frac{(-25.7 \pm 6) \text{ kJ/mol}}{RT}\right). \quad (14)$$

These values correspond to the GBs significantly covered with segregated Ag atoms.

3. Classification of Diffusion Kinetics in Two-scale Materials

Harrison’s classification⁶⁾ of diffusion processes in GBs is based on the classical Fisher’s model.³⁴⁾ Three regimes are introduced, A , B , and C in dependence on the given diffusion parameters.⁶⁾ Two of them (B and C) were partially described above. This classification was refined introducing subregimes A' , B_1 , B_2 , B_3 , B_4 , and C' for GB diffusion in poly- and bicrystals.¹⁾

However, in real materials different types of short-circuit diffusion paths can co-exist, a fact which modifies diffusional transport. For example, in presence of a dislocation network

Fig. 11 Segregation isotherm of Ag in Cu GBs at $T = 723$ K.³¹⁾

Fig. 12 Determination of Ag segregation factor s^{alloy} in the Cu(Ag) alloy by combined GB diffusion measurements in the B (P^{alloy} , circles) and C ($D_{\text{gb}}^{\text{alloy}}$, squares) kinetics. The filled squares represent the product $\delta \cdot D_{\text{gb}}^{\text{alloy}}$ calculated by using the directly measured $D_{\text{gb}}^{\text{alloy}}$ values and the open squares correspond to the results evaluated by using $D_{\text{gb}}^{\text{pure}}$.

tracer outdiffusion from GBs can occur at first along adjacent dislocation pipes with subsequent outdiffusion into bulk. Or, if each grain consists in a number of subgrains, the existence of both large-angle and small-angle boundaries should be taken into account. This was recognized by Klinger and Rabkin and they introduced new D_i regimes.³⁷⁾

Recently, a new, more transparent classification was introduced which explicitly reflects the existence of two types of short-circuit diffusion paths in the material.^{38–40)} This classification refers to the microstructure which is presented in Fig. 13(a) and is sketched in Fig. 13(b). This microstructure was observed in the nanocrystalline γ -FeNi material produced by compacting and sintering the powders of Fe and Ni oxides.^{39,41)} The individual nano-scale grains ($d \simeq 80\text{--}100\text{ nm}$) are arranged in micrometer-size clusters or agglomerates ($d_a \simeq 30\text{--}50\text{ }\mu\text{m}$). Accordingly, nanocrystalline GBs (intra-agglomerate boundaries) exist along with the inter-agglomerate boundaries.

3.1 Basic equations of GB diffusion in a two-scale material

Three diffusion fluxes generally coexist in such two-scale nanocrystalline material, Fig. 13(b): (i) direct bulk diffusion from the external surface into grain interior, $\bar{c}_1$, (ii) diffusion along nanocrystalline boundaries with subsequent outdiffusion into bulk, $\bar{c}_2$, and (iii) fast diffusion along inter-agglomerate boundaries with subsequent outdiffusion in the adjacent nanocrystalline GBs, diffusion along these GBs, and final outdiffusion into bulk of the grains, $\bar{c}_3$.

The flux $\bar{c}_3$ is specific for such two-scale structure. To

Fig. 13 Microstructure of the nanocrystalline γ -Fe-40 mass%Ni alloy³⁹⁾ (a) and its schematic presentation (b, c). The squares represent individual nano-grains with the bulk diffusivity D_v . The inter-agglomerate boundaries with a relatively larger fraction of the associated free volume (the diffusivity D_a and the width δ_a) and regular nanocrystalline boundaries (the diffusivity D_{gb} and the width δ) are distinguished.

describe the term $\bar{c}_3(y, t)$ the Fisher model³⁴⁾ was reformulated for inter-agglomerate boundary diffusion from a constant source.⁴⁰⁾ The tracer concentrations $c_v(x, y, t)$ in the bulk, $c_{\text{gb}}(x, y, t)$ in nanocrystalline grain boundaries, and $c_a(x, y, t)$ in inter-agglomerate boundaries are to be considered. The analytic solution was derived under following approximations (see Fig. 13(c)):

1. Diffusion in the nanocrystalline grains (bulk diffusion) occurs primarily normal to the local position of the GB, *i.e.* in the y direction in Fig. 13(c), $c_v(x, y, t) = c_v(y, t)$. The direct bulk diffusion from the surface into the grain is assumed to be negligible.
2. The relationship

$$D_a \gg D_{\text{gb}} \gg D_v \quad (15)$$

is supposed to be valid. Here D_a is the diffusion coefficient of the inter-agglomerate boundaries, D_{gb} the diffusivity of nanocrystalline GBs, and D_v the bulk diffusivity. Thus, the tracer atoms enter the GB slabs only by leaving the inter-agglomerate boundary along the x direction, while direct GB diffusion along the nanocrystalline GBs from the surface is neglected. Thus, $c_b(x, y, t) = c_b(x, t)$. Moreover, the condition $\partial c_b(x, t)/\partial t \approx 0$ is assumed when describing bulk diffusion. The latter means that outdiffusion from the

nanocrystalline GBs into the bulk occurs in nearly constant-source conditions.

