

WETTING AND PREMELTING PHASE TRANSITIONS ON THE 38° [100] TILT BOUNDARY IN ALLOY Fe–12 at.% Si–Zn NEAR A₂–B₂ ORDERING IN THE Fe–12 at.% Si VOLUME*

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An X-ray microspectral analysis is made of the permeation of zinc in 38° [100] tilt grain boundaries in bicrystals of the Fe–12 at.% Si alloy in which there is an A₂–B₂ ordering phase transition at $T = 770^{\circ}\text{C}$. All the observed results, including the disappearance of wetting and premelting at temperatures below the ordering point in the volume, can be explained on the basis of a phase transition on boundaries.

In our previous study, we looked at the permeation of tin and zinc on [100] tilt grain boundaries with a misorientation of 43° in bicrystals of the bcc alloy Fe–5 at.% Si [1]. This is the minimum quantity of silicon for which a range existence of γ -phase can be isolated on the phase diagram of Fe–Si and which allows the growth of single and bicrystals with bcc structure [2]. It was shown in [1] that when tin permeates these grain boundaries, a wetting phase transition is observed: above 810°C the contact angle at the place where the grain boundary emerges at the surface of the specimen on which the layer of tin was deposited before annealing, is equal (or very close) to zero. Below 810°C this angle becomes 180°. It grows from 0 to 180° over a temperature interval of no more than about 10°. A similar wetting transition has been observed before in other systems, such as Zn–Sn [3, 4], Al–Sn [5, 6], Al–Pb [5], Ag–Pb [7]. When the same boundaries are permeated by zinc, wetting of the boundaries by the melt is observed over the whole range 652–908°C studied in [1].

In the experiments of [1], the thickness of the layer of zinc or tin deposited on the surface of the specimen was chosen so that the wetting interlayer permeated along the grain boundary to a depth of 50–200 μm from the surface of the bicrystal. By studying the distribution of tin or zinc in the specimen at a greater depth than this interlayer, it was possible to determine the diffusion characteristics of the grain boundaries. It turned out that during diffusion of zinc there is a segment on the boundary (immediately behind the wetting interlayer) on which zinc diffusion is about two orders of magnitude faster than usual. The range of zinc concentrations in which such enhanced permeability of boundaries is observed extends from the volume solubility limit C_0 to

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a certain concentration C_{br} . At C_{br} the product of the grain boundary diffusion coefficient D_b by the diffusion thickness of the boundary δ falls rapidly. Below C_{br} the products $D_b\delta$ are close to their usual values for grain boundaries in iron and iron alloys [8].

It has been shown experimentally that the permeation depth of zinc on boundaries in the concentration range between C_0 and C_{br} is proportional to $t^{1/4}$, where t is the annealing time. This means that although zinc does permeate the boundaries at concentrations above C_{br} at a rate which is two orders of magnitude higher than usual, this is the same diffusion process as at concentrations below C_{br} . It has also been found that the concentration C_{br} at which $D_b\delta$ changes suddenly is closely dependent on the annealing temperature (see Fig. 1c). Above the Curie point in alloy Fe-5 at.% Si (740°C), the higher the solubility limit of zinc in the alloy C_0 , the lower the value of C_{br} , and below the Curie point C_{br} tends to the value C_0 , and yet wetting is still observed. If there is a decomposition maximum (possibly a "virtual" one) in the two-component system, then according to the theory of Cahn [9], there will be a prewetting phase transition near the critical point, one modification of which is the premelting transition. Premelting is similar to wetting in that a layer of new phase forms suddenly on the grain boundary at the transition point, but there is a difference in that the new phase is thermodynamically unstable in the volume and is microscopically thin rather than a macroscopic layer of volume phase, as in the wetting transition. Just near the Curie point on the $C_{br}(T)$ curve there is a protrusion towards lower concentrations.

