CONCENTRATIONAL PHASE TRANSITION ON THE INTERPHASE BOUNDARIES Sn/Ge AND ON THE GRAIN BOUNDARIES IN TIN : INDIUM DIFFUSION

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Abstract - The diffusion of indium along [001] tin-germanium interphase twist boundaries and [001] twist grain boundaries in tin has been studied in the vicinity of the β - γ', transition in the Sn-In system. The temperature of the β - γ' transition in the interphase boundaries and in the grain boundaries is lower than that in the bulk and depends on the boundary misorientation angle. In the tin-germanium interphase boundaries, near the temperature of β - γ' boundary transition, strong violations of the arrhenius law were observed. The observed decrease of the phase transition temperature at grain boundaries and interphase boundaries is explained in terms of a prewetting transition at the boundaries.

1 - INTRODUCTION

Phase transitions at grain boundaries and interphase boundaries attracts still greater attention of investigators. Various experimental data and computer simulation results [1-13] pertain to phase transitions occurring only at grain boundaries, and not accompanied by any phase transformations inside the grains which form the boundary. However of no less interest are grain boundary phase transitions occurring near bulk phase transitions. In these experiments, however, the object of the investigations, i.e., a grain boundary with definite crystallographic parameters must hold. Therefore these experiments involve 2nd order bulk phase transitions or "weak" 1st order transitions, close to 2nd order ones, with a small thermal and bulk effect. According to the results of our previous work [14] the Sn-In system is an appropriate candidate for such an investigation. The temperature dependence of the diffusion coefficient of In in tin does not have any abrupt discontinuities, but rather the slope of the Arrhenius plot changes abruptly at a temperature of about 180°C. This is a characteristic feature of a 2nd order transition or a "weak" 1st order phase transition.

2 - EXPERIMENTAL METHODS

In order to study bulk phase transitions at grain boundaries and interphase boundaries, we utilize the Sn-In system. Giessen [15] reported the existence at room temperature of the γ' - phase, whose homogeneity region is located on the tin-indium diagram between the γ - phase, with a simple hexagonal lattice, and the β

- tin-based solid solution. A simple hexagonal lattice of the γ - phase is formed from the β - tin structure by the displacement of sublattices by a quarter-period along the C-axis [16]. In the γ' - phase lattice the same displacement occurs by less than a quarter-period along the C-axis [15]; the elements of the γ' - phase crystalline lattice remain the same as in β - tin. Therefore in the first part of our work we determined more accurately the Sn-In phase diagram in the tin-rich side. For this we measured the homogeneity regions of β, γ and γ' - phases by means of an electron microprobe analysis of the concentration distributions in the diffusional layers, formed by bulk diffusion of indium in tin. To investigate grain boundary and interphase boundary properties in the vicinity of the bulk phase transition, we selected [001] twist boundaries. Tin bicrystals with misorientation angles 27.6, 28.1, 29.1, 30.2 and 31.1° (±0.5°) were grown. These angles are near the coincidence misorientation Σ=17. For the study of interphase boundaries we have grown tin-germanium bicrystals with misorientation angles 0°; 1°; 3° and 10° (±0.5°). The first three boundaries have a low surface tension, while their properties (activation energy and activation volume of diffusion) differ significantly from those of general boundaries. The fourth boundary is a general interphase boundary. As to the regions of existence of special and general grain boundaries, see [9]. Tin and tin-germanium bicrystals were grown by directed crystallization from 99.999 at. % pure tin and Sb-doped semiconducting germanium with a specific resistance of 5 $\Omega \cdot$ cm (the growth technique has been described in [14]). The indium layer was electolytically deposited on each bicrystal's surface.The diffusion anneals were carried out in a atmosphere of high-purity argon in a special furnace [17]. The distribution of indium concentrations was determined by electron microprobe analysis from the intensity of the InL_α line at an accelerating voltage of 15 kV.The product of the interphase boundary diffusion coefficient times the boundary width ($D'\delta$) was found using Fisher's method.

