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GRAIN BOUNDARIES: PHASE TRANSITIONS AND CRITICAL PHENOMENA

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ABSTRACT

Recent achievements in the investigation of grain boundary phase transitions are reviewed and results of experiments on the grain boundary roughening transition, the "special grain boundary-random grain boundary" phase transition, the prewetting and the premelting phase transition on grain boundaries are presented. Various types of grain boundary phase diagrams are constructed. The directions of possible further progress in that area are discussed.

1. INTRODUCTION

The problem of phase transitions on grain boundaries (**GBs**) always attracted great attention of specialists in materials science. Such interest has two main sources. Firstly, the progress in research of free surfaces stimulates analogous investigations on grain boundaries. Phase transitions on surfaces of solids are well-established and that area is now under intensive investigation [1,2]. Secondly, the problem of grain boundary phase transitions (**GBPTs**) is of a great practical importance, because in many cases GBs define the mechanical, electrical and magnetical properties of a polycrystal. Excellent review papers of Cahn [3] and Rottman [4] illustrate such interest. In the paper of Rottman [4], published in 1988, one can find a transparent classification of possible types of GBPTs as well as the critical review of experimental data known to that date. So in the present contribution we will mainly emphasize the progress in GBPT investigations achieved in the last four years.

2. GB MELTING

In a number of works where the molecular dynamics technique was employed for modelling of high temperature behavior of GBs (see [4] for review) it was found that GBs melt below the bulk melting point. For a quantitative characterization of a thermal disorder the order parameter is usually employed [5]:

$$\rho_j(\mathbf{k}) = \frac{1}{N_j} \sum_l \langle \mathrm{Re}\{\exp(i\mathbf{k}\mathbf{r}_l)\} \rangle \qquad (1)$$

where r is the coordinate of atom l, k is the fixed vector of reciprocal lattice, the angular brackets denote averaging over all generated trajectories and N is the total number of atoms in a selected part of a sample. Vanishing of the ρ value means that a corresponding part of a crystal is melted and a long-range order in atoms distribution is absent. In all works mentioned simple pairwise interatomic potentials were used. However, such ordinary potentials describe adequately only the crystals of inert gases. In real metals a significant contribution to the pairwise interactions is made by the conduction electrons. Presently the most advanced potential taking into account this contribution is the embedded-atom potential. It is widely employed for simulation of defects in metals [6]. This potential was used for an investigation of high-temperature behavior of an [001] Σ29 twist boundary in Cu [7] (here Σ is the inverse density of coincidence sites). It appeared that up to $T = 0.94T_m$ the order parameter was of a non-zero value in all atomic planes adjacent to the boundary. T is the absolute temperature and T_m is the bulk melting temperature. It was the first work where the embedded-atom potential was used, and the Σ29 boundary is a large-angle boundary possessing high surface tension. It has been concluded that the GB melting does not occur.

Recently Hsieh and Balluffi [8] tried to demonstrate a GB melting experimentally. In bicrystals of Al containing the tilt boundaries [001] Σ13(015), Σ17(014), and a random 45° [001] twist boundary delocalization of the secondary GB dislocation (**SGBD**) cores up to $T = 0.96T_m$ was not observed. Moreover, the aluminum foil was heated in the microscope column so that a part of it was melted. At this stage liquid Al was observed at the GBs in the unmelted part up to about 15 μm from the solid-liquid interface. Estimates made using the thermal conductivity equation demonstrated the fact that in this portion of the foil the temperature differed from the melting temperature by not more than 1°. Based on this the authors [8] concluded that the GBs in aluminum do not melt up to $0.999T_m$ although the boundaries are wetted by their own melt at $T = T_m$.

So the results of recent "computer" and "real" experiments give no evidence of GB melting below T_m in pure metals. One can come to the same conclusion considering the recent results in theory of crystal/melt interphase boundaries. It was shown [9] that the real width of this interphase boundary is approximately 4-5 interatomic spacings, so a liquid layer up to 8-10 lattice parameter thick would have a non-zero value for the order parameter in the boundary plane due to the disturbing influence of the adjacent crystalline grains. Based on the above arguments one can imagine the following scenario of GB melting (as confirmed by [5,7,8]): As the temperature increases the order parameter ρ in the boundary plane decreases monotonically and goes to zero as $T \rightarrow T_m$. At that temperature complete wetting of a boundary by its own melt is observed.

