E. Rabkin et al.: Interdiffusion Along a $38^\circ$ ⟨001⟩ Tilt Grain Boundary in (Fe–10 at. % Si)–Zn Bicrystals

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

Zinc penetration along a $38^\circ$ ⟨001⟩ 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, $\delta D_n$, 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 $\delta D_n$ is found for Zn concentrations close to the solidus/solvsus line in the bulk phase diagram. This is an indication that the grain boundary is in a quasi-liquid, premelting state. A simple thermodynamic model for the calculation of $\delta$ is developed, and the value of $\delta$ is estimated to be $\approx 20$ Å for the premelting grain boundary.

Chemische Diffusion in einer $38^\circ$ ⟨001⟩-Kippkornzgrenze eines (Fe–10 At. % Si)–Zn-Zweikristalls

Es wurde die Diffusion von Zn in einer $38^\circ$ ⟨001⟩-Kippkornzgrenze eines Fe–10 At. % Si-Zweikristalls im Temperaturbereich 700 bis 900°C untersucht. Die Konzentrationsabhängigkeit des Produktes aus dem Segregationsfaktor $\delta$, der Kornzgrenzdicke $\delta$ und dem Kornzgrenzdiffusionskoeffizient $D_n$ wurde mit einer neuen Methode aus gemessenen Eindringprofilen bestimmt. Die Aktivierungsgenergie von $\delta D_n$ bei Zn-Konzentrationen in der Nähe der Solidus/Solvus-Linien ist klein. Dies zeigt, daß sich die Kornzgrenzen in einem quasi-flüssigen, vorgeschmolzenen Zustand befinden. Zur Berechnung von $\delta$ wird ein einfaches thermodynamisches Modell entwickelt. Der $\delta$-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 $c_{eq}$ 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 $c_{eq}(T)$ 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 $c_{eq}(T)$ 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 $c_{eq}(T)$ 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 premelting 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 $D_n$). The segregation factor $\delta$ and the grain boundary width $\delta$ 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 premelting phase strongly, which would complicate the problem.

2 Experimental

The Fe–10 at. % Si bicrystal having a $38^\circ$ ⟨001⟩ 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 $1.5 \times 1.5$ mm$^2$ 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–K₄ and Si–K₄ 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, cₓ, 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 cₓ(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 FeSi–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, b, and D₀ are concentration independent, the GB penetration profile in the Bₗ-regime of GB diffusion in a bicrystal [4] can be satisfactorily approximated by Fishcr’s formula

\[ c_x = c_0 \exp \left( -\frac{z}{L_f} \right) \]  

(1)

where \( c_0 \) 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

\[ L_f = \frac{D_0 s t}{2} \]  

(2)

where \( D_0 \) 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 \( sD₀b \) is concentration dependent. According to [5], this concentration dependence can be determined from the GB penetration profile by the formula

\[ \frac{\partial \langle sD₀b \rangle}{\partial \langle c_x \rangle} = \frac{2 \left( \frac{\langle c_x \rangle}{c_0} \right)^{1/2} \int_c^z \frac{c_x(z') dz'}{c_0} + \frac{\langle c_x \rangle}{c_0} \langle sD₀b \rangle}{\int_c^z \frac{\langle c_x \rangle}{c_0} dz} \]  

(3)

The coordinate \( z^{*} \) on the GB penetration profile represents the point \( c_x(z^{*}) \) on this profile, which allows the exponential interpolation of \( c_x(z) \) 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 \( \langle sD₀b \rangle \) 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 \( s = \text{const} \). 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 \( c_0 \) even in the case of concentration-dependent \( sD₀b \). 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: \( D = 3 \times 10^{-5} \exp (-196649J/mol) \text{ m}^2/\text{s} \). The result of calculations of \( sD₀b \), for the penetration profile in Fig. 2a is in the interval of concentrations \( c_x(z^{*}) < c_0 \). where \( c_0 \) is the solubility concentration, is shown in Fig. 2b. The value of \( sD₀b \) 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 permelting hypothesis [1 to 3]. Indeed, in the premelting GB phase \( \delta \) corresponds to the width of the premelted layer, the latter being described by the following relationship [11]:

![Fig. 1. Schematic diagram illustrating the electron microprobe measurements of the Zn concentration at the GB.](image-url)
\[
\delta = \left( \frac{nW}{\Delta g} \right)^{1/2}
\]  
(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 \( W/\Delta g \), and \( \Delta g \) is the excess Gibbs energy of the liquid phase of concentration \( c_1 \) in contact with the solid solution of concentration \( c_0 \). 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 \( c = c_0 \), the value \( \Delta g = 0 \). A simple thermodynamic consideration for small deviations \( \Delta c \ll c_0 \) from \( c_0 \) leads to the following expression:

\[
\Delta g = \left( \frac{\partial^2 G}{\partial c^2} \right)_{c_0} (c_1 - c_0) \Delta c
\]  
(5)