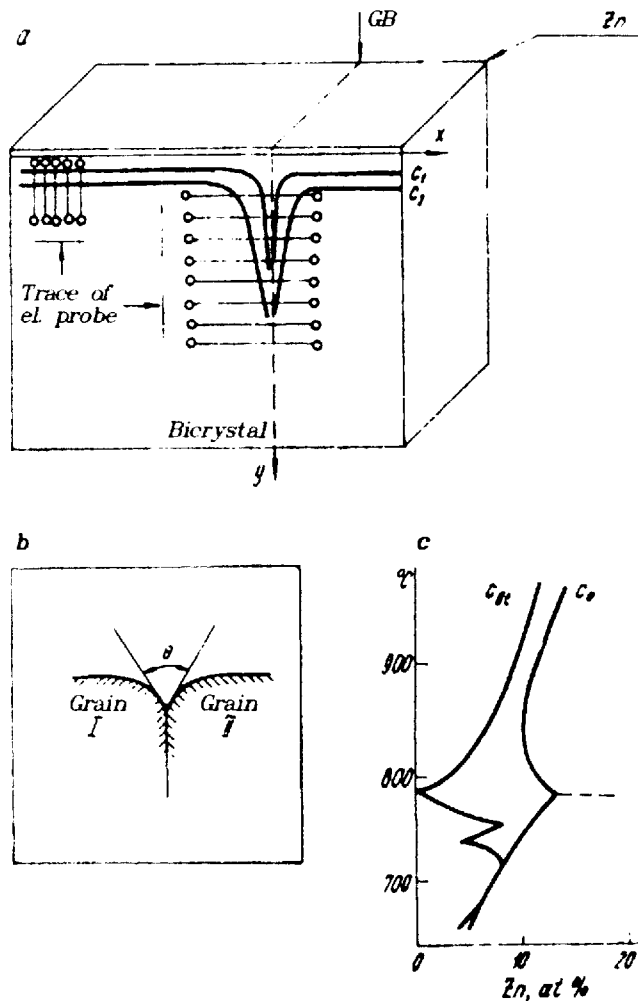


Fig. 1. Scheme of concentration distribution in bicrystal after diffusion annealing. Isoconcentrational lines and scheme of arrangement of electron probe for measurement by local X-ray spectral analysis (a). Measurement of angle θ at place where grain boundary emerges at surface of specimen (b) and grain-boundary and volume phase diagram of Fe-5 at.% Si-Zn [1] (c).

diffusion profiles perpendicular to the boundary, parallel to the surface of the specimen on which the diffusant has been deposited (see scheme in Fig. 1). The product of the grain-boundary diffusion coefficient D_b by the diffusion depth of the boundary δ was calculated with the formula of Fisher [13]

$$D_b \delta = 2(D/\pi t)^{1/2} y^2 / (\ln C_b/C_0)^2, \quad (1)$$

where C_b is the concentration on the grain boundary at depth y .

The Fisher formula can be used as an asymptotic representation of the solution of Whipple [14] for calculating $D_b \delta$ only if the Le Claire condition [15]

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

is satisfied, where $\eta = y/(Dt)^{1/2}$ and $\beta = \delta D_b / 2D^{3/2} t^{1/2}$. In our case this criterion is only satisfied for the shallow intercepts on the curves of zinc permeation on grain boundaries $C_b(y)$ (see Fig. 3), that is, the intercepts above the break point C_{bt} , where it exists (curves 4–7). In Fig. 4, for clarity, we also give the experimental points for the steeper intercepts of the $C_b(y)$ curves (the intercepts of curves 4–7 in Fig. 3 are below the break point C_{bt} and are straight lines with slope of the order $10^{-3} \mu\text{m}^{-1}$), where $\eta \beta^{-1/2}$ is small. If $\eta \beta^{-1/2} < 10$, then (1) gives understated values of $D_b \delta$ and the activation energy of grain-boundary diffusion E_b [16]. So, using formula (1) for small $\eta \beta^{-1/2}$, strictly speaking, it is not $D_b \delta$ that we are calculating, but a certain diffusion permeability of the boundary, which we denote by the symbol P . This has the same dimensions as $D_b \delta$.

RESULTS

Figure 2 shows the temperature dependence of the coefficient of volume diffusion of zinc in the Fe–12 at.% Si alloy. The coefficient was found on the same bicrystals as the product $D_b \delta$ for grain-boundary diffusion (see scheme in Fig. 1a). It is clear from Fig. 2 that the dependence $D(T)$ consists of two parts with different slopes, which intersect at about 770°C. This is close to the A_2 – B_2 ordering point in alloy Fe–12 at.% Si [2]. Above the ordering point T_{ord} the activation energy E of volume diffusion of zinc is 170 kJ/mol, below T_{ord} $E = 324$ kJ/mol.

