

GRAIN BOUNDARY DIFFUSION AND GRAIN BOUNDARY PHASE TRANSFORMATIONS

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Abstract

Grain boundary phase transformation can be divided into two large classes - peculiar grain boundary transformations, which do not involve the bulk of the crystal, and phase transformations, which demonstrate at grain boundaries some behaviour, different from that in the bulk.

The first class includes transformations "special grain boundary-general grain-boundary". Theoretical investigations and computer simulations in this area are discussed. Special attention is focussed on experimental research of these transformations and grain boundary diffusion in their vicinity.

The second class of transformations discussed comprises critical phenomena of grain boundary diffusion in the vicinity of phase transformations of the II kind /transition from ferromagnetic to paramagnetic state/, wetting and prewetting at grain and phase boundaries in the vicinity of "weak" phase transformations of I kind.

Introduction

Phase transitions on grain boundaries attract still greater attention of investigators. Computer simulation of the grain boundary structure shows that the grain boundary structure may depend both on the temperature and on the impurity content [6, 11-13, 17, 32].

The phase transition "special grain boundary - general grain boundary" was first experimentally observed in the work by Aleshin, Prokof'ev, Shvindlerman [1] during their studies of diffusion of nickel across the grain boundaries in copper in the vicinity of coincidence misorientation [5]. The possibility of special grain boundary-general grain boundary transition with varying temperature and/or misorientation angle was analyzed in detail [35]. Loikowski, Gleiter and Maurer [19] showed that the number of low energy special grain boundaries near the coincidence misorientation actually increased with decreasing temperature. Maksimova, Straumal, Shvindlerman [20, 22] experimentally constructed the region of existence of special boundaries near the coincidence misorientation $\Sigma 17$ in tin. Maksimova, Rabkin, Straumal, Shvindlerman established how the surface active impurity alters the temperature of the "special boundary-general boundary" phase transition in tin. Sickafus and Sass [36] showed experimentally that an increase of the impurity concentration in grain boundaries gives rise to a structural phase transition.

These experimental data and the computer simulation results pertain to phase transitions occurring only in grain boundaries and not followed by any phase transformations inside the grains which form the boundary. However of not less interest are the grain boundary phase transitions occurring near the bulk phase transitions. In these experiments, however, the object of the investigations, i.e. the grain boundary with definite crystallographic parameters must held. Therefore these experiments involve Kind II bulk phase transitions or Kind I "weak" transitions, close to Kind II ones, with a small thermal and bulk effect. Usually Kind I weak transitions are not accompanied by strong restructuring of the crystal-line lattice, in the process of transition the atoms are shifted by a spacing smaller than interatomic ones. These transitions may, under certain conditions, proceed like Kind II transitions, without the formation and growth of nuclei. On the external surface near weak Kind I phase transitions one may observe prewetting phenomena [5, 7].

Experimental technique. Sn-In phase diagram

In order to study the bulk phase transitions in grain boundaries, we have taken the Sn-In system. From the data [3, 14, 27] the region of the solid solution of indium in β -tin goes as far as 6-8 at. % indium with $T < 150-170^\circ\text{C}$, and between 10 and 23 at. % indium there is the γ -phase with a simple hexagonal lattice. The γ -phase is formed according to a peritectic or a peritectoid reaction from different data: 75°C [31], 250°C , 224°C [14, 27]. The width of the tin-base solid solution region, cited in these works, is unusually large: in the other tin-base

systems the solubility limit drops rapidly at temperatures below 170-150°C and does not exceed several tenths or hundredths percent [34]. Giessen [8] reports the existence at room temperature of the γ' -phase of which the homogeneity region is located on the tin-indium diagram between the γ -phase and the β -tin-base solid solution. The γ' -phases with analogous structure exist in the indium-bismuth and tellium-tin systems as well [8], and the γ -phases in the mercury-tin and cadmium-tin systems [33]. The position of the γ -phases on binary diagrams of B-metals is determined by their electron concentration (3,9 electron/atom). A simple hexagonal lattice of the γ -phase is formed from the β -tin structure by displacement of sublattices by a quarter-period along the C-axis [30]. In the γ' -phase lattice the same displacement occurs less than by a quarter-period along the X-axis [8], the elements of the γ' -phase crystalline lattice remain the same as in β -tin. Straumal, Klinger, Shvindlerman [37] determined the temperature dependence of the coefficient of interdiffusion in the indium-tin system within the concentration range of indium of 1-8 at. % indium. This temperature dependence exhibits two portions with different activation energy. On the high-temperature portion the activation energy agrees well with the published data on diffusion of isotopes whereas on the low-temperature portion it is approximately two times as low. A drastic change of the activation energy was not followed by a noticeable jump of the diffusion coefficient. This is a characteristic feature of the Kind II phase transition or the Kind I transition, close to Kind II.

Therefore in the first part of our work we determined more accurately the Sn-In phase diagram in the range of large concentrations of tin. For this we determined the homogeneity regions of β , γ and γ' -phases by means of an analysis of the concentration distributions in the diffusional layers, formed at interdiffusion of tin and indium.

To investigate the grain boundary properties in the vicinity of the bulk phase transition, we selected twist $\langle 001 \rangle$ boundaries. Like in the $\beta - \gamma'$ transition the atoms are displaced along the tetragonal $\langle 001 \rangle$ axis, whereas in the twist boundary plane with the $\langle 001 \rangle$ rotation axis the mutual location of the crystal-lattice sites is unchanged. Bicrystals with misorientation angles 27.6, 28.1, 29.1, 30.2 and 31.1° (+0.5°) were grown. These values of the angles are near the coincidence misorientation $\Sigma 17$. In the vicinity of the coincidence misorientation $\Sigma 17$ on tilt boundaries in tin we studied the "special grain boundary - general grain boundary" transition [20,22]. It takes place at temperatures close to melting temperatures (190-215°C), and the region of existence of $\Sigma 17$ special boundaries goes from 26 to 30°. Hence, four out of five twist boundaries are special at $T < 190^\circ\text{C}$, whereas a boundary with the misorientation angle of 31.1° is a general boundary. In order to study the behaviour of grain boundaries in the vicinity of the $\beta - \gamma'$ transition in tin indium alloys, we investigated the diffusion of indium on these twist boundaries in tin bicrystals.

