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PHASE TRANSITIONS ON GRAIN BOUNDARIES

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Topics: grain boundary phase transitions, grain boundary diffusion, wetting, premelting

ABSTRACT

Recent achievements in the investigation of grain boundary phase transitions are rewieved. Experimental results on the special to random grain boundary phase transition, the wetting, the premelting and the prewetting phenomena are presented. Various types of grain boundary phase diagrams are constructed. The influence of grain boundary phase transitions on grain boundary diffusion is discussed.

1. INTRODUCTION

The problem of phase transitions on grain boundaries (**GB**'s) has always attracted great attention of specialists in materials science. Such interest has two main sources. Firstly, progress in the research on free surfaces stimulates analogous investigations on grain boundaries. Phase transitions on surfaces of solids are well-established, and that area is now under extensive investigation [1,2]. Secondly, the problem of grain boundary phase transitions (**GBPT**'s) is of a great practical importance, because in many cases GB's define the mechanical and diffusional properties of a polycrystal. The excellent review papers of Cahn [3] and Rottman [4] illustrate such interest. In the paper of Rottman [4] one can find a clear classification of possible types of GBPT's as well as a critical review of experimental data known to that date. Thus, in the present contribution we will mainly emphasize the progress in GBPT investigations achieved in past four years.

2. SPECIAL - RANDOM GB PHASE TRANSITION

The GB's near the coincidence misorientations with low Σ (here Σ is the inverse density of coincidence sites) possess structure [5,6] and properties (energy [7], mobility [8], diffusivity [9]) different from those of GB's with general misorientations. With increasing temperature the characteristic cusps in

misorientation space, corresponding to the low values of Σ, may vanish. In [10] the experimental data on structure and properties of GB's in cubic lattices were analysed, and $T(\psi)$ phase diagrams were plotted. It was shown that the region of existence of GB's with special properties decreases as the Σ value increases, and at each temperature there exists a maximal Σ value above which GB properties vary monotonically with the misorientation angle ψ. That concept was successfully applied to the interpretation of observed changes in mobility and surface tension of symmetric [001] GB's in tin with misorientation angles near the coincidence misorientation Σ17 [11] and diffusional permeability of symmetric [001] GB's in copper near the coincidence misorientation Σ5 [13]. In figures 1 and 2 corresponding $T(\psi)$ phase diagrams are shown. Sharp changes in the temperature dependencies of GB surface tension (figure 1b) and discontinuities in the temperature dependencies of GB mobility (figure 1c) in tin as well as discontinuities in the GB diffusivity in copper (figure 2b) indicate that the transformation of special GB's to GB's with the properties of random boundaries proceeds like a first-order phase transition.

It should be noted that there exists a strong analogy between the GBPT under consideration and the GB roughening transition. Such phase transitions on GB's have recently been directly observed by Hsieh and Balluffi [14]. The cusps on the inclination dependence of the GB surface tension do not exist above the temperature of the roughening transition. Macroscopically the transition is manifested in defaceting of GB's. Microscopically the free energy of a step on the GB goes to zero at such transition, the spontaneous formation of steps begins and the GB becomes flat and diffuse [14]. The natural periodicity of the GB structure is the coincidence site lattice (**CSL**) spacing. Therefore, the steps responsible for the GB roughening should have a size comparable to that of CSL spacing. Let us consider a GB with a misorientation angle near one of the coincidence misorientations (special GB). The characteristic feature of such GB's are secondary GB dislocations (**SGBD**'s). The steps associated with SGBD's have the size of a displacement shift complete lattice (**DSC**). Therefore SGBD's may be considered as defects which lead to the roughening of the special GB structure and its transformation into a random one. Due to the fact that a long-range elastic field is associated with the SGBD's, such transformation may be of first order. The CSL lattice is a sublattice of the DSC lattice, and as the Σ value increases the period of the CSL also increases, while the period of DSC lattice decreases. So at high Σ *DSC roughening* should precede the *CSL roughening*. Since the CSL lattice is the sublattice of a DSC lattice, the GB which is rough in a DSC sense is also rough in a CSL sense. Therefore, at relatively high Σ the cusps associated with a given orientation and misorientation ψ should disappear simultaneously with a temperature increase. However, at low Σ the CSL-roughening may precede the DSC roughening. So on the low-Σ special GB's two GBPT's may take place with increasing temperature: the first phase transition is associated with *orientation* cusp vanishing and the second one with the *misorientation* cusp vanishing.

