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INFLUENCE OF AN IMPURITY ON THE TEMPERATURE OF TRANSFORMATION OF AΣ17 BOUNDARY TO A GENERAL BOUNDARY IN TIN*

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A study is made of the temperature dependences of the ratio of surface tension of a special boundary σ_{sp} to the surface tension of a general boundary σ_g from the shape of the triple junction on tilt boundaries [001] Σ17 in alloys of the tin–sodium system. The singularities on the (σ_{sp}/σ_g)–(T) curves for all the alloys are interpreted as a transformation of special boundaries to general boundaries. The experimental results agree with the thermodynamical analysis.

In [1–3] it has been shown that in the case of isolated tilt boundaries in tin in the angular range near special misorientation Σ17 ($\varphi = 28{\cdot}07°$) there is a change in the thermodynamic (energy) and kinetic (mobility) properties of the boundary, interpreted by the authors as a "special boundary–general boundary" phase transition. The presence of an impurity in the material might have a substantial influence on a grain boundary phase transition of this kind.

Our purpose here was to study the influence of an impurity on the "special boundary–general boundary" phase transition on tilt boundaries [001] in the tin–sodium system.

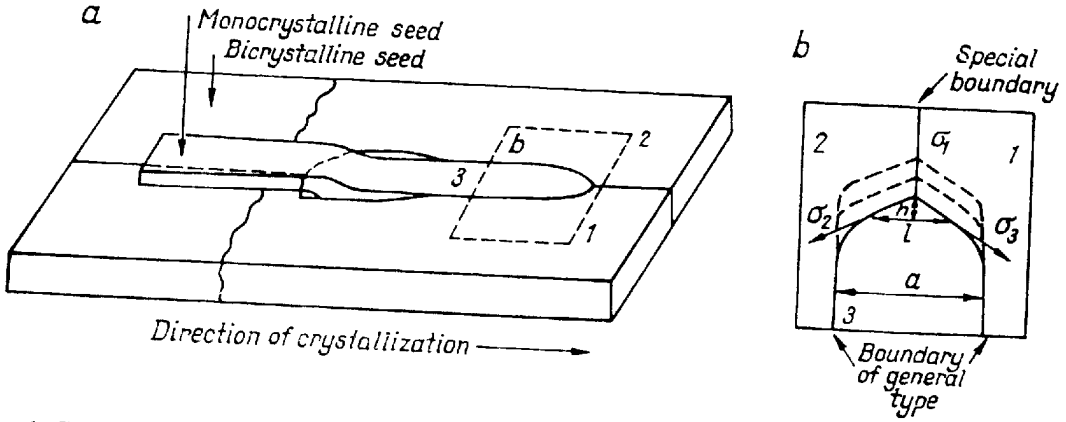

FIG. 1. Specimens with triple junctions: a – growth of tricrystal; b – successive positions of junction during change of temperature dependence of σ_{sp}/σ_g. Measurements taken of h and l, a = const.

Sodium was chosen as the impurity in tin, on which experiments were done in our previous work [1, 2]. Sodium dissolves in tin, forming a solid solution, up to ~0·48 wt.% (2·4 at.%) [4]. The impurity was inculated into tin OVCh-000 of nominal purity 99·9999%. The highest sodium concentration was $\sim 1 \times 10^{-1}$ at.%. The rest of the alloys were obtained by successive dilution. The sodium concentra-

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tion in the alloy with minimum impurity content was 1×10^{-4} %. The sodium content in the alloys was verified by mass-spectral analysis.

We studied the ratio of the surface tension of a special boundary σ_{sp} to σ_g of a genaral boundary from the shape of the triple junction, formed by one boundary with misorientation $\varphi=28{\cdot}3^\circ$ near the special angle $\varphi_c=28{\cdot}07^\circ$ ($\Sigma17$) and two general boundaries with angle φ defined by the relation $\varphi_2=\varphi_3=(90-\varphi_1/2)=30{\cdot}9^\circ$, lying a long way from the range of existence of special boundary $\Sigma17$.