Mono and bicrystals of tin were grown from tin grade 034-0000, with a nominal purity of 99.9999 at. % Sn by means

of a directed crystallization in a high-purity argon atmosphere. Special-purity graphite boats were employed for the crystal growth. The misorientation parameters were assigned by monocrystalline seed crystals in the process of growing. These seed crystals were oriented by means of a laser light source directly on an electric-spark cutting machine [28]. The indium layer was electrolytically deposited on the surface of mono- and bicrystals of tin. The layer thickness was 100-200 mkm. The diffusional anneals were conducted in a high-purity argon atmosphere in a special furnace, consisting of a thermostat and twelve small furnaces in which different temperatures were maintained [23]. The indium concentration distribution in the diffusional zones was determined by means of an electron microprobe analysis from the intensity of the InL line at an accelerating voltage of 15 kW. The coefficients of the bulk diffusion D of indium in the alloy were determined from

$$\frac{C}{C_0} = 1 - \operatorname{erf} \left(Y/2 \sqrt{Dt} \right)$$

Here C is the concentration of indium (diffusion into a semi-infinite sample via the surface with a constant concentration independent of time; Y is the distance; t is the annealing duration. The product of the grain boundary diffusion coefficient D' by the boundary width was determined by Fisher's method. The validity of utilization of Fisher's formula as an asymptotic form of Whipple's solution was analyzed by means of Le Claire's criteria (1963). The two-phase regions on the Sn-In diagram were determined by abrupt changes on the concentration curves in the zone of the interdiffusion of tin and indium.

Results

Fig. 1 presents the Sn-In diagram within the concentration range from 0 to 40 at. % indium. An analysis of one- and two-phase regions in the zones of interdiffusion of tin and indium enabled us to plot the boundaries of β , $\beta + \delta'$ and $\delta' + \delta$ regions. Also the diagram demonstrates the experimental points from the works [14,27], obtained by means of a differential thermal analysis and X-ray structural studies in a high-temperature chamber. Our data for the solidus line and the boundary of δ and $\delta + \delta'$ regions are seen to agree well with the published data. The data obtained by different authors for liquidus and eutectic are practically coincident, therefore they are shown in Fig. 1 in continuous lines. The studied portion of the Sn-In diagram exhibits similarity with the other diagrams where the solid solution disintegration followed by the formation of an intermediate phase with a wide homogeneity region is observed: iron-iridium (phase with ~ 40 at. % Ir), iron-nickel (phase FeNi₃), iron-palladium (phases FePd and FePd₃), vanadium-gallium (phase V₃Ga) [34].

Fig. 2 presents the temperature dependence of the coefficient of the interdiffusion of indium in tin for the range of indium concentrations from 2-4 to 8 %. At a temperature $T_0 =$

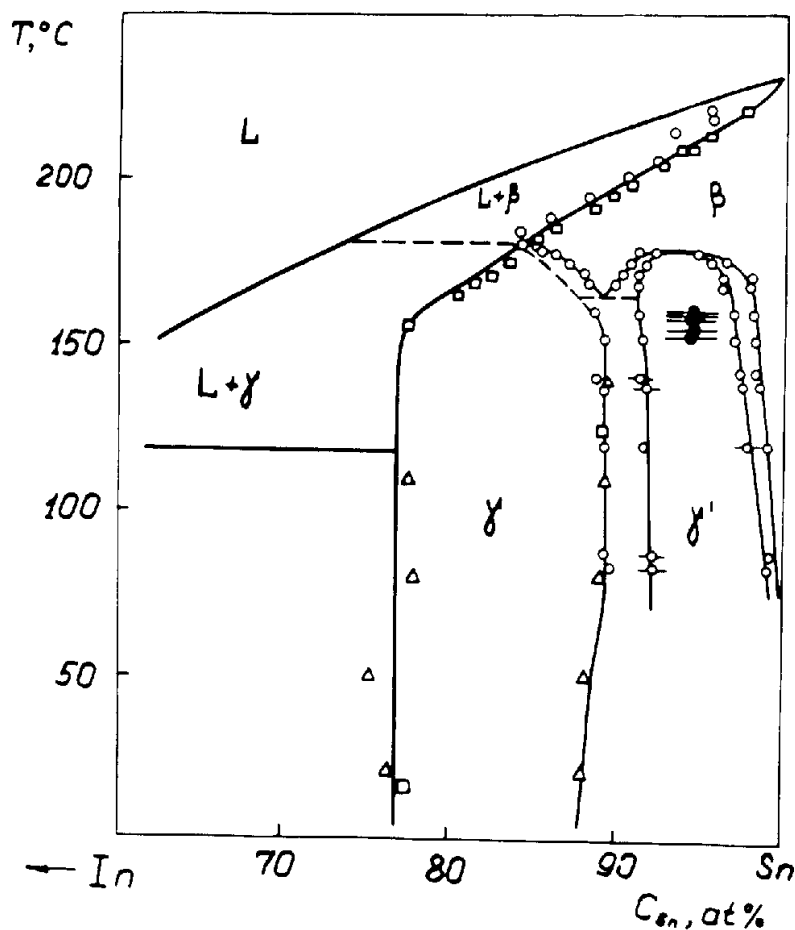


Figure 1. Portion of the Sn-In diagram. O - results of this work obtained from the concentration distribution in the region of interdiffusion of tin and indium; □ - data of differential thermal analysis (Predel, Godecke 1975); Δ - data of X-ray structural analysis in a high-temperature chamber (Heumann, Alpaut 1964); ● - β - γ' transition temperature on grain boundaries (see Figs 4,5).

$= 173.7 \pm 0.5^\circ\text{C}$ this dependence exhibits a discontinuity. Above and below T_c the diffusion coefficient obeys the Arrhenius law. The temperature T_c coincides with the temperature of the γ' -phase formation from the solid solution of indium in β -tin (see Fig. 1). As approaching T_c from the region of elevated temperatures the values of D deviate downward from the Arrhenius straight line, and as approaching T_c from the side of lower temperatures the diffusion coefficient deviates upward from the Arrhenius straight line.