3. GB WETTING, PREMELTING AND PREWETTING PHASE TRANSITIONS

One of the specific GB phase transformations is the wetting transition. What is it? Let us consider the two phase area (S+L) on a bulk phase diagram where the solid (S) and liquid (L) phases are in equilibrium. The angle θ is the angle between the solid-liquid interfaces at the intersection line between the GB in the solid phase S and the melt L. If the GB energy σ_b is higher than $2\sigma_{SL}$ (σ_{SL} is the energy of the liquid-solid phase boundary) the liquid wets the GB and θ=0. If the σ_b and σ_{SL} vary differently with temperature, the GB wetting phase transition can proceed at a wetting temperature T_W [15]. Above T_W the contact angle θ is zero because $2\sigma_{SL} < \sigma_b$ and the GB is wet. At temperatures far below the wetting transition temperature T_W the angle θ is larger than zero and is slightly dependent on the temperature, and

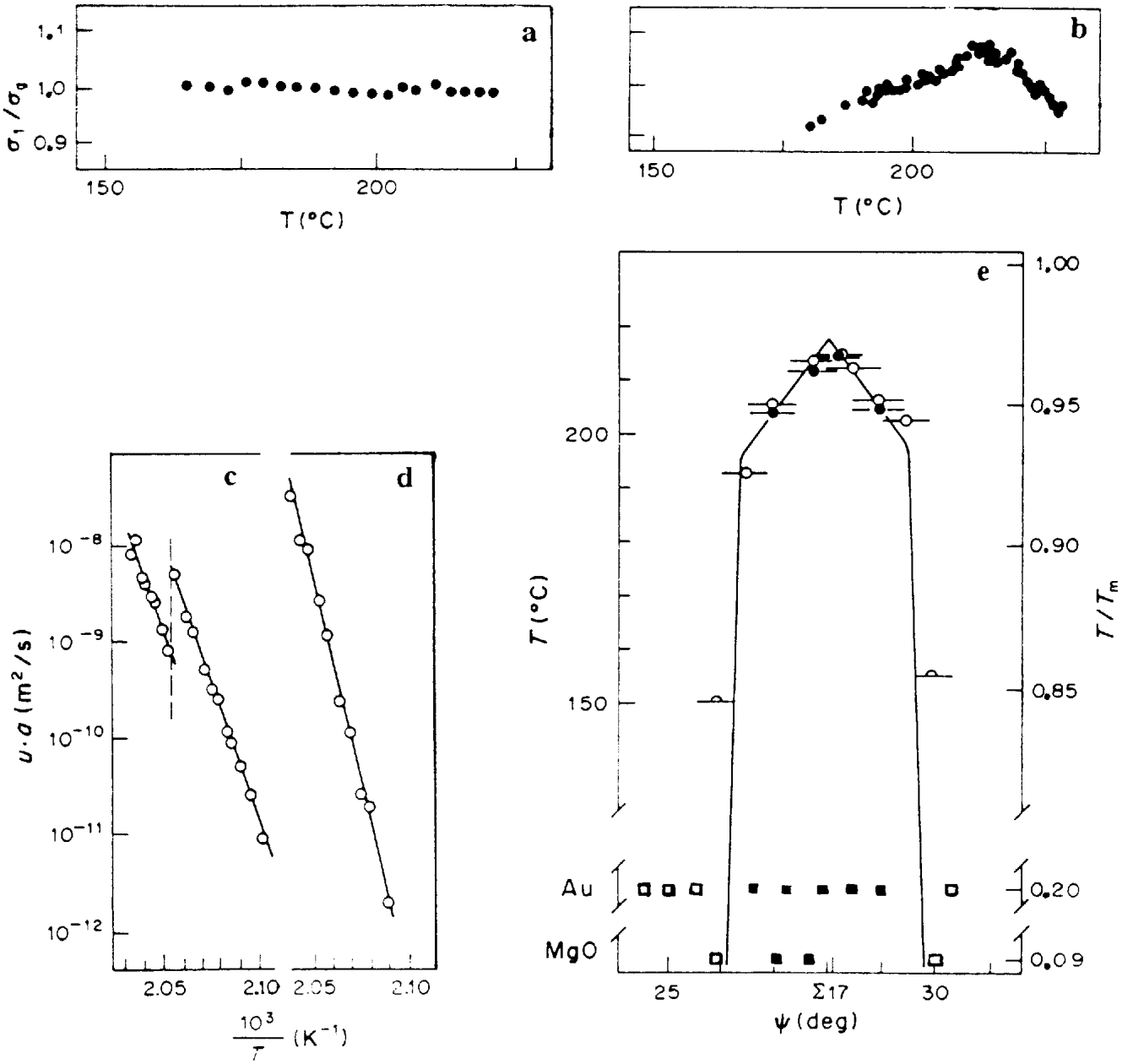

FIGURE 1.

Temperature dependencies of the ratio of the surface tension σ_l of special boundaries to that of general boundaries σ_g in tin for misorientation angles of 25.5° (**a**) and 28.2° (**b**) [11]. Temperature dependencies of the [001] tilt GB migration rate u normallized with respect to driving force (by multiplying by the GB radius of curvature a) in tin for misorientation angles of 28.2° (**c**) and 29.5° (**d**) [11]. (**e**) GB phase diagram for tilt GB's in tin near the Σ17 coincidence misorientation. Open circles stand for T_c values obtained from temperature dependencies of the surface tension [like (a) and (b)], solid circles for T_c values obtained, from the temperature dependencies of the GB migration rate [like (c) and (d)]. The lower part of the figure presents the data of GB's with misorientations near Σ17 in gold [5] and magnesium oxide [6]. Solid squares correspond to the GB's which exhibited secondary GB dislocations, open squares to the boundaries formed by primary GB dislocations alone.

