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Interdiffusion Along a $38^\circ \langle 001 \rangle$ Tilt Grain Boundary in (Fe–10 at.% Si)–Zn Bicrystals

Zinc penetration along a $38^\circ \langle 001 \rangle$ tilt grain boundary in Fe–10 at. % Si bicrystals has been studied at temperatures from 700 to 900 °C. A new method is used for determining the concentration dependence of the product, $s\delta D_b$, of the segregation factor, the grain boundary width and the grain boundary diffusion coefficient from experimentally determined penetration profiles. Only a very small activation energy for $s\delta D_b$ is found for Zn concentrations close to the solidus/solvus line in the bulk phase diagram. This is an indication that the grain boundary is in a quasi-liquid, premelted state. A simple thermodynamic model for the calculation of s is developed, and the value of δ is estimated to be ≈ 20 Å for the premelted grain boundary.

Chemische Diffusion in einer $38^\circ \langle 001 \rangle$ -Kippkorngrenze eines (Fe–10 At.% Si)–Zn–Zweikristalls

Es wurde die Diffusion von Zn in einer $38^\circ \langle 001 \rangle$ -Kippkorngrenze eines Fe–10 At.% Si-Zweikristalls im Temperaturbereich 700 bis 900 °C untersucht. Die Konzentrationsabhängigkeit des Produktes aus dem Segregationsfaktor s , der Korngrenzendicke δ und dem Korngrenzendiffusionskoeffizient D_b wurde mit einer neuen Methode aus gemessenen Eindringprofilen bestimmt. Die Aktivierungsenergie von $s\delta D_b$ bei Zn-Konzentrationen in der Nähe der Solidus/Solvus-Linien ist klein. Dies zeigt, daß sich die Korngrenzen in einem quasiflüssigen, vorgeschmolzenen Zustand befinden. Zur Berechnung von s wird ein einfaches thermodynamisches Modell entwickelt. Der δ -Wert wird zu $\delta \approx 20$ Å abgeschätzt.

1 Introduction

Recently, the interaction of Fe–Si bicrystals with molten Zn has been studied [1 to 3]. The complete wetting of the grain boundaries (GBs) by the Zn-rich melt was found to be accompanied by an unusually rapid Zn penetration along the GBs at Zn concentrations, at which the Fe(Si)–Zn solid solution was definitely in a single phase state. We interpreted this phenomenon as a premelting phase transition at the GBs. The concentration c_{bt} of Zn at the GBs, at which the premelting transition occurs, depends strongly on the temperature and bulk phase transitions in the system studied:

- In the Fe–5 at.% Si alloy, the $c_{bt}(T)$ line (here T is the absolute temperature) came very close to the bulk solidus line below the Curie temperature [1].

- In the Fe–12 at.% Si alloy, the $c_{bt}(T)$ line touched the bulk solidus line slightly below the A2–B2 ordering transition in the bulk. Simultaneously, the GB wetting phase transition occurred [3].
- In all Fe–Si alloys studied, the $c_{bt}(T)$ line had a protrusion to small Zn concentrations at the temperature close to the peritectic temperature in the binary Fe–Zn system.

An attempt to determine the GB diffusion coefficient in the premelted region has been made in [1, 3] by applying the Fisher solution of the simplest GB diffusion model [4] (concentration-independent grain boundary diffusion coefficient D_b , the segregation factor s and the grain boundary width δ) to the experimentally determined penetration profiles of Zn along GBs. Recently, the GB diffusion accompanied by the GB phase transition has been considered in a quasi steady-state approximation [5]. It was shown that the conventional procedure of determining the GB diffusivity cannot be directly applied to the solute-rich GB phase. Moreover, the apparent GB diffusivity in this phase determined from the slope of the penetration profile in the Fisher coordinates depends strongly on the interval of concentrations in which this phase exists. Therefore, in this work we reanalysed GB penetration profiles of Zn using the method suggested in [5].

