WETTING AND PREMELTING PHASE TRANSITIONS IN 43° <100> TILT GRAIN BOUNDARIES IN Fe-5at.% Si

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Abstract - Penetration of Sn and Zn along a 43° <100> tilt grain boundary (TiGB) in a body-centred cubic (bcc) Fe - 5 at.% Si alloy is studied in the temperature range of 652 - 975°C. Wetting transition of GB by the Sn-rich melt is observed at T_w = 810 ± 5°C. For Zn penetration along the GB, the wetting film is observed at all temperatures studied. The region behind the wetting film is observed to have an unusually high GB diffusivity of Zn (by two order of magnitude), followed by a region of "usual" GB diffusivity. The transition from usual to anomalous GB diffusivity $D'\delta$, where D' is the GB diffusion coefficient and δ is the GB width, takes place at the concentration C_{bt}. The value C_{bt} is independent of the annealing time, but depends strongly on the temperature. Such a phenomenon may be explained in terms of the so-called premelting phase transition "GB → thin wetting film on the boundary".

1. **Introduction** - Phase transitions in two-dimensional systems, particularly the phase transitions accompanying wetting on interfaces in solids [1], have attracted considerable attention in recent years. Wetting of GBs by the melt in two-component systems was evidenced in Zn-Sn [2], Al-Sn [3], Al-Pb [3], etc. The theoretically predicted [4] phase transitions accompanied by formation of thin liquid layers on boundaries (premelting, prewetting) were never observed experimentally in solids. The present study attempts to investigate the wetting and premelting transitions in two model systems having high enthalpy of mixing, namely Fe-Sn and Fe-Zn [5].

2. **Experimental Methods** - All experiments were carried out with 43° <100> TiGBs of an Fe - 5 at.% Si alloy. The bicrystals were grown by electron-beam zone melting technique in vacuum of the order of 10^{-6} Torr with a growth rate of 1 mm/min. A layer of Sn or Zn was applied to the specimens by immersing them into the melt. Before immersion the specimens were ground mechanically followed by chemical polishing in a solution containing 80% H_2O_2 + 14% H_2O + 6% HF. The samples were annealed in the temperature range of 652 -975°C. The Sn or Zn concentration profiles were determined by means of electron probe microanalysis (Fig.1a).

3. **Results** - Figures 1b and 1c reveal typical concentration profiles of Sn on the specimen cross-sections after two different diffusion annealing treatments. An alloyed layer formed by dissolution of Fe in liquid Sn during the initial period of annealing may be observed on the sample surface. The bulk diffusion layer may be found further deep inside the bicrystal. Isoconcentration lines parallel to the sample surface appears to suggest that no preferential penetration of Sn took place along GBs (Fig.1b). This is true for all bicrystal samples annealed at temperatures below 810 - 815°C. At temperatures above 810 - 815°C, the situation changes drastically. A thin (roughly 1 μm) layer enriched in Sn along GBs (Fig.1c) indicates that a phase transition of GB wetting by the melt (FeSi)-Sn has occured at T_w = 810 - 815°C. It is important to mention that wetting transition above T_w, perhaps, does not change the GB properties ahead of the Sn-enriched wetting layer. However, such changes in boundary properties ahead of the wetting layer have been observed in course of Zn penetration along the GBs. Figure 1d illustrates the Zn concentration distribution after annealing at 908°C for 3 h. The similarity between the concentration distributions between Figs.1c and 1d are worth noting. However, there is a distinct difference as far as Sn and Zn diffusion along the GB is concerned. A region with high diffusivity can be clearly seen below the GB layer only in Fig.1d (the beginning and end being marked by arrows). The GB diffusivity ($D'\delta$) in this region is very large, approximately 2 orders of magnitude higher than characteristic values of $D'\delta$ for GB self- and heterodiffusion in bcc Fe [6-9]. Following this region, the GB appears to have a $D'\delta$ value near to the usual one [6-9]. For estimating $D'\delta$, a sequence of concentration profiles perpendicular to the