Specimens with triple junctions were grown with the directed crystallization method in very pure argon atmosphere in a dish of especially pure graphite. A diagram of the tricrystal with triple junction is shown in Fig. 1. After it had grown, a specimen with triple junction was machined from the tricrystal (Fig. 1*b*), and after chemical polishing in a solution HNO_3–40% HF was placed in the high-temperature attachment to an optical microscope. Annealing was done in argon atmosphere, the temperature being maintained with accuracy $\pm0{\cdot}3^\circ$. The triple junction moved during successive annealings, as shown in Fig. 1*b*. Since $\sigma_2=\sigma_3=\sigma_g$, the special boundary with $\sigma_1=\sigma_{sp}$ remained flat throughout. The values h and l were found (see Fig. 1*b*), with $\sigma_{sp}/\sigma_g=\sigma_1/\sigma_2=\sigma_1/\sigma_3=2\cos[\arctan(l/2h)]$. Magnification was chosen so that measurements of h and l were taken near a junction where the boundaries with σ_2 and σ_3 were rectilinear, the ratio l/a did not exceed 0·1. In [1] it has been shown experimentally that the equilibrium value of the angle at the vertex of a triple junction can be measured with this technique.

RESULTS AND DISCUSSION

We studied the temperature dependences of σ_1/σ_g for five alloys of the Sn–Na system of content: 1×10^{-4}; 1×10^{-3}; 10^{-2}; 3×10^{-2}; 1×10^{-1} at.% Na with $\varphi=28{\cdot}3^\circ$ at temperatures from $0{\cdot}85T_m$ to T_m.

The error in determining the concentrations using mass spectral analysis were $\pm1\times10^{-3}$ at.%. The Na concentration in the most dilute specimen was taken equal to 1×10^{-4} at.% on the basis of the method used, of successive dilution with subsequent recrystallization in Ar atmosphere.

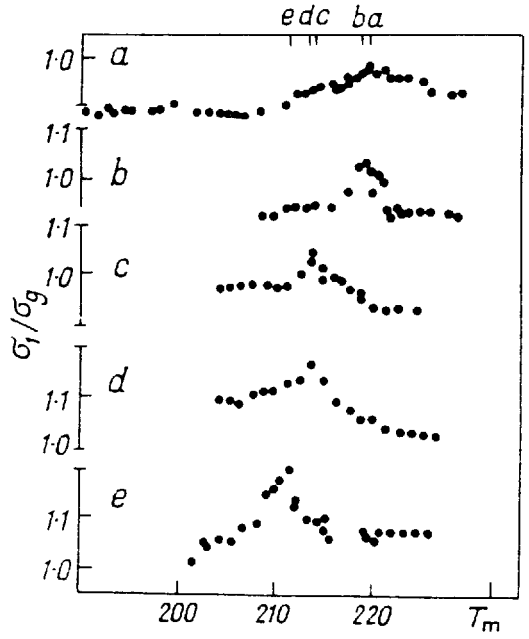

FIG. 2. Temperature dependences of ratio of surface tension $\sigma_1=\sigma_g$ of special boundaries to surface tension of general boundary $\sigma_2=\sigma_3=\sigma_g$ for alloys of concentrations: $a-1\times10^{-4}$ at.% Na; $b-1\times10^{-3}$ at.% Na; $c-1\times10^{-2}$ at.% Na; $d-3\times10^{-2}$ at.% Na; $e-1\times10^{-1}$ at.% Na.