3. With respect to GB diffusion, the tracer distribution within the inter-agglomerate boundaries is established within a very short period of time τ and the relations

$c_a(x, y, t) = c_a(y, t)$ and $\partial c_a(y, t)/\partial t|_{t>\tau} \approx 0$ is assumed. Considering the interfaces as homogeneous slabs with the given diffusivities and the given widths, Fig. 13(b), the following equations can be written for the concentrations c_a , c_b , and c_v :

$$\frac{\partial c_a(y, t)}{\partial t} = D_a \frac{\partial^2 c_a(y, t)}{\partial y^2} + \lambda \frac{2}{\delta_a} J_b \Big|_{|x|=\delta_a/2} + \frac{2}{\delta_a} J_v \Big|_{|x|=\delta_a/2}, \quad |x| < \frac{\delta_a}{2}, \quad (16)$$

$$\frac{\partial c_b(x, t)}{\partial t} = D_{gb} \frac{\partial^2 c_b(x, t)}{\partial x^2} + \frac{2D_v}{\delta} \frac{\partial c_v(y, t)}{\partial y} \Big|_{|y|=\delta/2}, \quad |x| > \frac{\delta_a}{2}, \quad |y| < \frac{\delta}{2}, \quad (17)$$

$$\frac{\partial c_v(x, y, t)}{\partial t} = D_v \left(\frac{\partial^2 c_v(x, y, t)}{\partial x^2} + \frac{\partial^2 c_v(x, y, t)}{\partial y^2} \right), \quad |x| > \delta_a/2, \quad |y| > \delta/2. \quad (18)$$

Here J_b and J_v are the fluxes of tracer atoms leaving the inter-agglomerate boundary through adjacent nanocrystalline GBs and the bulk, respectively. The factor λ takes into account that outdiffusion from an inter-agglomerate boundary takes place only through regions where nanocrystalline boundaries (of the width δ) cross the inter-agglomerate boundary. For cubic grains $\lambda = 2\delta/d$, while in a general case of a polyhedral grain shape $\lambda = \frac{\pi\delta}{2d}$.

A nomenclature combining two symbols, each one for the given type of boundaries, was introduced, for example a C – B regime. The first letter (in this example, C) indicates the diffusion regime in nano-GBs while the second one (B) diffusion regime in inter-agglomerate interfaces. The combined diffusion regimes depend on the standard parameters α , β , and Λ for nano-GB diffusion,

$$\alpha = \frac{\delta}{2\sqrt{D_v t}}, \quad \beta = \frac{\delta \cdot D_{gb}}{2D_v \sqrt{D_v t}}, \quad \Lambda = \frac{d}{\sqrt{D_v t}}, \quad (19)$$

and new parameters α_a , β_a , and Λ_a for inter-agglomerate boundary diffusion (see below).

Generally, the segregation factor s also enters these expressions, but the case of self-diffusion is considered here, $s = 1$. Large values of α ($\alpha > 1$) correspond to the conditions of negligible volume diffusion in which the diffusion process is confined to the interfaces of the thicknesses δ and δ_a . Otherwise, if $\alpha < 0.1$, bulk diffusion is strongly involved in the overall diffusion process.

3.2 The C – C diffusion regime

To satisfy the conditions of this regime very low temperatures and short diffusion times should be chosen that would suppress any outdiffusion from both types of interfaces. The conditions of the C – C regime are:

$$\alpha > 1; \quad \alpha_a = \frac{\delta_a}{2\lambda\sqrt{D_{gb}t}} > 1. \quad (20)$$

These conditions mean that tracer atoms do not leave both nanocrystalline and inter-agglomerate boundaries. For the instantaneous source conditions, the overall diffusion profile $\bar{c}(y, t)$ is represented by a sum of two Gaussians

$$\bar{c}(y, t) = q_3 \exp(-q_4 y^2) + q_5 \exp(-q_6 y^2) \quad (21)$$

which define the diffusivities D_{gb} and D_a by standard expressions:

$$D_{gb} = \frac{1}{4tq_4} \quad \text{and} \quad D_a = \frac{1}{4tq_6}. \quad (22)$$