The temperature dependence of the angle θ at the place where the boundary emerges at the surface of the specimen is shown in Fig. 5b (see scheme in Fig. 1). At low temperatures the angle θ is close to π . At $T_w = 749 \pm 4^\circ\text{C}$ the wetting phase transition takes place: above that temperature the grain boundary is wet by the zinc-base melt which appears when the diffusant melts when the specimen is placed in the oven for annealing. We note that the temperature of the wetting transition T_w is close to the temperature at which there is a maximum on $D_b(T)$.

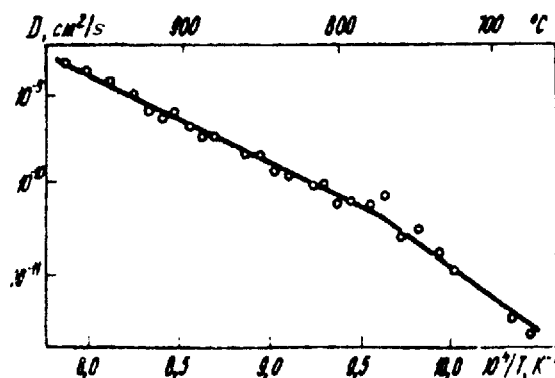


Fig. 2. Temperature dependence of coefficient of volume diffusion D of zinc in alloy Fe–12 at.% Si.

Figure 3 shows the dependences of zinc concentration on the boundary C_b on depth y (curves of diffusion permeation of zinc on boundaries), and Fig. 4 shows the temperature dependences of the product $D_b\delta$ and the permeability P . (The values of $D_b\delta$ and P are found with the same formula (1), but we obtain $D_b\delta$ for large, and P for small $\eta\beta^{-1/2}$.) We can see that the behaviour of the grain boundaries changes rapidly with temperature. Below T_w there is just one intercept on $C_b(y)$, with a large slope. Above T_w , in addition to the intercept with a steep slope, there is an intercept with a shallower slope (with higher grain-boundary diffusion coefficient). The two parts intersect at a certain concentration C_{bi} . On the less steep intercepts condition (2) applies and formula (1) gives $D_b\delta$. On the steeper parts (1) gives the diffusion permeability P . So two

