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GRAIN BOUNDARY ZINC PENETRATION IN Fe-Si ALLOYS: PREMELTING PHASE TRANSITION ON THE GRAIN BOUNDARIES

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ABSTRACT

Zinc penetration along a 38°<100> tilt grain boundary (GB) was studied in an Fe-10 at.% Si (disordered A2 phase) and Fe-14at.%Si (ordered B2 phase) alloys. In the entire temperature range studied (700-965°C) the GB's are wetted by the melt. In the Fe-10at.%Si alloy a region of accelerated GB diffusion is observed in the single-phase region of the (Fe-10at.%Si)-Zn diagram below the critical temperature T_{cr} =790±5°C. At a concentration $C_{b'}$ the product of the segregation factor, the thickness and the diffusion coefficient of the grain boundary, $s\delta D_b$ abruptly falls to a "normal" value. A singularity is observed in the $C_{b'}(T)$ curve at the peritectic temperature T_{per}. In the Fe-14at.% alloy no accelerated GB diffusion is observed. The data obtained confirm the previously proposed model of a GB premelting transition.

INTRODUCTION

In recent works the penetration along [100] tilt GB's was studied in bicrystals of the following body-centered cubic (bcc) alloys: Fe-5at.%Si [1], Fe-6at.%Si [2] and Fe-12at.%Si [3]. The Fe-5at.%Si and Fe-6at.%Si alloys undergo a magnetic ordering at about 730°C. Here the α phase is transformed from a paramagnetic state into a ferromagnetic one [4,5]. The Fe-12at.%Si alloy undergoes a A2-B2 ordering at 800°C [4]. It was shown [3] that a wetting transition occurs at T_W =794±4°C during zinc penetration along GB's. This means that the contact angle θ at the site of grain boundary intersection with the sample surface covered with a zinc layer has a non-zero value below the wetting temperature T_W. At $T=T_W$ the contact angle θ decreases from 180°C to zero rapidly, its value being zero at $T>T_W$. When the pressure is raised [2], wetting disappears at P_W= 0.5 GPa.

It was found that there exists a region on the GB (directly below the wetting interlayer) in which the rate of zinc diffusion is unusually high. Zinc concentrations for which such a permeability increase is observed ly in the range from C_s to $C_{b'}$. At the concentration $C_{b'}$ the value of the GB diffusivity, $s\delta D_b$ abruptly decreases (here s is the grain boundary segregation factor, δ is the grain boundary diffusional thickness and D_b is the grain boundary diffusion coefficient). Below $C_{b'}$ the values of $s\delta D_b$ are close to those characteristic for GB's in iron and its alloys [5]. It was also found that the concentration $C_{b'}$ strongly depends on the annealing temperature.

The temperature dependence of $C_{b'}$ is presented in Fig.2(a) and (c) along with solidus and solvus lines $C_s(T)$. In the Fe-5at.%Si alloy the discontinuity in $s\delta D_b$ at concentration $C_{b'}$, as well as wetting, is observed over in the whole temperature range (650-950°C) studied [Fig.2(a)] [1]. In the Fe-12at.%Si alloy the region of rapid GB diffusion disappears at $T<T_W$ (T_W=749±4°C) also simultaneously with wetting [Fig.1(c)]. In contrast to the (Fe-5at.%Si)-Zn alloys the $C_{b'}(T)$ line for the (Fe-12at.%Si)-Zn alloys is bounded by a critical point at temperature T_{cr}=801±2°C. Above T_{cr} the abrupt change of

GB diffusion coefficient gradually becomes "diffuse". At temperatures above about 870°C the diffusion profiles do not contain a region of rapid diffusion at all.