3. GB FACETING TRANSITION

It is known that special GBs of arbitrary orientation may be faceted, that is, they may be divided into planar sections with a special orientation. According to Cahn [3], each such section may be treated as a different GB phase with different values of the intensive thermodynamic parameter n (orientation). A similar phenomenon is observed also on the surface of solids. Many single crystals are of a faceted shape with flat sections corresponding to low index crystalline planes which possess particularly low surface tension. For a small deviation of a plane orientation from a low index orientation, steps occur on the surface and the energetically favorable orientation is partially conserved. In this case, however, the surface tension increases by a value proportional to the free energy of steps and their density (if the interaction between the steps is neglected). With increasing temperature the contribution of the steps to the entropy increases and at some temperature a formation of steps may become energetically favorable. Their spontaneous formation begins, and about every surface atom can be considered as being in a step. All the characteristic sizes in this process are in the order of interatomic distances. Transformation of an atomically flat surface into an atomically rough one occurs: that is, a roughening phase transition takes place. It is obvious from the above that the surface tension of the rough surface will vary smoothly with orientation and a crystal surface, corresponding to such orientations, must to be of a rounded (non-faceted) shape.

In principle, the same phenomenon may also be assumed to occur on GBs. With increasing temperature the boundary may become unstable with respect to the introduction of steps and transform into an atomically rough one. The surface tension of such a boundary will vary smoothly with orientation, and macroscopically the transition is manifested in defaceting. The boundary

becomes flat but somewhat diffuse. According to Rottman's classification [4], such a transition, followed by the disappearance of cusps on the surface tension vs n curve, should be of second order. For low-angle GBs such GBPTs have been predicted theoretically [10] but have never been observed experimentally. For large-angle GBs such an experiment has recently been performed by Hsieh and Balluffi [11]. In that work asymmetrical $\Sigma 3$ <111> tilt boundaries in gold and aluminum and an asymmetric $\Sigma 11$ boundary in aluminum were obtained. At room temperature all the boundaries possessed a clearly defined facet structure. A direct observation of the boundaries on heating inside an electron microscope demonstrated that with a temperature increase the facets gradually became diffused and at a high temperature the boundaries became flat. As temperature decreased the boundaries resumed their faceted structure again.

Note also that the reversible faceting/defaceting of a GB in a copper film was observed under saturation/evaporation of bismuth [12].

4. "SPECIAL GB- RANDOM GB" PHASE TRANSITION

Analogous to the fact that for a temperature increase the characteristic cusps at the preferred GB orientations n disappear, the cusps in misorientation space, corresponding to low values of Σ, may also vanish. A set of experimental data on the structure and properties of symmetrical [001] GBs in cubic lattices from the literature was analyzed, and T- θ phase diagrams were plotted, where θ is the tilt angle [13]. It was shown that the region of existence of GBs with special properties in T-θ space decreases as the Σ value increases, and at each temperature there exists a maximal Σ value above which GB properties vary monotonically with θ. That concept was successfully applied to the interpretation of observed changes in the mobility and surface tension of symmetrical [001] tilt GBs in tin with the misorientation angles near the coincidence misorientation $\Sigma 17$ [14,15]. In Fig.1 the corresponding T-θ phase diagram is shown. Sharp changes in the temperature dependence of GB surface tension and discontinuities in the temperature dependence of GB mobility indicate that the transformation of special GBs to GBs with the properties of random boundaries proceeds like a first-order phase transition. This is an interesting result showing that at high temperatures there should be breaks in the dependence of GB surface tension on misorientation θ (Fig.2) separating regions of special GBs from random ones. Such breaks have not been observed in computer calculations of GB energy, but this may be a resolution effect. Because the structural unit model [16] predicts the gradual change of GB energy vs misorientation angle for [001] tilt GBs, the validity of that model at high temperatures is rather doubtful.

