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PHASE TRANSITIONS AT GRAIN BOUNDARIES IN THE PRESENCE OF IMPURITIES

E. L. MAKSIMOVA, E. I. RABKIN, L. S. SHVINDLERMAN and B. B. STRAUMAL
Institute of Solid State Physics, Academy of Sciences of the U.S.S.R., Chernoglovka, Moscow District, 142432, U.S.S.R.

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Abstract—Phase transitions at grain boundaries have analyzed thermodynamically in two-component systems. Possible types of phase diagrams for grain boundaries in such systems are studied. The effect of the second component on the "special grain boundary–general boundary" phase transition has been examined experimentally. The temperature of such transition at the grain boundaries in tin has been shown to decrease in proportion to the logarithm of sodium concentration in the bulk. A comparison of the experimental results and the thermodynamical model shows that the grain-boundary sodium solution in tin is saturated.

Résumé—Nous présentons une analyse thermodynamique des transitions de phases aux Joints de grains dans des systèmes à deux composants. Nous avons recherché les différents types possibles de diagrammes de phases pour les joints de grains dans de tels systèmes, et étudié expérimentalement l'effet du second composant sur la transition de phases "joint de grain particulier–joint général". La température de cette transition intergranulaire dans l'étain décroît proportionnellement au logarithme de la concentration volumique en sodium. La comparaison de ces résultats expérimentaux et du modèle thermodynamique montre qu'aux joints de grains, la solution de sodium dans l'étain est saturée.

Zusammenfassung—Die Phasenumwandlungen an Korngrenzen in zweikomponentigen Systemen wurden thermodynamisch analysiert. Es werden mögliche Typen von Phasendiagrammen für die Korngrenzen entworfen. Der Einfluß der zweiten Komponente auf die Phasenumwandlung "spezielle Korngrenzeallgemeine Korngrenze" wurde untersucht. Es wird gezeigt, daß die Temperatur für eine solche Umwandlung von Korngrenzen in Zinn proportional zum Logarithmus der Natriumvolumkmonzentration abnimmt. Der Vergleich der experimentellen Ergebnisse mit dem Modell ergibt, daß im Zinn die Natriumlösung in der Korngrenze gesättigt ist.

1. INTRODUCTION

In the last few years phase transitions in low dimensionality systems have received wide-spread attention. Beside the phase transitions on the surface, researchers began studying phase transitions at grain boundaries. Theoretical papers [1–3], computer simulation of boundaries [4–6], experimental studies [7–9] (see also review [10] and references therein) are now available. For instance, in a number of papers, devoted to grain-boundary segregation, strong interaction of atoms adsorbed at the boundary has been shown to lead to a two-dimensional grain-boundary phase transition which does not occur in a pure material (see paper [11] and references).

In the present paper we perform a thermodynamical analysis of the situation when a grain-boundary transition occurs in a pure material. To compare theory and experiment we have studied the effect of a surface-active impurity (sodium) on the temperature of the "special grain boundary Σ17–general boundary" phase transition in tin. We have recently analyzed in detail such a transition on an example of pure tin [9]. And also we considered variation of the parameters of boundary migration under such a transition and showed the singularities on temperature dependences of the surface tension [9]. At the end of the present paper we compare the experimental results obtained with the thermodynamical model.

2. THERMODYNAMICAL MODEL OF THE EFFECT OF IMPURITY ON THE GRAIN-BOUNDARY PHASE TRANSITION

We consider a situation when a phase transition takes place on a grain boundary, but the bulk phase remains stable. Then three phases, one bulk and two grain-boundary ones, coexist at the temperature of the grain-boundary phase transition. Such type phase transitions involve the transition observed in paper [8] and also the "special grain boundary–general boundary" transition [7, 9]. Further the low-temperature phase at the boundary will be designated by A and the high-temperature one by B. In the case of "special grain boundary–general boundary" transition A is a special boundary and B is a general type boundary. The quantities with primes will be referred to impurity atoms, Those without primes to matrix atoms, and the ones with the sign p will denote solutions in general. In order to describe the

thermodynamical equilibrium at grain boundaries, geometrical variables should be used besides common thermodynamical variables, such as pressure and temperature. The geometrical variables indicate boundary orientation and misorientation of grains [2]. In this paper we consider only the case of symmetrical tilt boundaries, their structure being determined by the misorientation angle only.

