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MIGRATION OF [001] TILT BOUNDARIES IN TIN NEAR THE $\Sigma 17$–$\Sigma 1$ GRAIN BOUNDARY PHASE TRANSITION*

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A study is made of the temperature dependences of the migration velocity of tilt boundaries with misorientation close to 28·07° ($\Sigma 17$). There are discontinuities on the curves at points T_c, which coincide with the temperatures of phase transition of special boundaries $\Sigma 17$ to boundaries of general type obtained in the study of the temperature curves of surface tension of these boundaries [1]. From the values T_c and the data of [1] the phase diagram of existence of boundaries $\Sigma 17$ is formed. The shape of the phase equilibrium line is discussed on the basis of the thermodynamics of grain boundary phase transitions and ideas on the dislocation structure of grain boundaries.

In [2] we showed, on the basis of existing experimental data on the structure and properties of grain boundaries, that special grain boundaries exist in a restricted range of temperature and misorientation angles. The width of the angular range in which the boundaries possess special structure and properties decreases exponentially with growth of Σ – the reciprocal density of coincident sites. The maximum temperature of existence of special boundaries also falls with rise of Σ. So at a given temperature, only boundaries with Σ less than a certain Σ_{max} possess special structure and properties. In [2] we suggested that, for certain values of the misorientation angles and temperature, a phase transition from a special boundary to a non-special boundary can be observed.

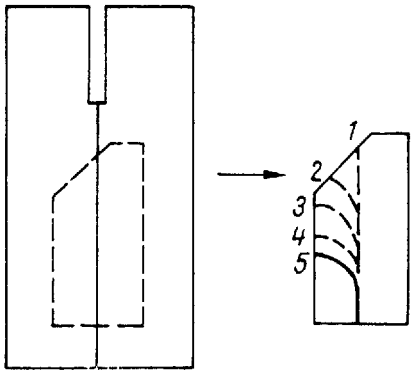

FIG. 1. Bicrystalline specimen for determining grain boundary mobility in the presence of a constant driving force. *1*, *2*, *3*, *4*, *5* – successive positions of grain boundary during migration.

In [1] we made an experimental study, on tricrystals with triple junctions with prescribed misorientation of boundaries, of the temperature dependences of surface tension σ of tilt boundaries [001] in tin in the misorientation range of φ from 25·5 to 30°. There were breaks on the curves of boundaries with σ closest to φ ($\Sigma 17$)=28·07°. The T_c position of those breaks depends only on misorientation

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of the boundaries and is independent of other thermodynamic, kinetic and geometric parameters of the triple junctions. In [1] the existence of breaks is explained by a grain boundary phase transformation of special boundaries $\Sigma 17$ into non-special boundaries. From temperatures T_c we constructed the line of equilibrium of grain boundary phases separating the ranges of existence of boundaries $\Sigma 17$ and non-special boundaries. This line is bell-shaped, consistent with ideas on the dislocation structure of special boundaries and defined by the law $\Delta T \sim \sin \Delta\varphi(B - \ln \Delta\varphi)$. The surface tension of boundaries σ is their principal thermodynamic function. So the results of [1] uniquely characterize the equilibrium line of phases $\Sigma 17$ and $\Sigma 1$ for tilt boundaries [001]. It is therefore interesting to find out about change of the kinetic properties of the boundaries, and their mobility in particular, near the temperature of the grain boundary phase transition.