It should be noted that there exists a strong analogy between the GBPT under consideration and the GB roughening transition discussed above. Steps which are responsible for GB roughening should have the size of the coincidence site lattice (**CSL**) because this is the only natural periodicity of the GB structure. It follows from the geometrical theory of GB structure that the steps of the unit vector of the displacement shift complete (**DSC**) lattice are associated with SGBDs, which are the characteristic feature of a special GB structure. So SGBDs may be considered as defects which lead to the roughening of the special GB structure and its transformation into of a random one. Due to the fact that a long-range elastic field is associated with the SGBDs, such transformations 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 lattice increases while the period of the DSC lattice decreases. So at high Σ "DSC-roughening" should precede the "CSL roughening". Since the CSL lattice is a sublattice of a DSC lattice, the GB which is rough in the "DSC sense" is also rough in the "CSL sense". So at relatively high Σ the cusps associated with the orientation n and misorientation θ should disappear simultaneously with a temperature increase. However, at low Σ the "CSL roughening" may precede the "DSC roughening". So on low-Σ special GBs the sequence of two GBPTs may take place as the temperature increases: The first phase transition is associated with orientation cusp vanishing and the second one with the misorientation cusp vanishing. The unusual results of [17], where the GB diffusion and surface tension of near-$\Sigma 5$ tilt GBs in Cu were studied may be explained by such concept.