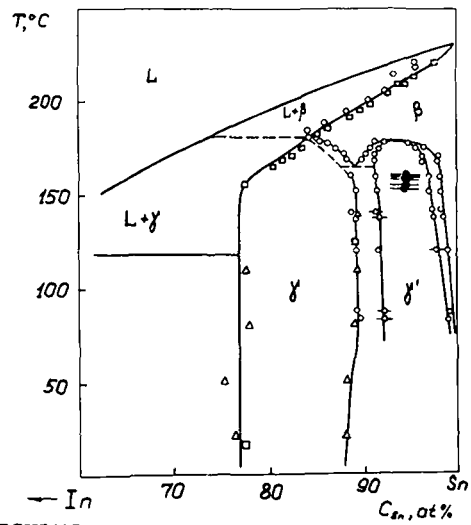

Fig.1. A portion of the Sn-In diagram; o(open circles) - results of this work obtained from the concentration distribution in the region of interdiffusion of tin and indium; □ - data of differential thermal analysis [19]; Δ - data of X-ray structural analysis in a high-temperature chamber [19];

3 - RESULTS

Fig.1 presents the Sn-In diagram within the concentration range from 0 to 40 at. % indium. An analysis of the single and two-phase

regions in the zones of interdiffusion of tin and indium enabled us to plot the boundaries of the β, $\beta + \gamma'$ and $\gamma' + \gamma$ regions. Also the phase diagram exhibits experimental points from other works [18,19], obtained by means of a differential thermal analysis and X-ray structural studies in a high-temperature chamber. Fig.2 presents the temperature dependence of the coefficient of the bulk interdiffusion of indium in tin for the range of indium concentrations from 2-4 to 8%. At a temperature T_c = 178.7 ± 0.5°C this dependence exhibits a discontinuity. Above and below T_c the diffusion coefficient obeys an 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).

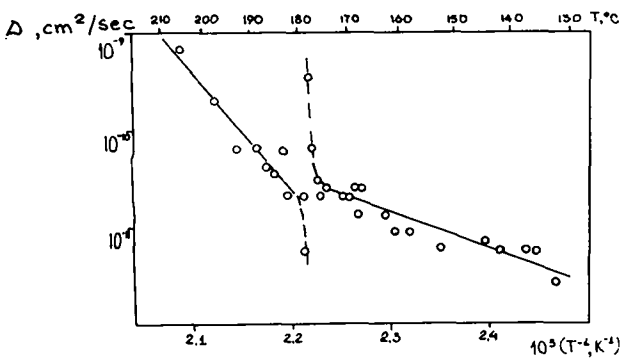

Fig.2. Temperature dependence of the bulk interdiffusion coefficient of indium in tin in the concentration range from 2 to 8 at % In. The discontinuity in the temperature dependence at T_c corresponds to the β-γ' transition (see Fig.1). Deviations from an Arrhenius law near T_c are seen.

To determine grain boundary diffusion coefficients for indium, we determined a number of diffusion profiles across the boundary parallel to the sample's surface. Fig.3 presents the maximum concentration of indium in grain boundaries C_b as a function of depth in Fisher's coordinates ($\ln C_b$ -y). All these dependences have the form of straight lines. The coefficients for grain boundary diffusion, as the D values for the bulk interdiffusion, were determined in the concentration range from 2-4 to 8 at % indium. The same dependences for tin-germanium interphase boundaries are similar to these.

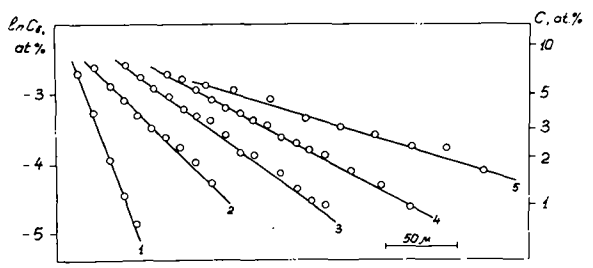

Fig.3. Logarithm of the indium concentration at a grain boundary as a function of the depth.
1 - φ=31.1°, T=158.5°C, t=160 h;
2 - φ=30.2°, T=175.2°C, t=160 h;
3 - φ=29.1°, T=136.9°C, t=122 h;
4 - φ=27.6°, T=144.8°C, t=122 h;
5 - φ=30.2°, T=158.5°C, t=160 h.

Fig.4 a presents the temperature dependences of the product D'δ for 5 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

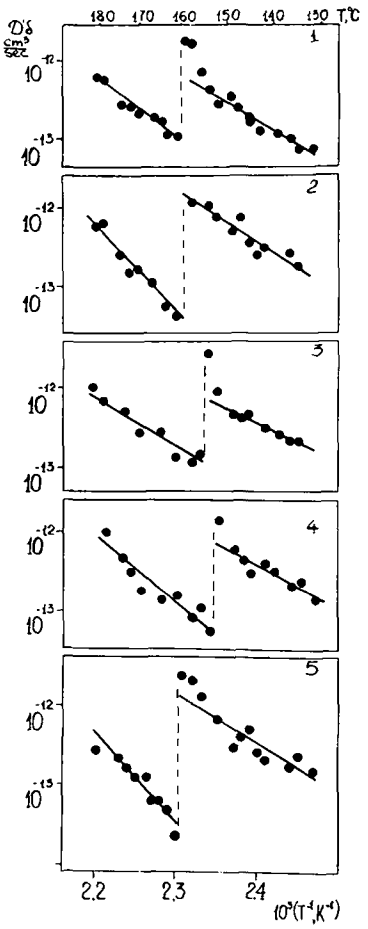

Fig.4a. Temperature dependence of the product of the grain boundary diffusion coefficient of indium D' and the boundary width (δ) for grain boundaries with different misorientation angles φ: 1 - 28.1°; 2 - 29.1°; 3 - 27.6°; 4 - 30.2° and 5 - 31.1°