There exists a number of theoretical works in which the phase transitions on interfaces acompanying wetting are predicted [6-8]. They are related to the formation of a thermodynamically stable thin liquid (quasi-liquid) interlayer on interfaces. In the system Fe-Si-Zn the abrupt change in the GB properties at concentration C_{bt} assumed to be a premelting transition. In this case the increase of $s\delta D_b$ may be explained by the formation of a quasi-liquid interlayer on the GB, for which the diffusional thickness of the interface δ is increased by a factor of 10-100. All of the necessary conditions for a premelting transition to occur are satisfied by the system. These are (1) a high positive value of the enthalpy of mixing of the solution components, (2) a wetting of GB's in the two-phase region "solid-melt", and (3) the fact that the phenomena mentioned are observed on GB's of the component having the higher melting temperature (iron). Therefore, it is quite reasonable to say that a premelting transition is observed on GB's.

The temperature dependencies of $C_{bt}(T)$ for the Fe-5at.%Si and Fe-12at.%Si from our previous works [1,3] presented in Fig.2(a) and (c) with the new data obtained in this work [Fig.2(b) and (d)] contain singularities of the following three different types: (1) At temperatures close to bulk ordering (magnetic [1] and concentrational [3]), the lines $C_{bt}(T)$ have protuberances directed towards lower concentrations; (2) Ordering leads to the disappearance of the region of rapid grain boundary diffusion. At temperatures below the Curie point, the $C_{bt}(T)$ line nearly merges with the C_s line. At temperatures below the A2-B2 ordering point the region of rapid grain boundary diffusion disappears simultaneously with wetting; (3) At $T=T_{per}$ the zinc solubility C_s in the Fe-5 at.%Si alloy increases abruptly, while C_{bt} decreases nearly to zero.

The aim of the present paper was to find experimental answers to the following questions: (1) Is it true that the protuberances directed towards lower concentrations on the $C_{bt}(T)$ curves are caused by bulk magnetic or concentration ordering? (2) Is it true that bulk ordering "suppresses" the GB premelting transition and leads to the disappearance of the region of rapid GB diffusion? (3). Is it true that C_{bt} increases as C_s decreases and vice versa for the disordered phase?

EXPERIMENTAL

The above questions can be answered by investigation of zinc GB penetration into the Fe-10 at.% Si and Fe-14at.%Si alloys. Above 700°C this alloys do not undergo either magnetic or concentrational ordering, which are assumed [1,3] to cause the appearance of the discontinuity in the $C_{bt}(T)$ line. In the temperature interval studied the Fe-10at.%Si alloy has a disordered A2 structure and Fe-14at.%Si alloy has an ordered B2 structure. At the same time the Fe-10at.%Si alloy can be expected to exhibit stronger changes in C_s in the vicinity of T_{per} than those exhibited by the Fe-12at.% Si alloy [4,5]. To demonstrate this, the Fe-10 at.%Si and Fe-14at.%Si bicrystals having a 38°<100> tilt GB (where the tilt angle is measured between {100} planes) were grown by the electron beam zone melting method. The silicon concentration at various locations in the bicrystal ranged from 9.9 to10.1 at.% and from 13.8 to 14.1 at.% respectively. After spark erosion cutting and mechanically grinding the surfaces of the specimens and chemically polishing them in an 80% H_2O_2, 14%H_2O and 6% HF solution, a 100-150 μm Zn layer (99.998% Zn) was applied to the two opposite surfaces perpendicular to the tilt axis. These specimens were then encapsulated in evacuated (< $4\cdot10^{-4}$ Pa) silica tubes and annealed in a furnace at constant temperature ($\pm$0.5°C) between 700 and 950°C. Electron probe microanalysis (EPMA) measurements were carried out by wave length dispersive analysis on a JEOL 6400 electron probe microanalyser operated at 15 kV. The Al and Zn concentrations were obtained utilizing a program, which applied both ZAF and background corrections. For the determination of the concentration profiles the beam was stepped at 1 to 5 μm intervals