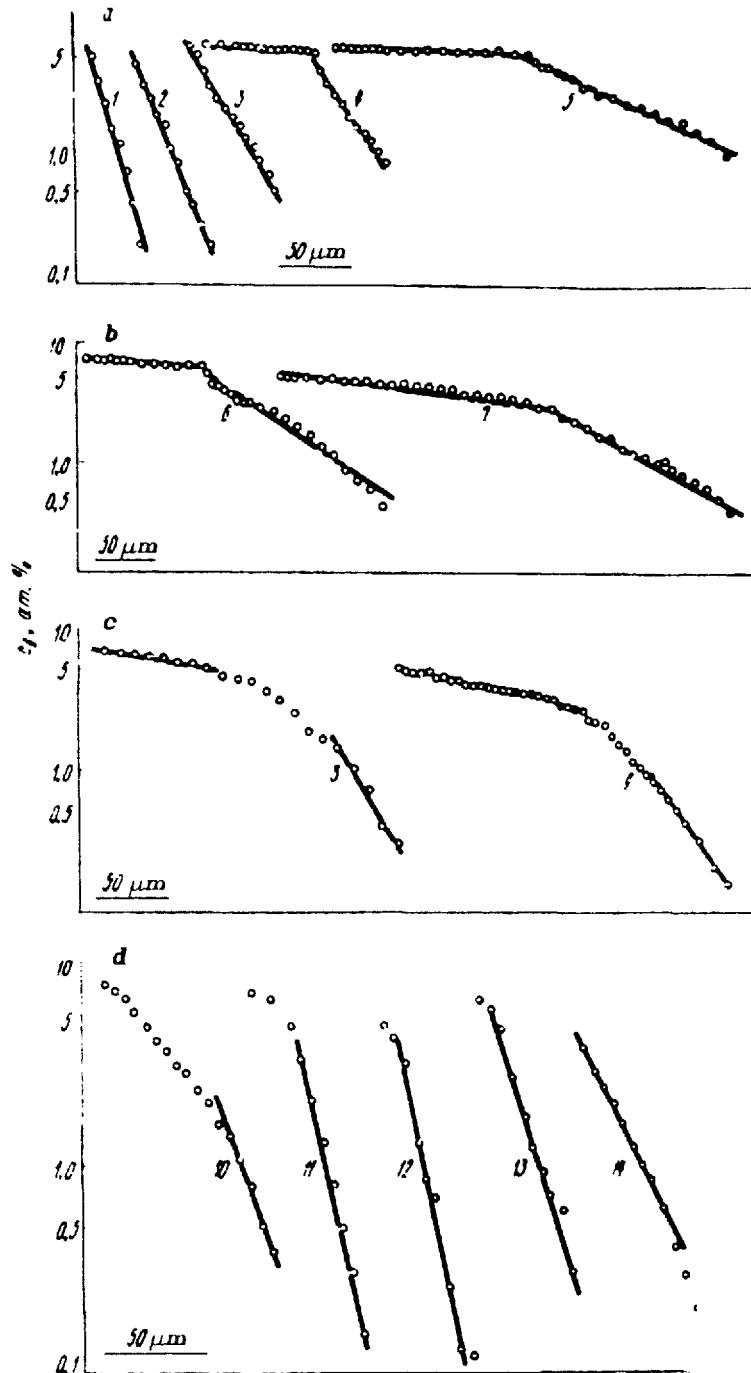


Fig. 3. Dependences of zinc concentration on grain boundaries C_b on depth y (curves of diffusion permeation of zinc along boundaries). The concentration C_{bi} is found from the breaks on $C_b(T)$: 1 — 724°C, 241 h; 2 — 743°C, 184 h; 3 — 754°C, 110.5 h; 4 — 764°C, 65 h; 5 — 774°C, 50 h; 6 — 784°C, 50 h; 7 — 804°C, 30 h; 8 — 810°C, 18 h; 9 — 830°C, 10 h; 10 — 834°C, 14 h; 11 — 844°C, 10.2 h; 12 — 874°C, 6.5 h; 13 — 934°C, 5 h; 14 — 994°C, 5.4 h.

points in Fig. 4 correspond to each curve $C_b(y)$ containing steep and shallow intercepts. As the temperature rises $D_b\delta$ and P increase rapidly and both reach a maximum at 774°C .

In the range of concentrations from C_0 to C_{br} the product $D_b\delta$ is 10–100 times larger than P at concentrations below C_{br} . The transition from “normal” to accelerated grain-boundary diffusion takes place suddenly at a certain concentration C_{br} , at which there is a break on the $C_b(y)$ curves. Before, we found [1] that C_{br} is an equilibrium parameter of grain boundaries. In particular, it is independent of the annealing time. At temperature above $T_{cr} = 807 \pm 2^\circ\text{C}$ the breaks on $C_b(y)$ disappear. Above the critical point T_{cr} in an interval of about $30\text{--}40^\circ\text{C}$ the $C_b(y)$ curves are essentially non-linear, showing traces of a shallow intercept. At a temperature above about 840°C the $C_b(y)$ curves again have only a steep intercept.

The diffusion permeability of boundaries falls rapidly in the temperature range $774\text{--}840^\circ\text{C}$ (starting from the ordering point). From about 870°C the diffusion permeability again increases with temperature by the Arrhenius law.

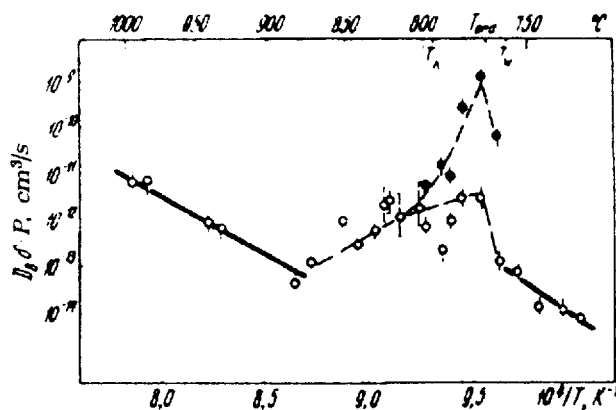


Fig. 4. Temperature dependence of product $D_b\delta$ (and/or diffusion permeability of boundaries P). Closed points — values for $C_0 > C_b > C_{br}$.