We have chosen the Fe–10 at.% Si alloy, because there is neither magnetic nor atomic ordering in the bulk of this alloy in the temperature interval in which the GB premelting transition occurs. Such bulk transitions change the concentration interval of stability of the GB premelted phase strongly, which would complicate the problem.

2 Experimental

The Fe–10 at.% Si bicrystal having a $38^\circ \langle 001 \rangle$ tilt GB was grown by the electron beam zone melting method. The technique of growth of Fe–Si single crystals and bicrystals is described in details elsewhere [6]. Samples 6 to 10 mm long and 1.5×1.5 mm² in cross-section were cut from the bicrystal by spark erosion. After mechanical and chemical polishing, a layer of pure Zn was applied to the samples by immersion in a Zn melt at approx. 500 °C for a few seconds. The samples were then sealed in evacuated silica ampoules and annealed in the temperature range 700 to 900 °C. After annealing, the samples were embedded in a holder and mechanically ground and polished. The Zn concentration in the vicinity of the GB was measured using a JEOL-6400 electron microprobe, in which the sample could be positioned with an accuracy of 1 µm. The intensities of the

Zn–K_α and Si–K_α X-ray lines, the microprobe current and the background to the left and right of the lines were measured. The concentrations of Zn, Si and Fe were evaluated using the standard software for the quantitative microprobe analysis. Firstly, the dependence of the Zn concentration on the distance along the *x*-axis (perpendicular to the GB) was determined (Fig. 1). That dependence has a maximum at the GB position. The concentration of the maximum, *c_b*, is accepted as the Zn concentration in the bulk layers adjacent to the GB and in local thermodynamic equilibrium with it. Such measurements were repeated along the GB (*z*-axis), the distance between adjacent profiles being 2 to 5 μm. Secondly, the *c_b*(*z*) dependence (GB penetration profile) was determined from the primary diffusion profiles (Fig. 1). As it was shown in previous works [1 to 3], the GB penetration profiles in the Fe(Si)–Zn system exhibit two different parts with a low and high slopes, respectively. The part with a low slope was interpreted as a manifestation of the quasi-liquid character of the GBs at high Zn concentrations.

3 Results and Discussion

3.1 Processing of the GB Penetration Profiles

A typical GB penetration profile of Zn is shown in Fig. 2a. If the values of *s*, *δ* and *D_b* are concentration independent, the GB penetration profile in the B₂-regime of GB diffusion in a bicrystal [4] can be satisfactory approximated by Fisher’s formula

$$c_b = c_0 \exp\left(-\frac{z}{L_F}\right) \tag{1}$$

where *c₀* is the concentration of diffusant in the constant source on the surface of the bicrystal, and *L_F* is the Fisher length determined by the equation

$$L_F^2 = \frac{D_b s \delta}{2} \left(\frac{\pi t}{D}\right)^{1/2} \tag{2}$$

where *D_b* and *t* are the bulk diffusion coefficient and the annealing time, respectively. It is obvious from Fig. 2a that only a few points of the penetration profile at large *z* could be interpolated by the exponent like in Eq. (1). Therefore, the triple product *sδD_b* is concentration dependent. According to [5], this concentration dependence can be determined from the GB penetration profile by the formula

