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WETTING AND PREMELTING PHASE TRANSITIONS IN 38° [100] TILT GRAIN BOUNDARY IN (Fe–12 at.% Si)–Zn ALLOY IN THE VICINITY OF THE A_2–B_2 BULK ORDERING IN Fe–12 at.% Si ALLOY

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Abstract—Zinc penetration along grain boundary tilt of 38° [100] in bicrystals of the Fe–12 at.% Si alloy is studied by means of an electron microprobe analysis. At $T_{\mathrm{ord}} = 770°\mathrm{C}$ the alloy undergoes an A_2–B_2 ordering transition. At $T_w = 749°\mathrm{C}$ a wetting transition occurs in grain boundaries of the alloy. At temperature above T_w, the diffusion permeability of the grain boundaries changes abruptly at C_{bt}. This change may be explained, assuming a premelting transition to occur in grain boundaries. The $C_{\mathrm{bt}}(T)$ line on the phase diagram terminates by critical point at $T_{\mathrm{crit}} = 807 \pm 2°\mathrm{C}$. A protrusion can be seen on the $C_{\mathrm{bt}}(T)$ line and on the solvus line near T_{ord}. The maximum on the temperature dependence of the diffusion permeability of grain boundaries corresponds to approximately the same temperature. The hypothesis of a premelting transition on grain boundaries provides possibility of explaining all the observed phenomena, in particular, the disappearance of wetting and premelting below the ordering temperature in the bulk.

Résumé—On étudie la pénétration du zinc le long d'un joint de grains de flexion de 38° [100] dans des bicristaux de l'alliage Fe–12 at.% Si, par microanalyse électronique. A $T_{\mathrm{ord}} = 770°\mathrm{C}$ l'alliage subit une transition d'ordre A_2–B_2. A $T_m = 749°\mathrm{C}$ une transition de mouillage se produit dans les joints de grains de l'alliage. Aux températures supérieures à T_m la perméabilité de diffusion de joints de grains change brusquement à C_{tj}. Cette variation peut s'expliquer en supposant qu' une transition de préfusion se produit dans les joints de grains. La courbe C_{tj} (T) sur le diagramme de phases se termine par un point critique à $T_{\mathrm{crit}} = 807 \pm 2°\mathrm{C}$. Une excroissance peut se produire sur la courbe C_{tj} (T) et sur la ligne de solvus prés de T_{ord}. Le maximum de la dépendance de la perméabilité de diffusion vis à vis de la température correspond approximativement à la même température. L'hypothèse d'une transition de préfusion sur les joints de grains donne la possibilité d'expliquer tous les phénomènes observés, en particulier la disparition du mouillage et de la préfusion au dessous de la température de mise en ordre globale de l'échantillon.

Zusammenfassung—Das Eindringen von Zink entlang von einer 38°/[100]-Korngrenze in Bikristallen der Legierung Fe–12 At.-% Si wird mit der Elektronenmikrosonde untersucht. Bei der Temperatur $T_{\mathrm{ord}} = 770°\mathrm{C}$ durchläuft die Legierung einen A_2–B_2-Ordnungsübergang. Bei $T_w = 749°\mathrm{C}$ tritt ein Benetzungsübergang in den Korngrenzen der Legierung auf. Bei Temperaturen oberhalb von T_w ändert sich die Diffusionspermeabilität der Korngrenzen abrupt bei C_{bt}. Diese Änderung kann mit der Ännahme erklärt werden, daß ein Vorschmelzübergang in den Korngrenzen auftritt. Die $C_{\mathrm{bt}}(T)$-Linie im Phasendiagramm endet am kritischen Punkt bei $T_{\mathrm{crit}} = 807 \pm 2°\mathrm{C}$. Auf der $C_{\mathrm{bt}}(T)$-Linie und auf der Solvuslinie in der Nähe von T_{ord} kann eine Vorstülpung gesehen werden. Das Maximum in der Temperaturabhängigkeit der Diffusionspermeabilität der Korngrenzen entspricht etwa derselben Temperatur. Mit der Hypothese eines Vorschmelzüberganges ergibt sich eine Möglichkeit, alle die beobachteten Erscheinungen, insbesondere das Verschwinden der Benetzung und das Vorschmelzen unterhalb der Volumen-Ordnungstemperatur, zu erklären.