Fig. 3 presents a maximal concentration of indium in grain boundaries G_0 as a function of depth in Fisher's coordi-

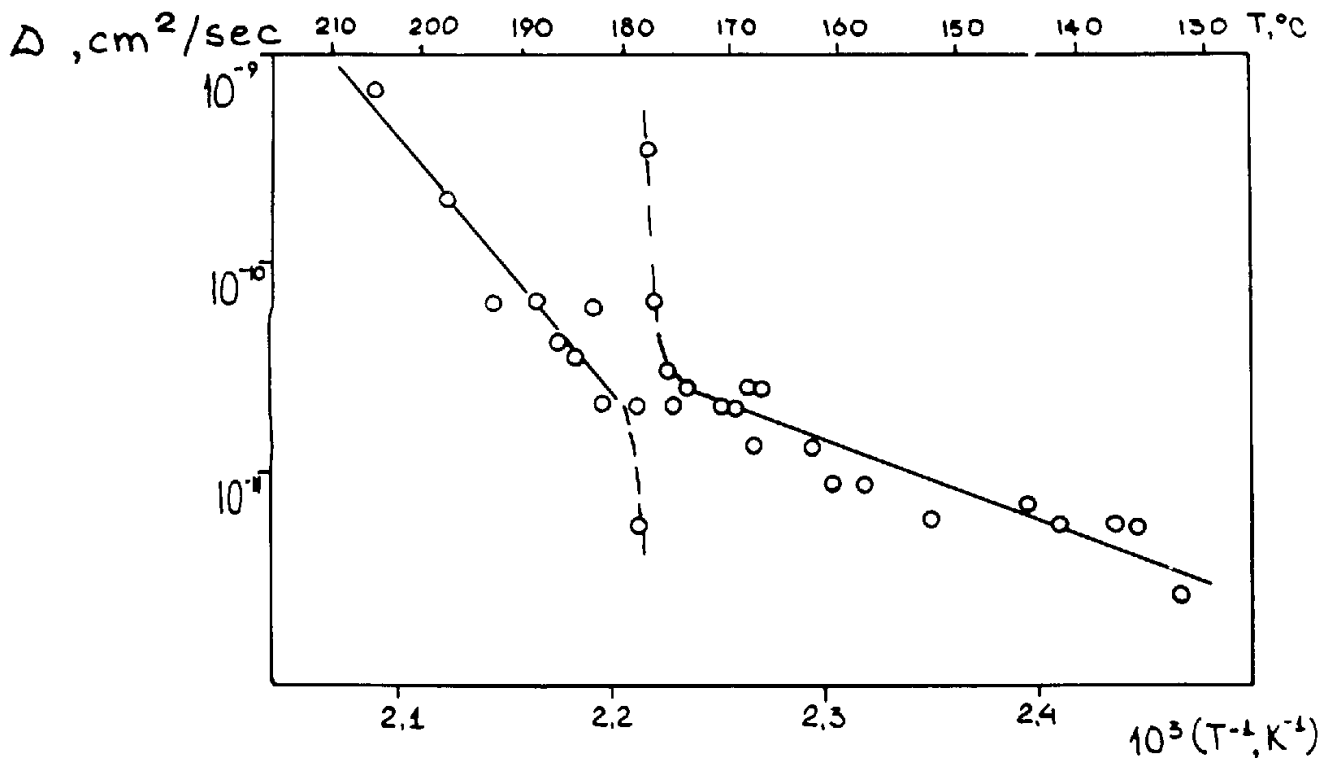


Figure 2. Temperature dependence of the bulk diffusion coefficient of indium in the concentration range from 1 to 8 at. % In. The discontinuity on the temperature dependence at T_c corresponds to the $\beta - \beta'$ transition (see Fig. 1). Deviations from the Arrhenius law near T_c are seen.

nates. All these dependences have the form of straight lines. The coefficients of the boundary diffusion, like D values for the bulk diffusion were determined in the concentration range from 2-4 to 8 at. % indium. Fig. 4 presents the temperature dependences of the product $D'\delta$ for 5 studied twist boundaries with different misorientation angles. Each of these dependences exhibits two regions: high- and low-temperature ones. At some temperature T_c^b the diffusion coefficient changes abruptly.

Temperatures T_c^b are different for different boundaries, they are by 17-25°C lower as compared with T_c for the bulk diffusion coefficient. At a temperature T_c for the bulk diffusion coefficient. At a temperature T_c of the bulk phase transition $\beta - \beta'$, where an abrupt change of D is observed, the dependences $D'\delta(\varphi)$ for grain boundaries exhibit no singularities.

Fig. 5 presents T_c^b as a function of misorientation angle of grain boundaries. It is seen that when a misorientation angle φ deviates from the coincidence misorientation

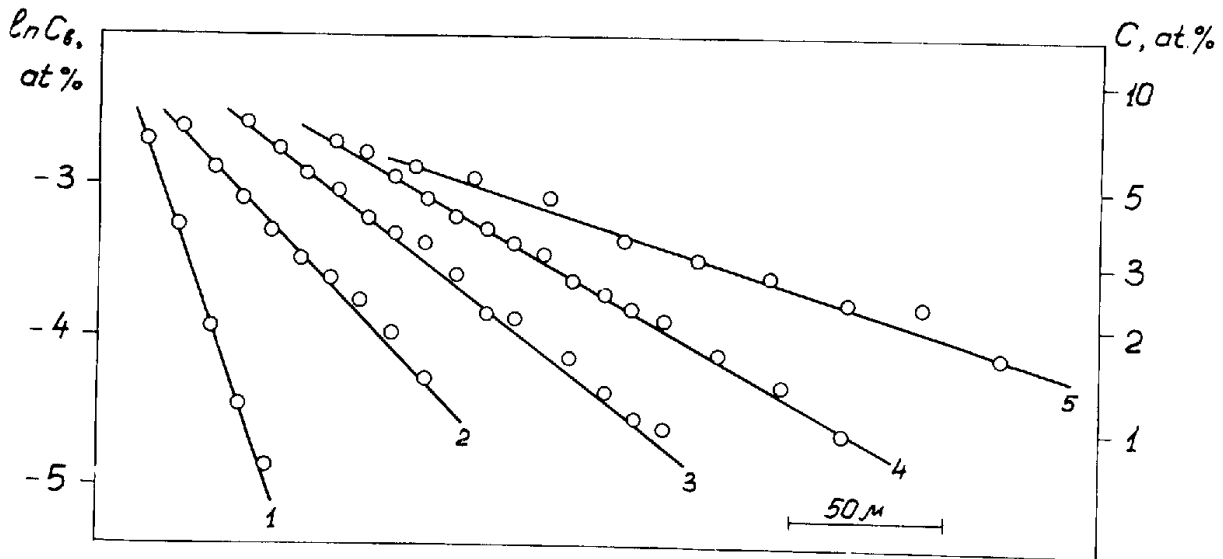


Figure 3. Logarithm of the indium concentration on the grain boundary as a function of the depth.