We apply the generalized Clausius–Clapeyron equation. Unlike Hart [1], we use the Gibbs method, in which the surface excess of volume is supposed to be zero

$$0 = (S^{\sigma}_{A} - S^{\sigma}_{B})\,dT + (\Gamma_A - \Gamma_B)\,d\mu + (\Gamma'_A - \Gamma'_B)\,d\mu + \left[\left(\frac{\partial\sigma}{\partial\varphi}\right)^{\sigma}_{B} - \left(\frac{\partial\sigma}{\partial\varphi}\right)^{\sigma}_{A}\right] d\varphi \quad (1)$$

where S is the surface excesses of entropy, Γ are the values of adsorption, μ are chemical potentials. As compared to the equation proposed by Hart, equation (1) takes account of the dependence of the boundary surface tension on the angle of grain misorientation, φ. Further development of formula (1) depends on the model of bulk and grain-boundary solutions we use. Let's consider the case of small volume concentrations of impurity, the solution being assumed to be ideal. Then

$$d\mu' = RT\,d\ln C_v + (R\ln C_v - S'_v)\,dT$$
$$d\mu = -RT\,dC_v - (RC_v + S_v)\,dT. \quad (2)$$

Combining equations (1) and (2) we get the formula relating the temperature of the grain-boundary phase transition with the volume concentration of impurity and with the values of adsorption at the boundaries, and also with angle φ

$$dT = RT\,\frac{(\Gamma'_A - \Gamma'_B)\,d\ln C_v - (\Gamma_A - \Gamma_B)\,dC_v + \left[\left(\frac{\partial\sigma}{\partial\varphi}\right)^{\sigma}_{B} - \left(\frac{\partial\sigma}{\partial\varphi}\right)^{\sigma}_{A}\right]\frac{d\varphi}{RT}}{S^{\sigma}_{B} - S^{\sigma}_{A} - (\Gamma'_A - \Gamma'_B)(R\ln C_v - S'_v) + (\Gamma_A - \Gamma_B)(RC_v + S_v)} \quad (3)$$

We analyze the case when the grain-boundary phase transition occurs already in a pure material (without impurities). Equation (3) allows calculating the temperature variation of this transition when small amounts of impurity are introduced into the material.

Further we restrict our analysis to a most simple case, when the adsorption at the boundary is given by the Langmuir–McLean equation

$$A\Gamma'_{A,B} = r_{A,B}B_{A,B}C_v/(1 + B_{A,B}C_v) \quad (4)$$

here r is the mole fraction of adsorption sites, $B_{A,B} = \exp\{g_{A,B}/RT\}$, and $g_{A,B}$ is the free energy of impurity atom adsorption at the boundaries, A is the area per a mole of the grain-boundary substance. In what follows we shall assume the values of adsorptions small, and from surface excesses we pass to the values of entropies and concentrations. Besides, we