3.3 The C – B diffusion regime

As the temperature increases, tracer atoms can leave inter-agglomerate boundaries by outdiffusion along adjacent nanocrystalline boundaries. Since bulk diffusion is still frozen out, the tracer will then diffuse only along nanocrystalline GBs. The conditions of the C – B diffusion regime are:

$$\alpha > 1; \quad \alpha_a < 0.1, \quad \beta_a = \frac{P_a}{2D_{gb}\sqrt{D_{gb}t}} \geq 2, \quad \frac{d_a}{L_{gb}} > 4. \quad (23)$$

Here L_{gb} is the diffusion length along the nanocrystalline GBs, $L_{gb} = \sqrt{D_{gb}t}$. The condition $d_a/L_{gb} > 4$ limits the B regime.³⁸⁾ The diffusion process is confined to nano-GBs and inter-agglomerate boundaries.

The overall diffusion profile $\bar{c}(y, t)$ is:

$$\bar{c}(y, t) = q_3 \exp(-q_4 y^2) + q_5 \exp(-q_6 y^{6/5}). \quad (24)$$

The first term, $\bar{c}_2(y, t) = q_3 \exp(-q_4 y^2)$, corresponds to direct diffusion from the surface into nanocrystalline GBs, which occurs in the C regime, while the second term, $\bar{c}_3(y, t) = q_5 \exp(-q_6 y^{6/5})$, represents a faster diffusion mode from the surface into inter-agglomerate boundaries with subsequent outdiffusion into adjacent nanocrystalline GBs. Since this outdiffusion is quite significant, $\sqrt{D_{gb}t} \gg \delta_a/\lambda$, the formal B -type conditions of interface diffusion are fulfilled for the term $\bar{c}_3(y, t)$.³⁹⁾ The parameter q_4 allows to calculate the diffusivity of nano-GBs, D_{gb} , and the inter-agglomerate boundary diffusivity $P_a = \delta_a \cdot D_a/\lambda$ is defined as solution of eqs. (16)–(18) in the given conditions:⁴²⁾

$$P_a = 0.661 \left(\frac{4D_{gb}}{t} \right)^{1/2} q_6^{-5/3}. \quad (25)$$

Penetration profiles measured for Ni diffusion in nano- γ -Fe–Ni in the B – C regime along with the fits according to eq. (24) are presented in Fig. 14.

Fig. 14 Penetration profiles of Ni GB diffusion in nano- γ -Fe-Ni in the C-B regime.⁴⁰⁾

Fig. 15 Penetration profiles of Ni GB diffusion in nano- γ -Fe-Ni in the B-B regime.⁴⁰⁾

3.4 The B-B diffusion regime

If temperature increases further, the bulk diffusion flux becomes more significant and cannot be neglected. As a result, three diffusion modes contribute to the overall penetration profile $\bar{c}(y, t)$:

$$\bar{c}(y, t) = q_1 \exp(-q_2 y^2) + q_3 \exp(-q_4 y^{6/5}) + q_5 \exp(-q_6 y). \quad (26)$$

Here $\bar{c}_1(y, t) = q_1 \exp(-q_2 y^2)$ represents the contribution of direct volume diffusion from the sample surface into the nano-grains, $\bar{c}_2(y, t) = q_3 \exp(-q_4 y^{6/5})$ corresponds to the tracer which comes into the bulk through GB diffusion along nanocrystalline boundaries with subsequent outdiffusion into the grain interior, and $\bar{c}_3(y, t) = q_5 \exp(-q_6 y)$ represents the amount of tracer which diffuses along inter-agglomerate boundaries with subsequent outdiffusion to nano-boundaries and then into the grains. Since the bulk diffusion length is smaller than grain size, $\sqrt{D_v t} < d \simeq 100$ nm, the first term cannot be measured by the conventional radiotracer method and the experimental profiles should be fitted with four unknown parameters q_3 , q_4 , q_5 , and q_6 .

The term $\bar{c}_2(y, t)$ in eq. (26) corresponds to GB diffusion in the B regime. The last term $\bar{c}_3(y, t)$ yields the product $P_a = \delta_a D_a / \lambda$ for inter-agglomerate boundary diffusion in the B-B kinetic regime as it was derived by solving eqs. (16)–(18):⁴⁰⁾

$$P_a = 1.798 \sqrt{\frac{D_{gb}}{\delta}} \left(\frac{D_v}{t} \right)^{1/4} (q_6)^{-2}. \quad (27)$$