- | | | | |
|-----|--------------------------|-----------------------------|-----------------------|
| 1 - | $\varphi = 31.1^\circ$; | $T = 158.5^\circ\text{C}$; | $t = 160 \text{ h}$; |
| 2 - | $\varphi = 30.2^\circ$; | $T = 175.2^\circ\text{C}$; | $t = 160 \text{ h}$; |
| 3 - | $\varphi = 29.1^\circ$; | $T = 136.9^\circ\text{C}$; | $t = 122 \text{ h}$; |
| 4 - | $\varphi = 27.6^\circ$; | $T = 144.8^\circ\text{C}$; | $t = 122 \text{ h}$; |
| 5 - | $\varphi = 30.2^\circ$; | $T = 158.5^\circ\text{C}$; | $t = 160 \text{ h}$. |

$\varphi_{\Sigma 17} = 28.1^\circ$, the temperature drops. T_c^b decreases within the region of existence of special $\Sigma 17$ boundaries (Shvindlerman, Straumal 1985, Maksimova et al. 1987, 1988). Beyond this region T_c^b increases again. Fig. 5 also presents the slags of the difference between the temperatures T_c in the bulk and T_c^b on the boundaries.

Discussion

A comparison of Figs 1 and 2 shows that the formation of the γ' -phase from the β -tin-base solid solution is accompanied by the discontinuity on the temperature dependence of the bulk diffusion coefficient of indium and a decrease of the activation energy of diffusion. The discontinuities on the temperature dependences of the boundary diffusion coefficients are displaced from the bulk value of T_c towards lower temperatures, and at T_c no singularities are seen on $D^b \delta(T)$. To our opinion this suggests that the $\beta - \gamma'$ transition on the grain boundaries occurs at a lower temperature as compared with the bulk. In Fig. 1 in the homogeneity region of the bulk γ' -phase the dark points indicate the temperatures of the grain boundary $\beta - \gamma'$ transition for the boundaries studied. It follows from

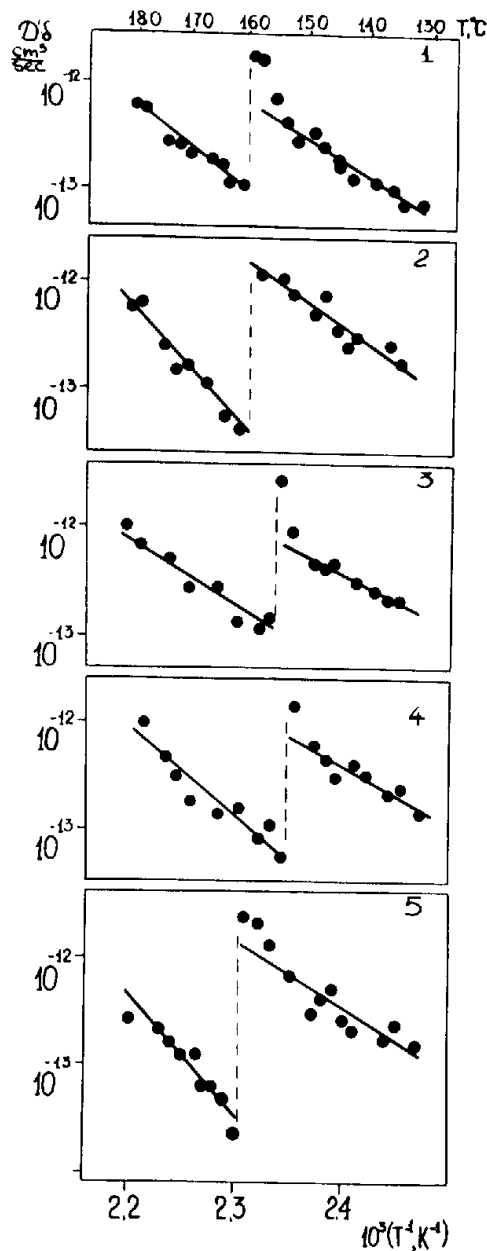


Figure 4. Temperature dependences of the product of the grain boundary diffusion of indium D' by the boundary width δ for boundaries with different misorientation angles
 1 - 28.1° ; 2 - 29.1° ;
 3 - 27.6° ; 4 - 30.2° ;
 5 - 31.1° .

the Gibbs rule for grain boundary phase transitions in two-component systems that the two-phase region $\beta + \gamma'$ is transformed to a line on the grain boundary phase diagram. In Fig. 1 these lines are drawn through each point designating the temperature of the grain boundary $\beta - \gamma'$ transition. In the studied range of concentrations the lines of the grain boundary phase equilibrium are nearly horizontal: already at a small temperature decrease (approximately by 0.5°C) the diffusion coefficient increases sharply as a result of transition from the grain boundary β -phase to the grain boundary γ' -phase. Should these lines noticeably curve, some of Fisher's straight lines (see Fig. 2) would exhibit two differently sloping portions at temperatu-

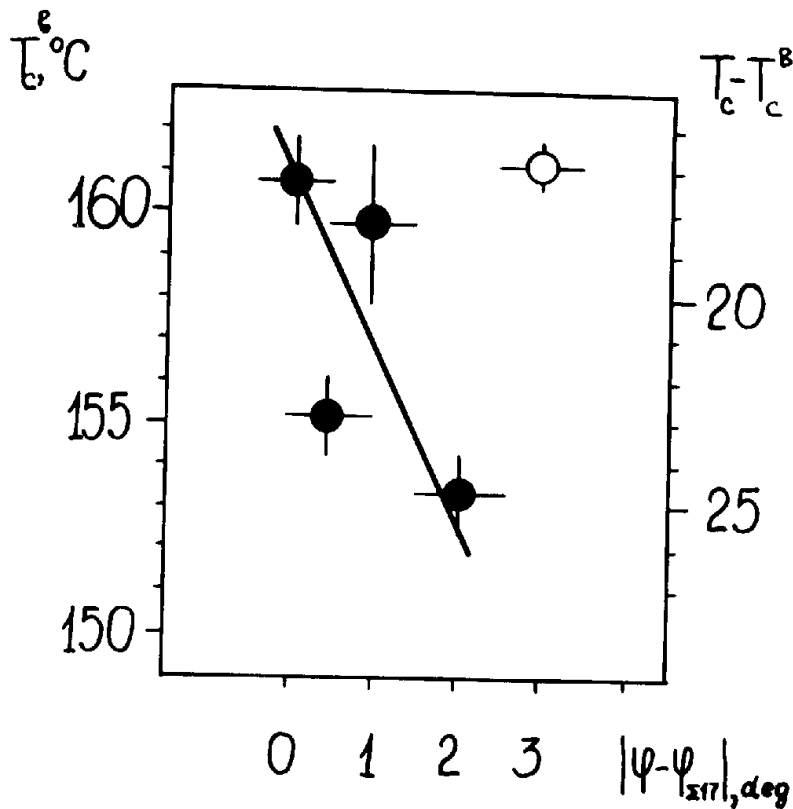


Figure 5. Dependence of the $\beta - \gamma'$ transition temperature T_c^b on the grain boundaries on the misorientation angle φ . T_c^B is the $\beta - \gamma'$ transition temperature in the bulk. ● - boundaries lying within the region of existence of special boundaries $\Sigma 17$, ○ - a general boundary, $\varphi_{\Sigma} = 28.1^\circ$ ($\Sigma 17$).