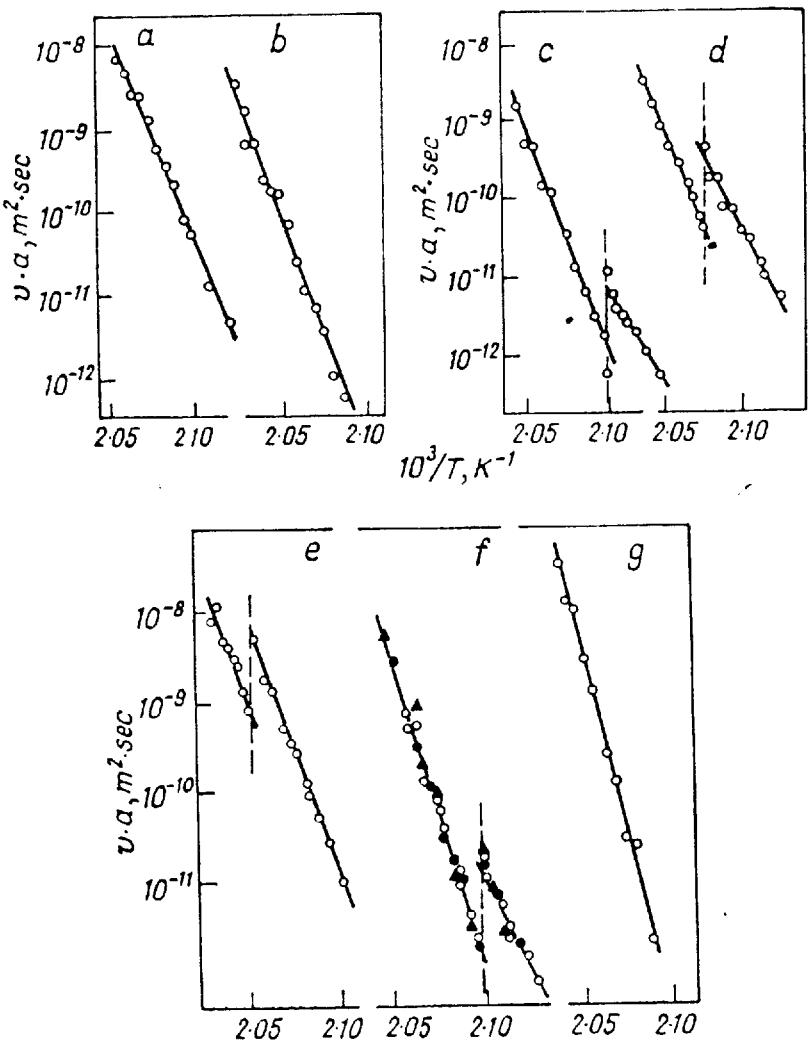

FIG. 2. Temperature dependence of velocity of [001] tilt boundaries in tin, relative to identical driving force. Misorientation angles: a – 26·0; b – 26·5; c – 27·0; d – 27·7; e – 28·2; f – 29·0; g – 29·5°. Figure 2f shows the results for specimens with different driving forces a: a_1(▲) : a_2(●) : a_3(○) = 2·9 : 1·5 : 1. T_c is clearly independent of the driving force of migration.

In [3–6] it has been shown that the parameters of grain boundary migration are a non-monotonic function of the misorientation angle: in sufficiently pure metals with from 10^{-1} to 10^{-4} at.% impurity level there are maxima of boundary mobility and minima of the activation parameters of their migration (activation energy, pre-exponential multiplier, that is, of migration entropy, and activation volume),

near special misorientation angles. These extrema have only been observed on special boundaries with $\Sigma \leqslant \Sigma$ 19. This is explained [2] by the fact that the mobility measurements were taken at fairly high temperatures T/T_m, where boundaries with $\Sigma > \Sigma$ 19 no longer exhibit special properties.

Our purpose here is to measure the migration parameters of grain boundaries [001] in tin near the equilibrium line of phases Σ 17 and Σ 1 [1].

The bicrystals for measurement of the migration parameters were grown by direct crystallization in argon atmosphere OSCh, in dishes of specially pure graphite, from tin OVCh-0000 of nominal purity 99·9999 at.%. The manner in which the bicrystal was cut to prepare the specimen on which the boundary mobility was measured, with a constant driving force of migration, is depicted in Fig. 1. Specimens were machined on an electrospark device, and then polished chemically in a solution of HNO_3–40% HF. To determine the mobility, annealing was done in a high-temperature attachment to an optical microscope in argon atmosphere OSCh. The position of the boundary before and after annealing was found from the thermal etching channel. The temperature was maintained during annealing to within $\pm 0{\cdot}3$°C.

Usually, during the study of boundary migration, curves of boundary mobility are plotted without allowing for change of the driving force with the temperature and misorientation of boundaries determined by surface tension of boundaries. In our case this is clearly not true (see [1]). However, in our range of temperatures and misorientation angles the surface tension does not change by more than 40–60% [1] and the migration rate by 3–4 orders of amgnitude (see Fig. 2 for instance). We have therefore constructed the curves of reduced velocity v/a m²/sec vs. T^{-1}.