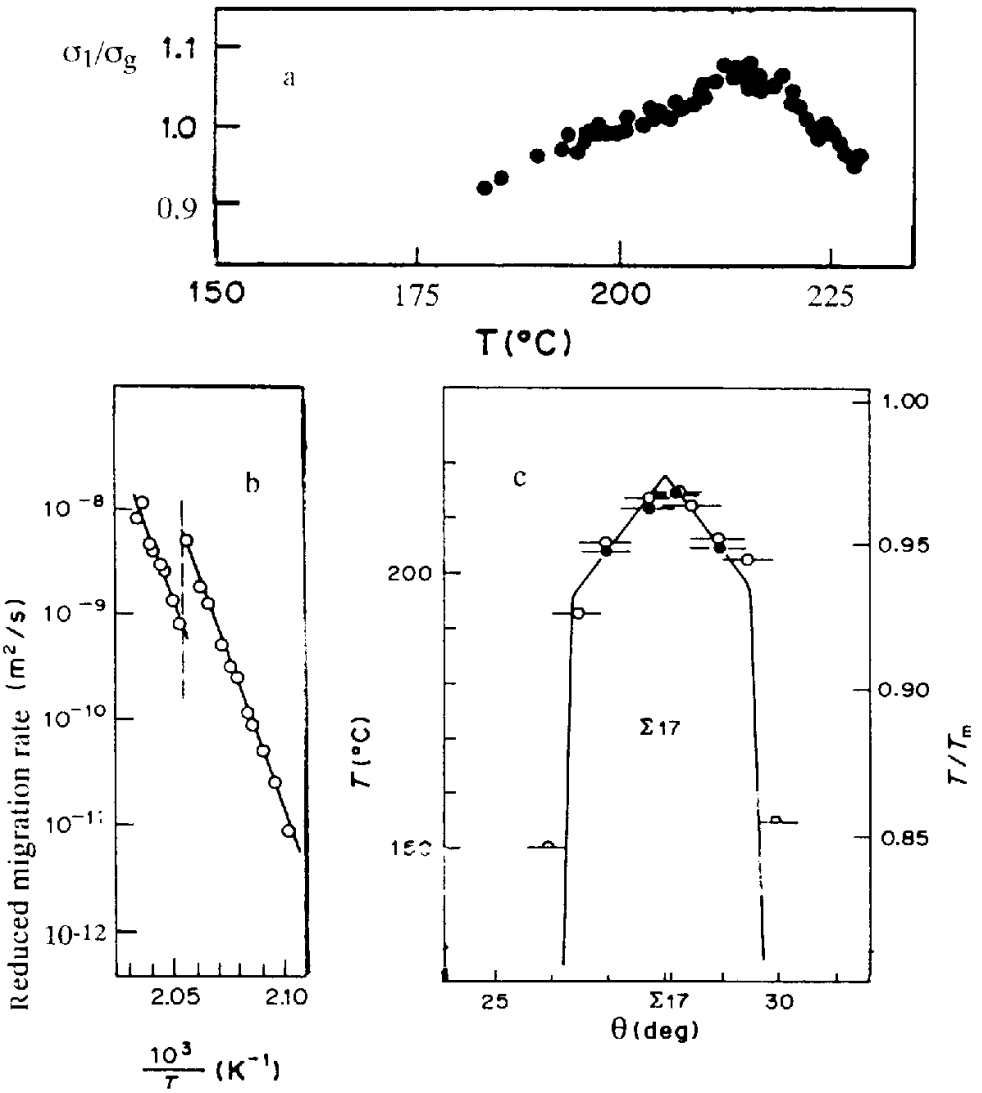

Fig.1. (**a**) The temperature dependence of the ratio σ_1/σ_g, where σ_1 is the surface tension of near-Σ17 special GB and σ_g is the surface tension of a random GB in Sn. (**b**) The temperature dependence of the migration rate of near-Σ17 special GB in Sn. (**c**) Phase diagram for a special Σ17 GB in Sn in the coordinates "temperature-misorientation". Inside the dome-like curve GBs posess special properties. o - migration data, o - surface tension data.

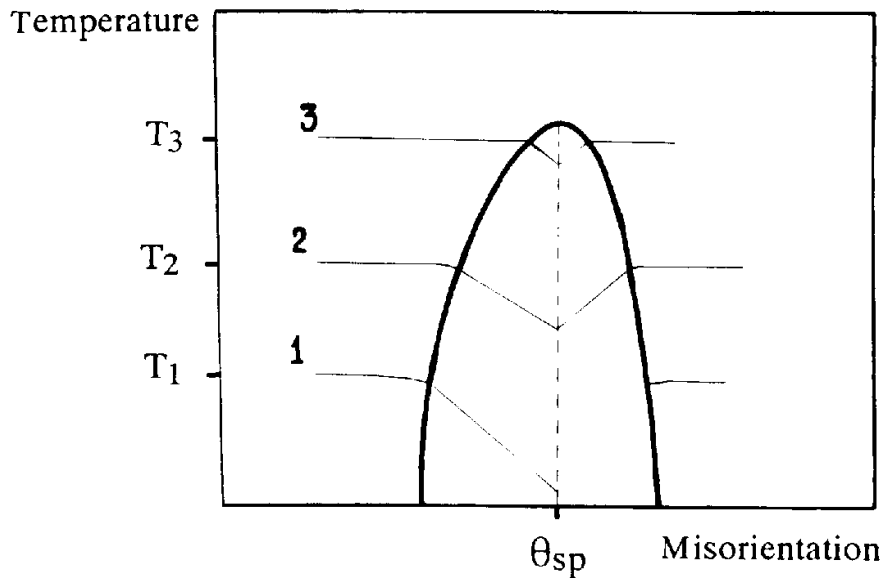

Fig.2. Schematic dependence of GB surface tesion vs misorientation angle according to data from [14]. θ_{sp} is the misorientation angle corresponding to special GB structure.

5. GB PREMELTING AND PREWETTING IN ALLOYS

It was pointed out by Cahn [3] that, when the critical consolution point of two phases is approached, GBs of one critical phase should be wetted by the layer of another critical phase, and in the one-phase region of a phase diagram there should be a singularity connected with an abrupt transition to a microscopic wetting layer. In our further consideration we will distinguish two possible situations: the first one, when a layer of new phase is formed on the GB (prewetting transition), and the second one, when the GB is replaced by the layer of a new phase (premelting phase transition) (Fig.3). 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 GBs in the Sn-In system [18,19]. 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 model of the prewetting transition shown in Fig.3, assuming that the diffusion path is strictly two-dimensional.