res slightly below T_c^b . So, the $\beta - \gamma'$ phase transition on grain boundaries proceeds the transition in the bulk. What is this behaviour caused by? How can one explain the observed dependence of the grain boundary transition temperature on the misorientation angle? To our opinion there is a certain analogy between the grain boundary phase transition, observed in this work, and so-called prewetting phase transition. We shall consider adsorption of liquid or gas on a solid substrate. If we are on the line of co-existence of gas and liquid of the phase p-T-diagram from the side of the gas phase and the temperature is low enough, then there is a thin layer of a liquid-like phase of a microscopic thickness l . The l value will be growing in this case. At some temperature T_w , l becomes infinite. If this growth is continuous then we are dealing with critical wetting, and if l changes abruptly at T_w from a finite value to infinity then this is Kind I wetting transition. This infinite abrupt change of the l value during the motion along the phase co-existence line at T_w is an ultimate form of abrupt changes of a finite quantity, observable in the one-phase region of the p-T-diagram. This phenomenon when the thickness l of the liquid-like layer on the substrate increases abruptly is called a prewetting transition. A phenomenological description of these transitions was first done in the work by Cahn [5]. These presentations hold for phase transitions of solids as well (see, for example the review by

Dietrich [10]). If at some temperature T_c the order-disorder transition takes place in the crystal bulk then the disordered phase wets "the crystal-vacuum" interphase as it approaches T_c . If ordering occurs as Kind I phase transition, then in this system one can observe pre-wetting transitions too. The experimental results in this field are, however, meager [2,16,24,26]. We assume that in the system in question near the bulk phase transition $\beta - \gamma'$ on the grain boundaries the β -phase can be abruptly transformed to the γ' -phase. In our discussion we shall use Cahn's presentations [5].

We shall consider a solid near a weak bulk phase transition of Kind I. We shall describe its state by means of a scalar order parameter h . The quantity $h = 0$ corresponds to a high-temperature disordered phase, and the quantity $h = h_v$ to a low-temperature phase. Let h_s be the quantity of the order parameter in the atomic layers directly adjoining the grain boundary. At a temperature lower than the bulk transition temperature T_c h_s , generally speaking, is not coincident with h_v due to disturbing action of the boundary. The corresponding contribution to the free energy of the system is given by some functional of h_s . In this presentation our problem is equivalent to Cahn's model [5]. It should only be born in mind that the h_s value is closely connected with the boundary structure. Correspondingly, any variation of h_s is connected with a boundary structure variation. Under appropriate conditions the prewetting transition occurs in this system. This transition consists in that the h_s value decreases abruptly. Fig. 6 shows schematically the phase diagram analogous to that in the work by Dietrich [10] for the gas adsorption on the substrate. It is seen that at a temperature $T_c^0 < T_c$ h_s decreases in an abrupt manner and the grain boundary structure changes.

So, already such a simple analogy suggests that phase transitions, similar from the thermodynamical view point, to prewetting transitions can occur on grain boundaries. However, the bulk phase transitions are not always preceded by the grain boundary transitions. There are two important limitations inherent in this model. Firstly, the phase transition must have a small thermal effect, that is it must be close to Kind II transition. Only in this case one can use continual approximation. Secondly, an alteration of the order parameter at the phase transition does not have to affect the mutual arrangement of crystal-lattice sites of two grains in the boundary. Only in this case the contribution of the boundary to the free energy of the system may be present by a quadratic form like in the work by Cahn [5].

Both these conditions are likely to be fulfilled for the $\beta - \gamma'$ transition in the tin-indium system. Firstly, the thermal effect of the $\beta - \gamma'$ transition is small the boundaries of the two-phase regions ($\beta + \gamma'$) were not registered by the DTA method in the works dealing with the study of the equilibrium diagram of Sn-In, and the boundary of the γ' and ($\gamma' + \beta$) regions was interpreted as a solubility limit of indium in the β -phase [27] or, else, it was not registered at all [14]. Secondly, during the $\beta - \gamma'$ transition one of the BCT-sublattices is displaced along the tetragonal C-axis at a spacing of less