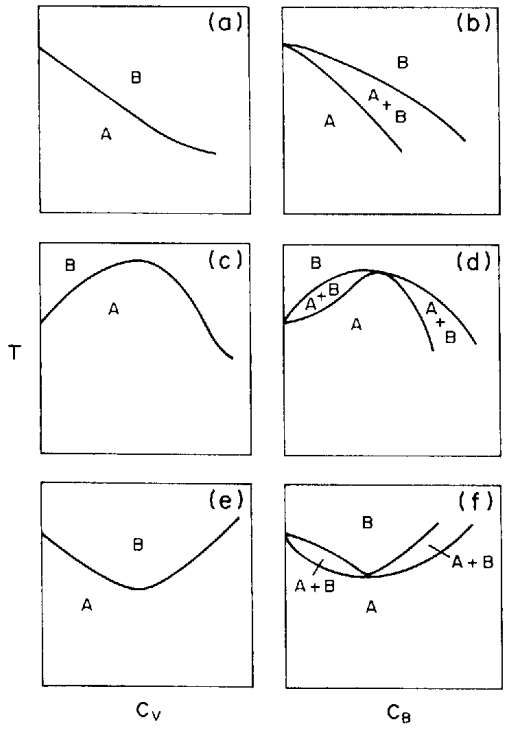

Fig. 1. Phase diagrams for two grain-boundary phases A and B in the "temperature–bulk impurity concentration" coordinates (a, c, e) and in the "temperature–boundary impurity concentration" coordinates (b, d, f): (a, b)—$r_B > r_A$, $g_B \sim g_A$; (c, d)—$r_B > r_A$, $g_A \gg g_B$; (e, f)—$r_B < r_A$, $g_A \ll g_B$ [see equation (5)].

neglect a change in the mole area under the phase transition, in other words, we assume that $A_A \sim A_B \sim A$. Substituting (4) into (3) and integrating from 0 to C_v, we get the following, taking into account all the previous simplifications

$$\Delta T \simeq \frac{RT^2}{q_{tr}}\left\{\frac{r_A g_A - \tau_B g_B}{RT} + r_A \ln\left(C_v + \frac{1}{B_A}\right) - r_B \ln\left(C_v + \frac{1}{B_B}\right)\right\}, \quad (5)$$

where $q_{tr} = T(S^{\sigma}_{B} - S^{\sigma}_{A})$ is the heat of the grain-boundary phase transition, and the misorientation angle, φ, is considered to be constant. Using formula (5), one can obtain several types of grain-boundary phase diagrams, depending on the ratios between parameters r_A, r_B and g_A, g_B. Figure 1 (a, c, e) shows schematically such diagrams in the "temperature–volume impurity concentration" coordinates. The impurity concentration is restricted by the solubility limit for a volume solution. It follows from the Gibbs phase rule [11] that two grain-boundary phases may coexist at a single value of the volume concentration, C_v. So, the diagrams in Fig. 1 (a, c, e) do not have any two-phase regions. Figure 1 (b, d, f) depicts the same diagrams, but they are plotted in the "temperature-boundary impurity concentration" coordinates. They involve two-phase regions, related to the jump of adsorption under a grain-boundary phase transition [1].

3. EXPERIMENTAL

Sodium was chosen as impurity for the tin on which our previous experiments [9] had been carried out. Sodium dissolves in tin forming a solid solution to a concentration of ~0.48 wt % (2.4 at.%) [12]. The impurity was introduced into the tin of a nominal purity of 99.9999% Sn. The maximum concentration of sodium in the Sn–Na alloys under study was $1 \cdot 10^{-1}$ at.%. The four other alloys with lower concentration of sodium were produced by successive dilution. The minimum concentration of sodium in the alloys came to $1 \cdot 10^{-4}$ at.%. The impurity content was controlled by mass-spectrometric analysis.

The ratio of the special boundary surface tension to that of general boundary, σ_{sp}/σ_g, was studied by the triple junction is formed by a boundary with the misorientation angle $\varphi_1 = 28.3°$ near the special angle $\varphi_s = 28.07$ ($\Sigma 17$) and by two general boundaries with the angle φ determined by the relationship $\varphi_2 = \varphi_3 = (90 - \varphi_1)/2 = 30.9°$ and situating far from the region of the existence of the $\Sigma 17$ special boundary.

The triple junction specimens were grown by the technique of directed crystallisation in an atmosphere of high-purity argon in ultra-pure graphite crucible. The specimen containing triple junction was cut out of the tricrystal, chemically polished in a mixture of HNO_3–40% HF and then placed into a high-temperature attachment to an optical microscope. Anneals were carried out in the HP argon, the temperature was maintained with an accuracy to $\pm 0.3°$. At successive anneals the triple junction shifted. Since $\varphi_2 = \varphi_3 = \varphi_g$, the special boundary with $\sigma_1 = \sigma_{sp}$ remained flat all the time. The triple junction vertex angle was measured after sample anneal. It has been shown experimentally in paper [9] that by this technique we can measure the equilibrium value of the triple junction vertex angle.