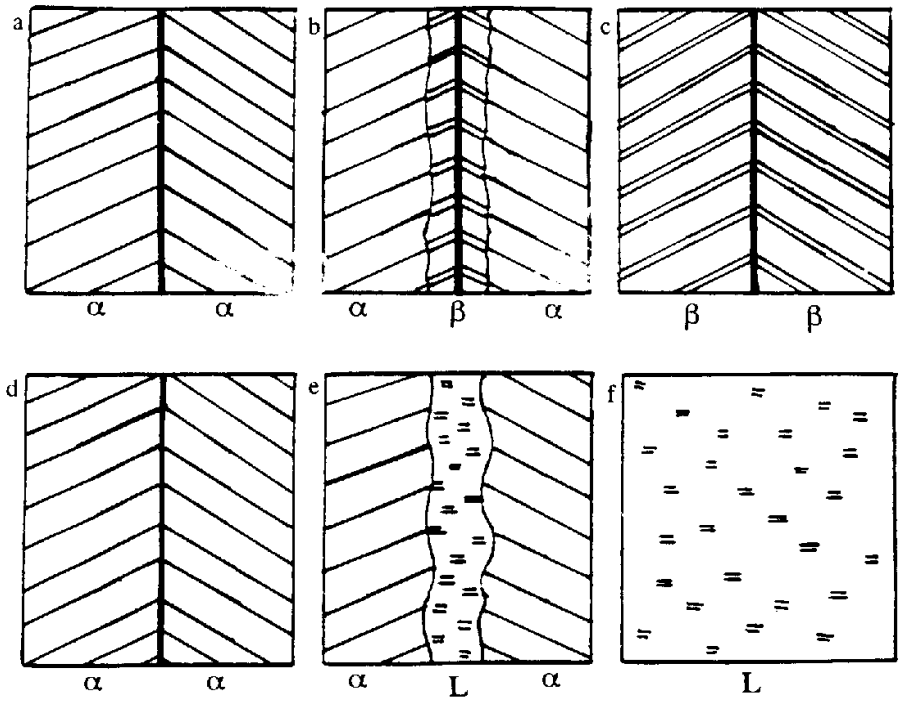

Fig.3.(**a-c**) Prewetting transition. (**a**) A GB in α - phase. (**b**) A GB in the thin quasi-β layer between two α-crystals near the bulk α–β transition. (**c**) A GB in the β–phase. (**d-f**) Premelting transition. (**d**) A GB in the α - phase. (**e**) Thin liquid layer (L) between two α - crystals near the solid-liquid coexi-stence line. (**f**) The liquid at $T>T_m$.

In [20-24] the premelting transition has been revealed in the ternary Fe-Si-Zn system during a study of Zn diffusion along tilt GBs in Fe-Si alloys. It was found that the penetration profiles of Zn along GBs in Fisher coordinates (log c_b vs y, where c_b is the Zn concentration at the GB and y is distance) consist of two sections, one with a small slope at high Zn concentrations and one with a large slope at low Zn concentrations (Fig.4). The transition from one type of behavior to the other was found to occur at a definite Zn concentration c_{bl} at the GB , which is an equilibrium characteristic of a GB and depends on the temperature. The ratio of the GB diffusivities in the two regions was approximately 10^2 which is an indication of a quasiliquid layer present in the GBs at high Zn concentration. The dependencies of c_{bl} upon temperature (GB phase diagrams) have been determined for alloys with different Si contents. Let us summarize the main features of these diagrams.

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) (Fig.5). The nature of that peak is connected with the fact that in the Fe-Zn system the "virtual" critical point of solid solution decomposition lies only slightly above the peritectic temperature. It was shown [20] that

the concentration c_{bt} at which a GBPT occurs depends on the GB surface tension σ_{gb} and the surface tension σ_{cm} of "crystal-melt" interface according to following expression:

$$c_{bt} = c_s - \frac{(\sigma_{gb}-2\sigma_{cm})^{(n+1)/n}}{b(Wn)^{1/n}(1+n^{-1})^{(n+1)/n}} \quad . \qquad (2)$$

Here c_s is the solubility limit of Zn in the alloy, W and n are the constants describing the repulsive interaction between two "crystal-melt" interfaces, and b is a constant which may be determined from the thermodynamic data describing the ternary Fe-Si-Zn alloys. In the vicinity of the critical point, σ_{cm} decreases rapidly, and according to equation (2), c_{bt} also decreases.