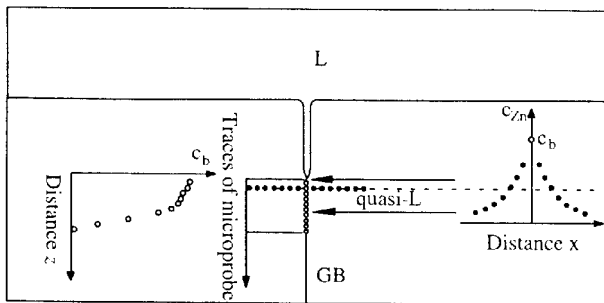
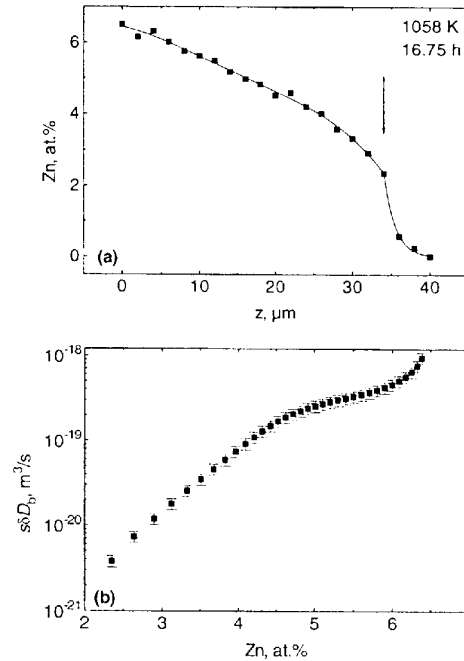


Fig. 1. Schematic diagram illustrating the electron microprobe measurements of the Zn concentration at the GB.



Figs. 2a and b. (a) The penetration profile of Zn along the GB. The experimental points are interpolated by a polynomial (left from the arrow) and by an exponent (right from the arrow). (b) concentration dependence of *sδD_b*.

$$(s\delta D_b)_z = \frac{2\left(\frac{D}{\pi}\right)^{1/2} \int_0^{z^*} c_b(\zeta) d\zeta + \left.\frac{\partial c_b}{\partial z}\right|_{z=z^*} (s\delta D_b)^*}{\left.\frac{\partial c_b}{\partial z}\right|_z} \tag{3}$$

The coordinate *z** on the GB penetration profile represents the point *c_b*(*z**) on this profile, which allows the exponential interpolation of *c_b*(*z*) for *z* > *z** with a reasonable accuracy on the one hand, but leaves enough experimental points for interpolation on the other hand. From this exponential fit the value of (*sδD_b*)* should be determined according to Eqs. (1) and (2). The coordinate *z** is marked by an arrow in Fig. 2a. Equation (3) results from a direct integration of Fisher’s equations under the assumption *s* = const. The possibility for integration was proved in [5], where it was shown that in the quasi-steady state regime of the GB diffusion the GB penetration profile obeys Eq. (1) for large *z* and small *c_b* even in the case of concentration-dependent *δD_b*. We have interpolated the GB penetration profiles for *z* < *z** by the polynomial of a 5th degree. We used also the following relationship for *D*, which we obtained by the interpolation of the bulk interdiffusion data for alloys containing 5 and 12 at.% Si [1, 3] to 10 at.% Si: *D* = 3 × 10⁻⁵ exp(-196 649 J · mol⁻¹/RT) m²/s. The result of calculations of *sδD_b* for the penetration profile in Fig. 2a in the interval of concentrations *c_b*(*z**) < *c_b* < *c_S*, where *c_S* is the solidus concentration, is shown in Fig. 2b. The value of *sδD_b* changes more than by two orders of magnitude in the interval of concentration 2 to 6.5 at.% Zn. This increase is consistent with the premelting hypothesis [1 to 3]. Indeed, in the premelted GB phase *δ* corresponds to the width of the premelted layer, the latter being described by the following relationship [1]:

$$\delta = \left(\frac{nW}{\Delta g} \right)^{\frac{1}{n-1}} \quad (4)$$

where W and n are the force constants describing the interaction of the two solid/liquid interfaces, contributing to the excess Gibbs energy of the quasi-liquid layer by the term W/δ^n , and Δg is the excess Gibbs energy of the liquid phase of concentration c_L in contact with the solid solution of concentration c_b . The repulsive interaction of two metallic solid/liquid interfaces at small distances between them has been demonstrated experimentally in the systems Fe–Hg and Cu–Ga [7, 8]. For $c = c_S$, the value $\Delta g = 0$. A simple thermodynamic consideration for small deviations $\Delta c \ll c_S$ from c_S leads to the following expression:

$$\Delta g = \left(\frac{\partial^2 G}{\partial c^2} \right)_{c_S} (c_L - c_S) \Delta c \quad (5)$$

where G is the Gibbs energy of the bulk solid solution. It follows from Eqs. (4) and (5) that δ should grow when approaching c_S according to the power law $\delta \propto (\Delta c)^{-1/n-1}$. Therefore, taking into account the temperature dependence of c_S , one should compare the $s\delta D_b$ values for different temperatures not for fixed Zn concentrations, but for the fixed