GB and parallel to the sample surface has been measured (Fig.1a), and the C_b values have been calculated from the maxima of these profiles corresponding to the GB position. The D'δ values can be determined from the slope of the variation of $\log C_b$ against the depth y. These $\log C_b$-y plots for different temperatures are displayed in Fig.2. These plots consist of an initial part having a low gradient followed by a steep slope. The concentration C_{bt} (the concentration at which D'δ changes) has been obtained from the point of intersection of these two parts having different slopes. From experimental evidences in Fig.2 it may be suggested that a phase transition accompanies by the formation of the thin wetting layer at C_{bt} near the GBs. However, similar transition has not been observed in the experiments with Sn. At the points of intersection in Fig.2, the GB thickness δ may increase abruptly. Assuming D' constant above and below C_{bt}, the GB thickness δ can be estimated by ratio of D'δ above and below C_{bt}. The value of δ, so obtained is approximately 10^2. The temperature dependence of C_{bt} is displayed in Fig.3 in which the variation of C_{bt} appears rather complicated. Above the Curie point, the greater the bulk solubility limit C_o the lower is the corresponding C_{bt}. Near the Curie point, this correlation may not be valid since the line has a protuberance towards the lower Zn concentrations.
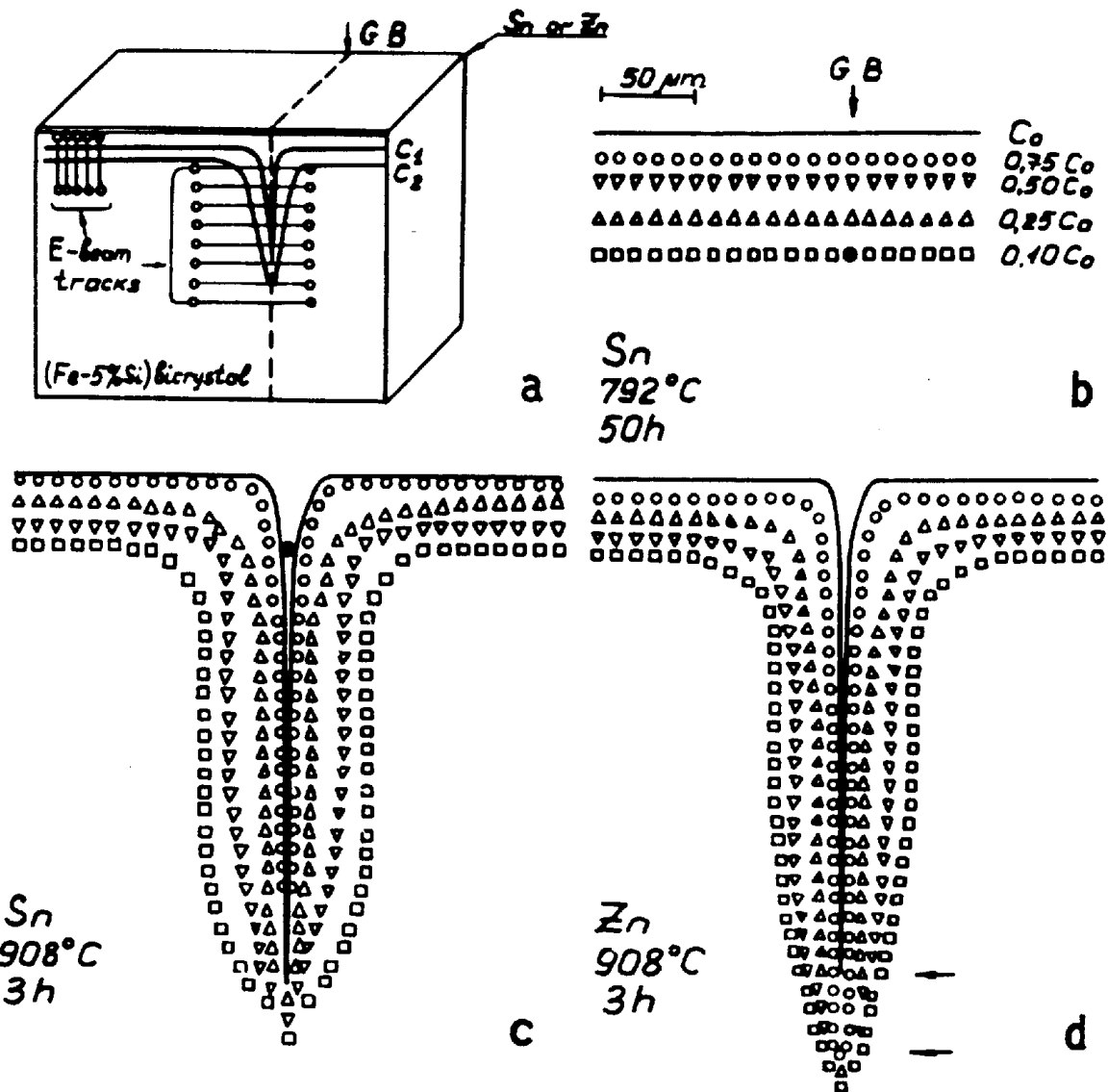