1. INTRODUCTION

In their previous work the authors studied the process of penetration of tin and zinc along 43° [100] tilt grain boundaries in bicrystals of b.c.c. Fe–5 at.% Si alloy [1]. This is the smallest silicon content which isolates the region of existence of γ-phase on the Fe–Si phase diagram [2]. This enables growing single- and bicrystals with the b.c.c. lattice. Wetting transition was experimentally shown to occur when tin penetrates along these grain boundaries: above 810°C, the contact angle at the grain boundary intersection with the sample surface is equal (or very near) to zero. Below 810°C, this angle becomes 180°. It grows from 0 to 180° in the temperature range as small as about 10°C. Similar wetting transition was earlier observed in other systems too, e.g. in Zn–Sn [3, 4], Al–Sn [5–7], Al–Pb [5], Ag–Pb [8]. During penetration of zinc along the same grain boundaries the wetting of interfaces with the melt was observed in the whole temperature range studied, 652–908°C [1]. In the experiments [1] the thickness of a zinc or tin layer applied to the surface was selected so that to provide penetration of the wetting interlayer along the interface to the depth of 50–200 μm from the surface. Studying the distribution of tin or zinc in the sample below this interlayer, one could define the behaviour of diffusion of the grain boundaries. It was found that during zinc diffusion there exists a region at the grain boundary (directly below the wetting interlayer) in which the zinc diffusion rate is two orders of magnitude higher than the common one is. Zinc concentrations displaying such elevated permeability range from the bulk solubility limit C_o to some concentration C_{bt}. At concentration C_{bt} the value of product of grain boundary diffusion coefficient D_b and diffusional thickness of grain boundary δ abruptly decreased. Below C_{bt}, the values of $D_b\ \delta$ are close to those characteristic of grain boundaries in iron and its alloys. The depth of zinc penetration in the concentration range from C_o to C_{bt} was shown to be proportional to $t^{1/4}$, t being the time of annealing. This means that although zinc penetrates along the interfaces at the rate of two orders of magnitude greater than usual, at a concentration above C_{bt}—it is still a diffusional process similar to that occurring at the concentration below C_{bt}. It was also found that the concentration C when the abrupt change of $D_b\,\delta$ occurs, depends strongly on the annealing temperature [see Fig. 1(c)]. Above the Curie point the C_{bt} value is the lower, the higher is the limit of zinc solubility in the alloy, while below the Curie point the C_{bt} value approaches the solubility limit C_o but, nevertheless, the wetting occurs. In the vicinity of the Curie point, a protrusion towards lower concentrations is observed on the dependence $C_{bt}(T)$.

There exists a number of theoretical works in which the phase transitions in interfaces accompanying the wetting are predicted [9–11]. Such transition include premelting, prewetting, layering, etc. They are connected with the formation of a thin liquid (or quasi-liquid) thermodynamically equilibrium interlayer in interfaces. In the Fe–5 at.% Si system, a phase transition occurs on grain boundaries at concentration C_{bt}. We suppose it to be a premelting transition. In this case an increase of $D_b\delta$ may be explained by formation of a quasi-liquid interlayer on grain boundary: the diffusional thickness of the interface δ increases approximately by a factor of 100. All the necessary conditions for a premelting transition to exist are satisfied in the studied system: high positive value of enthalpy of mixing the solution components, the wetting of grain boundaries in the two-phase "solid–melt" region, as well as the fact that the mentioned phenomena are observed on grain boundaries of the component with a higher temperature of melting (iron). Therefore, it is quite reasonable to say that we do observe a premelting transition on grain boundaries.

The aim of the present paper is to determine how the phase transition of the concentration ordering in the bulk affects the process of zinc penetration along the grain boundaries in the Fe–Si system, the grain boundary wetting and the premelting transition. Besides, we intend to compare the influence of the atomic ordering with that of the spin ordering studied in the previous paper [1].

2. EXPERIMENTAL

To perform the experiments, a bicrystal of the Fe–12 at.% Si alloy was grown. In this alloy the atomic ordering of the iron–silicon solid solution occurs: with decreasing temperature the disordered b.c.c. lattice (A_2 structure) is transformed into the ordered one (B_2 structure) [2]. The bicrystals of the Fe–12 at.% Si alloy were grown using the method of the electron-beam melting. The silicon content in the alloy was selected to provide A_2–B_2 transition to occur at approximately 800°C: this temperature is convenient for diffusion experiments since the duration of diffusional anneal at the upper limit of the temperature range to be studied, 1000°C, is not very short (about an hour), while at the lower limit, 700°C, it is not very long: about 500 h (see the table). A bicrystal of 12 mm in diameter with the 38° [100] tilt grain boundary was grown. It was cut in a spark cutter into 6–12 mm samples, cross-section being 1.5 × 1.5 mm. The grain boundary was disposed in the middle of the sample, normal to its longer part. The zinc layer was applied to the sample by immersion into melt. Before immersion, the samples were mechanically ground and chemically polished in the solution of 80% H_2O_2–14% H_2O–6% HF. Then the applied zinc layer was completely removed from two lateral faces of the samples. From the other two sides the excess of zinc was removed so that only a 100–150 μm thick layer remained on them.