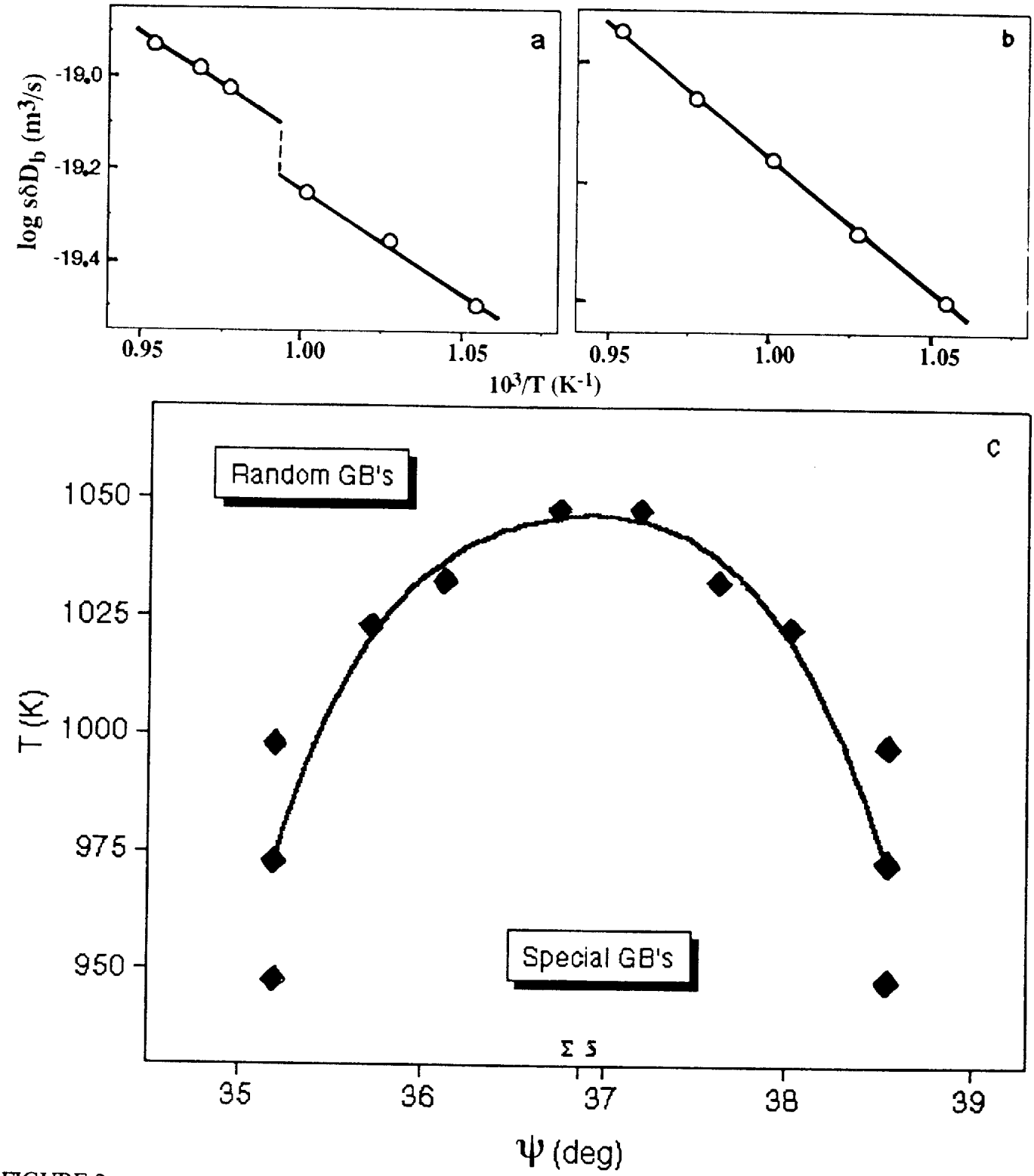

FIGURE 2.

Temperature dependencies of the GB diffusivity $s\delta D_b$ (s is the GB segregation factor, δ is the GB width and D_b is the GB diffusion coefficient) for misorientation angles of 38.08° (**a**) and 38.80° (**b**) [13]. (**c**) GB phase diagram for tilt GB's in copper near the Σ5 coincidence misorientation. The points stand for T values obtained from the gaps in the temperature dependencies of $s\delta D_b$.