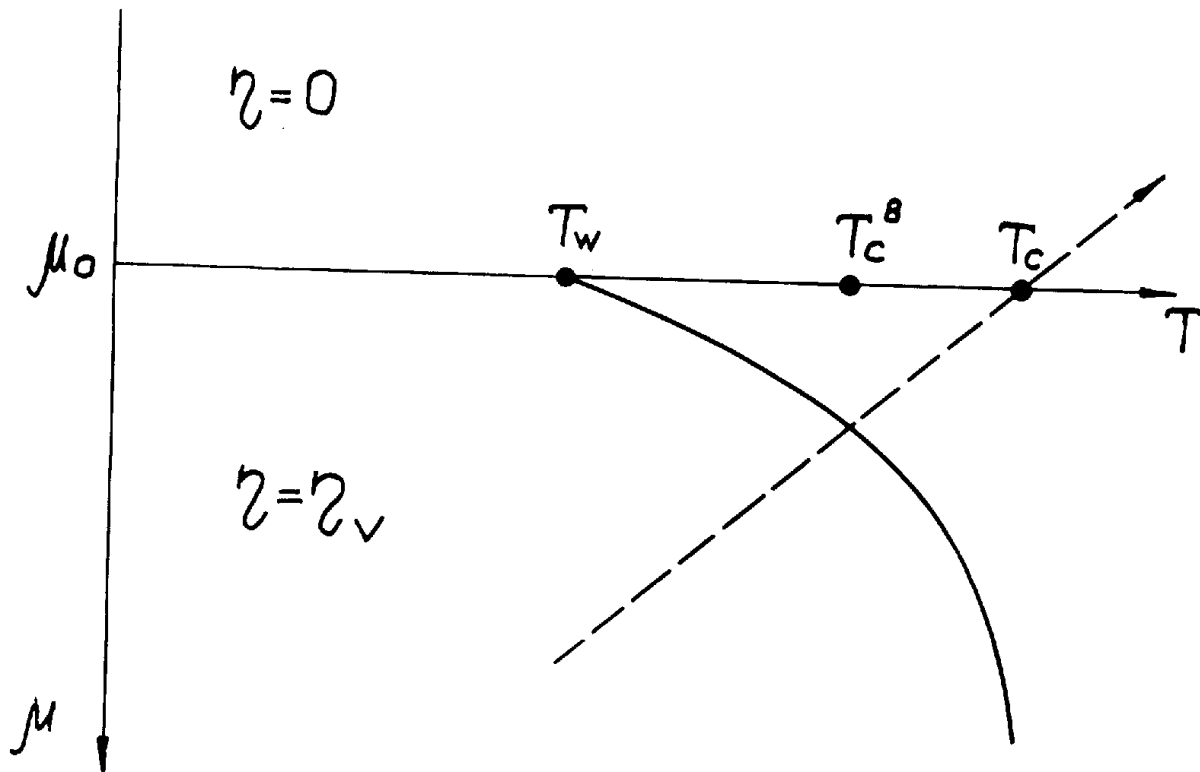


Figure 6. Schematic presentation of the μ - T phase diagram of the Sn-In system. Dashed line shows a change of the chemical potential of tin atoms with increasing temperature ($P = \text{const.}$). Temperature T_c corresponds to the β - γ' transition in the bulk, temperature T_c^b corresponds to the prewetting transition on the boundary.

than $4/C$ [8]. The plane of a twist $\langle 001 \rangle$ boundary is perpendicular to the C -axis along which these displacements occur. Therefore, during the β - γ' transition the geometry of crystal-lattice coincidence of two grains on the studied twist $\langle 001 \rangle$ boundaries does not change.

So, the observed abrupt changes on the temperature dependences of the grain boundary diffusion coefficient in the system tin-indium, observed by us, is attributed to the γ' - β transition on the boundaries, that precedes the γ' - β transition in the bulk. The small thermal effect of the transition and the geometry of the atomic displacements at the transition enable us to describe it in terms of the model analogous to that for the prewetting transition [5]. We shall consider what follows from this boundary transition model. How does the temperature T_c^b of the prewetting transition on grain boundaries have to depend on the misorientation angle of the boundaries φ in the vicinity of the coincidence misorientation φ_Σ ? How will T_c^b change on going out of the region of existence of special boundaries into the region of existence of general boundaries? It is known that at a small deviation of $\Delta\varphi$ from the coincidence misorientation φ_Σ a network of so called 'secondary grain boundary dislocations' SGBD with a period $d = b_\Sigma / 2\sin(\Delta\varphi/2)$. b_Σ being the Burgers vector of SGBD's is formed on special boundaries. We shall consider a simplest assumption that the

core structure of SGBD's corresponds to the structure of the high temperature grain boundary phase. Generally speaking, in this case, one has to solve a two-dimensional problem

$\eta = \eta(x, Y)$, we shall, however, simplify considerably the calculations by considering the prewetting phase transition only in one grain boundary phase, irrespective of the grain volume.

The thermodynamical potential of the unit volume of the grain boundary phase as a function of the order parameter has the form shown in Fig. 7. η_s is the quantity of the order parameter in the layers adjoining the low-temperature grain boundary phase. As the temperature is increased the "thermodynamical gap" Δ is decreased, and with $T = T_c^{SP}$ it vanishes. Here T_c^{SP} is the temperature of the prewetting transition on the boundary with $\varphi = \varphi_c$. With account taken of our assumption on the core structure of SGBD we minimize the functional

$$\Phi_B = \int_0^d \left\{ \frac{1}{2} m \left(\frac{\partial \eta}{\partial x} \right)^2 + \varphi(\eta) \right\} dx$$

with the boundary conditions

$$\eta(0) = \eta(d) = 0 \quad ; \quad \frac{\partial \eta}{\partial x} \Big|_{x=0} = \frac{\partial \eta}{\partial x} \Big|_{x=d} = 0$$

We approximate the $\varphi(\eta)$ function by the 4-th order polynomial

$$\varphi(\eta) = (\eta - \eta_s)^2 \left(\frac{\Delta}{\eta_s^2} + \frac{2\Delta}{\eta_s^3} \eta + \eta^2 \right)$$

We seek for the solution in the form

$$\eta(x) = \begin{cases} \frac{1}{2} \eta_s \left(1 - \cos \frac{\pi x}{h} \right) & ; \quad 0 \leq y \leq h \\ \eta_s & \quad h \leq y \leq d-h \\ \frac{1}{2} \eta_s \left(1 - \cos \frac{\pi(d-x)}{h} \right) & \quad d-h < y \leq d \end{cases}$$

After the optimization with respect to h we obtain that with

$$\Delta = (m\pi^2 \eta_s^2 + \sqrt{m^2 \pi^4 \eta_s^4 + \frac{35}{2} m \pi^2 \eta_s^6 d^2}) / 8d^2$$

the solution $\eta(x) = 0$ corresponds to a minimum of the energy. With $\Delta \varphi \rightarrow 0$ ($d \rightarrow \infty$) we have

$$\Delta T = T_c^{SP} - T_c \sim \Delta \sim d^{-2} \sim \Delta \varphi$$

So, at deviation of the misorientation angle of the grains from the coincidence misorientation φ_c by a small angle $\Delta \varphi$ the prewetting transition temperature on the boundary drops in proportion to $\Delta \varphi$. If $\Delta \varphi$ is such that the misorientation