The phase diagram is shown in Fig. 5a. The open points show the values of the volume solubility limit of zinc in the Fe–12 at. % Si alloy (solvus line). The closed points show the values of C_{br} at which breaks are observed on $C_b(y)$ and the diffusion permeability of boundaries changes suddenly. At T_w the wetting phase transition takes place. It is evident that the line $C_{br}(T)$ merges with the solvus line $C_0(T)$ at T_w . In fact, both wetting of grain boundaries and the shallow intercepts on the $C_b(y)$ curves disappear at that temperature.

Above T_w the line $C_{br}(T)$ gradually moves away from $C_0(T)$ and ends in a critical point at $804^\circ\text{C} < T_{cr} < 810^\circ\text{C}$. At $T = 804^\circ\text{C}$ there is still a break on $C_b(y)$, but there is no longer one at $T = 810^\circ\text{C}$, although there are still signs of steeper and less steep intercepts on the permeation curve (see Fig. 3). Near the ordering point in the volume, the $C_{br}(T)$ contains protrusions in the direction of lower concentrations. Similar protrusions (within the experimental error) were noted on the phase diagram on $C_0(T)$.

DISCUSSION

It is known that ordering (atomic, spin, etc.) always leads to an increase in the activation energy of diffusion (see [17] for example), including grain boundary diffusion [8]. This is understandable at a qualitative level: the formation and migration of vacancies in an ordered alloy

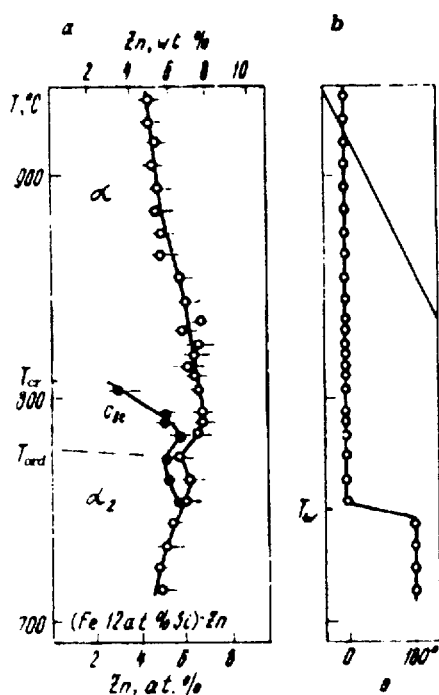


Fig. 5. Phase diagram of Fe-12 at.% Si-Zn: T_{ord} — temperature of A_2 - B_2 transformation in volume; T_{cr} — critical point on phase transformation line $C_{bt}(T)$ (a) and temperature dependence of angle θ at place where boundary emerges at surface; T_w is the temperature of wetting grain-boundary transition (b).

involves the “tearing” of supplementary bonds. This contribution is described by the extra term in the activation energy of diffusion, which is roughly proportional to the square of the order parameter [18]. But the order parameter itself changes rapidly near the ordering temperature, leading to a strong temperature dependence of the diffusion coefficient and high “apparent” activation energies. In fact, the value that we have obtained from the activation energy for diffusion in the ordered state is appreciably higher than the usual value for iron and iron alloys [19].

It is interesting that, below the ordering point, at which the activation energy of volume diffusion grows suddenly, wetting of boundaries disappears. In our previous study [1] we showed that the transition from a disordered paramagnetic state to ordered ferromagnetic state should suppress both wetting and the formation of different thin equilibrium interlayers on boundaries (premelting, prewetting, etc.).

We have already seen [1] that wetting and a region of rapid diffusion are observed simultaneously in grain boundaries over the whole range of temperatures that have been investigated. Under high pressure, wetting disappears at about 0.5 GPa [20], and the region of rapid grain-boundary diffusion disappears at the same time. The result that we obtained in [20], together with those in [1], suggest that the premelting phase transition takes place on the grain boundary at C_{bt} . This leads to the formation of a thin, thermodynamically equilibrium interlayer of a quasiliquid phase on the grain boundary.