The prepared samples were soldered in evacuated silica ampules, then annealed in an oven in temperature range of 714–994°C. The temperature was maintained with an accuracy of ±0.5°C. After annealing the samples were fixed in a holder using Wood alloy, then mechanically ground and polished. The polished surface of samples was etched for 10–15 s to reveal the grain boundaries and make it possible to study the samples by means of optical microscopy. The site of grain boundary intersection with the sample surface was marked by imprints of the indentor of a microhardness meter. Then the sample was mechanically repolished: the traces of chemical etching were removed, while the indentor imprints remained visible. On the samples produced the zinc content distribution was determined by means of an electron microprobe analysis (see Fig. 1). To determine the concentration by the intensity of the characteristic X-ray radiation, the necessary corrections of standard methods of quantitative electron microprobe analysis were introduced [15].

In order to determine the bulk diffusion coefficient of zinc, the diffusion profiles were measured far from the grain boundary, perpendicularly to the sample

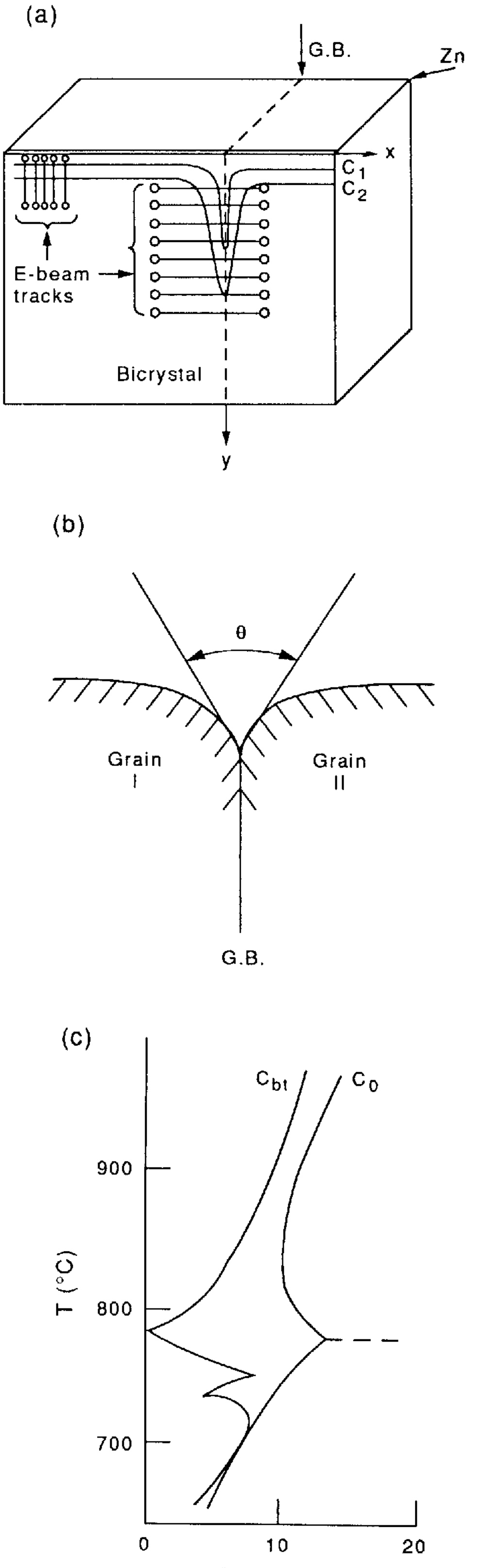

Fig. 1. (a) The schematic diagram of measurements of zinc concentration in a bicrystal after diffusional anneal. The trajectories of electron microprobe during measurements of bulk and grain boundary diffusion coefficients are presented. (b) The schematic diagram of measurement of a contact angle θ at the site of grain boundary intersection of bulk and grain boundary diffusion coefficients are presented. (c) Grain boundary and bulk phase diagrams of the system (Fe–5 at.% Si)–Zn [1].

surface, along the [100] axis (see the schematic diagram in Fig. 1). The values of D were determined from 5 to 7 diffusion profiles according to the procedure, described in the previous work [1], where we used Lyubov's method, taking into account the dependence of the bulk diffusion coefficient D on bulk concentration C. For determining the coefficients of zinc grain boundary diffusion, series of diffusion profiles were measured perpendicularly to the grain boundaries, parallel to the sample surface to which the diffusing impurity was applied (see the schematic diagram in Fig. 1). The value of the product of the grain boundary diffusion coefficient D_b and the diffusion thickness of the grain boundary δ was determined using the Fisher equation [16] with the correction for the concentrational dependence of the bulk diffusion coefficient D [1]

$$D_b\delta = 2\,(D^\circ/\pi t)^{1/2}\, y^2\,(1 + 2\beta C_o/3\pi)/(\ln C_b/C_o)^2. \quad (1)$$