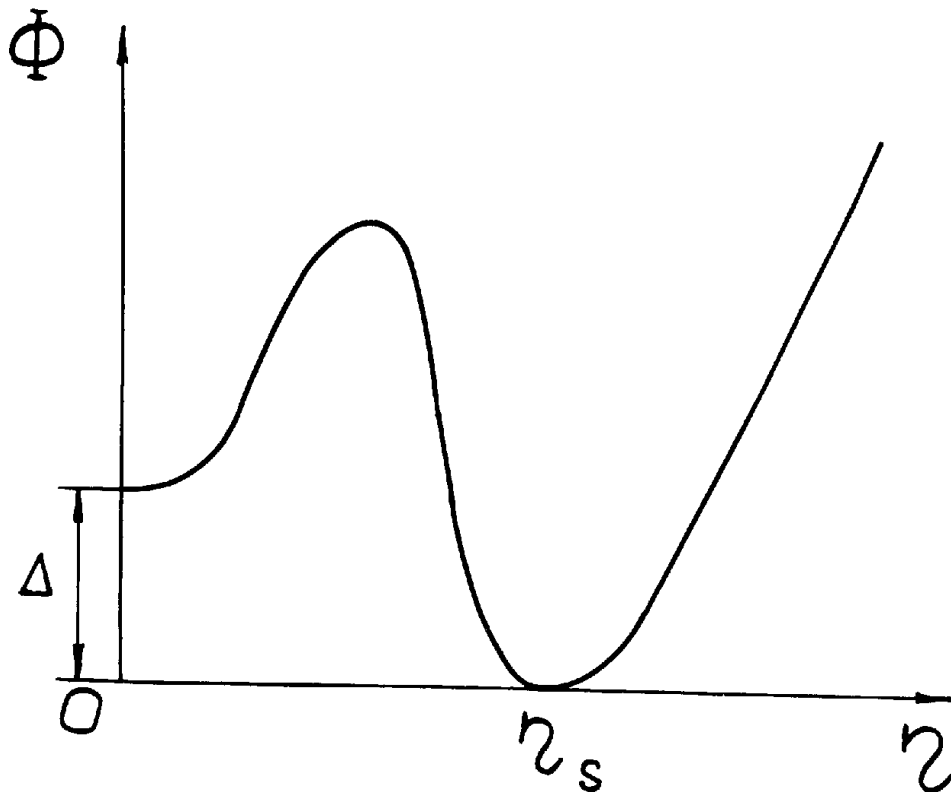


Figure 7. Schematic dependence of the volumetric density of free energy Φ for a grain boundary on the order parameter ζ . At low temperatures the disordered phase ($\zeta = 0$) is separated from the ordered phase by a "thermodynamical gap" Δ . As the temperature grows Δ decreases and vanishes at the temperature of the grain boundary phase transition on the special boundary.

angle goes beyond the limits of existence region of the given special boundary (Shvindlerman, Straumal 1985), then this boundary will no longer exhibit large inhomogeneities. The prewetting transition on such a boundary will occur at a higher temperature as compared with a special boundary with a close misorientation angle. All these explain qualitatively our experimental dependence $T_b^0(\varphi)$.

It is to be pointed out that though the above stated presentations are applicable only to weak transitions of Kind I, the computer simulation in terms of the lattice gas model and molecular dynamic simulation [4, 15] show that at a temperature lower than the melting temperature a liquid-like phase layer is formed on the special boundary. Our model suggests that secondary grain boundary dislocations are wetted by the high-temperature phase. Then at a certain temperature T_0 , lower than the melting temperature, the SGBD network in the special boundary may disappear. It is one of the possible mechanisms of the "special boundary-general boundary" transition [20-22, 35]. This approach explains why this transition occurs at a change of both the temperature and the misorientation angle: in either case the SGBD cores begin to overlap, in the former case due to

geometrical, in the latter case due to thermodynamical causative factors.

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References

- 1) Aleshin, A.N., Prokofjev, S.I., Shvindlerman, L.S.: 1985, *Scripta Metall.*, 19, 1135.
- 2) Alvarado, S.F., Campagna, M., Fattah, A., Uelhoff, W.: 1987, *Z. Phys.*, B66, 103.
- 3) Blade, J.C., Ellwood, E.C., 1956-57, *J. Inst. Met.*: 85, 30.
- 4) Broughton, J.Q., Gilmer, G.H.: 1986, *Phys. Rev. Letters*, 56, 2692.
- 5) Cahn, J.W.: 1977, *J. Chem. Phys.*, 66, 3667.
- 6) Cicotti, G., Guillope, M., Pontikis, V.: 1983, *Phys. Rev. B*, 27, 5576.
- 7) De Gennes, P.G.: 1985, *Rev. of Mod. Phys.*, 57, 827.
- 8) Giessen, B.C.: 1969, *Advances in X-ray Analysis*, 12 (New York: Plenum Press), p. 23.
- 9) Greenberg, A., Komeno, Y.: 1983, *Scripta Metall.*, 17, 405.
- 10) Dietrich, S.: 1988, *Phase transitions and critical phenomena*, v. 12 (London: Academic Press), in press.
- 11) Hasimoto, M., Ishida, I., Yamamoto, R., Doyama, M.: 1981, *Acta Metall.*, 29, 617.
- 12) Hasimoto, M., Ishida, Y., Yamamoto, R., Doyama, M., Fujiwara, T.: 1982, *Scripta Metall.*, 16, 267.
- 13) Hashimoto, M., Ishida, Y., Yamamoto, R., Doyama, M.: 1984, *Acta Metall.*, 32, 1.
- 14) Heumann, T., Alpaut, O., 1964: *J. Less-Common Metals*, 6, 108.
- 15) Ho, P.S., Kwok, T., Nguen, T., Nitta, C., Yip, S.: 1985, *Scripta Metall.*, 19, 993.
- 16) Jamison, K.D., Lind, D.M., Dunning, F.B., Walters, G.K.: 1985, *Surf. Sci.*, 159, L451.
- 17) Kikuchi, R., Cahn, J.W.: 1980, *Phys. Rev. B*, 21, 1983; 1987, *Phys. Rev. B*, 36, 418.
- 18) Le Claire, A.D.: 1963, *Brit. J. Appl. Phys.*, 14, 351.
- 19) Łoikowski, V., Gleiter, H., Maurer, R.: 1988, *Acta Metall.*, 36 (in press).
- 20) Maksimova, E.L., Straumal, B.B., Shvindlerman, L.S.: 1987, *Fiz. Mat. Metalloved.*, 63, 886.
- 21) Maksimova, E.L., Rabkin, E.I., Straumal, B.B., Shvindlerman, L.S.: 1987, *Fizika Metallov Metalloved.*, 64, 511.
- 22) Maksimova, E.L., Shvindlerman, L.S., Straumal, B.B.: 1988, *Acta Metall.*, 36 (in press).
- 23) Maksimova, E.L., Straumal, B.B., Fradkov, V.E., Shvindlerman, L.S.: 1983, *Fizika Met. Metalloved.*, 56, 979.
- 24) McRae, E.G., Malic, R.A.: 1984, *Surf. Sci.*, 148, 551.
- 25) Nguen, T., Ho, P.S., Kwok, T., Nitta, C., Yip, S.: 1986, *Phys. Rev. Letters*, 57, 1919.
- 26) Potter, H.C., Blakely, J.H.: 1975, *J. Vac. Sci. Technol.*, 12, 635.