where \( G \) is the Gibbs energy of the bulk solid solution. It follows from Eqs. (4) and (5) that \( \delta \) should grow when approaching \( c_0 \) according to the power law \( \delta \propto (\Delta c)^{-1/2} \). Therefore, taking into account the temperature dependence of \( c_0 \), one should compare the \( sD_b \) values for different temperatures not for fixed Zn concentrations, but for the fixed values \( \Delta c \) of the deviation from the solidus/solvisus concentration. These dependencies of \( sD_b \) on \( \Delta c \), 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 \( sD_b \) increases almost linearly as approaching \( c_0 \). This exponential growth of \( sD_b \) is even stronger than the power growth like in Eq. (4), which one would expect if the concentration dependence of \( \delta \) 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 \( c_0 \). 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/solvisus 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 \( \delta \) of the quasi-liquid layer [see Eq. (4)]. Unfortunately, the accuracy of the microprobe measurements (not better than \( \pm 0.1 \) at. % Zn) did not allow us to determine the critical index for this divergence. The critical index determined formally by plotting \( sD_b \) vs. \( \Delta c \) in log-log coordinates expresses the highest degree of the polynomial term, which contribute to the extremum on the GB penetration profile at \( \Delta c \to 0 \) 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 \( sD_b \) 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: \( sD_b = (1.6 \pm 3.4) \times 10^{-17} \exp \left(-35 \pm 18 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{RT}^{-1}\right) \text{m}^2/\text{s} \)

and

for \( \Delta c = 0.2 \) at. % Zn: \( sD_b = (1.5 \pm 4) \times 10^{-18} \exp \left(-1 \pm 23 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{RT}^{-1}\right) \text{m}^2/\text{s} \).

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Fig. 3. Concentration dependencies of \( sD_b \) for the temperatures studied and in the interval of concentrations \( c_0 - c_0 \) between 0.2 and 1.5 at. % Zn.

Fig. 4. The temperature dependence of \( sD_b \) in Arrhenius coordinates.
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]:

\[ z = \frac{s \Delta D_s}{2 \sqrt{D_t}} \]  
\[ (6a) \]

and

\[ \beta = \frac{s \Delta D_s}{2D_t \sqrt{D_t}} \]  
\[ (6b) \]

In our experimental conditions \( z \lesssim 10^{-5} \) and \( \beta \) vary from \( \approx 1 \) for \( s \Delta D_s = 10^{-19} \text{ m}^2/\text{s} \) to \( \approx 10 \) for \( s \Delta D_s = 10^{-18} \text{ m}^2/\text{s} \). Therefore, for \( \beta \approx 10 \) our experimental conditions correspond to the B2 regime, in which the distribution of the diffusant in the GB is quasi-steady state (\( \Delta c_s/\Delta t \approx 0 \)) 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 \( s \Delta D_s \) was derived for this regime. The value of \( \beta \approx 1 \) corresponds to the B2 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 model [Eq. (1)] with the exact solution of Fisher’s model for concentration-independent \( s \Delta D_s \), shows that the application of Eq. (1) to the experimental penetration profiles leads to a slight overestimation of \( s \Delta D_s \). For \( s \Delta D_s < 10^{-19} \text{ m}^2/\text{s} \) \( \beta < 1 \), which corresponds to the B2 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 \( s \Delta D_s < 10^{-18} \text{ m}^2/\text{s} \) (see Fig. 2b) cannot be considered as reliable. This is the reason why we have not shown the values of \( s \Delta D_s \) which are below \( 10^{-19} \text{ m}^2/\text{s} \) for all temperatures studied. However, the numerical analysis of Eq. (3) showed that the values of \( s \Delta D_s \) which are above \( 10^{-19} \text{ m}^2/\text{s} \) do not change more than by 10% with the variation of \( (s \Delta D_s) \) by one or two orders of magnitude. This is below the experimental error in the determination of \( s \Delta D_s \), and the data in Fig. 3 can be considered as reliable.

Moreover, there are reasons to extend the region of the B2 regime in our case up to the lowest values of \( s \Delta D_s \approx 10^{-20} \text{ m}^2/\text{s} \) obtained. Indeed, the classification of the regimes of GB diffusion in bicrystal given in [4] was derived for concentration-independent \( s \Delta D_s \) values, which is not the case in our experimental situation. Let us rewrite the definition of \( \beta \) [Eq. (6b)] using Eq. (2):
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 $c_{gb} = k c_b^{n}$ 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:

$$c_{gb} = c_b - \frac{\Delta G_s}{RT} \left( c_b - c_s \right)$$

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):

$$s = \frac{\Delta G_s}{RT}$$

For the Fe–Zn system $s \approx 0.15$ and we get $\delta \approx 20 \text{ Å}$, 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/solubility Zn concentration are an indication of a quasi-liquid state of the GB.

(ii) The concentration dependence of the triple product $\delta D_e$ has been determined using the method suggested recently [5]. $\delta D_e$ increases as the Zn concentration approaches the solidus/solubility concentration. For all concentration dependencies the region exists, in which $\delta D_e$ increases exponentially with the concentration. In the direct vicinity of the solidus/solubility line ($\Delta c_b < 0.5$ at. % Zn) the upward deviations from the exponential increase of $\delta D_e$ are observed.

(iii) The low values of activation energies for the GB diffusion (35 ± 18 and 23 ± 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 “premelted” GB has been estimated to be approx. 20 Å.

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Literature


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