Fig.1 (a) The scheme of concentration measurement in a bicrystal after diffusional annealing. The isoconcentration lines and the plot of electron probe shift are drawn. The measurements were carried out by local X-ray spectral analysis. (b) Five isoconcentration profiles of Sn after annealing at 792°C for 50 h. C_o is the Sn solubility limit. (c,d) The Sn and Zn concentrations in the same bicrystal after annealing at 908°C for 3 h. The region of rapid GB diffusion below the wetting layer is marked by the arrows.
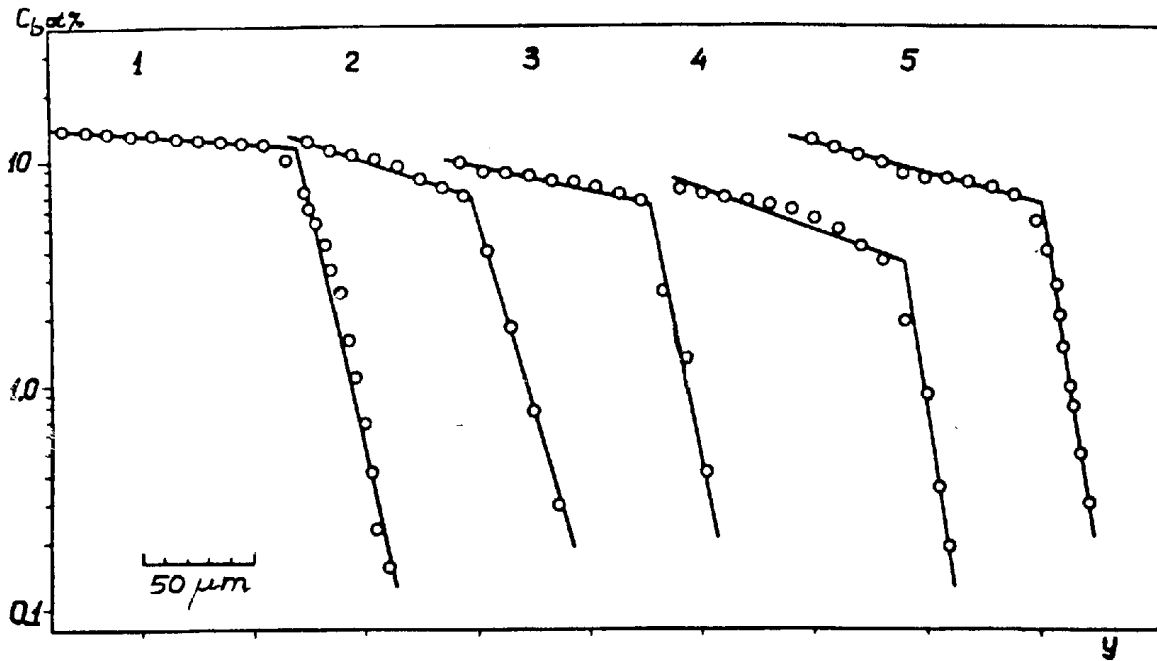
Fig.2 The dependence of Zn concentration on boundaries C_b on the depth y for different temperatures. For C_{bt}, the value of GB diffusivity $D'\delta$ changes abruptly. $D'\delta$ is measured from the slope of C_b vs. y plot. The concentration C_{bt} corresponding to the change of $D'\delta$ slope changes with temperature (cf. Fig.3). (1) 975°C, 1.75 h; (2) 857°C, 7.5 h; (3) 809°C, 21 h; (4) 790°C, 63 h; (5) 745°C, 102 h.
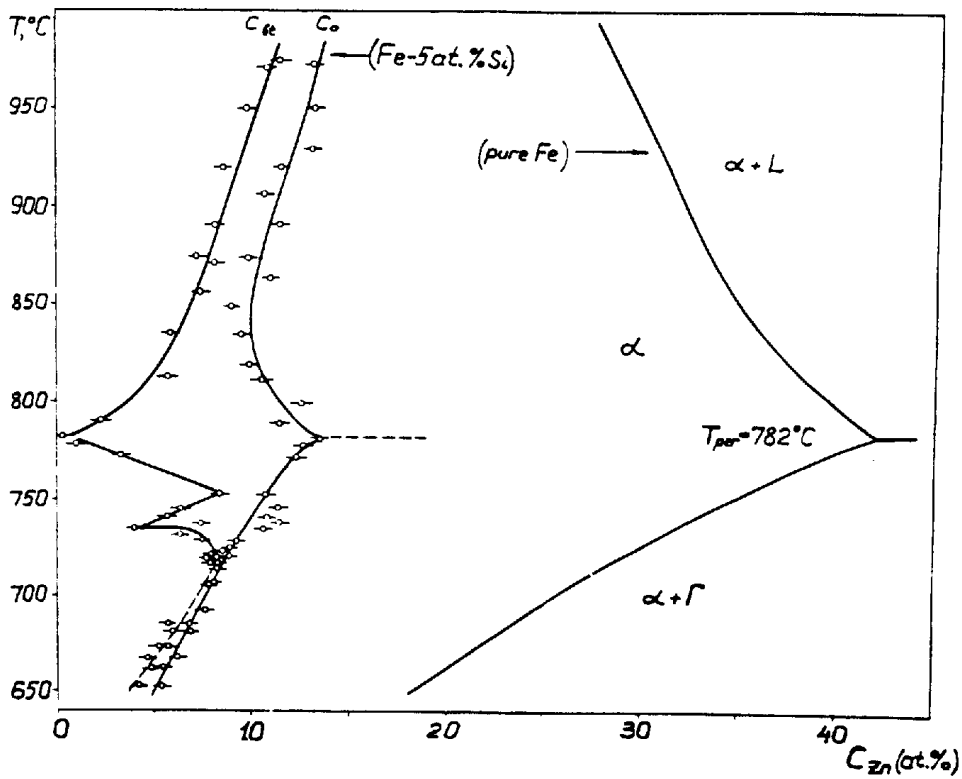