The parameters α'_a and β'_a , which characterize the B-B regime have to be redefined as⁴⁰⁾

$$\alpha'_a = \frac{\delta_a}{\lambda \sqrt{\delta D_{gb}}} \left(\frac{4D_v}{\pi t} \right)^{1/4}, \quad \beta'_a = \frac{P_a}{D_{gb} \sqrt{\delta D_{gb}}} \left(\frac{4D_v}{\pi t} \right)^{1/4}. \quad (28)$$

The formal conditions of the B-B diffusion regime are determined by the relations:

$$\alpha < 0.1, \quad \beta \geq 2, \quad \frac{d}{\sqrt{D_v t}} > 4; \quad (29)$$

$$\alpha'_a < 0.1, \quad \beta'_a \geq 2, \quad \frac{d_a}{L_{gb}} > 4.$$

Here $L_{gb} = \sqrt{\delta D_{gb}} / (4D_v / \pi t)^{1/4}$ is the diffusion length along nano-GBs. Monte-Carlo simulation of combined inter-agglomerate boundary, nanocrystalline GB, and bulk diffusion in the case of cubic grains resulted in almost linear dependence of $\ln \bar{c}$ against y^n with $n \simeq 1.05 \pm 0.02$.⁴⁰⁾ Therefore n can be well approximated by unity and the diffusivity P_a of the inter-agglomerate boundaries can be reliably calculated from eq. (27).

Typical penetration profiles measured for Ni diffusion in nano- γ -Fe-Ni along with the fits according to eq. (26) are presented in Fig. 15.

3.5 The A-B diffusion regime

As the annealing temperature increases further, the bulk diffusion flux increases until the condition $\sqrt{D_v t} > d$ is established and the regime of diffusion along nanocrystalline GBs changes. In this new regime the clusters of the nano-grains as a whole are characterized by an effective diffusivity D_{eff} , which according to Hart⁴³⁾ is given by

$$D_{\text{eff}} = f_{\text{gb}} \cdot D_{\text{gb}} + (1 - f_{\text{gb}}) \cdot D_{\text{v}}. \quad (30)$$

Here f_{gb} is the volume fraction of the nanocrystalline GBs, which is $f_{\text{gb}} = g \frac{\delta}{d}$ (where g is a geometrical factor of about unity). Taking into account that in typical case $D_{\text{eff}} \gg D_{\text{v}}$, eq. (30) becomes

$$D_{\text{eff}} \cong f_{\text{gb}} \cdot D_{\text{gb}}. \quad (31)$$

Then, the penetration profile is composed of two parts:

$$\bar{c}(y, t) = q_1 \exp(-q_2 y^2) + q_5 \exp(-q_6 y^{6/5}). \quad (32)$$

Here $\bar{c}_{12}(y, t) = q_1 \exp(-q_2 y^2)$ represents the contribution of direct diffusion from the sample surface into the clusters of the nano-grains characterized by the effective diffusivity D_{eff} , whereas $\bar{c}_3(y, t) = q_5 \exp(-q_6 y^{6/5})$ represents the amount of tracer which diffuses along inter-agglomerate boundaries with subsequent outdiffusion into the agglomerates.

Under these conditions the inter-agglomerate boundary diffusion problem is mathematically identical to the standard GB diffusion problem characterized by the ‘GB diffusivity’ $P'_a = \delta_a \cdot D_a$ and the effective ‘bulk diffusivity’ D_{eff} . The parameters that define this regime are:

$$\alpha'_a = \frac{\delta_a}{2\sqrt{D_{\text{eff}}t}}, \quad \beta'_a = \frac{P'_a}{2D_{\text{eff}}\sqrt{D_{\text{eff}}t}}. \quad (33)$$

The diffusivity of the inter-agglomerate boundaries can be calculated as:

$$P'_a = \delta_a \cdot D_a = 1.308 \left(\frac{D_{\text{eff}}}{t} \right)^{1/2} q_6^{-5/3}. \quad (34)$$

Summarizing, the conditions of the *A-B* diffusion regime in the two-scale structure are determined by the relations:

$$\begin{aligned} \alpha < 0.1, \quad \frac{d}{\sqrt{D_{\text{v}}t}} < 0.3; \\ \alpha'_a < 0.1, \quad \beta'_a \geq 2, \quad \frac{d_a}{L_{\text{gb}}} > 4. \end{aligned} \quad (35)$$

Here $L_{\text{gb}} = \sqrt{D_{\text{eff}}t}$ is the diffusion length with respect to the agglomerate interior in the *A* regime. Experimentally these conditions were satisfied for Fe diffusion in nano- γ -Fe-Ni,³⁹ Fig. 16.