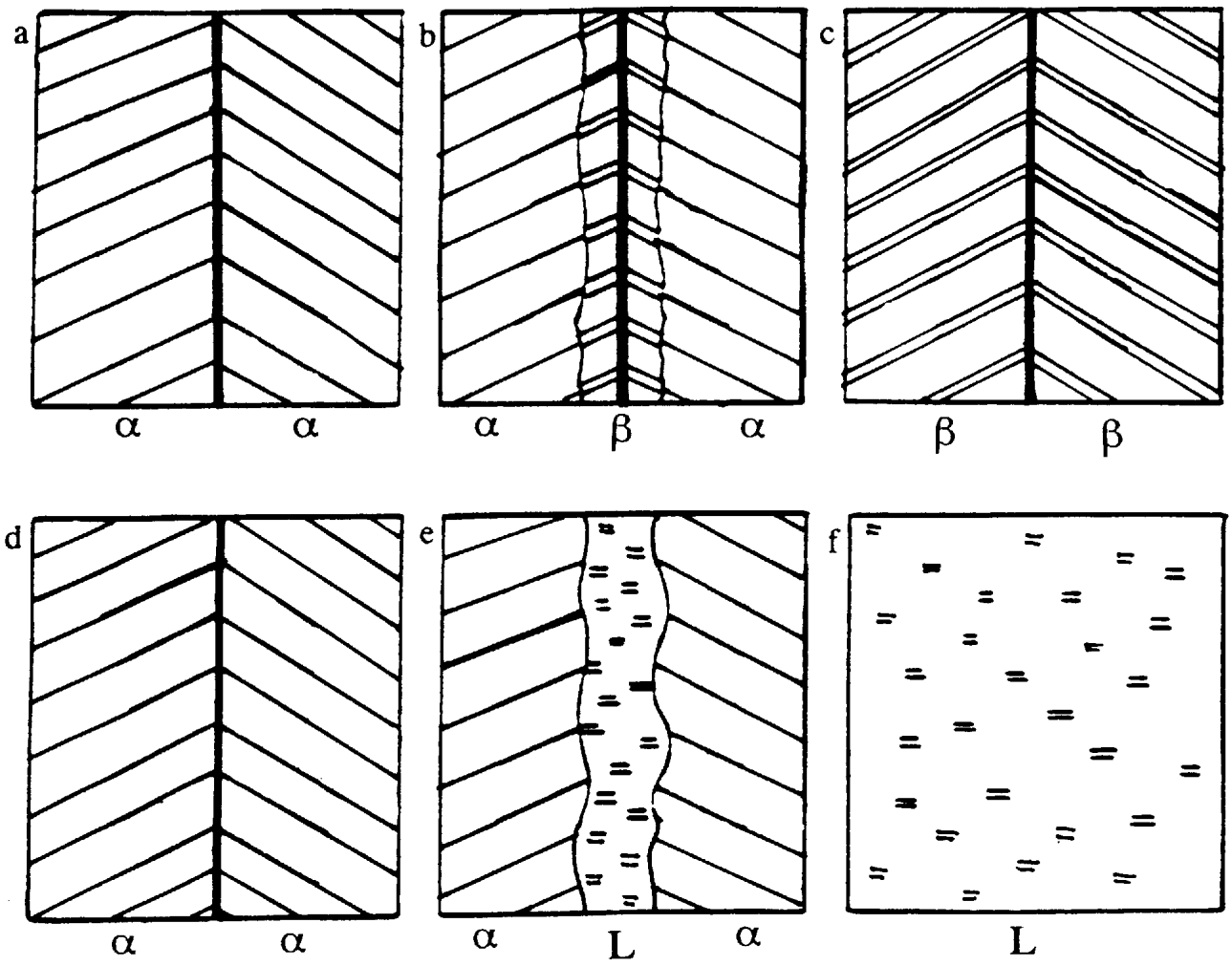

FIGURE 3.
(**a-c**) Prewetting transition. Three interfaces are forming in place of the single GB, a new GB and two *crystal-wetting phase* interfaces: (**a**) GB in the α-phase; (**b**) GB in the thin quasi-β layer between two α-crystals near the bulk α–β transition, and (**c**) GB in the β-phase. (**d-f**) Premelting transition. The GB is completely replaced by the wetting phase interlayer: (**d**) GB in the α-phase: (**e**) thin liquid layer between two α-crystals near the solid-liquid coexistence line, and(**f**) liquid phase for $T > T_m$.

and the GB is not wet. θ approaches zero in a small temperature interval near T_w. At the temperature T_w of the GB wetting phase transition the horizontal line (conode) will appear in the two-phase area (S+L) of the bulk phase diagram. Above this line the GB can no longer exist in equilibrium with the melt, and liquid layer must form between the corresponding grains.

It was pointed out by Cahn [3] that when the critical consolution point of two phases is approached, GB's of one critical phase should be always wetted by the layer of another critical phase, and in the one-phase region of a phase diagram there should be the singularity connected with an abrupt transition to a microscopic wetting layer. In our further consideration we will distinguish two possible situations. In the first a layer of new phase is formed on a GB (prewetting transition, figure 3a-c); in the second the GB is replaced by a layer of new phase (premelting phase transition, figure 3d-f). At the prewetting transition the difference between two phases must be small, while at the premelting transition the wetting phase may differ from that of the bulk dramatically. There exists strong evidence for a prewetting phase transition on