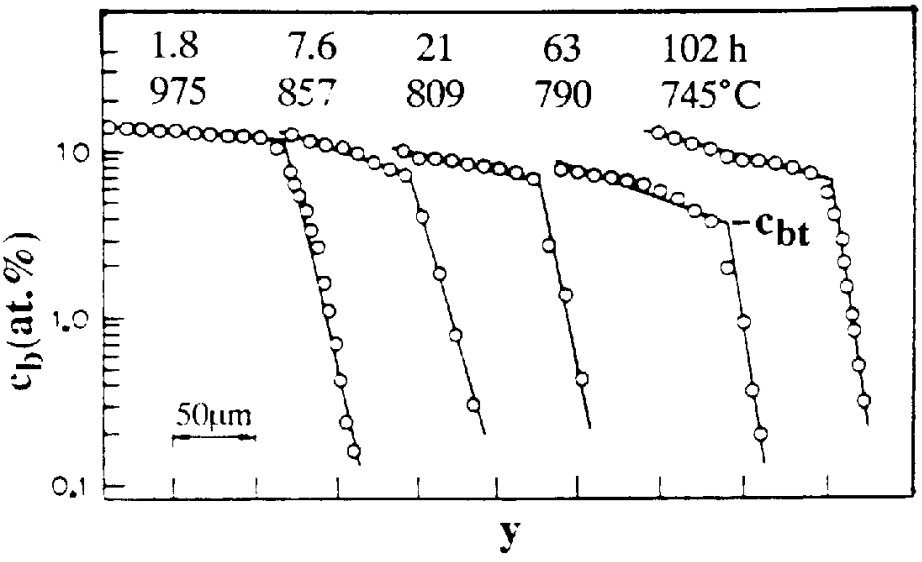

Fig.4. The dependencies of zinc concentration c_b on GBs, on the depth y for different temperatures. At concentration c_{bt} the value of GB diffusivity changes abruptly.

2. In an 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 (Fig.5). Such effects are often observed at the intersection of the line of a second-order phase transition with the line of a first-order phase transition [25]. This can be illustrated within the framework of a simple thermodynamical theory [26]. In alloys containing 10 and 12 at.% Si the Curie temperature is below the temperature interval studied and such peaks have not been observed. All of the above may be illustrated by a three-dimensional GB phase diagram having the coordinates "temperature - Zn concentration - Si concentration" (Fig.6). Such a diagram looks like a two-dimensional surface below which (at low Zn concentrations) GBs with low zinc adsorption are stable, and above which GBs exist in a premelted state. Two channels are clearly seen on that surface. The first at constant temperature is associated with the peritectic temperature, and the second, which is bent in direction of low temperatures is associated with the "ferromagnetic-paramagnetic" transition.

3. Below the Curie point for the Fe-5 at.% Si alloy the premelting line is very close to the bulk solubility limit line, and below the atomic ordering A2-B2 temperature in an alloy containing 12 at.% Si the complete wetting of the GB by the zinc-rich melt disappears simultaneously with the GB premelting phase transition. So it may be concluded that atomic and spin ordering shortens the region of stability of a GB in a premelted state. 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. The origin of such contribution is an attraction of two ferromagnetic fragments divided by the paramagnetic premelting layer along the GB. In the case of atomic ordering A2-B2 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 the premelting layer with a liquid-like structure is more disordered than the GB, such a contribution should be greater for a premelting layer and it looses its stability in bulk ordered state.

