THE ZINC PENETRATION ALONG TILT GRAIN BOUNDARY 38° [100] IN Fe-12at.%Si ALLOY NEAR ORDERING A₂ - B₂ IN THE BULK

O.I. Noskovich, E.I. Rabkin, V.N. Semenov, B.B. Strauman*  
Institute of solid state physics, Academy of sciences of the USSR  
Chernogolovka, Moscow district, 142432, USSR  
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Introduction

In their previous work, the authors studied the process of penetration of tin and zinc along tilt grain boundaries 43° [100] in the bicrystals of bcc alloy Fe-5at.%Si [1]. In the whole studied temperature range, wetting and the region of rapid diffusion are observed simultaneously on grain boundaries in the alloy Fe-5at.%Si. When the samples are subjected to high pressure, the wetting disappears at about 0.5 GPa [2]. The region of accelerated diffusion between the bulk solubility limit of zinc Ω₀ and a concentration C₀ disappears simultaneously. The experimental data obtained by us in [2], along with the results of [1], provide evidence that at C₀ a premelting transition occurs on the grain boundary which leads to the formation of a thin thermodynamic equilibrium interlayer of quasi-liquid phase on the grain boundary. There exist a number of theoretical works where such phase transitions on interfaces accompanying wetting are predicted [3-5].

All necessary conditions for a premelting transition to exist are satisfied in the studied system: high positive value of enthalpy of mixing of solution components, wetting of grain boundaries in the two-phase region, "solid-melt" as well as the fact that the phenomena mentioned are observed on grain boundaries of the component having 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 concentration ordering in the bulk affects the process of zinc penetration along the grain boundaries in the system Fe-Si, the grain boundary wetting and premelting transition.

Experimental

To perform the experiments, a bicrystal of alloy Fe-12at.%Si with tilt grain boundary 38° [100] was grown. In this alloy atomic ordering of the solid solution iron-silicon occurs: when the temperature is decreased, the disordered bcc lattice (A₂ structure) is transformed into the ordered one (B₂ structure) [6]. It was cut on a spark outer into samples of length 6...12 mm and cross-section 1.5 x 1.5 mm. The grain boundary was disposed in the middle of the sample, perpendicularly to its longer part. The zinc layer was applied to the sample by immersion into melt. The prepared samples were soldered in evacuated silica ampules, then annealed in an oven in temperature 714...994° C.

* Now at MPI Metallforshung, Seestrasse 75, D-7000 Stuttgart 1, Germany
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 at the site of grain boundary intersection with the sample surface.

c - Grain boundary and bulk phase diagram of the system (Fe-5at.%Si)-Zn [1].

Fig. 2. The temperature dependence of the bulk diffusion coefficient $D$ of zinc in the alloy Fe-12at.%Si.
The temperature was maintained with accuracy ±0.5°C. On the obtained samples, the zinc content distribution was determined by means of electron microprobe analysis (see fig.1). To determine the concentration by intensity of the characteristic X-ray radiation, the necessary corrections of the standard methods of quantitative electron microprobe analysis were introduced [7].

The value of product of the grain boundary diffusion coefficient \( D_b \) and the diffusion thickness of the grain boundary \( \delta \) was determined using the Fisher's equation with the correction for concentrational dependence of the bulk diffusion coefficient \( D \) [8]:

\[
D_b\delta=2y^2\left(D^0/\pi t\right)^{1/2}(1+2\beta C_0/3\pi)/(\log C_b/C_0)^2
\]

Here, \( y \) is distance to sample surface, \( t \) - anneal duration, \( D^0 \) and \( \beta \) are parameters.

Fig. 3. The dependence 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 h;
- d - 764°C, 65 h;
- e - 774°C, 65 h;
- f - 784°C, 50 h;
- g - 804°C, 30 h;
- h - 824°C, 18 h;
- i - 834°C, 14 h;
- j - 844°C, 10 h;
- k - 874°C, 6.5 h.
Results

In fig.2, the temperature dependence of zinc bulk diffusion coefficient for the alloy Fe-12at.%Si is presented. It can be seen that the temperature dependence \( D(T) \) consists of two regions with different slope. They intersect at about 770°C. This temperature is close to the \( A_2-B_2 \) ordering temperature in the alloy Fe-12at.%Si [6]. Above the ordering temperature \( T_{ord} \), the activation energy of the bulk zinc diffusion \( E \) is 170 kJ/mole, below \( T_{ord} \), \( E=324 \) kJ/mole.

In fig.4b, the temperature dependence of the angle \( \theta \) at the site of intersection of grain boundary with the sample surface is presented (for determination of \( \theta \) see the diagram in fig.1). At lower temperatures, the \( \theta \) angle is nearly 180°. At the temperature \( T_w = 749 \pm 4°C \), the wetting transition occurs: above this temperature the grain boundary is wettable by the Zn-based solution, which is formed due to melting of the surface layer of the diffusant during the anneal. In fig.3 the dependencies of grain-boundary zinc concentration \( C_b \) upon the depth \( y \) (the curves of zinc diffusional penetration along the grain boundaries) are presented, while fig.5 displays the temperature dependences of value of the product \( D\Delta \). The grain boundary behavior can be seen to depend on the temperature strongly. Below the temperature \( T_w \) the dependence \( C_b(y) \) contain a steep region only. Above the temperature \( T_w \) there appears a "gentle region (corresponding to high diffusivity) along with the steep one. The steep and gentle regions intersect at a concentration \( C_{bt} \). Therefore, to each curve of zinc diffusional penetration along the grain boundaries \( C_b(y) \) correspond two points in fig.5. The values of \( D\Delta \) for both gentle and steep parts of \( C_b(y) \) increase drastically with the temperature and approach their maxima simultaneously at 774°C.