RESULTS AND DISCUSSION

Fig. 1 shows the dependences of the GB concentration maxima C_b upon depth y plotted in so-called Fisher's coordinates ($\log C_b$ vs y)[4]. If Fisher's model is valid, the slope of a diffusion profile in these coordinates is proportional to the GB diffusivity $s\delta D_b$. The first five diffusion profiles for the Fe-10at.%Si alloy $C_b(y)$ contain two distinct linear regions. They intersect at concentration C_{bt}. In the concentration range from C_s to C_{bt} the slope of the lines is small (large $s\delta D_b$). At concentration C_{bt}, the profiles have a knee. The region with steep slope (small $s\delta D_b$) corresponds to $C<C_{bt}$. At $T>790$°C, the knee on $C_{bt}(T)$ curves becomes diffuse. However, some vestiges of the high and low slope regions on the $C_b(y)$ curves are preserved at $T>T_{cr}$ in the temperature interval about 50-70°C. At the highest temperature interval studied the diffusion profiles $C_b(y)$ contain only the steep slope region. The $C_b(y)$ profiles for Fe-14at.%Si alloy in the all temperature intervall studied contain only the large slope region. In the temperature range studied for both alloys (700-900°C for Fe-10at.%Si and

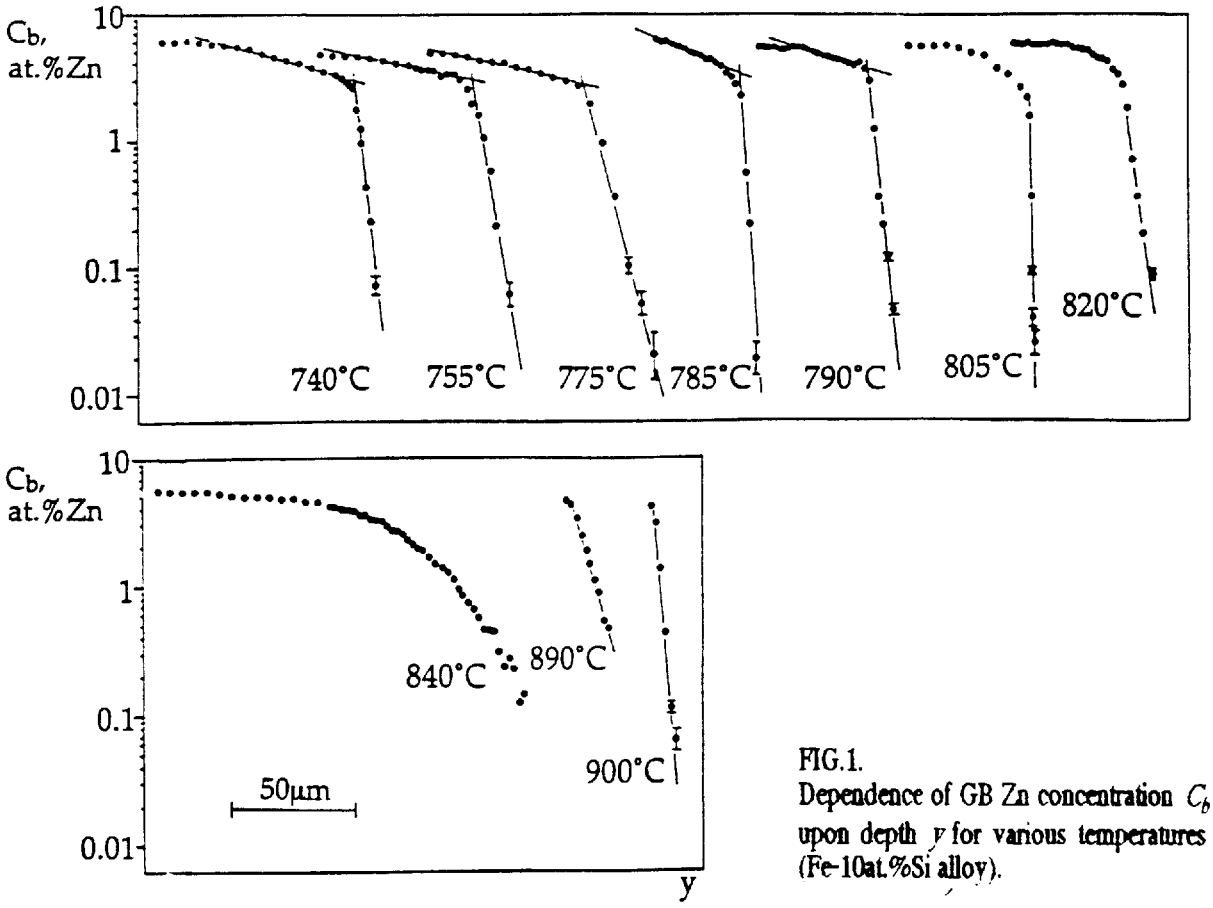

FIG.1.
Dependence of GB Zn concentration C_b upon depth y for various temperatures (Fe-10at.%Si alloy).

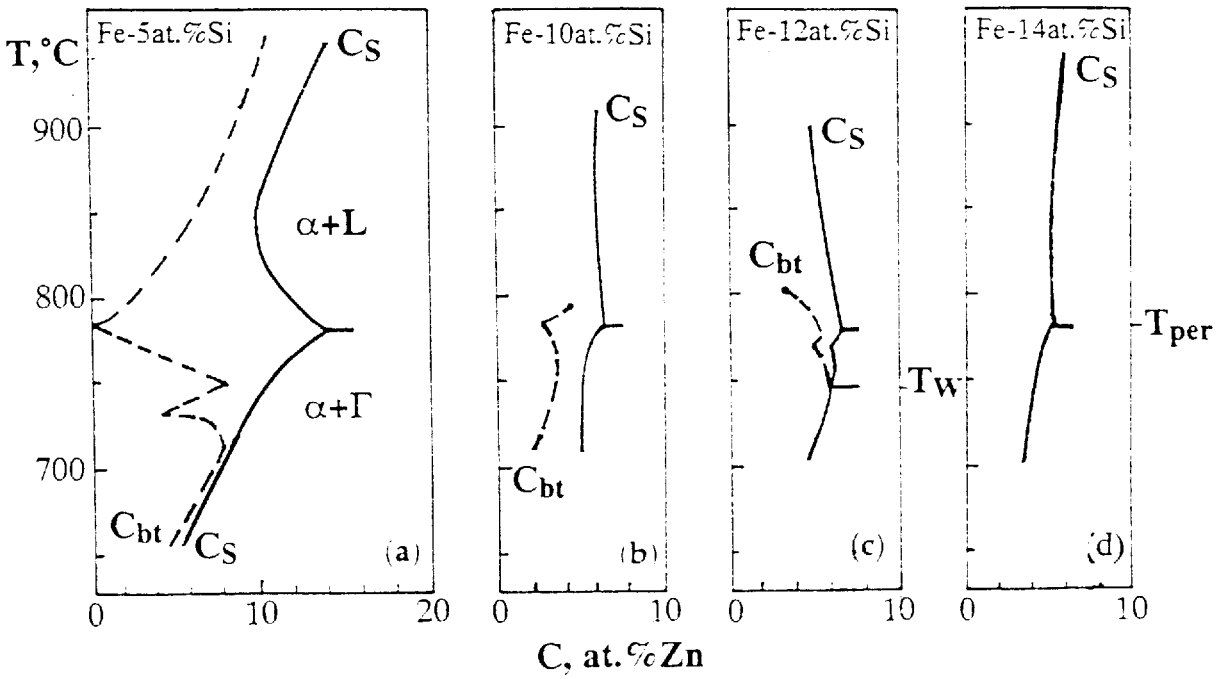

FIG.2.
(a) (Fe-5at.%Si)-Zn phase diagram. (b) (Fe-10at%Si)-Zn phase diagram. (c) (Fe-12at.%Si)-Zn phase diagram. (d) (Fe-10at%Si)-Zn phase diagram. The dotted lines on the diagrams (a)-(c) are $C_{bt}(T)$ lines for the grain boundary premelting phase transition.