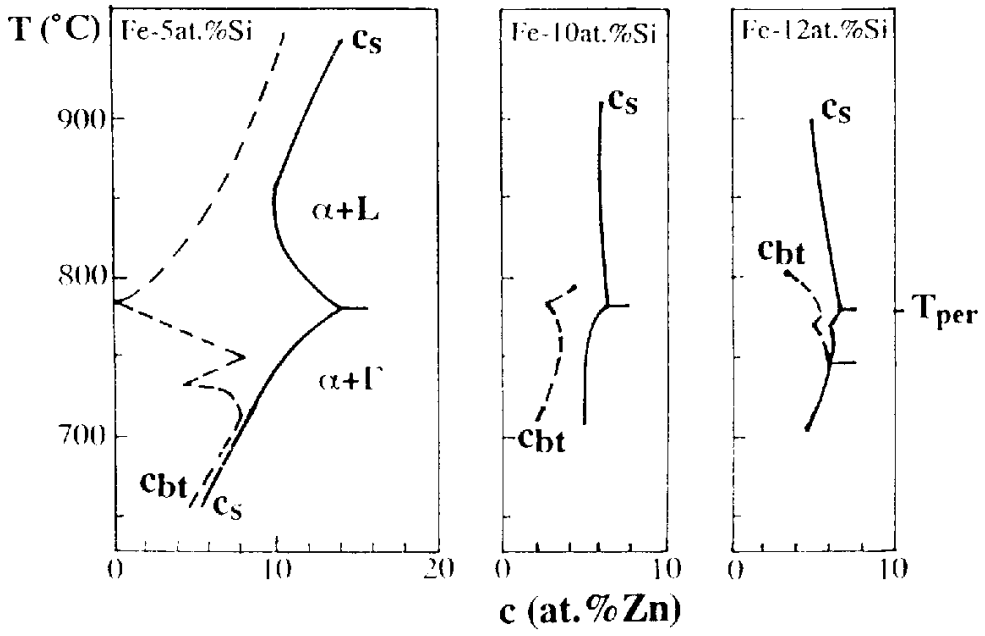

Fig.5. Fe-Zn-Si phase diagrams for alloys with different Si contents: (**a**) 5%, (**b**) 10%, (**c**) 12%. c_{bt} is the concentration at which the GB diffusivity changes dramatically (premelting phase transition). c_s is the bulk solubility limit of Zn is the Fe-Si alloys, T_{per} - peritectic temperature of binary Fe-Zn system.

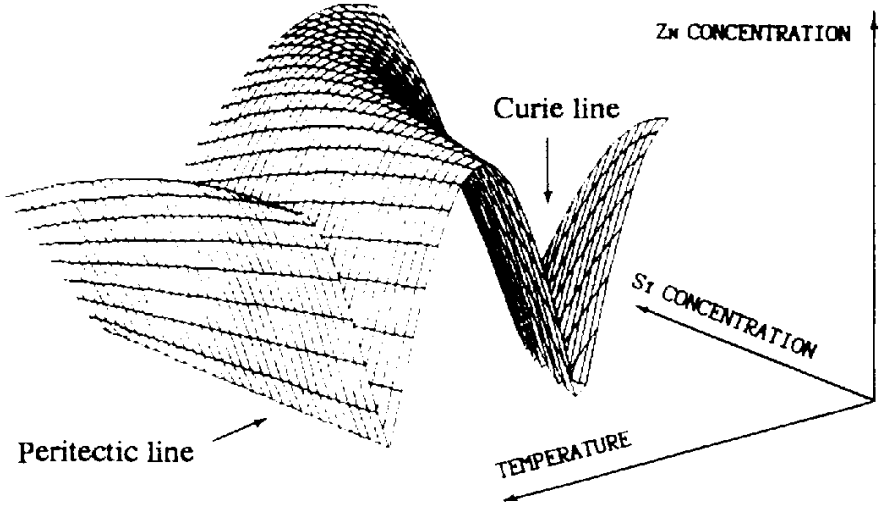

Fig.6. Two-dimesional GB premelting surface in "Zn concentration - Si concentration - temperature" space.

4. It was shown [23] that when hydrostatic pressure is increased the region of stability of the premelting layer on a GB decreases and at some critical pressure p_w one can observe the transition from complete to incomplete wetting of a GB by the Zn-rich melt with the simultaneous disappearance of GB premelting transition. In Fig.7 a schematic three-dimensional GB phase diagram in coordinates "temperature-Zn concentration-pressure" is shown in two sections, at p=0 (isobaric) and at T=905 °C for different pressures (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. It was shown [24] that the difference in excess volumes of premelted and "ordinary" GBs is higher near the peritectic temperature. This is summarized in the three-dimensional GB phase diagram in the coordinates "temperature-Zn concentration-pressure" (Fig.8). As in the case for Fig.6, below this two-dimensional GB premelting surface (at low Zn concentrations) GBs with low zinc adsorption are stable; above it GBs exists in a premelted state. Isothermal (T=const) sections of this surface look like straight lines with the slope determined by the difference in excess volumes of two GB phases. It is clearly seen that in the vicinity of the peritectic temperature the slope has the highest value.