- 27) Predel, B., Gödecke, T.: 1975, Z. Metall., 66, 654.
- 28) Prokofjev, S.I., Straumal, B.B., Zorin, I.M.: 1984, Zavodskaya laboratoriya, 50, 45.
- 29) Rabkin, E.I., Maksimova, E.L., Shvindlerman, L.S., Straumal, B.B.: 1988, Acta Metall., 36 (in press).
- 30) Raynor, G.V., Lee, J.A.: 1954, Acta Metall., 2, 617.
- 31) Rhines, F.N., Urquart, W.M., Hogl, H.P.: 1947, Trans. ASM, 39, 694.
- 32) Röttman, C.: 1987, Phil. Mag. A, 55, 499.
- 33) Schubert, K., Rosler, U., Mahler, W., Dorre, E., Schütt, W.: 1954, Z. Metallkunde, 54, 643.
- 34) Shunk, F.A.: 1969, Constitution of binary alloys. Suppl. 2. (New-York a.o.: McGraw Hill).
- 35) Shvindlerman, L.S., Straumal, B.B.: 1985, Acta Metall., 33, 1735.
- 36) Sickafus, K.E., Sass, S.: 1987, Acta Metall., 35, 69.
- 37) Straumal, B.B., Klinger, L.M., Shvindlerman, L.S.: 1984, Acta Metall., 32, 1355.

DISCUSSION

W. Gust

How is it possible for you to determine the misorientation angle with accuracy of 0.1 degree?

L.S. Shvindlerman

In fact this problem consists of two tasks: the first - preparation of bicrystals with parameters of the boundary within a very narrow range, the second - the accuracy of measurement. The first task was performed by means of optical orientation, which allowed to obtain specimens with accuracy of 0.1° . Precise values of the parameters of misorientation of already grown bicrystals were found by means of diffraction patterns obtained by a wide X-ray beam. The accuracy was $0.02-0.05^\circ$.

K.T. Aust

You showed a curve for diffusion coefficient vs. deviation from exact coincidence ($\Delta\theta$) for a $\Sigma 17$ grain boundary. Do your experiments show a dependence of such a curve on the Σ value?

L.S. Shvindlerman

We studied a phase transformation "a special grain boundary - a general grain boundary" on tilt boundaries $\langle 100 \rangle$ in copper ($\Sigma 5$) and $\langle 001 \rangle$ in tin ($\Sigma 17$). Such diagrams of state can be obtained for other materials too. In fact, this is not a simple task because for the boundaries with high density of coincidence lattice sites (low Σ) the temperature of phase transition is quite close to melting temperature, and for big Σ the transition temperatures are too low for the diffusion.

G. Erdélyi

1. Have you observed a grain boundary migration during your diffusion experiments? 2. The cusp on the g.-b. energy-misorientation curve was observed to be sensitive to the pressure. It was considered to be a possible pressure-induced g.-b. phase transformations. Have you observed similar phenomena in your experiments?

L.S. Shvindlerman

1. We observed no migration during diffusion experiments. 2. No doubt, pressure can change the parameters of phase transitions in a boundary as well as produce new ones (as was shown experimentally by Prof H. Gleiter for sintered monocrystalline balls, where pressure changed the number of special grain boundaries observed). Pressure is also useful to obtain the difference of specific volumes of grain boundary phases from the Clausius-Clapeyron equation. However, we did not carry out these experiments.

Ch. Herzig

Have you observed the effect of the ferromagnetic phase transition on grain boundary diffusion only in iron alloys or also in pure alpha-iron? We found* such an effect when ^{65}Zn and ^{59}Fe tracers were simultaneously diffusing in $\alpha\text{-Fe}$. In this case the Arrhenius plot of both tracers was curved. When, however, Fe self-diffusion alone was investigated in the same $\alpha\text{-Fe}$ material a linear Arrhenius was observed. Therefore the anomaly may be related more to a change in segregation than to a structural change in the grain boundary.

L.S. Shvindlerman

We investigated volume diffusion of zinc and tin in Fe-Si alloys and grain-boundary diffusion in the same alloys along an individual grain-boundary. The fact that the anomaly is observed both for the volume and grain boundary diffusion brings support to the point of view that the anomalous behaviour of the diffusion coefficient is caused by the magnetic transformation and not by segregation changes. For the grain boundary diffusion the anomaly is stronger. It should be noted that the interval of the anomalous behaviour of the diffusion coefficient is not quite wide - a few dozens of degrees. The distance between temperature points in our experiment is $\sim 3^{\circ}\text{C}$, in the experiment of Prof. Herzig it is about $10^{\circ}\text{-}20^{\circ}\text{C}$. It may account for the instability of the anomaly.

K. Lücke

According to your ideas must the breakaway of a grain-boundary from solute atoms, as described by the impurity drag theory, be included in the theory of grain boundary phase transformation or must it be treated separately?

*Proceedings of the Conference on Solute-Defect Interaction-Theory and Experiment, Kingston, 1985.

L.S. Shvindlerman

The question whether temperature dependence of migration should be explained by the breakaway of the boundary from the solute atoms is quite natural. If the mobility jumps are in fact connected to an equilibrium phase transition in grain boundaries, then T_c should not depend on the driving force of the migration. In our experiment the driving force was increased up to 3 times the initial value, but no change in T_c (within the experimental error $\sim 1^\circ\text{C}$) was observed. For a breakaway even small deviations in driving force cause considerable shifts of the breakaway temperature. It was found in our experiments on breakaway of the special boundary $\langle 111 \rangle \Sigma 19$ in aluminium**. The change in the driving force by a factor of 1.5 shifted breakaway temperature by 25°C . At last, the kinetic explanation of the jumps is contradicted by the angle dependence of the jump temperature. For the breakaway the temperature is lower for more "special" boundaries (i.e., for smaller deviations from special misorientation). For an equilibrium phase transition "special grain boundary - general grain boundary" the dependence is inverse, which was in fact observed in our experiments.

** Molodov, D.A., Kopeczky Ch.V., Shvindlerman L.S. - Solid State Physics, 1981, v.23, No.10, p.29-46 (in Russian).