Fig.3 The temperature dependences of C_{bt} and C_o. The line of solubility limit of Zn in pure Fe is also included (both solidus and solvus) [10]. Γ is an intermetallic compound and L is the liquid.
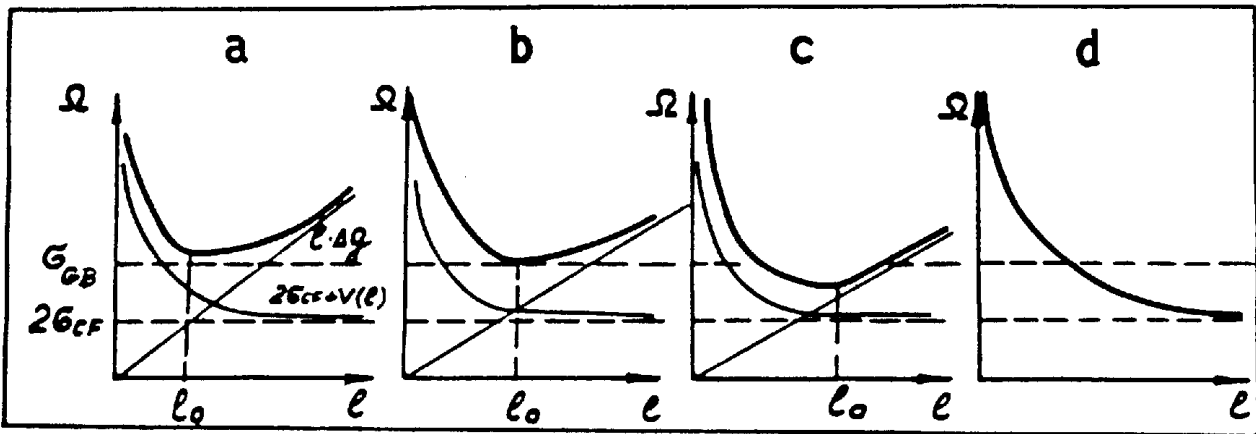
Fig.4 The dependences of excess free energy of wetting layer Ω on the layer thickness 1. σ_{CF} is the surface tension of the interphase "crystal-wetting phase", σ_{CB} is the GB surface tension (marked by dashed horizontal lines). The hyperbola V(l) and the straight line $1 \cdot \Delta g$ (a-c) may yield Ω as per Eq.(1). (a) Wetting layer on a boundary is not feasible. (b) σ_{GB} is tangent to Ω, and a thin layer of thickness 1_o appears on the boundary (the premelting transition). (c) In course of further decrease in Δg, the layer thickness grows. (d) At $\Delta g = 0$, the layer thickness 1 approaches infinity (complete wetting).