Figure 2 shows the temperature dependences of σ_1/σ_g. They lie in increasing order of Na concentration. Near a certain temperature T_c the ratio σ_1/σ_g starts to grow, then reaches a maximum, after which it falls. T_c falls as the sodium content rises from specimen to specimen. The position of the breaks on σ_1/σ_g is independent of the driving force of motion of the junction, the sequence in which the temperature dependences were taken with rise or fall of temperature and of the angles of misorientation of general grain boundaries in the junction [1]. Thus, the position of the breaks on the temper-

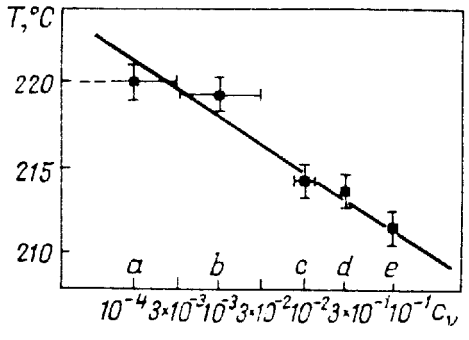

FIG. 3

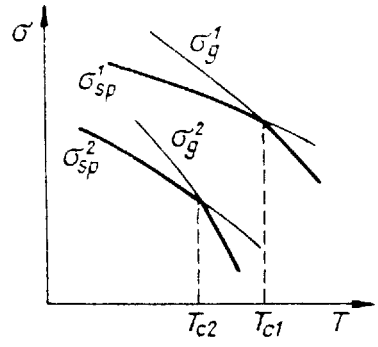

FIG. 4

FIG. 3. Dependence of temperature T_c of break on curves σ_{sp}/σ_g on logarithm of sodium concentration. Same notation as Fig. 2.

FIG. 4. Schematic temperature dependences of surface tension of special boundaries σ_{sp} and general boundaries σ_g: σ_{sp}^1, σ_g^1 – surface tension of boundaries in pure material; σ_{sp}^2, σ_g^2 – in material with impurity.

ature curves of σ_1/σ_g depends only on the impurity content and is independent of other factors, within the experimental accuracy. We have observed similar behaviour previously in pure tin [1, 2]. It is clear from Fig. 3 that T_c falls with rise of sodium content.

Figure 4 gives a schematic diagram of the temperature dependences of surface tension of special boundaries σ_{sp} and general boundaries σ_g, with $(\partial\sigma/\partial T)_g > (\partial\sigma/\partial T_{sp})$, since the general boundaries are less ordered and their entropy is higher than in special boundaries.

If the temperature curves of surface tension $\sigma_{sp}(T)$ and $\sigma_g(T)$ intersect below the melting point, a boundary with special structure transforms to a general boundary. There will be a break on the $\sigma(T)$ curves during a first-order phase transition. Furthermore, the entropy of boundaries in a material with an impurity is higher, and the surface tension lower than in the pure material. If the surface tension of a general boundary diminishes more with rise of impurity concentration than that of a special boundary, the temperature T_{c1} at which the structure of a general boundary becomes more favourable as regards energy is lower than T_{c2} for the pure material ($T_{c1} > T_{c2}$, Fig. 4).

The shape of the curves in Fig. 2 allows us to speak of breaks on the $\sigma_{sp}/\sigma_g(T)$ curves. Figure 3 shows the diminution of T_c with rise of impurity concentration. Together with the results of [1, 2], these results suggest that there is a "special boundary–general boundary" phase transition at T_c. Judging from the shape of the temperature dependences of surface tension, it is a first-order transformation.

Two grain-boundary and a volume phase coexist at the grain-boundary phase transition point. The Gibbs adsorption equation for the two grain-boundary phases – special boundary and general boundary [5] is

$$A_{sp}^s d\sigma = -S_{sp}^s dT - N_{sp}' d\mu_{sp}' - N_{sp} d\mu_{sp};$$

$$A_g^s d\sigma = -S_g^s dT - N_g' d\mu_g' - N_g d\mu_g, \qquad (1)$$

where A is the molar area in the grain-boundary solution; S and N – surface excesses of entropy and cocentration respectively; μ – chemical potential; σ – surface tension; "sp" and "g" denote a special boundary and a general boundary, primed values refer to sodium atoms, unprimed – tin atoms, values with superscript "s" to the solutions as a whole.