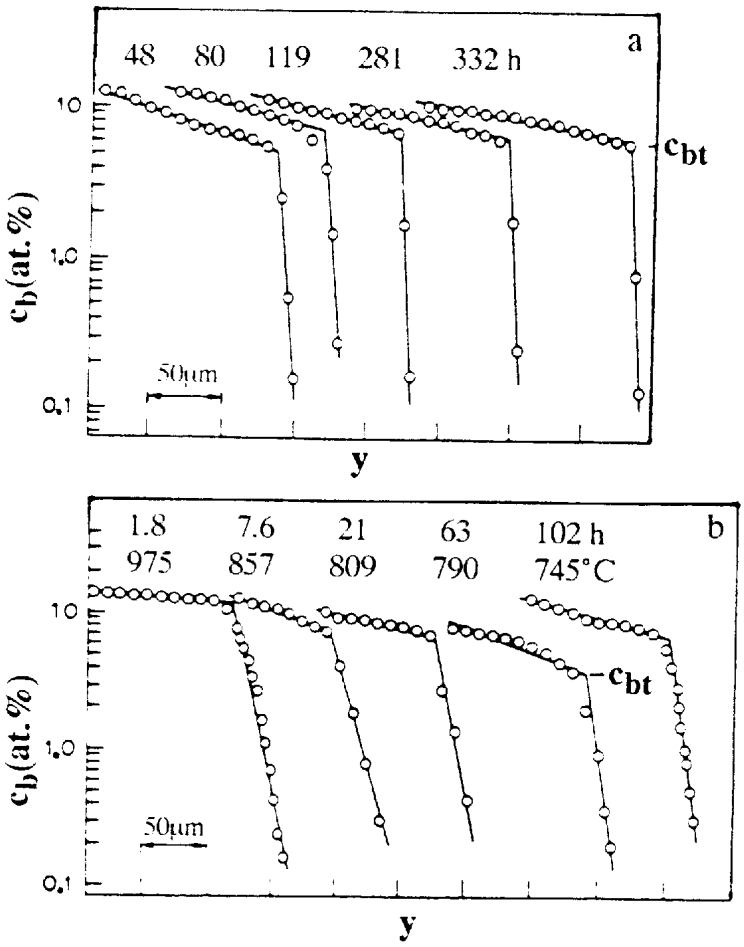

FIGURE 4.
The dependencies of GB zinc concentration c_b on depth y in an Fe-5at.%Si alloy [18]. (**a**) At concentration c_{bt} the value of GB diffusivity $s\delta D_b$ changes abruptly at a constant temperature of 735°C and various annealing times t. It can be seen that c_{bt} does not depend on t.

(**b**) At concentration c_{bt} the value of GB diffusivity $s\delta D_b$ changes abruptly. The concentartion c_{bt} depends on the temperature.

GB's in the tin-indium system [16,17]. In these works bulk and GB diffusion of tin in indium was studied, and it was shown that there is a discontinuity in the temperature dependence of the bulk interdiffusion coefficient at the temperature of the critical point of the β–γ′ phase transition in the bulk. Analogously, but at lower temperatures, discontinuities were also observed in the temperature dependence of GB diffusivity, while at the bulk critical temperature these dependencies exhibited no singularities. Such behavior may be understood according to the scheme of the prewetting transition shown in figure 3, assuming that the diffusion path is strictly two-dimensional.

The premelting transition has been observed in the ternary Fe-Si-Zn system during Zn diffusion along tilt GB's in Fe-Si alloys [18-21]. It was found that the profiles of Zn penetration along GB's in Fisher coordinates ($\log c_b$ vs y , where c_b is Zn concentration at the GB and y is the distance) consist of two sections, one with a small slope at high Zn concentrations and one with a steep slope at low Zn concentrations (figure 4). The transition from one type of behavior to the other was found to occur at a definite Zn concentration c_{bt} at the GB. This is an equilibrium characteristic of the GB. The concentration c_{bt} does not depend on the annealing time (figure 4a), but does depend on temperature (figure 4b). The ratio of GB diffusivities in the two regions was approximately $10\text{-}10^2$, which is an indication of the presence of a quasiliquid layer at the GB at high Zn concentrations. c_{bt} dependencies upon temperature (GB phase diagrams, figure 5) have been determined for alloys with different Si contents [18-21]. Let us summarize the main features of these diagrams.