Here C_b is the grain boundary concentration measured at the depth y. C_o—solubility limit, t—anneal duration, β and D° are parameters. The Fisher equation can be used as an asimptotic representation of the Wipple solution [17] for calculation of $D_b\delta$ only if the Le Claire condition is satisfied [18]

$$\eta\beta^{-1/2} > 10. \quad (2)$$

Here $\eta = y/(Dt)^{1/2}$ and $\beta = \delta D_b/2D^{3/2}\,t^{1/2}$. In our case, this relation is true only for the gentle regions of zinc penetration along the grain boundaries $C_b(y)$ (see Fig. 3). In Fig. 4, however, the experimental data for the steep regions of $C_b(y)$ curves, where $\eta\beta^{-1/2}$ is small are also presented for illustration. If $\eta\beta^{-1/2} < 10$, equation (1) yields under estimated values for $D_b\delta$ and grain boundary diffusion activation energy E_b [19]. Therefore, using equation (1) for small $\eta\beta^{-1/2} < 10$, the diffusional permeability of the grain boundary (denoted by Π) is determined rather than the ordinary parameter $D_b\delta$. The diffusional permeability Π has the same dimensionality as $D_b\delta$.

3. RESULTS

Figure 2 shows the temperature dependence of the bulk zinc diffusion coefficient for the Fe–12 at.% Zn alloy. The bulk diffusion coefficient was determined on the same bicrystals as the values of product $D_b\delta$ for the grain boundary diffusion (see the schematic diagram Fig. 1). It can be seen from Fig. 2 that the temperature dependence $D(T)$ consists of two regions with different slopes. They intersect at about 770°C. This temperature is close to the A_2–B_2 ordering temperature in the Fe–12 at.% Si alloy [2]. Above the ordering temperature, $T_{\rm ord}$, the activation energy of the bulk zinc diffusion E is 170 kJ/mol, below $T_{\rm ord}$ $E = 324$ kJ/mol.

In Fig. 5(b), the temperature dependence of angle θ at the site of intersection of grain boundary with the sample surface is presented (for θ see the schematic

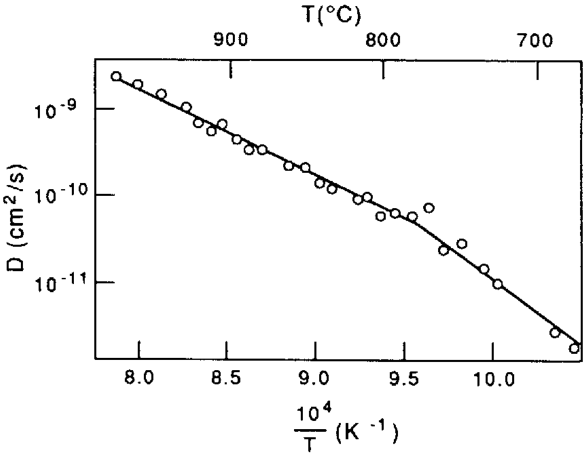

Fig. 2. The temperature dependence of the bulk diffusion coefficient D of zinc in the alloy Fe–12 at.% Si.

diagram in Fig. 1). At lower temperature, angle θ is almost equal to π. At the temperature $T = 749 \pm 4°C$ the wetting transition occurs: above this temperature the grain boundary is wetted by the Zn-based solution, which is formed due to melting of the surface layer of the diffusant during the anneal. It should be noted that the temperature of the wetting transition is close to that at which the temperature dependence of the grain boundary coefficient diffusion $D_b(T)$ reaches its maximum.

In Fig. 3 the dependences of zinc concentrations, C_b, at the grain boundary upon the depth y (the curves of zinc diffusional penetration along the grain boundaries) are presented, while Fig. 4 displays temperature dependences of the value of product $D_b\delta$ and of permeability Π. [Values of $D_b\delta$ and Π are determined using the same equation (1), but for high values of $\eta\beta^{-1/2}$, $D_b\delta$ is obtained, while for small ones Π]. The grain boundary behaviour can be seen to depend strongly on temperature. Below temperature T_w the dependence $C_b(y)$ contain a steep region only. Above temperature T_w there exists both a gentle region (corresponding to high diffusivity) and the steep one. The steep and gentle regions intersect at a concentration C_{bt}. For gentle regions the Le-Claire condition is satisfied, and equation (2) does yield $D_b\delta$.

Therefore, two points in Fig. 4 correspond to each curve of zinc diffusional penetration along the grain boundaries, $C(y)$. $D_b\delta$ and Π increase drastically with temperature and approach their maxima simultaneously at 774°C.