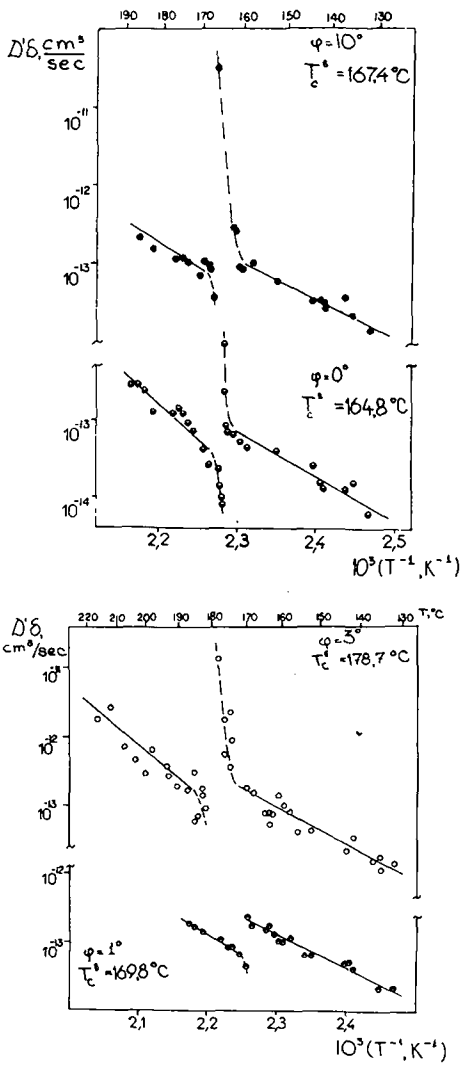

Fig.4b. The temperature dependences of the product of the boundary diffusion coefficient of indium and boundary width D'δ for four twist [001] tin-germanium interphase boundaries. The misorientation angles and temperatures of the transitions β -γ' on the boundaries are shown on the figures.

are different for different boundaries; they are 17 to 25°C lower when compared with T_c for the bulk interdiffusion coefficient. At a temperature T_c of the bulk phase transition β - γ', where an abrupt change of D is observed, the dependences D'δ(T) for grain boundaries exhibit no singularities. The D'δ values for

tin-germanium interphase boundaries are given in Fig.4b for the concentration range 2-8 at % In. All the temperature dependences of $D'\delta$ in Fig.4b deviate from an Arrhenius law near T_c^b . On approaching T_c^b from low temperature region the diffusion coefficients deviate greatly from the Arrhenius plot upwards, whereas on approaching T_c^b from high temperatures they deviate downwards. The deviations are observed within the temperature range $T_c^b \pm 5\ C^\circ$.

4 - DISCUSSION

A comparison of Figs.1 and 2 demonstrates that the formation of the γ' - phase from the β - tin-base solid solution is accompanied by a discontinuity in the temperature dependence of the bulk interdiffusion coefficient of indium , and a decrease of the activation energy for interdiffusion. The discontinuities in 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 in $D'\delta(T)$. This suggests that the $\beta - \gamma'$ transition in the grain boundaries and interphase boundaries occurs at a lower temperature than in the bulk. In our opinion there is a certain analogy between a grain boundary phase transition, observed in this work, and a so-called prewetting phase transition [20]. At such transition a thin equilibrium layer of another phase, which is unstable in the bulk, is formed at the interface. We consider a solid near a weak 1st order phase transition. We describe its state by means of a scalar order parameter η. The quantity $\eta = 0$ corresponds to a high-temperature disordered phase, and the quantity $\eta = \eta_v$ to a low-temperature phase. Let η_s be the quantity of the order parameter in the atomic layers directly adjoining the grain boundary or interphase boundary from the tin side. At a temperature lower than the bulk transition temperature T_c the quantity η_s , generally speaking, is not coincident with η_v due to the disturbing action of the boundary. The corresponding contribution to the free energy of the system is given by some functional of η_s. In this presentation our problem is equivalent to Cahn's model [21]. It should be born in mind that the η_s value is closely connected with the structure of a grain boundary. Correspondin g ly, any variation of η_s is connected with a variation of a grain boundary's structure. Under appropriate conditions the prewetting transition occurs in this system. This transition is marked by the fact that the η_s value decreases abruptly. In grain boundaries there are no anomalously strong deviations of the diffusion coefficient from the Arrhenius law. How can we explain this critical phenomena in the interphase boundaries ? The anomalous decrease of the diffusion coefficient is connected with the thermodynamics of the solid solution of In in β - Sn near the critical point of the $\beta - \gamma'$ transition. The thermodynamic factor for the interdiffusion coefficient can be expressed as $(\partial^2 F/\partial C^2)$, where F is the solid solution's Helmholtz free energy, C the concentration. According to Landau theory,