In the Fe-12 at.% Si alloy we also see that, above T_w , a region of accelerated diffusion appears on the grain boundary in the concentration range between C_0 and C_{bt} . To all appearances, once again we are dealing with the premelting grain boundary phase transition, as in the alloy with lower silicon content. Now, however, the situation is more complicated: firstly, ordering in the volume suppresses wetting and premelting on boundaries and, secondly, the line of the premelting transition on the phase diagram does not continue to the high temperature range as in [1], but

stops at a critical point. At the same time, near the atomic ordering point for the volume T_{ord} , as in [1] near T_c , a protrusion is observed on the premelting phase transition line, towards lower zinc concentration. A similar protrusion can be seen on the solvus line $C_0(T)$. Protrusions of this kind always arise at the intersection of second-order phase and first-order phase transition lines [21, 22] and, in the Fe–Si–Zn system, are of interest from the point of view of the influence of magnetic and concentrational ordering in the matrix on the premelting grain boundary transition.

Why is it that atomic ordering suppresses wetting and premelting on grain boundaries? A necessary (but not sufficient) condition for total wetting is $\sigma_{gb} > 2\sigma_{cf}$, where σ_{gb} is the surface tension of the boundary and σ_{cf} is the surface tension of the “crystal–wetting phase” interface. The value $2\sigma_{cf}$ grows faster than σ_{gb} with the transition to ordered state, and this can destroy the wetting condition. This can be explained in qualitative terms as follows: the ordering process can be represented nominally as an increase in the number of bonds between A and B atoms. The wetting interlayer breaks all these bonds, whereas they are partly preserved on the boundary. So ordering makes a larger contribution to $2\sigma_{cf}$ than to σ_{gb} . This helps to explain why wetting vanishes slightly below the atomic ordering point.

How is the fall of the diffusion permeability above the critical point in a temperature interval 30–40°C to be explained? If there were no critical point in the system, the grain-boundary phase diagram would look like that in the Fe–5 at.% Si system (Fig. 1c). The presence of a critical point means that there is a continuous transition of the boundary to premelting state and the corresponding breaks on the curves of zinc permeation of boundaries broaden out, the slope of these curves being determined not solely by the coefficient of boundary diffusion, but also by the concentrational range of existence of the premelted state. This range decreases with rise of temperature (see Figs 3 and 4) and the corresponding slope increases. This results in diminution of the effective coefficient of grain-boundary diffusion with rise of temperature.

CONCLUSIONS

1. When zinc permeates 38°[100] tilt grain boundaries, a wetting phase transition takes place at $T_w = 749 \pm 4^\circ\text{C}$.

2. From T_w to $T_{cr} = 807 \pm 2^\circ\text{C}$, grain boundaries contain a region of accelerated diffusion in the range of concentrations from C_0 (solubility limit of zinc in the volume) to C_{bt} . At C_{bt} , the rate of zinc diffusion along grain boundaries decreases suddenly to values which are typical for iron. At C_{bt} , there is a break on the permeation curves. The existence of a region of rapid diffusion on grain boundaries can be explained by the premelting phase transition and the formation of a thin equilibrium interlayer of liquid or quasiliquid phase.

3. The break on the curve disappears at $T_{cr} = 807 \pm 2^\circ\text{C}$, but signs of accelerated diffusion are observed even up to a temperature 30–40°C above T_{cr} .

4. Below T_w the diffusion permeability of boundaries increases with temperature by the Arrhenius law. Starting from T_w , the $D_b\delta(T)$ and $P(T)$ curves deviate strongly from the Arrhenius law, reaching a maximum near the ordering point in the volume T_{ord} (roughly 30°C below T_{cr}), after which they again fall. From about 870°C the diffusion permeability of boundaries again grows with temperature by the Arrhenius law.

5. The hypothesis that a premelting phase transition takes place on grain boundaries provides a clear explanation for the reason why a region of accelerated diffusion appears on grain boundaries and why it and wetting disappear below the ordering point in the volume.

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