4. Discussion - The GB wetting phenomena, along with the common features of the surface wetting, deserves special attention for many reasons. In general, the wetting layer free energy Ω_s may be expressed as follows [1]:

$$\Omega_s = 2\sigma_{CF} + 1\Delta g + V(1) , \qquad (1)$$

where σ_{CF} is the surface tension of the "crystal-wetting phase" interphase, 1 is the wetting layer thickness and Δg is the excess free energy of the wetting phase. The last term describes the interaction of the "crystal-wetting phase" interphases. The situation in which the wetting layer thickness approaches infinity $(1 \rightarrow \infty)$ and the concerned phases tend to coexist $(\Delta g \rightarrow 0)$ is called the complete wetting. In order to analyse the Ω behaviour, V(1) may be assumed to have a simple hyperbolic form,

$$V(1) = W/1^n . \qquad (2)$$

The function $\Omega_s(1)$ defined by Eqs.(1) and (2) has a minimum at $1 = 1_o$. If Δg value is large (far from phase coexistence line), then $\Omega_s(1_o) > \sigma_{GB}$, and the wetting layer on the boundary is not noticeable (i.e. the boundary is "clean") (Fig.4a). When Δg is such that $\Omega_s(1_o) = \sigma_{GB}$, the boundary transforms into a thin layer of a wetting phase of thickness 1 (Fig.4b). This is the so-called premelting transition of GB if the wetting phase is liquid. When Δg decreases, the 1_o value increases and approaches infinity at $\Delta g = 0$ (Figs.4c,d). The experimental data substantiates the scheme displayed in Figs.4a-d by showing a wetting layer on GB above the region of accelerated GB diffusion. Consequently, complete wetting occurs in the systems as explained in Fig.4d. At $C_b = C_o$, $\Delta g = 0$ and for small deviations in C_o, Δg may be expanded into a series in terms of $C_o - C_b$. Truncating the first term of this expansion, it follows

$$g = b(C_o - C_b) . \qquad (3)$$

The $\Omega(1)$ function determined by use of Eqs.(1) to (3) has a minimum at $1_o = [b(C_o - C_b)/nW]^{-1/(n+1)}$:

$$\Omega(1_o) = \Omega_o = 2\sigma_{CF} + (nW)^{1/n+1} [b(C_o - C_b)]^{n/(n+1)}(1 + W^{-1}) .$$

When the condition $\Omega_o = \sigma_{GB}$ is satisfied, then the premelting transition occurs, and the GB is replaced by a layer of a Zn-enriched phase. For this condition one may obtain:

$$C_{bt} = C_o - \frac{(\sigma_{GB} - 2\sigma_{CF})^{(n+1)/n}}{b(Wn)^{1/n}(1+W^{-1})^{(n+1)/n}} \ . \tag{4}$$

The Eq.(4) correlates the bulk solubility limit with the concentration at which the pre-melting transition occurs at the boundary. But the surface tensions σ_{GB} and σ_{CF} also depend on the concentration. Thus comparison of Eq.(4) with the experimental data may not be feasible. The solid solubility limit line (solvus) in Fe-Zn system is near to the metastable curve of solid solution decomposition [10]. This means that the σ_{CF} value decreases sharply as the peritectic transformation point is approached ($T_{per} = 782°C$). According to Eq.(4), this leads to a decrease in C_{bt}, which is also observed in the concerned experiment (Fig.3).

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