In the concentration range of C_0–C_{bt} the product $D_b\delta$ is 10–100 times as great as the diffusion permeability Π at concentrations below C_{bt}. The transformation from the "usual" to accelerated grain boundary diffusion occurs abruptly at concentration C_{bt}. At this concentration a knee is observed on the curves of zinc diffusional penetration along the grain boundaries $C_b(y)$. Concentration C_{bt} was earlier shown to be an equilibrium parameter of grain boundaries. In particular, it does not depend upon the annealing time. At a temperature above $T_{crit} = 801 \pm 2°C$ the knees disappear from dependences $C_b(y)$. In the interval of 30–40°C above the critical temperature T_{crit}, curves $C_b(y)$ are essentially non-linear. They still contain traces of the gentle region. At the temperature above approximately 840°C, the curves again contain a steep region only.

In the temperature range 774–840°C (beginning from the ordering temperature), the diffusion permeability of grain boundaries decreases strongly. Beginning from the temperature 870°C, the permeability grows again with temperature, according to the Arrhenius law.

In Fig. 5(a) the phase diagram is presented. White points indicate the values of the bulk solubility limit of zinc in the Fe–12 at.% Si alloy (solvus line). Black points correspond to the values of concentration C_{bt}, at which the knees on curves $C_b(y)$ are observed, and the diffusion permeability of the grain boundaries undergoes abrupt change. At T_w the wetting transition occurs. It can be clearly seen, that the $C_{bt}(T)$ line unites with the solvus line $C_0(T)$ at temperature T_w. Indeed, at this temperature the wetting of grain boundaries and gentle region on the zinc grain boundary diffusion curves $C_b(y)$ disappear simultaneously.

Above T_w the $C_{bt}(T)$ line generally goes away from the solvus line $C_0(T)$, and is ended by a critical point at $804°C < T < 810°C$. At temperature 804°C, the penetration curve $C_b(y)$ still contains a knee, while at $T = 810°C$ such a knee is absent, although the penetration curve has some traces of steep and gentle regions (see Fig. 3). In the vicinity of the bulk ordering temperature, protrusions directed towards the region of low concentrations can be seen on the line $C_{bt}(T)$ and the solvus line $C_0(T)$.

4. DISCUSSION

It is known that any ordering (spin, atomic, etc.) always causes an increase of the diffusion activation energy (see e.g. [20–22]), including the grain boundary diffusion [9]. It is quite understandable qualitatively: formation and migration of vacancies in an ordered alloy are connected with "breaking" of additional bonds. This contribution can be represented by an additional term in the activation energy of diffusion, roughly proportional to the square of the order parameter [23]. But the order parameters itself undergoes significant changes in the vicinity of the ordering temperature. This leads to strong temperature dependence and to high "effective" values of the activation energy. Really, the activation energy value obtained for bulk diffusion in the ordered state significantly exceeds common parameters of iron and its alloys [25].

It is interesting that below the ordering temperature, at which the bulk diffusion activation energy grows abruptly, the grain boundary wetting also