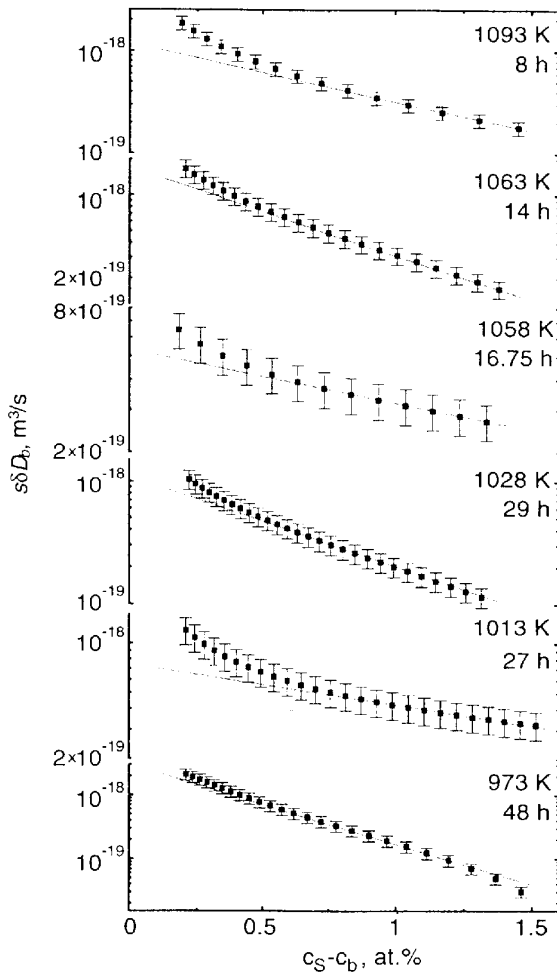


Fig. 3. Concentration dependencies of $s\delta D_b$ for the temperatures studied and in the interval of concentrations $c_S - c_b$ between 0.2 and 1.5 at. % Zn.

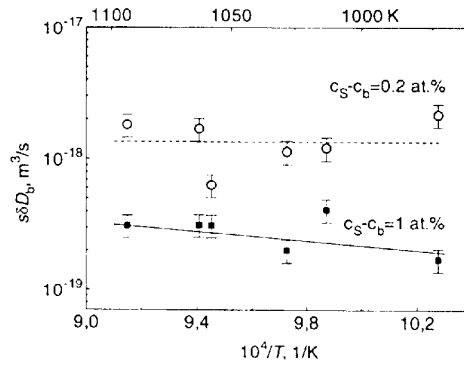


Fig. 4. The temperature dependence of $s\delta D_b$ in Arrhenius coordinates.