3.6 Transition regime *AB* and subregime *AB-B*

If the conditions of the *A* diffusion regime are not strictly satisfied and the volume diffusion penetration $\sqrt{D_{\text{v}}t}$ is about the grain size d , a transition regime *AB* can be defined.³⁸ The strict condition of the transition *AB* regime are: $0.3 < \frac{d}{\sqrt{D_{\text{v}}t}} < 4$ and the corresponding part of the penetration profile should be linear in coordinates of logarithm of concentration vs. $y^{3/2}$.³⁸ Then, the penetration profile in a two-scale material is composed of two parts:

$$\bar{c}(y, t) = q_1 \exp(-q_2 y^{3/2}) + q_5 \exp(-q_6 y^{6/5}). \quad (36)$$

The GB diffusivity can then be calculated from the first part of the penetration profiles as:³⁸

$$D_{\text{gb}} \cong 16.48 \frac{D_{\text{v}}^{0.1}}{\delta^{0.2} t^{0.9}} q_2^{-4/3}. \quad (37)$$

Fig. 16 Penetration profile of Fe GB diffusion in nano- γ -Fe-Ni in the *A-B* regime.³⁹ The dashed line indicates the contribution of inter-agglomerate boundary diffusion. The fit was performed according to eq. (32).

The product P'_a is suggested to estimate from eq. (34) with D_{eff} calculated through eq. (31). This introduces an error in the analysis, but it should not be too large since P'_a depends on the square root of D_{eff} , see eq. (33). Experimental profile and the fit according to eq. (36) are shown in Fig. 17.

3.7 GB diffusion in nanocrystalline Fe-Ni alloy

Using the derived mathematical treatment, eqs. (15)–(37), Ni and Fe diffusion in the two-scale nanocrystalline γ -Fe-Ni alloy was measured with the radiotracers ^{63}Ni and ^{59}Fe and subsequently analyzed.^{39,40} In the case described, Ni diffusion along nanocrystalline GBs was measured in the *C*, *B*, and *AB* conditions, with the GB diffusivity D_{gb} measured directly in the *C* and *AB* regimes and the product $P = \delta \cdot D_{\text{gb}}$ determined in the *B* regime. Summarizing all results derived in different regimes of GB diffusion and assuming $\delta \simeq 0.5$ nm, the temperature dependence of the GB-diffusion coefficient D_{gb} in the nanocrystals is plotted in Fig. 18. Different symbols are used to distinguish between the different regimes. Although quite different shapes of the penetration profiles were observed in different regimes and the profiles were processes in different ways, the whole set of data reveals a good systematics and the following summarizing Arrhenius dependence can be derived:

$$D_{\text{gb}} = (9.3^{+23.9}_{-6.7}) \times 10^{-4} \exp \left\{ - \frac{(177 \pm 8) \text{ kJ/mol}}{RT} \right\} \text{ m}^2/\text{s}. \quad (38)$$

Since Ni GB diffusion in coarse-grained γ -Fe-Ni alloys has not been measured, the diffusivity of nanocrystalline GBs

Fig. 17 Penetration profiles of Ni GB diffusion in nano- γ -Fe-Ni in the AB-B regime.⁴⁰⁾

Fig. 18 Arrhenius plot of Ni GB diffusion in two-scale nanocrystalline γ -Fe-Ni in different kinetic regimes⁴⁰⁾ in comparison with Ni GB diffusion in coarse-grained γ -Fe measured in Refs. 44) (dashed line) and 45) (dashed-dotted line).

can be compared with Ni GB diffusion in coarse-grained γ -Fe^{44,45)} (Fig. 18). While Ni bulk diffusion was found to depend only slightly on the composition of the γ -FeNi alloys

and is similar to Ni diffusivity in pure γ -Fe,⁴⁶⁾ a similar trend is expected also for GB diffusion in such alloys. Figure 18 suggests that Ni GB diffusivity in nanocrystalline GBs of the γ -Fe-40 mass%Ni alloy is close to that in conventional coarse-grained γ -Fe. The same feature was observed for Fe GB diffusion in nanocrystalline γ -Fe-40 mass%Ni.³⁹⁾

The temperature dependence of Ni inter-agglomerate boundary diffusion D_a is also presented in Fig. 18. The inter-agglomerate boundary width δ_a was taken as $\delta_a \simeq 1$ nm. The different symbols are used to distinguish between the data derived in different GB diffusion regimes. The whole set of data can be approximated by the following Arrhenius dependence:

$$D_a = (1.9^{+1.9}_{-1.0}) \times 10^{-3} \exp \left\{ - \frac{(134 \pm 7) \text{ kJ/mol}}{RT} \right\} \text{ m}^2/\text{s}. \quad (39)$$

Inter-agglomerate boundary diffusion is orders of magnitude faster than Ni GB diffusion along nanocrystalline GBs while the corresponding activation enthalpy Q_a is smaller.