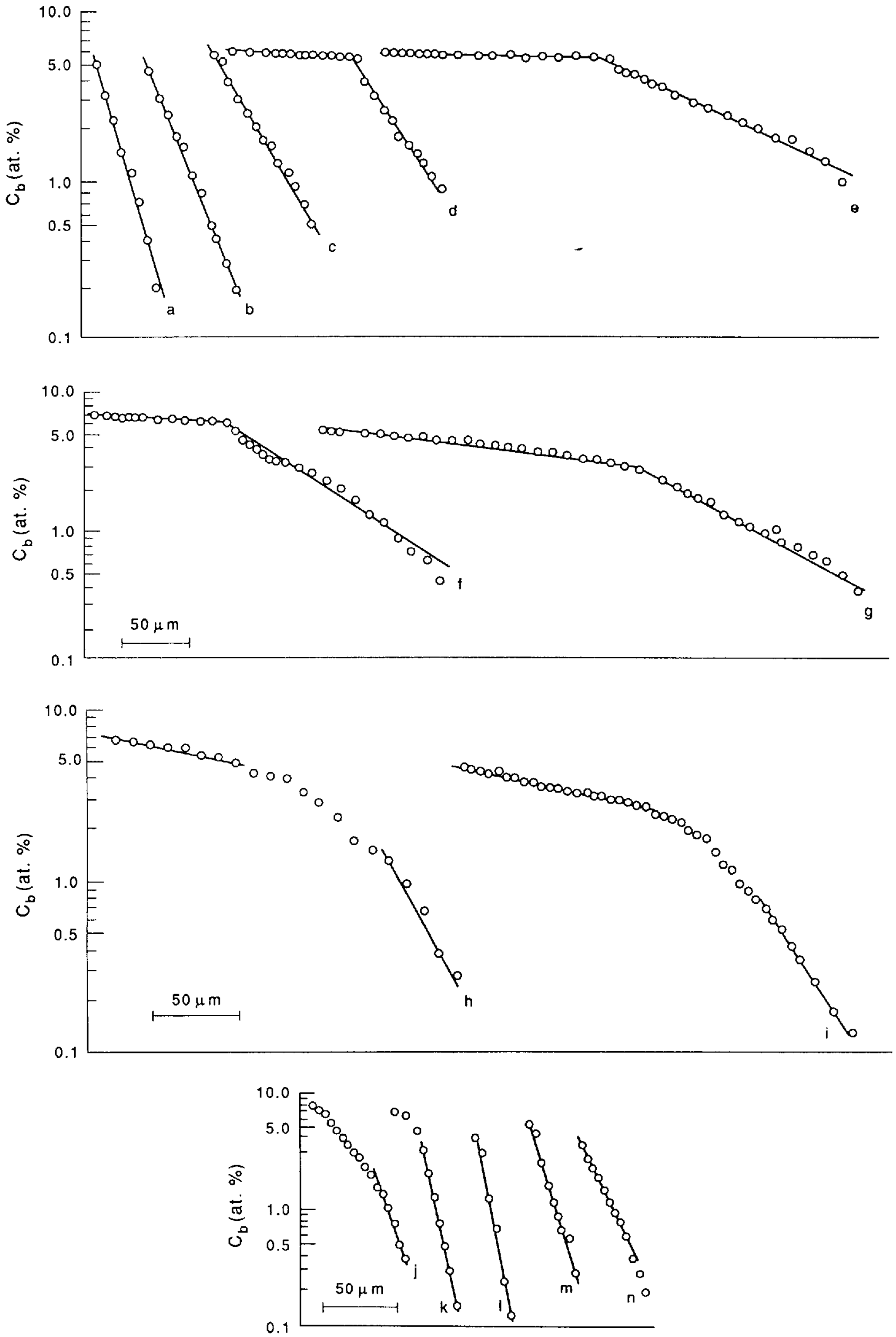

Fig. 3. The dependences of grain boundary zinc concentration C_b upon the depth y (the curves of zinc diffusional penetration along the grain boundaries). The concentration C_{bt} corresponds to the knees on the dependences $C_b(y)$: (a) 724°C, 241 h; (b) 734°C, 184 h; (c) 754°C, 110.5 h; (d) 764°C, 65 h; (e) 774°C, 50 h; (f) 784°C, 50 h; (g) 804°C, 30 h; (h) 810°C, 18 h; (i) 830°C, 10 h; (j) 834°C, 14 h; (k) 844°C, 10.2 h; (l) 874°C, 6.5 h; (m) 934°C, 5 h; (n) 994°C, 4.5 h.

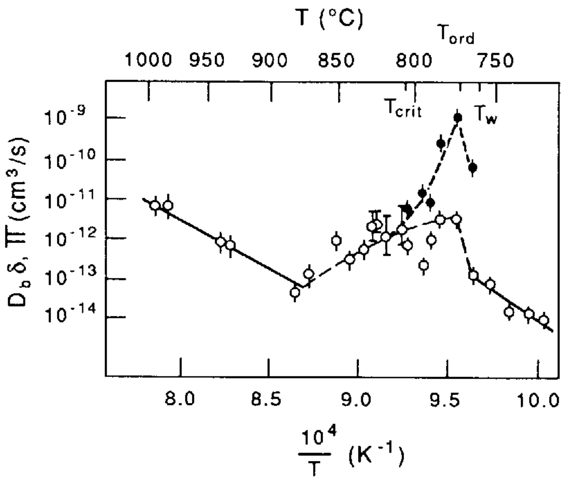

Fig. 4. The temperature dependence of the value of product $D_b\delta$ (and/or diffusion permeability of grain boundaries Π). Black points correspond to concentrations in range from C_0 to C_{bt}.

disappears. As was shown in the previous paper [1], the transition from the disordered paramagnetic state into an ordered ferromagnetic one must suppress both the wetting and the process of formation of thin equilibrium interlayers on grain boundaries (premelting, prewetting, etc.).

As has been shown in [1], in the whole temperature range the wetting and rapid diffusion in some region are observed simultaneously on grain boundaries of the Fe–5 at.% Si alloy. When the samples are subjected to high pressure, no wetting is observed at about 0.5 GPa [26]. The region of accelerated diffusion disappears simultaneously. The experimental data obtained by us in [26], along with the results of [1], provide evidence that at C_{bt} a premelting transition occurs on the grain boundary. This leads to the formation of a thin thermodynamically equilibrium interlayer of quasiliquid phase on the grain boundary.