values Δc of the deviation from the solidus/solvus concentration. These dependencies of $s\delta D_b$ on Δc , calculated from the GB penetration profiles by using Eq. (3), are shown in Fig. 3 for the most interesting interval of small deviations: $0.2 < \Delta c$ (at. % Zn) < 1.5 . The results for temperatures above 1093 K are not shown in this figure, because these temperatures are above the critical point of the GB premelting phase transition [2], and the presence of a quasi-liquid layer on the GB is problematic there. It can be seen from Fig. 3 that for $0.5 < \Delta c$ (at. % Zn) < 1.5 the $\log(s\delta D_b)$ increases almost linearly as approaching c_S . This exponential growth of $s\delta D_b$ is even stronger than the power growth like in Eq. (4), which one would expect if the concentration dependence of δ only is taken into account. Such exponential growth can be only caused by a linear decrease of the activation energy for the GB diffusion as approaching c_S . It is known that the activation energy for diffusion in liquids is much lower than the activation energy of GB diffusion and even surface diffusion [4]. Therefore, we can conclude that for $0.5 < \Delta c$ (at. % Zn) < 1.5 the degree of thermal disordering at the GB increases as the solidus/solvus line is approached and the boundary layer gradually transforms from an ordered structure into a disordered liquid. For $\Delta c < 0.5$ at. % Zn the upward deviations from the exponential growth can be clearly seen in Fig. 3. Such deviations could be connected with the divergence of the width δ of the quasi-liquid layer [see Eq. (4)]. Unfortunately, the accuracy of the microprobe measurements (not better than ± 0.1 at. % Zn) did not allow us to determine the critical index for this divergence. The critical index determined formally by plotting $s\delta D_b$ vs. Δc in log-log coordinates expresses the highest degree of the polynomial term, which contribute to the extremum on the GB penetration profile at $\Delta c \rightarrow 0$ and has no any physical meaning, because the error of concentration measurements is comparable with the region of concentrations, in which the critical divergence is observed.

The temperature dependence of $s\delta D_b$ for $\Delta c = 0.2$ at. % Zn and $\Delta c = 1$ at. % Zn is shown in Fig. 4. The relevant Arrhenius equations are the following.

For $\Delta c = 1$ at. % Zn: $s\delta D_b = (1.6 \pm 3.4) \times 10^{-17} \exp(-35 \pm 18 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{ m}^3/\text{s}$

and

for $\Delta c = 0.2$ at. % Zn: $s\delta D_b = (1.5 \pm 4) \times 10^{-18} \exp(-1 \pm 23 \text{ kJ} \cdot \text{mol}^{-1}/RT) \text{ m}^3/\text{s}$.

From this data one can see that the activation energy for the GB diffusion is indeed very small if compared with the activation energy for bulk interdiffusion (197 kJ/mol) or with the activation energy for GB interdiffusion in the Fe–Zn system (187 kJ/mol), extracted from the experimental data on the diffusion-induced GB migration [9]. This confirms the quasi-liquid character of the GBs in the pre-melted state close to the solidus/solvus line in the bulk phase diagram.

From the obtained data it is possible to estimate with which regime of the GB diffusion our experimental data are consistent. There are two parameters on which the classification of the GB diffusion regimes in a bicrystal is based [4]:

$$\alpha = \frac{s\delta}{2\sqrt{Dt}} \quad (6a)$$

and

$$\beta = \frac{s\delta D_b}{2D\sqrt{Dt}} \quad (6b)$$

In our experimental conditions $\alpha \leq 10^{-5}$ and β vary from ≈ 1 for $s\delta D_b = 10^{-19} \text{ m}^3/\text{s}$ to ≈ 10 for $s\delta D_b = 10^{-18} \text{ m}^3/\text{s}$. Therefore, for $\beta \approx 10$ our experimental conditions correspond to the B_2 regime, in which the distribution of the diffusant in the GB is quasi-steady state ($\partial c_b/\partial t \approx 0$) and the lateral volume diffusion from the GB into the bulk dominates over the bulk diffusion along the z -axis. Equation (3) which we used for determining the concentration dependence of $s\delta D_b$ was derived for this regime. The value of $\beta \approx 1$ corresponds to the B_3 regime, in which the distribution of the diffusant in the GB is still quasi-steady state, but the bulk diffusion along the z -axis contributes considerably to the total mass balance at the GB. A comparison of Fisher's formula [Eq. (1)] with the exact solution of Fisher's model for concentration-independent $s\delta D_b$ shows that the application of Eq. (1) to the experimental penetration profiles leads to a slight overestimation of $s\delta D_b$. For $s\delta D_b < 10^{-19} \text{ m}^3/\text{s}$ $\beta < 1$, which corresponds to the B_4 regime of the GB diffusion, in which the diffusant distribution in the GB is not quasi-steady state anymore, and the bulk diffusion in the z -direction dominates in the mass balance. In principle, the application of Eq. (3) for the processing of the experimental data is not justified in this case and respective results for $s\delta D_b < 10^{-19} \text{ m}^3/\text{s}$ (see Fig. 2b) cannot be considered as reliable. This is the reason why we have not shown the values of $(s\delta D_b)^*$ which are below $10^{-20} \text{ m}^3/\text{s}$ for all temperatures studied. However, the numerical analysis of Eq. (3) showed that the values of $s\delta D_b$ which are above $10^{-19} \text{ m}^3/\text{s}$ do not change more than by 10% with the variation of $(s\delta D_b)^*$ by one or two orders of magnitude. This is below the experimental error in the determination of $s\delta D_b$, and the data in Fig. 3 can be considered as reliable.