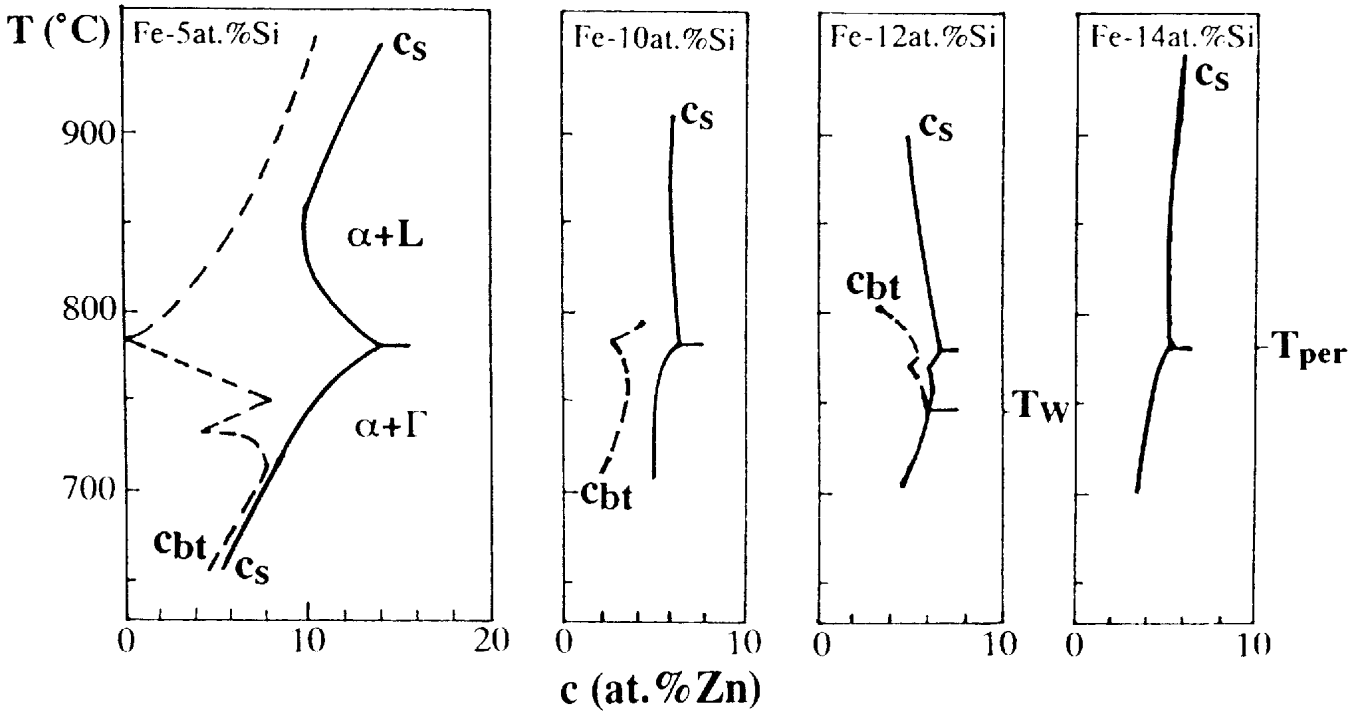

FIGURE 5.
Fe-Si-Zn phase diagrams for alloys with different silicon contents. The dotted lines show the temperature dependencies of the concentration c_{bt} at which the GB diffusivity changes dramatically (premelting phase transition). c_s is the bulk solubility limit of Zn in the Fe-Si alloys. T_{per} is the peritectic temperature of the binary Fe-Zn system [18-21].

1. For all Si contents sharp peaks directed towards low Zn concentrations were observed on GB phase diagrams at the peritectic temperature of the Fe-Zn system (782°C) (figure 5). The nature of that peak is connected with the fact that in the Fe-Zn system the "virtual" critical point of the solid solution decomposition lies only slightly above the peritectic temperature. It has been shown [18] that the concentration c_{bt} at which GBPT occur depends on the GB surface tension σ_b and the surface tension σ_{SL} of the solid-liquid interface according to the following expression:

$$c_{bt} = c_0 - \frac{(\sigma_b - 2\sigma_{SL})^{(n+1)/n}}{b\,(Wn)^{1/n}(1+n^{-1})^{(n+1)/n}} \qquad (1)$$

Here c_0 is a solubility limit of Zn in alloy, W and n are the constants describing the repulsive interaction between two solid-liquid interfaces, and b is a constant which may be determined from the thermodynamic data describing the ternary Fe-Si-Zn alloy. In the vicinity of the critical point, σ_{CM} decreases rapidly, and according to equation 1 c_{bt} also decreases.

2. In the alloy containing 5 at.% Si a peak on the GB phase diagram directed towards low Zn content was also observed in the temperature vicinity of the Curie point (figure 5). Such effects are often observed at the intersection of a line of a second-order phase transition with the line of a first-order phase transition [22]. This can be illustrated within the framework of a simple thermodynamic theory [23]. In alloys containing 10 and 12 at.% Si the Curie temperature is below the temperature interval studied and such peaks have not been observed.