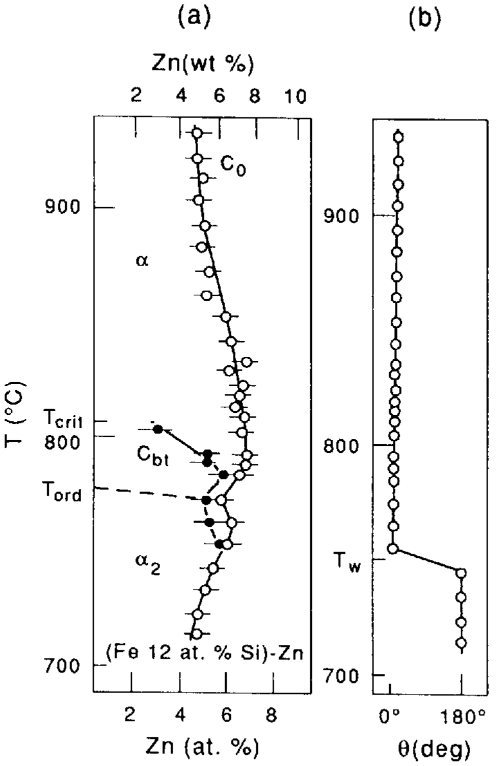

Fig. 5. (a) Phase diagram of the system (Fe–12 at.% Si)–Zn. T_{ord}–temperature of the bulk ordering A_2–B_2; T_{crit}–the critical point on the line $C_{bt}(T)$ of grain boundary premelting transition. (b) Temperature dependence of the angle θ in site of the grain boundary intersection with the surface. T_w–temperature of grain boundary wetting transition.

In the Fe–12 at.% Si alloy we also see that above the wetting transition temperature, T_w, a region of accelerated diffusion appears on the grain boundary in the concentration range from C_0 to C_{bt}. Apparently we deal again with the same grain boundary premelting transition as in the alloy with a lower silicon content. However, now the situation is more complicated: first, we see that the bulk ordering suppresses wetting and premelting on grain boundaries, and second, the line of the premelting transition does not reach the region of high temperatures, as was the case in [1], but culminates with a critical point. Strictly speaking, the line of the premelting phase transitions cannot terminate in the critical point, since a continuous transition from the state with a non-zero long range order parameter to a state with a zero parameter is impossible. However, it may happen that above T_{crit} the premelting transition occurs as a second order phase transition. In this case there will be no typical knee on the curve of penetration $C_b(y)$, though it will display traces of steep and gentle slopes, that has been observed in the experiment. The premelting phase transition line continuous thus even above T_{crit}, but it is already a second order phase transition line. Unfortunately, the technique of diffusion measurements does not permit defining the position of this line in the phase diagram, and in Fig. 5(a) it is not depicted. In the phase transition theory such a point, separating the second order phase transition line from that of first order transitions, is called a tricritical point, though in what follows we shall call a critical point. On the other hand, a protrusion directed towards the low zinc content is observed on the line of premelting transition in the vicinity of the atomic ordering temperature T_{ord}, a similar one can be seen near the Curie point T_c in [1]. The same protrusion can be observed on the solvus line $C_0(T)$. Such protrusions are always formed when the lines of second order and first order phase transitions intersect [28].

Why does ordering suppress wetting and premelting on grain boundaries? A necessary (but not significant) condition of complete wetting is relation $\sigma_{gb} > 2\sigma_{cf}$, where σ_{gb} is the surface tension of a grain boundary, and σ_{cf} is the surface tension of the "crystal-wetting phase" interface. Below the transition temperature in an ordered state positive terms due to the long-distance order of the alloy are added to these parameters. Actually, ordering leads to the corresponding decrease of the alloy free energy. If the grain boundary may be assumed completely or partially disordered, then the decrease of the free energy due to the transition into ordered state will be lower near the grain boundary than in the bulk. Since the surface tension of a grain boundary is equal to its excess free energy, the grain boundary surface tension must obviously increase when the alloy is transformed into the ordered state.

Therefore, the problem of the ordering influence on wetting is reduced to the question, which parameter, σ_{gb} or $2\sigma_{cf}$ grows faster during transition into the ordering state. This is to be discussed in the framework of a simplest geometrical model, in which the atomic relaxation is neglected. This approach was used by Takasugi and Izumi for calculation of the energy of various types of grain boundaries in ordered alloys having the stoichiometric composition [25]. For simplicity, we consider the symmetrical grain boundary tilt $\Sigma = 5$ with the misorientation angle $\phi = 36{,}9^\circ$ in the AB alloy. In the same assumptions in [25], for the completely ordered 'state, we obtained the following

$$\sigma_{gb}^{ord} = \frac{V_1(BB) + V_1(AA) - 2V_1(AB) - V_2(AA) - V_2(BB)}{a^2 10^{1/2}} \tag{3}$$

$$\sigma_{cf}^{ord} = \frac{2[V(AW) + V(BW) - 2V(WW)] - 3V(AB) - 3/2[V_2(AA) + V_2(BB)]}{a^2(10)^{1/2}}. \tag{4}$$