700-965°C for Fe-14at.%Si) the GB's were wetted by the melt.

Figure 2(b) presents the (Fe-10 at.% Si)-Zn phase diagram. The plot contains two lines, the zinc bulk solubility limit $C_s(T)$ and the $C_{bt}(T)$ line. $C_s(T)$ is a solidus line at $T>T_{per}$, while at $T<T_{per}$ it is a solvus line. $C_s(T)$ contains a characteristic singularity at $T=T_{per}$. At this point C_s reaches its maximum, while the $C_{bt}(T)$ line reaches its minimum at the same temperature. Above T=790°C the C_{bt} line comes to an end, because the sharp transition of the slope on the $C_b(y)$ profiles disappears. At temperatures below T_{per} the C_{bt} curves do not contain any singularities down to T=700°C. On the whole the curves $C_s(T)$ and $C_{bt}(T)$ seem to be inverted with respect to each another, that is C_{bt} decreases as C_s increases and vice versa.

Figure 2(d) presents the (Fe-14at.% Si)-Zn phase diagram. The plot contains only one line, the zinc bulk solubility limit $C_s(T)$, because all the diffusion profiles $C_b(y)$ contain only the steep slope region. $C_s(T)$ is a solidus line at $T>T_{per}$, while at $T<T_{per}$ it is a solvus line.

Comparing Figs 2(a),(b) and (c) it can be seen that the disappearance of GB premelting and wetting in the systems (Fe-5 at.%Si)-Zn and (Fe-12 at.%Si)-Zn is really caused by the bulk ordering. The only difference between the Fe-10 at.%Si alloy and the Fe-5at.%Si and Fe-12 at.%Si alloys is the absence of an ordering transition in the temperature range from 700-800°C. It can also be seen that grain boundary premelting and wetting transitions really do not disappear with temperature decrease in the Fe-10 at%Si alloy. The region of the grain boundary diffusion in the Fe-12at.%Si alloy disappears together with the wetting by the transition from the disordered A2 to the ordered B2 phase [3] In the Fe-14at.%Si alloy, "deep in the ordered region", we really do not see the fast grain boundary diffusion, but wetting appears again.

CONCLUSIONS

1. GB wetting by a zinc-based melt during zinc penetration of 38°<100> tilt boundaries in the Fe-10 at.%Si and Fe-14at.%Si alloys is observed over the entire temperature range studied.

2. In the Fe-10at.% Si alloy in the range from the lowest temperature studied (700°C) up to T_{cr} =790±5°C a region of accelerated diffusion is observed on GB's in the concentration range from C_s (bulk solubility limit for zinc) to C_{bt}. At concentration C_{bt} the rate of zinc GB diffusion abruptly decreases to typical values for GB diffusion in iron. At C_{bt} a knee is observed in curves of GB zinc penetration. We explain the existence of a region of rapid GB diffusion in terms of a premelting transition and the formation of an thin equilibrium layer of a liquid or quasi-liquid phase. In the Fe-14at.%Si alloy the region of accelerated diffusion is not observed at all.

3. The above mentioned knee in the Fe-10at.%Si alloy disappears at T_{cr}=790±5°C, but certain features of rapid GB diffusion are also observed at higher temperatures.

4. At T_{per} in the Fe-10at.%Si alloy C_{bt} reaches its minimum. At the same temperature the bulk zinc solubility is maximal. In contrast to the previously studied ordering Fe-Si alloys the $C_{bt}(T)$ line for the alloy in this study does not have any singularities below T_{per}. Also the regions of accelerated GB diffusion and wetting do not disappear.

5. Thus, the singularities in the $C_{bt}(T)$ curve related to the miscibility gap and bulk ordering can also be observed separately. This further supports the hypothesis of the GB premelting proposed in [1-3] as an approach to explaning the accelerated zinc diffusion along GB's in Fe-Si alloys.

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