Moreover, there are reasons to extend the region of the B_2 regime in our case up to the lowest values of $s\delta D_b \approx 10^{-20} \text{ m}^3/\text{s}$ obtained. Indeed, the classification of the regimes of GB diffusion in bicrystal given in [4] was derived for concentration-independent $s\delta D_b$ values, which is not the case in our experimental situation. Let us rewrite the definition of β [Eq. (6b)] using Eq. (2):

$$\beta = \frac{1}{\sqrt{\pi}} \left(\frac{L_F}{\sqrt{Dt}} \right)^2 \quad (7)$$

Written in such a form, β represents the ratio of the penetration depth of the diffusant along the GB to the penetration depth in the bulk. For concentration-dependent $s\delta D_b$, the penetration depth along the GB is determined by the maximal values of $s\delta D_b$ [5]. In any case, the L_F can be estimated roughly by the distance, at which the Zn concentration at the GB decreases from c_S to c_S/e in the experimental penetration profile. This distance varies between 35 and 100 μm in our experiments. The value of \sqrt{Dt} varies between 10 and 15 μm , therefore, the minimal value of β is ≈ 3 . Therefore, the GB diffusion process proceeds in the B_2 regime for all GB concentrations. Qualitatively, the following interpretation can be given for this: the "advancing" part of the penetration profile, at which the value of $s\delta D_b$ is low, moves along the GB in z -direction with a velocity determined by the high values of $s\delta D_b$ at Zn concentrations close to c_S . After the zone of bulk diffusion is formed, the part of the penetration profile with low $s\delta D_b$ advances further in the bulk regions free from diffusant with a high velocity, and the process of formation of the bulk diffusion zone repeats again. The effective time, during which the zone of bulk diffusion is forming around the part of GB with low $s\delta D_b$ is much more lower than the total annealing time t , which, according to Eq. (6b), increases the value of β .

3.2 Calculation of the Segregation Factor

It follows from Figs. 3 and 4 that $s\delta D_b \approx 10^{-18} \text{ m}^3/\text{s}$ close to the bulk solidus/solvus line at all temperatures, at which the GB premelting occurs. As far as the diffusion coefficient in the melted metal at the melting temperature is approximately $3 \times 10^{-9} \text{ m}^2/\text{s}$, the width, δ , of the premelted GB can be estimated if the segregation factor s is known. Because the ternary Fe–Si–Zn phase diagram is not known in details, we will use the binary Fe–Zn phase diagram for estimations [10]. From this diagram, $c_L \approx 92 \text{ at.}\% \text{ Zn}$ and $c_S \approx 29 \text{ at.}\% \text{ Zn}$ at the peritectic temperature of 782 °C. However, one cannot use the standard definition of the segregation factor [4] for the quasi-liquid film on the GB, from which it would follow $s = c_L/c_S \approx 3.2$. The reason for this is the fact that the relationship between