Assuming the volume solution to be perfect, due to the thermodynamic equilibrium conditions we have:

$$d\mu'_{sp}=d\mu'_g=d\mu'_v=RTd\ln c_v+(R\ln c_v-S'_v)\,dT;$$
$$d\mu_{sp}=d\mu_g=d\mu_v=-RTdc_v-(Rc_v+S_v)\,dT. \tag{2}$$

Here S'_v and S_v are the entropies per Na and Sn atom in the volume solution.

The differences between adsorption on a special boundary and a general boundary are assumed to be small; then from (1) and (2) we have

$$dT=RT\frac{N'_{sp}A^s_g-N'_gA^s_{sp}}{S'^s_gA^s_{sp}-S^s_{sp}A'^s_g}d\ln c-RT\frac{N_{sp}A^s_g-N_gA^s_{sp}}{S'^s_gA^s_{sp}-S^s_{sp}A'^s_g}dc, \tag{3}$$

where terms which contain the differences of adsorptions on both boundaries have been omitted from the denominator. The change in molar area is not more than a few percent and so we shall assume below that $A^s_g\simeq A^s_{sp}=A$. Then equation (3) can be written

$$dT\simeq RT\frac{N'_{sp}-N'_g}{S^s_g-S^s_{sp}}d\ln c-RT\frac{N_{sp}-N_g}{S^s_g-S^s_{sp}}dc. \tag{4}$$

The differences in the surface excesses in the numerators and denominators of (4) coincide with the differences of the actual grain-boundary concentrations and entropies.

For the pure material $S^s_g-S^{sp}_s=q_{tr}/T$, where q_{tr} is the heat of the grain boundary phase transition. For the solution the first non-vanishing correction to this value is linear in N'_{sp} and N'_g and so can be neglected for adsorption of the order of a few percent. Let us examine some limiting cases.

1. Both grain boundary solutions are infinitely dilute; then $\Gamma_{sp,g}=j_{sp,g}+$terms of higher orders in c, where Γ is grain boundary adsorption, j_{sp}, j_g – adsorption constants. From (4)

$$\Delta T\approx\frac{RT^2}{q_{tr}}(j_{sp}-j_g-N_{sp}+N_g)\,\Delta c.$$

We take the value q_{tr} equal in order of magnitude to the heat of melting of tin $q_{tr}\simeq 7{\cdot}1$ kJ/mole [6].

2. Both grain boundary solutions are saturated: $N'_{sp}\simeq$ const, $N'_g\approx$ const. Considering that at low concentrations $|c|\ll|\ln c|$ we have

$$\Delta T\simeq\frac{RT^2}{q_{tr}}(N'_{sp}-N'_g)\,\Delta\ln c.$$

This corresponds to the experimental dependence of $\Delta T(c)$ (see Fig. 2). Here $N'_g-N'_{sp}\approx 5\times10^{-3}$, that is, the absolute difference in the number of adsorption sites in a general boundary and a special boundary is $\sim 0{\cdot}5\,\%$ of the total number of sites in the boundary.

The simplest thermodynamic model can be constructed as follows: a limited number of adsorption sites is allocated to impurity atoms (Na) in the boundary, their molar fractions r_{sp} and r_g respectively. The change in configurational entropy associated with the formation of grain boundary solutions is

$$\Delta S=R\ln\left(\frac{[(n_{Sn}+n_{Na})\,r]!}{n_{Na}![(n_{Sn}+n_{Na})\,r-n_{Na}]!}\right), \tag{5}$$

where n_i is the number of atoms of the corresponding component. The chemical potentials of sodium and tin atoms are equal respectively to

$$\mu_{Na}=\mu_{Na}^{st}(\sigma, T)+RT\ln\frac{c_{Na}r}{r-c_{Na}}-RTr\ln\frac{r}{r-c_{Na}};$$

$$\mu_{Sn}=\mu_{Sn}^{st}(\sigma, T)-RTr\ln\frac{r}{r-c_{Na}}. \qquad (6)$$

c_{Na} – sodium concentration in solution.