For completely disordered state, when the probability of finding the atom A or B in the given lattice site is 0.5, we have

$$\sigma_{gb}^{dis} = \frac{-1/2[V_2(AA) + V_2(BB)]}{a^2(10)^{1/2}} \tag{5}$$

$$\begin{aligned}\sigma_{cf}^{dis} = \{&2[V(AW) + V(BW) - 2V(WW)] \\ &- 3/4V_2(AA) - 3/4V_2(BB) - 3/2V(AB) \\ &- 3/4V_1(BB) - 3/4V_1(AA)\}/a^2(10)^{1/2}.\end{aligned} \tag{6}$$

Here, V denotes the potential of interatomic interaction (V_1 regarding the interaction with nearest neighbours, V_2 next nearest), a denotes lattice parameter, W corresponds to an averaged atom on the wetting interlayer. Combining (2)–(5), we obtain the equations

$$\begin{aligned}\sigma_{gb}^{ord} = \sigma_{gb}^{dis} &+ \frac{2V_1(AB)}{a^2(10)^{1/2}} \\ &- \frac{1/2[V_2(AA) + V_2(BB)]}{a^2(10)^{1/2}}\end{aligned} \tag{7}$$

$$\begin{aligned}\sigma_{cf}^{ord} = \sigma_{cf}^{dis} &+ \frac{3/2\,V_1(AB)}{a^2(10)^{1/2}} \\ &- \frac{3/4[V_2(AA) + V_2(BB)]}{a^2(10)^{1/2}}\end{aligned} \tag{8}$$

where $V(AB) = V_1(BB) + V_1(AA) - 2V_1(AB)$.

All values are negative, $V_1(AB) > 0$ (in the other case, the alloy would be unstable). Comparing (7) and (8), we see that the contributions to $2\sigma_{cf}^{ord}$ connected with the ordering exceed those to σ_{gb}^{ord}. Therefore, during transition into ordered state, $2\sigma_{cf}$ value grows faster than σ_{gb} which may violate the wetting condition $\sigma_{gb} > 2\sigma_{cf}$. Qualitatively, it may be explained in the following way. Ordering may be considered to be the process of formation of additional bonds between atoms A and B. The wetting interlayer breaks all such bonds, while on the coincidence grain boundary they are partially conserved. Therefore, the contribution of ordering to $2\sigma_{cf}$ is greater than that to σ_{gb}. All this explains why wetting disappears at a temperature slightly lower than the ordering temperature.

How can we explain the fact that in the temperature range 30–40°C above the critical point the diffusion permeability decreases with temperature growth? If the system studied had not contained a critical point, the grain boundary phase diagram would have had the same shape as for the Fe–5 at.% Si system [see Fig. 1(c)]. In the presence of the critical point, the grain boundary transformation into the premelted state becomes continuous, the corresponding knees on the zinc penetration curves being diffused. Here the measured slope of this dependence is determined not only by the coefficient of the grain boundary diffusion, but also by concentrational region of existence of a premelted state. This range becomes smaller with growing temperature at $T > T_{crit}$ (see Figs 3 and 4), the corresponding slope increasing. This causes a decrease of the effective grain boundary diffusion coefficient with the increasing temperature.

5. CONCLUSIONS

1. Wetting transition is observed during penetration of zinc along the grain boundary tilt 38° of [100] in Fe–12 at.% Si alloy at $T_w = 749 \pm 4^\circ C$.

2. Above T_w to $T_{crit} = 807 \pm 2^\circ C$, a region of accelerated diffusion is observed on grain boundaries in the concentration range from C_o (the bulk solubility limit of zinc) up to C_{bt}. At concentration C_{bt}, the rate of zinc diffusion along grain boundaries decreases abruptly to the values common for iron. At C_{bt}, a knee is observed on the curves of zinc penetration along grain boundaries. The existence of a region of rapid diffusion on grain boundaries may be explained by a premelting transition and formation of thin equilibrium interlayer of liquid or quasi-liquid phase.

3. At temperature $T_{crit} = 807 \pm 2^\circ C$, this knee disappears, but traces of accelerated diffusion are conserved in the temperature range of 30–40°C above T_{crit}.

4. Below T_w the diffusion permeability of grain boundaries grows with temperature according to the Arrhenius law. Beginning with T_w, curves $D_b\,\delta(T)$ and $\Pi(T)$ deviate abruptly from the Arrhenius straight line and reach their maxima in the vicinity of the bulk ordering temperature T_{ord} (about 30°C below T_{crit}), after which the values of $D_b\delta$ and Π decrease again. Beginning from approximately 870°C, the diffusion permeability of grain boundaries grows again with temperature according to the Arrhenius law.

5. The hypothesis of a premelting transition on grain boundaries allows to give a self-consistent explanation of the appearance of a region of accelerated diffusion on the grain boundary as well as the fact that it disappears simultaneously with wetting at a temperature below bulk ordering point.

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