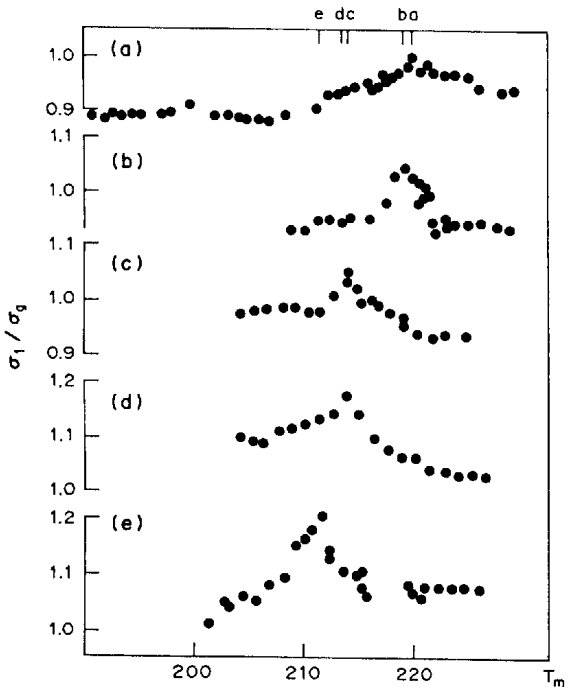

Fig. 2. Temperature dependences of the ratio of the special boundary tension $\sigma_1 = \sigma_{sp}$ to the general boundary tension $\sigma_2 = \sigma_3 = \sigma_g$ for alloys of following concentrations: (a) $1 \cdot 10^{-4}$ at.% Na; (b) $1 \cdot 10^{-3}$ at.% Na; (c) $1 \cdot 10^{-2}$ at.% Na; (d) $3 \cdot 10^{-2}$ at.% Na; (e) $1 \cdot 10^{-1}$ at.% Na.

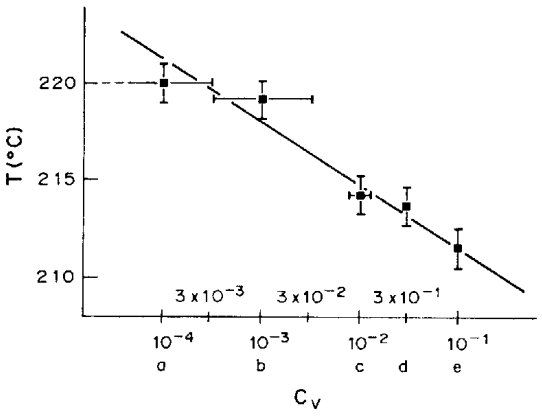

Fig. 3. The dependence of break temperature T_c on sodium concentration in the alloys studied.

4. RESULTS AND DISCUSSION

The temperature dependence of σ_{sp}/σ_g in the Sn–Na system has been studied for 5 alloys of the following concentrations: $1 \cdot 10^{-4}$; $1 \cdot 10^{-3}$; $1 \cdot 10^{-2}$; $3 \cdot 10^{-2}$; $1 \cdot 10^{-1}$ at.% Na and for the misorientation angle $\varphi = 28.3°$ at temperatures from 0.85 T_m to T_m.

The error of the mass-spectrometric analysis was $\pm 1 \cdot 10^{-3}$ at.%. The concentration of Na in the most diluted specimen is assumed to be $1 \cdot 10^{-4}$ at.% Na proceeding from the technique of its production by successive dilution and subsequent recrystallisation in the Ar atmosphere.

Figure 2 illustrates the temperature dependences of the ratio σ_1/σ_g. The curves are arranged in order of increasing concentration of Na in the alloys. Near some temperature T_c the ratio σ_1/σ_g begins to grow, at T_c it reaches its maximum and after that falls down. The temperature decreases from specimen to specimen as the sodium concentration in alloys is increased. The position of breaks in the temperature curves of σ_1/σ_g does not depend on the driving force of the junction displacement, the sequence of the measurements and the misorientation angles of general grain boundaries in the junction [9]. Thus the position of breaks in the temperature dependences of σ_1/σ_g only is determined by the impurity concentration and within the limits of experimental error is independent of the other factors. Earlier [9] we have observed similar features in the temperature dependences of the surface tension ratio σ_{sp}/σ_g.