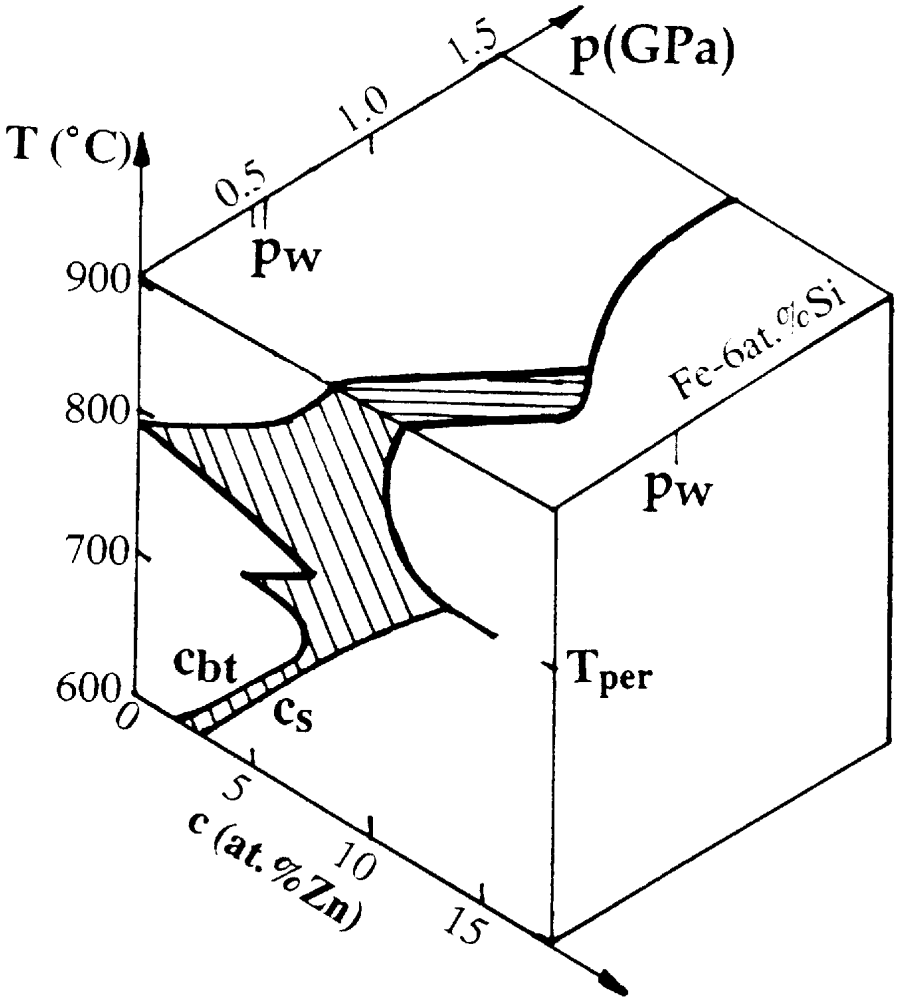

FIGURE 6.
Three-dimensional phase diagram with the coordinates temperature - Zn concentration - pressure. In the shadowed area between $c_{bt}(T,p)$ and $c_s(T,p)$ the premelting layer with high diffusivity exists on the GB [21]

3. Below the Curie point in the Fe-5 at.%Si alloy, the premelting line lies very close to the bulk solubility limit line. Below the A2-B2 atomic ordering temperature in the Fe-12 at.%Si alloy, the complete wetting of the GB by the zinc-rich melt disappears simultaneously with the GB premelting phase transition. Therefore, it may be concluded that atomic and spin ordering suppress the GB premelting. In the case of the ferromagnetic transition it is connected with the long-range attractive contribution to the free energy of the premelting layer, which is known to prevent wetting. This contribution is due to the attraction of two ferromagnetic fragments divided by the paramagnetic GB premelting. In the case of A2-B2 atomic ordering in the bulk an additional contribution to the free energy of both the GB and the premelting layer arises due to the disorder in the interface core. Since a premelting layer with a liquid-like structure is more disordered than a GB, such a contribution should be greater for a premelting layer, and it looses its stability in the bulk ordered state.

4. The region of stability of the GB premelting layer decreases with increasing hydrostatic pressure [21]. At some critical pressure p_W one can observe the transition from complete to incomplete wetting of a GB by the Zn-rich melt. The GB premelting transition also disappears at p_W . In figure 6 the schematic three-dimensional GB phase diagram is shown in two sections, p=0 (isobaric) and T=905°C (isothermal). The disappearance of GB wetting and premelting is connected with the higher excess volume of the premelting layer when compared with that of an "ordinary" GB. An estimation showed that the premelted GB is approximately 20-30 times as thick as an ordinary one.

4. THE DIRECTIONS OF FURTHER RESEARCH

Further research work should go in the following directions.

1. More detailed investigations of the GB wetting transition and complete wetting by the melt. In spite of the large amounts of data, many important questions still remain to be answered. What is the dependence of the phase transition point upon the GB type? What is the order of the wetting transition? What is it determined by? For example, to determine the order of the wetting transition, it is necessary to measure the temperature dependence of angle θ at the tip of the GB groove accurately in a narrow temperature range below the wetting transition temperature T_w. This dependence is continuous both for the first- and the second-order phase transitions. They can be distinguished only by the power of the law correlating θ with $|T - T_w|$ [1]. As far as we know, such studies have not been yet carried out.

2. Search of different types of GB roughening. If for low-Σ GB's the CSL roughening can precede the DSC one, then there should be a temperature interval in which the cusp in the GB energy vs orientation curve is absent and the cusp in the energy vs misorientation curve still exists. Note that the GB roughening may be observed by methods other than direct observation and measurement of the GB energy. If GB migration occurs by step nucleation and spreading, then at low temperatures the activation energy for GB migration should include the formation energy of a step, and at temperatures above the roughening temperature, when the concentration of steps is about 1, only the energy of step migration should be represented in the GB migration activation energy. So the GB roughening transition should manifest itself in upward curvature of Arrhenius plot for the GB mobility.