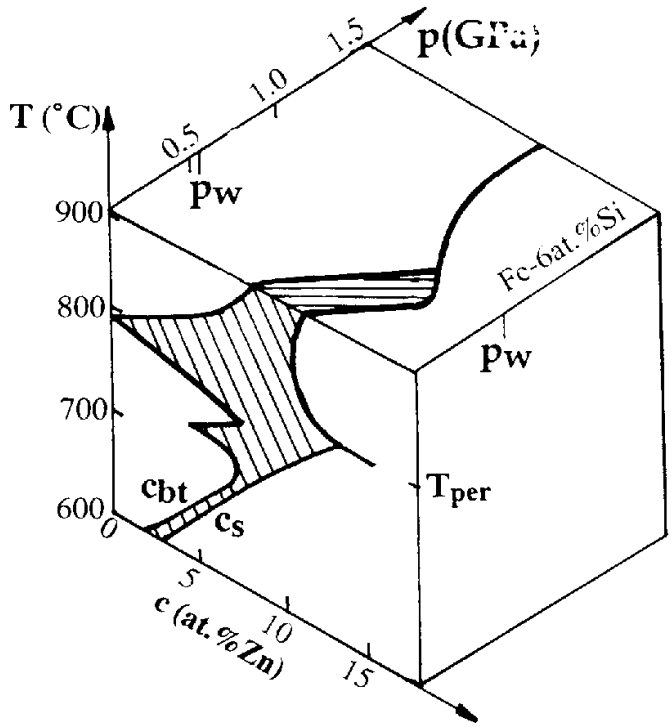

Fig.7. Three-dimensional phase diagram on which the locations of the bulk solubility limit of Zn (c_s) and the concentrations of the premelting transitions on GBs, c_{bt}, are shown [23].

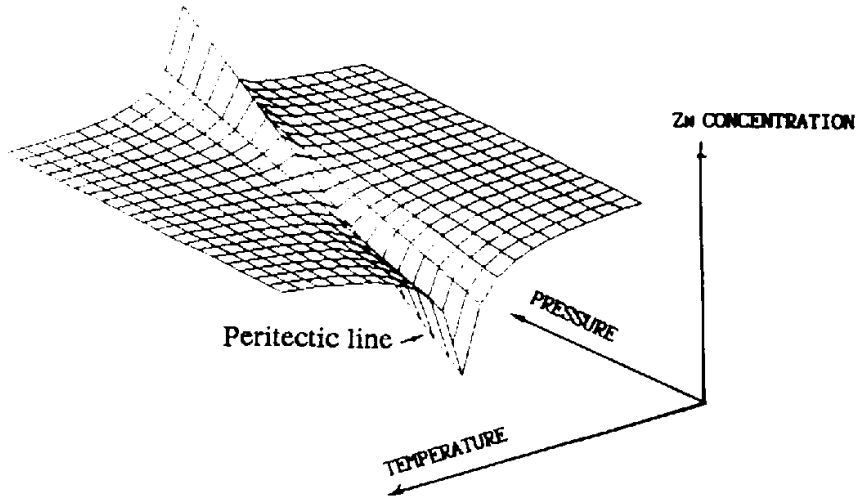

Fig.8. Two-dimesional GB premelting surface in "Zn concentration - pressure - temperature" space.

6. SOME IDEAS REGARDING FUTURE DIRECTIONS OF RESEARCH

1. More detailed investigations of the GB wetting transition and complete wetting by the melt. In spite of 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 (recently it was shown for Cu(In) [27] that the GB wetting transition temperature is higher for GBs with low surface tension)? What is the order of the wetting transition? What is the order determined by? For example, to determine the order of the wetting transition, it is necessary to measure the temperature dependence of the angle Φ at the tip of a GB groove accurately in a narrow temperature range below the wetting transition temperature T_w. This dependence is continuous both for first- and second-order phase transitions. They can be distinguished only by the power of the law correlating Φ 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 GBs the CSL roughening can precede for the DSC, then there should be a temperature interval in which the cusp in GB energy vs orientation is absent, and the cusp in energy vs misorientation 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 an upward curvature of an Arrhenius plot for GB mobility.

3. As we have already seen, there exist many types of GBPTs, 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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