In the concentration range from \( C_c \) to \( C_{bt} \) the product \( D\Delta \) is 10-100 times more than 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 \( C_b(y) \). The concentration \( C_{bt} \) was earlier shown to be an equilibrium parameter of the grain boundaries. In particular, it does not depend upon the annealing time. At a temperature above \( T_w = 809 \pm 4°C \) the knees disappear from the dependence \( C_b(y) \). In the interval \( 30 - 40°C \) above the critical temperature \( T_w \), the 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 contain only the steep region again. In the temperature range 774...840°C (beginning from the disordering temperature), the diffusion permeability of grain boundaries decreases strongly.

In fig.4a, the phase diagram is presented. White points indicate the values of the bulk solubility limit of zinc in the alloy Fe-12at.%Si (solvus line). Black points correspond to the values of concentration \( C_{bt} \), at which the knees on the curves \( C_b(y) \) are observed, and the diffusion permeability of the grain boundaries undergoes abrupt change. At the temperature \( T_w \) the wetting transition occurs. It can be clearly seen that the \( C_{bt}(T) \) line unites with the solvus line \( C_c(T) \) at the temperature \( T_w \). Really, at this temperature the grain boundary wetting and gentle region on the zinc grain boundary diffusion curves \( C_b(y) \) disappear simultaneously. Above \( T_w \), the \( C_c(T) \) line gradually goes away from the solvus line \( C_c(T) \), and is ended by a critical point at 804°C \( \pm 10°C \). At the temperature 804°C, the penetration curve \( C_b(y) \) still contains a knee, while at \( T=810°C \) such knee is absent, although the penetration curve has some traces of steep and gentle regions (see fig.5). In
the vicinity of the bulk ordering temperature $T_{ord}$ protrusions directed towards the region of low concentrations can be seen on the line $C_{bt}(T)$ and the solvus line $C_e(T)$.

**Discussion**

It is known that any ordering (spin, atomic, etc) always cause the increase of the diffusion activation energy (see e.g. [9,10,11]), including the grain-boundary diffusion [11]. Qualitatively it is quite understandable:

![Figure 4a: Phase diagram of the system (Fe-12at.%Si)-Zn.](image)

**Fig.4 a.** Phase diagram of the system (Fe-12at.%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. $T_e$—temperature of grain boundary wetting transition.

![Figure 5: Temperature dependence of the value of product $D_e$.](image)

**Fig.5** The temperature dependence of the value of product $D_e$. Solid points correspond to concentration in range from $C_o$ to $C_{bt}$.

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 [13]. But the order parameter 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 obtained value of the activation energy of bulk diffusion in the ordered state significantly exceeds usual parameters of iron and its alloys [14].

It is interesting that below the ordering temperature, at which the bulk diffusion activation energy grows abruptly, the grain boundary wetting also disappears. The transition from the disordered paramagnetic state into ordered ferromagnetic state (as was shown in the previous paper [1]) must suppress both wetting and the process of formation of thin equilibrium interlayers on grain boundaries (premelting, prewetting, etc.).
In the alloy Fe-12at.%Si we also see that above the temperature of
wetting transition $T_w$, a region of accelerated diffusion appears on the grain
boundary in the concentration range from $C_o$ to $C_{bt}$. Apparently we again deal
with the same grain boundary melting transition as in the alloy with lower
silicon content. However, now the situation is more complex: we see
first that the bulk ordering suppresses wetting and premelting on grain
boundaries; second, the line of the premelting transition does not reach the region of high temperatures, as in [1], but is finished by a
critical point. On the other hand, a protrusion directed towards low zinc
content is observed on the line of premelting transition in the vicinity of
the atomic ordering temperature $T_{ord}$, similar to that observed near Curie
point $T_c$ in [1]. A similar protrusion can be observed on the solvus line
$C_o(T)$. Such protrusions are always formed when a line of second order phase
transitions intersects a line of first order phase transitions [15].

Why does ordering suppress wetting and premelting on grain boundaries? A
necessary (but not sufficient) condition of complete wetting is the relation
$\sigma_{gb} > 2 \sigma_{if}$, where $\sigma_{gb}$ is the surface tension of a grain boundary, and $\sigma_{if}$ is
the surface tension of the interphase boundary "crystal-wetting phase". Ordering may be considered to be a process of formation of additional
bonds between the atoms A and B. Wetting interlayer breaks all such bonds,
while on the coincidence grain boundary they are partially conserved.
Therefore, the contribution of ordering into $\Delta \sigma_{gb}$ is greater than into $\sigma_{if}$.

In ref. [16] an anomalous behavior of diffusion coefficient directly near
the phase transition is studied theoretically. We suppose that in our case we
have observed something like that.

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