The difference between D_{gb} and D_a was explained by the relaxed state of the nanocrystalline GBs and a non-equilibrium character of the inter-agglomerate boundaries^{39,40)} resulting from the specific preparation method of the nanocrystalline γ -Fe-Ni alloy which allowed growth of the nano-grains from about 20 to about 100 nm of the grain diameter during the heat treatment of the powder sintered.

4. Conclusions

GB diffusion measurements are shown to represent a powerful tool for studying GB equilibrium segregation in true dilute (Henry) limit. At present there exist already ample information on equilibrium segregation of different solutes in Cu and Ag.

GB diffusion measurements on bicrystals yield specific and unique information on linear and non-linear segregation behavior. Compiling a large body of experimental data concerning Ag GB diffusion in high-purity polycrystalline Cu, Cu-Ag polycrystalline alloys, and in Cu bicrystals allowed to extract the corresponding segregation isotherm from GB diffusion data.

Combination of GB diffusion measurements in pure and alloyed metals and in pure and pre-alloyed bicrystals allowed to draw justified conclusions and to distinguish the effects of moving boundaries, non-linear segregation, and a hypothetical variation of the GB diffusivities D_{gb} .

Harrison's classification scheme of GB diffusion regimes was extended including two-scale nanocrystalline materials. Rigorous application of the derived mathematical treatment allowed to extract the GB diffusivity of both nanocrystalline and inter-agglomerate boundaries from the results of radio-tracer measurements in the two-scale nanocrystalline γ -Fe-Ni alloy.

There are further crucial developments in the field of GB diffusion research which were not directly addressed here but are of prime importance. In following they will be briefly presented.

GB diffusion in intermetallic compounds. Considerable progress was recently achieved in GB diffusion in ordered intermetallics. However, GB diffusion is still investigated to a much smaller extent than bulk diffusion. Experimental information is available already for Ni-,^{47–50)} Ti-,⁵¹⁾ and Fe-⁵²⁾ aluminides and a few other compounds, e.g. Ni₂Si,⁵³⁾ Ni₂Si₅ and CoSi₂.⁵⁴⁾ The effect of composition on GB diffusion in intermetallic compounds, which accommodate large deviations from the stoichiometric composition, was carefully studied in Ni-^{47,55)} and Ti-⁵¹⁾ aluminides. While in Ni₃Al and Ti₃Al a remarkable compositional dependence of both the triple product P and the activation enthalpy Q_{gb} was observed, such a dependence was in the limits of experimental uncertainties in equiatomic NiAl and TiAl in the studied compositional intervals. Moreover, GB diffusion was slowest in stoichiometric Ni₃Al, whereas Al-richest Ti₃Al alloys reveal the smallest GB diffusivity P and the largest activation enthalpy Q_{gb} . These features still wait for a reliable explanation from an atomistic point of view. Other feature, which should be explained, is the large ratio of the activation enthalpies of GB and bulk diffusion, which can amount up to 0.9 and even higher.^{51,54)}

Recently, experimental data on GB diffusivity of interphase boundaries in technologically important polysynthetically twinned (PST) TiAl alloy were obtained.⁵⁶⁾ Titanium diffusion along the α_2/γ boundaries turned out to be similar to the Ti GB diffusivity of the Al-richest α_2 -Ti₃Al phase and by two orders of magnitude smaller than Ti GB diffusion in the γ -TiAl.⁵⁶⁾ This effect was explained by the specific atomistic structure of the α_2/γ interfaces.⁵⁷⁾

Our general understanding of GB diffusion in intermetallic compounds has still to be improved on the atomistic level in many details. For example, particular diffusion mechanisms in GBs, the effect of the order and of structural multiplicity are not well elucidated.⁵⁸⁾ It is not clear if the local disorder at GBs occurs by the same mechanism as in the bulk, i.e. by means of anti-structure atoms or structural vacancy formation.⁵⁸⁾

GB phase transitions. It was recently recognized that the phase transitions in GBs may reveal their own specific features.^{59,60)} GB wetting phase transition occurs for some systems in the liquid–solid two-phase area of the bulk phase diagram. Above the given temperature (the wetting temperature) a GB cannot exist in equilibrium with the liquid and the liquid phase substitutes the GB and separates the two grains.⁶⁰⁾ Most prominent examples of such behavior are the Cu–Bi and Al–Ga systems. It was suggested that below the solidus prewetting phenomena may occur that can drastically influence the GB diffusivity in such systems.⁵⁹⁾ Systematic GB diffusion measurements are required to prove the predictions of the prewetting theory.