$$F = F_o(T) + A(T)(C-C_c)^2 + B(T)(C-C_c)^4 + D(T)(C-C_c)^6,$$

where $A(T) = \alpha(T - T_c^b)$

Then $\left.\frac{\partial^2 F}{\partial C^2}\right|_{C=C_c} \sim |T - T_c^b|$

Therefore when $T \to T_c^b + 0$, the coefficient of interdiffusion should decrease proportionally to $|T - T_c^b|$. The case of anomalous growth of $D'\delta$ at $T \to T_c^b - 0$ are not very clear. It can be only said that this growth is due to fluctuations of an order parameter in an ordered phase in the vicinity of the $\beta - \gamma'$ transition point. The scale of these fluctuations divergrs as $|T - T_c^b|^{-\nu}$, where $\nu=0.63$ for 3-dimensional case and $\nu=1$ for 2-dimensional case. Because the diffusion coefficient is proportional to the second power of length, then the law $D'\delta \sim |T - T_c^b|^{-2\nu}$ may be expected in the vicinity of a transition point. The experimental value of the critical index of $D'\delta$ is 1.5 ± 0.2, which lies in the interval from 1.29 (2ν for 3 dimensions) up to 2 (2ν for 2 dimensions). Therefore, interphase boundaries occupy an intermediate position (regarding the diffusional properties) between two- and three-dimensional objects.

REFERENCES

/1/ R.Kikuchi and J.W.Cahn, Phys.Rev.B, 21 (1980) 1983.
/2/ R.Kikuchi and J.W.Cahn, Phys.Rev.B, 36 (1987) 418.
/3/ M.Hashimoto, Y.Ishida, R.Yamamoto, M.Doyama and T.Fujiwara, Scripta Metall, 16 (1982) 267.
/4/ G.Cicotti, M.Guillope and V.Potikis, Phys.Rev.B., 27 (1983) 5576.
/5/ M.Hashimoto, Y.Ishida, R.Yamamoto and M.Doyama, Acta Metall, 29 (1981) 617.
/6/ M.Hashimoto, Y.Ishida, R.Yamamoto and M.Doyama, Acta Metall, 32 (1984) 1.
/7/ C.Rottman, Phil.Mag.A, 55 (1987) 499.
/8/ A.N.Aleshin, S.I.Prokofjev and L.S.Shvindlerman, Scripta Metall., 19 (1985) 1135.
/9/ L.S.Shvindlerman and B.B.Straumal, Acta Metall., 33 (1985) 1735.
/10/ W.Łojkowski, H.Gleiter and R.Maurer, Acta Metall., 36 (1988).
/11/ E.L.Maksimova, L.S.Shvindlerman and B.B.Straumal, Acta Metall., 36 (1988) 1573.
/12/ E.I.Rabkin, E.L.Maksimova, L.S.Shvindlerman and B.B.Straumal Acta Metal, 37 (1989) in press.
/13/ K.E.Sickafus and S.L.Sass, Acta Metall., 35 (1987) 69.
/14/ B.B.Straumal, L.M.Klinger and L.S.Shvindlerman, Acta metall., 32 (1984) 1355.
/15/ B.C.Giessen, Advances in X-ray Analysis, vol.12, Plenum Press, New York, 1969, p.23.
/16/ G.V.Raynor and J.A.Lee, Acta metall., 2 (1954) 617.
/17/ E.L.Maksimova, B.B.Straumal, V..E.Fradkov and L.S.Shvindlerman, Fizika Met. Metalloved., 56 (1983) 979.
/18/ T.Heumann and O.Alpaut, J.Less-Common Metals, 6 (1964) 108.
/19/ B.Prédel and T.Gödecke, Z.Metallkde, 66 (1975) 654.
/20/ P.G.De Gennes, Rev. of Mod.Phys., 57 (1985) 827.
/21/ J.W.Cahn, J.Chem. Phys., 66 (1977) 3667.