3. As we have already seen, there exist many types of GBPT's, both in alloys and pure metals. So, it is interesting to investigate the mutual influence of various phase transitions. From this data, complete GB phase diagrams, analogous to bulk or surface phase diagrams can be plotted. Such diagrams could find important practical applications.

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REFERENCES

1) Dietrich S., in Phase Transitions and Critical Phenomena, edited by C. Domb and J. Lebowitz (Academic Press, London) 1988, vol. 12, p.1.
2) Proceedings of 11th European Congress on Surface Science: Surface Sci., 1991, 251-252.
3) Cahn J.W.: J.Phys.(Paris), 1982, 43, C6-199.
4) Rottman C.: J.Phys.(Paris), 1988, 49, C5-313.
5) Tan T.Y., Sass S.L. and Balluffi R.W.: Phil. Mag., 1975, 31, 575.
6) Sun C.P. and Balluffi R.W.: Phil. Mag., 1982, A46, 49.
7) Hasson G.C. and Goux C.: Scripta metall.., 1971, 5,889.
8) Fridman E.M., Kopezky Ch.V. and Shvindlerman L.S.: Z. Metallk., 1975, 60, 533.
9) Aleshin A.N., Aristov V.Yu., Bokstein B.S. and Shvindlerman L.S.: phys. stat. sol. (a), 1978, 45, 359.
10) Shvindlerman L.S. and Straumal B.B.: Acta metall., 1985, 33, 1735.

11) Maksimova E.L., Shvindlerman L.S. and Straumal B.B.: Acta metall., 1988, 36, 1573.
12) Maksimova E.L., Rabkin E.I., Shvindlerman L.S. and Straumal B.B.: Acta metall., 1989, 37, 1995.
13) Aleshin A.N., Prokofjev S.I. and Shvindlerman L.S.: Scripta metall., 1985, 19, 1135.
14) Hsieh T.E. and Balluffi R.W.: Acta metall., 1989, 37, 2133.
15) de Gennes P.G.: Rev. Mod. Phys.: 1985, 57, 827.
16) Rabkin E. I., Shvindlerman L.S. and Straumal B.B.: J. Less - Common Met., 1990, 158, 23.
17) Rabkin E. I., Shvindlerman L.S. and Straumal B.B.: J. Less - Common Met., 1990, 159, 43.
18) Rabkin E.I, Semenov V.N., Shvindlerman L.S. and Straumal B.B.: Acta metall. mater.,1991, 39, 627.
19) Noskovich O.I., Rabkin E.I., Semenov V.N., Shvindlerman L.S. and Straumal B.B.: Acta metall. mater., 1991, 39, 3091.
20) Straumal B.B., Noskovich O.I., Shvindlerman L.S., Semenov V.N., Gust W. and Predel B.: Acta metall. mater., 1992, 40, 795.
21) Shvindlerman L.S., Lojkowski W., Rabkin E.I. and Straumal B.B.: J. Physique Colloq., 1982, C1, 51, 629.
22) Binary Alloy Phase Diagrams, edited by T.B.Massalski, H.Okamoto, P.R.Subramanian and L.Kacprzak, Second Edition (ASM International, Materials Park, Ohio) 1990.
23) Nishizawa T., Hasebe M. and Ko M.: Acta metall., 1979, 27, 817.

DISCUSSION

Philibert, J.

Q Your results remind me some studies performed a long time ago in Professor Lacombe's laboratory on the grain boundary diffusion of gallium in aluminium. Do you think the processes observed in Al–Ga system are identical to yours?

Shvindlerman, L. S.

A Thank you for a nice question. Indeed, the Al–Ga system is one of the oldest and may be the most famous between the liquid metals wetted systems. Of course, the wetting by liquid metal is necessary for the premelting phase transition. There is no premelting phase transition without wetting one, as I mentioned above.

Danielewski, M.

Q Have you measured the effect of pressure on the phase equilibrium at interfaces? What do you expect from the present state of knowledge?

Shvindlerman, L. S.

A We measured the effect of high hydrostatic pressure in the center of High Pressure of Polish Academy of Sciences in collaboration with Dr W. Lojkowski. These measurements give us, particularly, the excess of volume of the premelting layer.

Kikuchi, R.

C In the paper, Kikuchi, R., and Cahn, J. W.: *Phys. Rev.* B, 1980, 21, 1893, we calculated the structure of a $\Sigma 5$ coincident boundary in 2-D. We found this grain boundary makes a gradual transition from the low temperature structure to a high temperature structure at around a half of the bulk melting temperature. In the high–T regime the grain boundary widens and the center region approaches the liquid state.

Shvindlerman, L. S.

A There may be two reasons for such disagreements. (Kikuchi, R.: I thought my calculation supports the author's experiments.) First the grain boundary studied in your work was a coincidence grain boundary. In a real experiment it is principally impossible to reproduce exact coincidence boundaries. In our experiments the boundaries were near to the special (coincidence) misorientation. The structure of such grain boundaries is different from the structure of a special boundary. Then the phase transition in the exact special boundary may be different from that in the near special boundary. Second, the type of phase transition in the computer simulation may be determined by the theoretical and calculational approach. Anyway the type of phase transition should be determined by experiments.