Atomistic mechanisms of GB diffusion. Remarkable progress was recently achieved in our understanding of underlying mechanisms of GB diffusion in pure metals. Both, vacancies and interstitials were found to be formed in a GB core, with vacancy delocalization and instability at certain GB positions being important features.^{61,62)} Different atomistic mechanisms were established for a GB: a vacancy can move by single-atom exchanges or perform collective jumps which involves several atoms. Even defect-free ring disla-

cements of several atoms in a GB core were observed.⁶²⁾ Interstitials move predominantly by the interstitialcy mechanism involving several atoms.⁶²⁾ However, the calculation of the GB diffusivity as a function of misorientation in comparison with available experimental data presents still a challenging problem.

Acknowledgment

The present investigation was supported by funds of the Deutsche Forschungsgemeinschaft (Project He848/24-1).

REFERENCES

- 1) I. Kaur, Y. Mishin and W. Gust: *Fundamentals of Grain and Interphase Boundary Diffusion* (Wiley & Sons LTD, Chichester, New York, 1995).
- 2) I. Kaur, W. Gust and L. Kozma: *Handbook of Grain and Interphase Boundary Diffusion Data*, (Ziegler, Stuttgart, 1989).
- 3) Y. Mishin, Chr. Herzig, J. Bernardini and W. Gust: *Int. Mater. Rev.* **42** (1997) 155.
- 4) Y. Mishin and Chr. Herzig: *Mater. Sci. Eng. A* **260** (1999) 55.
- 5) Y. Mishin and Chr. Herzig: *Grain Boundary Diffusion in Metals*, in: *Diffusion in Condensed Matter*, (eds.) J. Kärger, P. Heitjans, and R. Haberlandt (Vieweg & Sohn Verlagsgesellschaft mbH, Braunschweig/Wiesbaden, 1998).
- 6) L. G. Harrison: *Trans. Faraday Soc.* **57** (1961) 597.
- 7) S. V. Divinski, M. Lohmann and Chr. Herzig: *Acta Mater.* **49** (2001) 249.
- 8) P. Gas, D. L. Beke and J. Bernardini: *Philos. Mag. Lett.* **65** (1992) 133.
- 9) J. Sommer and Chr. Herzig: *J. Appl. Phys.* **72** (1992) 2758.
- 10) T. Surholt and Chr. Herzig: *Acta Metall.* **45** (1997) 3817.
- 11) T. Surholt, C. Minkwitz and Chr. Herzig: *Acta Mater.* **46** (1998) 1849.
- 12) Chr. Herzig, J. Geise and Y. Mishin: *Acta Metall. Mater.* **41** (1993) 1683.
- 13) T. Surholt, Y. Mishin and Chr. Herzig: *Phys. Rev. B* **50** (1994) 3577.
- 14) E. D. Hondros and M. P. Seah: *Met. Trans. A* **8** (1977) 1363.
- 15) E. D. Hondros: *Interfaces*, (ed. R.C. Gifkins) (London, Butterworths, 1969), 77.
- 16) P. Gas, M. Guttman and J. Bernardini: *Acta Metall.* **30** (1982) 1309.
- 17) P. Gas, S. Poize and J. Bernardini: *Acta Metall.* **34** (1986) 359.
- 18) P. Gas, S. Poize, J. Bernardini, F. Cabane and J. Cabane: *Defect Diffusion Forum* **66–69** (1989) 905.
- 19) Z. Erdélyi, Ch. Girardeaux, G. A. Langer, D. L. Beke, A. Rolland and J. Bernardini: *J. Appl. Phys.* **89** (2001) 3971.
- 20) J. Bernardini, Zs. Tôkei and D. L. Beke: *Philos. Mag. A* **73** (1996) 237.
- 21) B. S. Bokstein, V. E. Fradkov and D. L. Beke: *Philos. Mag. A* **65** (1992) 277.
- 22) Y. Mishin and Chr. Herzig: *J. Appl. Phys.* **73** (1993) 8206.
- 23) B. Bokstein, A. Ostrovsky and J. Bernardini: *Mater. Science Forum* **294–296** (1999) 581.
- 24) F. Güthoff, Y. Mishin and Chr. Herzig: *Z. Metallkd.* **84** (1993) 584.
- 25) D. L. Beke, I. Gödény, G. Erdélyi and F. J. Kedves: *Philos. Mag. A* **56** (1987) 659.
- 26) D. Gupta: *Defect Diff. Forum* **156** (1998) 43.
- 27) S. V. Divinski, M. Lohmann, T. Surholt and Chr. Herzig: *Interface Sci.* **9** (2001) 357.
- 28) J. Bernardini and G. Martin: *Scr. Metall.* **10** (1976) 833.
- 29) J. Bernardini and P. Gas: *Defect Diffusion Forum* **95–98** (1993) 393.
- 30) D. McLean: *Grain Boundaries in Metals*, (Clarendon Press, Oxford, 1957).
- 31) S. V. Divinski, M. Lohmann and Chr. Herzig: *Interface Sci.* **11** (2003) 21.
- 32) T. Suzuoka: *J. Phys. Soc. Japan* **19** (1964) 839.
- 33) E. Budke, T. Surholt, S. I. Prokofjev, L. S. Shvindlerman and Chr. Herzig: *Acta Mater.* **47** (1999) 385.
- 34) J. C. Fisher: *J. Appl. Phys.* **22** (1951) 74.
- 35) V. J. Keast and D. B. Williams: *Acta Mater.* **47** (1999) 3999.
- 36) J. L. Murray: *Metall. Trans. A* **15** (1984) 261.