The shape of curves in Fig. 2 allows us to speak about breaks in the $\sigma_{sp}/\sigma_g(T)$ dependences. Figure 3 shows how T_c decreases with increasing impurity concentration. All this along with our previous results [9], enables us to suppose that at temperature T_c a phase transition from special to general grain

boundary takes place. Judging by appearances of the surface tension temperature dependences, this is a first-kind phase transition.

The dependence of the temperature of the "special boundary Σ17–general boundary Σ1" transition on sodium concentration allows estimating the difference of adsorption capacities of both boundaries and the heat of sodium adsorption at the boundaries. Suppose all the assumptions made upon derivation of equation (5) are fulfilled. Then, provided

$$C_v \gg \exp\left\{-\frac{g_{A,B}}{RT}\right\},$$

which corresponds to saturation of grain-boundary solutions, we get from (5) the equation

$$\Delta T \simeq \frac{RT^2}{q_{tr}}\left\{\frac{r_A g_A - r_B g_B}{RT} + (\tau_A - \tau_B)\ln C_v\right\}. \quad (6)$$

This is a logarithmic dependence of the transition temperature on the impurity concentration, that is in agreement with the experiment.

Let's present numerical estimates. For this purpose we take typical "bulk" values: for instance, q_{tr} will be estimated by the melting heat of tin, $q_{tr} \simeq 7.1$ kJ/mol. The quantities g_A and g_B will be taken equal in a zero approximation. Then $r_B - r_A \simeq 5 \cdot 10^{-3}$, $g_{A,B} \simeq 50$ kJ/mol.

The fact, that the adsorption capacity of the general type boundary is higher than that of a special one, well agrees with the up-to-date representations of the grain-boundary segregation [13]. The results of computer simulation indicate that adsorption heats at the boundary vary highly from site to site, provided the impurity forms a substitution solution [14]. In case the size of an impurity atom is larger than that of a matrix atom, the extended boundary regions, if compared to those of lattice, will possess the greatest adsorption heat. The metal radius of Na, 1.92 Å, much exceeds the radius of Sn, 1.57 Å [15]. Therefore, in the case of Na adsorption the above characteristic properties should be well most pronounced. Na atoms first occupy the boundary areas with the highest adsorption heat. The results, obtained in our paper, that grain-boundary solutions are saturated already at negligible volume concentrations of sodium may be related to the fact that such regions turn out to be already occupied. In case the structure of the general type boundary is more "friable" than that of a special one, it involves more extended regions and, consequently, more adsorption sites. This is in agreement with the results of our thermodynamical analysis. How do we visualize the "special boundary Σ17–general boundary Σ1" transition, occurring as the impurity concentration increases? In our previous paper [9] we have proposed a hypothesis that at such a transition the SGBD's wall at the boundary vanishes. Gleiter has derived an expression for the SGBD's core width [16]

$$W \sim (dE/d\theta)^{-1}. \quad (7)$$

Since the adsorption capacity of the general boundaries is higher, their energy will decrease faster than that of special boundaries, provided the Na content in the alloy increases. The "gaps", corresponding to special boundaries in the "energy–misorientation angle" graph, become more shallow and the SGBD's core width increases, according to equation (7). At a certain Na concentration the cores will overlap each other, and the structure of the special boundary will be energetically disadvantageous.

The authors of paper [17] proposed the same interpretation of an interesting effect, discovered by them: electron-microscopic images of dislocations in small-angle thin-filmed bicrystals of gold vanished when implanted into films of chromium and cobalt ions.

It should be noted, however, that the analysis performed by Gleiter referred namely to secondary grain-boundary dislocations. And in our case such considerations are more valid as well.

A similar phenomenon, suppression of facetting the grain boundaries in zinc with increasing the impurity content, was also observed in [18].

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