Now let us write out the conditions for thermodynamic equilibrium of the two components in all three phases, expanding $\mu^{st}(\sigma, T)$ in series of powers of $\Delta\sigma=\sigma-\sigma_0$ and $\Delta T=T-T_0$, where σ_0 and T_0 are the surface tension and phase transition temperature in pure tin, and the standard state for sodium is chosen as the dilute solution in which $\sigma\approx\sigma_0$ and $T\approx T_0$. We obtain a system of four non-linear equations with four unknowns: ΔT, $\Delta\sigma$, c_{sp}, c_g (c_{sp}; c_g are the sodium concentrations in the respective grain boundary solutions which make it possible to obtain an exact solutions). Analysis of this system in the limiting cases described above gives results which agree with the purely thermodynamic approach. In case 2, for instance, we have

$$\Delta T\simeq\frac{RT^2}{q_{tr}}(r_{sp}-r_g)\ln c+T\frac{r_{sp}g_{sp}-r_g g_g+RT(r_g\ln r_g-r_{sp}\ln r_{sp})}{q_{tr}},$$

where g_{sp}, g_g are the free adsorption energies in a infinitely dilute solution on the respective boundaries. The same result is obtained from relation (3) by substitution of Langmuir isotherms

$$\Gamma'_{sp,g}=\frac{r_{sp,g}c\exp(g_{sp,g}/RT)}{r_{sp,g}+c\exp(g_{sp,g}/RT)}.$$

Let c_0 be any value of the volume concentration for which the assumptions made above are valid; ΔT^0 – the corresponding displacement of the phase equilibrium point. Then

$$r_{sp}g_{sp}-r_g g_g=q_{tr}\frac{\Delta T^0}{T}+RT\left((r_g-r_{sp})\ln c_0-r_g\ln r_g+r_{sp}\ln r_{sp}\right).$$

Choosing $g_{sp}=g_g=g$ as the "null" approximation, we find that for r_{sp} of order 1% the adsorption energy is 30–35 kJ/mole, which seems reasonable [8].

Thus, the temperature of the "special boundary" [100] Σ17–general boundary" phase transition falls with rise of impurity concentration. There is numerical agreement between the results and the conclusions of a thermodynamic analysis of the effect, from which it follows that the sodium solution on grain boundaries in tin is saturated.

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REFERENCES

1. Ye. L. Maksimova, B. B. Straumal and L. S. Shvindlerman, (Surface tension of [001] tilt boundaries in tin in the region of transition of special Σ17 boundaries to general boundaries), *Fiz. tverd. tel*, **28**, 3059 (1986).
2. Ye. L. Maksimova, B. B. Straumal and L. S. Shvindlerman, (Migration of [001] tilt boundaries in tin in region of Σ17–Σ1 phase transition), *Fiz. metal. metalloved.*, **63**, 885 (1987).
3. A. N. Aleshin, S. I. Prokofjev and L. S. Shwindlerman, Evidence of structure transformation in $\Sigma=5$ near-coincidence grain boundaries, *Scripta Met.*, **19**, 1135 (1985).
4. M. Hansen and K. Anderko, *Structures of Binary Alloys*, Vol. 2, Moscow, Metallurgizdat (1962).

5. V. Ye. Fradkov and L. S. Shvindlerman, (Thermodynamics of grain boundaries. Surface tension and adsorption in binary systems), *Fiz. metal. metalloved.*, **48**, 297 (1979).
6. *Tablitsy fizicheskikh velichin* (*Tables of Physical Constants*), Moscow, Atomizdat (1978).
7. A. A. Zhukhovitskiy and L. A. Shvartsman, *Fizicheskaya khimiya* (*Physical Chemistry*), Moscow, Metallurgizdat (1976).
8. V. L. Aleksandrovich, V. Ye. Fradkov and L. S. Shvindlerman, (Thermodynamics of adsorption on grain boundaries in systems with limited solubility), *Fiz. metal. metalloved.*, **54**, 986 (1982).