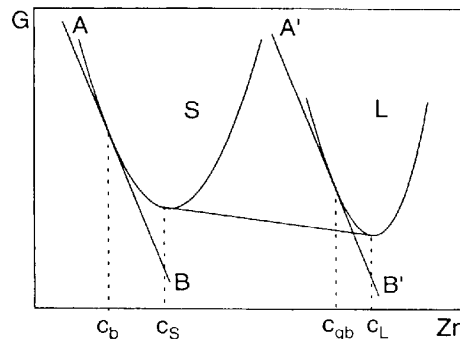


Fig. 5. Schematic Gibbs energy-concentration diagram. The common tangent to the Gibbs energies for the solid (S) and liquid (L) phases determines the solidus (c_S) and liquidus (c_L) concentrations of Zn. The parallel tangents AB and A'B' determine the concentration of Zn, c_{gb} , in the quasi-liquid phase on the GB in equilibrium with the solid in which the Zn concentration is c_b .

the bulk concentration near the GB c_b and the Zn concentration inside the GB c_{gb} does not obey the Henry-type adsorption isotherm of the type $c_{gb} = sc_b$ in the vicinity of solid-liquid equilibrium. A simple "Gibbs energy – concentration" construction (Fig. 5) is useful for establishing the true relationship between c_{gb} and c_b . It follows from Fig. 5:

$$c_{gb} - c_L = \frac{(\partial^2 G_S / \partial c^2)}{(\partial^2 G_L / \partial c^2)} (c_b - c_S) \quad (8)$$

where G_S and G_L are the Gibbs energies of the solid and liquid phase, respectively. At a constant temperature the values of c_L and c_S are also constant, and the fraction in the right hand side of Eq. (8) can be estimated from the slope of the solidus and liquidus line at the respective temperature. By calculation of the atom flux along the GB the constant additive terms from Eq. (8) vanish, and we get for the segregation factor (in the sense of the GB diffusion):

$$s = \frac{(\partial c_L / T)}{(\partial c_S / T)} \quad (9)$$

For the Fe–Zn system $s \approx 0.15$ and we get $\delta \approx 20 \text{ \AA}$, which is considerably higher than the crystallographic width of the GBs in metals of approx. 5 Å [4]. This value of the width of the premelted layer is in a good correlation with the equilibrium thickness of the intergranular amorphous phase in various ceramics [11].

4 Conclusions

The following conclusions can be drawn.

(i) The penetration of Zn along a 38° {001} tilt GB in Fe–10 at.% Si bicrystals has been studied and the GB Zn penetration profiles (Zn concentration at GB vs. distance along the GB) after annealing in the temperature interval 700 to 900 °C has been determined by the electron probe microanalysis. The GB penetration profiles at temperatures below 820 °C exhibit two distinct regions with a small and a large slope. The regions with a small slope at high Zn concentrations close to the bulk solidus/solvus Zn concentration are an indication of a quasi-liquid state of the GB.

(ii) The concentration dependence of the triple product $s\delta D_b$ has been determined using the method suggested recently [5]. $s\delta D_b$ increases as the Zn concentration ap-

proaches the solidus/solvus concentration. For all concentration dependencies the region exists, in which $s\delta D_b$ increases exponentially with the concentration. In the direct vicinity of the solidus/solvus line ($\Delta c_b \leq 0.5$ at. % Zn) the upward deviations from the exponential increase of $s\delta D_b$ are observed.

(iii) The low values of activation energies for the GB diffusion (35 ± 18 and 1 ± 23 kJ/mol for $\Delta c_b = 1$ and 0.2 at.% Zn, respectively) are consistent with the premelting hypothesis, because the activation energy for the diffusion in liquids is low.

4. The relationship between the bulk concentration near the GB c_b and the Zn concentration inside the GB c_{gb} in the vicinity of the solid-liquid equilibrium has been established and the segregation factor s has been estimated ($s \approx 0.15$, in spite of the fact that Zn concentration in the liquid phase exceeds those in the solid by a factor of 3.2). The width of the "premelting" GB has been estimated to be approx. 20 Å.

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