- 37) L. Klinger and E. Rabkin: *Acta Metall.* **47** (1999) 725.
- 38) S. V. Divinski, F. Hisker, Y.-S. Kang, J.-S. Lee and Chr. Herzig: *Z. Metallkd.* **93** (2002) 256.
- 39) S. V. Divinski, F. Hisker, Y.-S. Kang, J.-S. Lee and Chr. Herzig: *Z. Metallkd.* **93** (2002) 265.
- 40) S. V. Divinski, F. Hisker, Y.-S. Kang, J.-S. Lee and Chr. Herzig: *Interface Sci.* **11** (2003) 67.
- 41) P. Knorr, J. G. Nam and J. S. Lee: *Metall. Mater. Trans. A* **31** (2000) 503.
- 42) I. L. Balandin, B. S. Bokstein, V. K. Egorov and P. V. Kurkin: *Nanostr. Mater.* **8** (1997) 37.
- 43) E. W. Hart: *Acta Metall.* **5** (1957) 597.
- 44) Y. Hanatate, K. Majima and H. Mitani: *Trans. JIM* **19** (1978) 669.
- 45) M. A. Krishtal, A. P. Mokrov, O. V. Stepanov and L. A. Goncharenko: *Zashch. Pokryt. Metal.* **2** (1968) 201.
- 46) P. Million, J. Ruzickova, J. Velisek and J. Vrestal: *Mater. Sci. Engng.* **50** (1995) 43.
- 47) St. Frank and Chr. Herzig: *Mater. Sci. Engng.* **239–240** (1997) 882.
- 48) J. Cermak, J. Ruzickova, I. Stloukal and A. Pokorna: *Scr. Mater.* **37** (1997) 31.
- 49) J. Cermak, I. Stloukal, J. Ruzickova and A. Pokorna: *Intermetallics* **6** (1998) 21.
- 50) N. P. Zulina, E. V. Bolberova and I. M. Razumovski: *Defect Diffusion Forum* **143–147** (1997) 1453.
- 51) Chr. Herzig, T. Wilger, T. Przeorski, F. Hisker and S. V. Divinski: *Intermetallics* **9** (2001) 431.
- 52) Zs. Tôkei, J. Bernardini and D. L. Beke: *Acta Mater.* **47** (1999) 1371.
- 53) J. C. Ciccariello, S. Poize and P. Gas: *J. Appl. Phys.* **67** (1990) 3315.
- 54) T. Barge, P. Gas and F. M. d'Heurle: *J. Mater. Res.* **10** (1995) 1134.
- 55) Chr. Herzig, S. V. Divinski, St. Frank and T. Przeorski: *Defect Diffusion Forum* **194–199** (2001) 389.
- 56) S. V. Divinski, F. Hisker, A. Bartels and Chr. Herzig: *Scr. Mater.* **45** (2001) 161.
- 57) Chr. Herzig, Y. Mishin and S. V. Divinski: *Metal. Mater. Trans. A* **33** (2002) 765.
- 58) Yu. Mishin: *Defect Diffusion Forum* **194–199** (2001) 1113.
- 59) B. B. Straumal, S. I. Prokofjev, L.-S. Chang, N. E. Sluchanko, B. Barezky, W. Gust and E. J. Mittemeijer: *Defect Diffusion Forum* **194–199** (2001) 1343.
- 60) B. B. Straumal, P. Zieba and W. Gust: *Int. J. Inorg. Mater.* **3** (2001) 1113.
- 61) P. Keblinski, D. Wolf, S. R. Phillpot and H. Gleiter: *Philos. Mag. A* **79** (1999) 2735.
- 62) M. R. Sorensen, Y. Mishin and A. F. Voter: *Phys. Rev. B* **62** (2000) 2658.