EXPERIMENTAL RESULTS AND DISCUSSION

We have studied the migration of seven tilt boundaries [001] in tin with misorientation from 26 to 29·5° in the temperature range from 0·93 to 0·99 T_m. The resulting curves are shown in Fig. 2. The first two curves (Fig. 2*a*, *b*) are in the form of straight lines in Arrhenius coordinates over the whole temperature range studied. In the next four curves (Figs. 2*c–f*) there is a sudden fall in mobility with rise of temperature at the points denoted by T_c. Below and above T_c the mobility behaves according to the Arrhenius law. At the point T_c the mobility falls by roughly an order of magnitude with rise of temperature. T_c first grows with misorientation angle (Fig. 2*c*, *d*) and then, after reaching a maximum (Fig. 2*e*) falls again (Fig. 2*f*). There are no singularities on the last of the curves (Fig. 2*g*).

The equilibrium line of phases Σ 17 and Σ 1 obtained in [1] is shown in Fig. 3, together with the temperatures T_c at which the boundary mobility changes suddenly. The temperatures T_c found from the jumps in mobility clearly coincide with the Σ 17–Σ 1 transition temperatures, found from the breaks on the temperature dependences of surface tension in [1]. Published data from investigation of the structure of twist boundaries in gold and magnesium oxide [12, 13] is also given here. The result for the boundary Σ 17 lies in the angular range where the images of secondary grain boundary dislocations disappear.

If the jumps in mobility are indeed associated with the equilibrium phase transition on boundaries, rather than any kinetic processes (the influence of the impurity, for example) the temperature T_c will be independent of the driving force of migration. The driving force, according to its dimensionality and physical meaning, is the pressure exerted on the boundary. In the migration scheme that we have used, the driving force is governed by the capillary pressure of the curved grain boundary. This pressure is relatively small: $\Delta F = P = 10^3$ Pa. It is clear that such a low pressure cannot produce any substantial change in the temperature of transition in a condensed phase. The change of T_c can be estimated numerically using the Clapeyron–Clausius equation. We use typical values of the parameters for phase transitions in condensed phases. Then the change in temperature of the phase transition ΔT_c under the

effect of pressure P is equal to $\Delta T_c \sim T_c \Delta P \Delta P/\lambda$. Here λ is the heat of the transition, and ΔV the volume change during the transition. From this we find $\Delta T_c \sim 10^{-5}$ K.

A jump in migration velocity, outwardly similar to that discussed here, has previously been observed on special and close to special grain boundaries in aluminium [7]. In that work, the discontinuities were explained by breakaway of the moving boundary from the cloud of the adsorbed impurity,

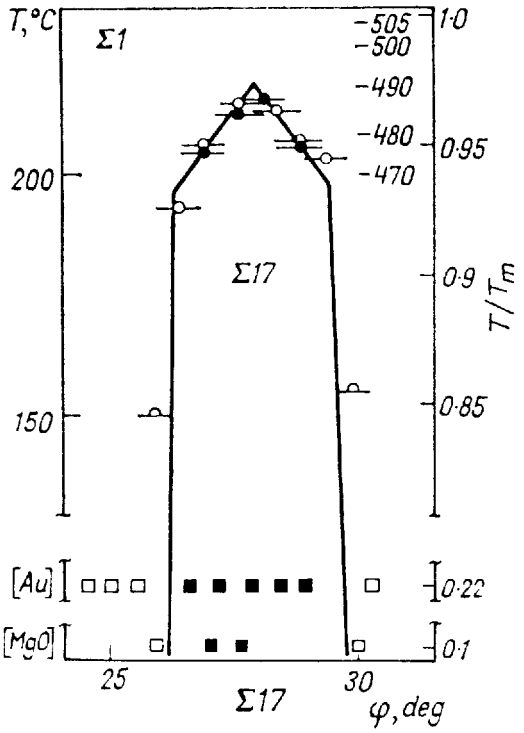

FIG. 3

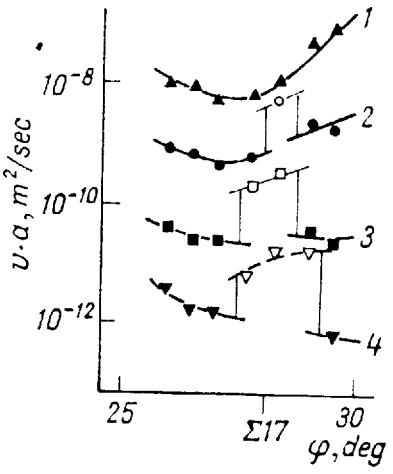

FIG. 4

FIG. 3. Phase equilibrium line of special boundaries $\Sigma 17$ and general boundaries $\Sigma 1$ in tin, constructed from temperatures T_c: ○ – values of T_c found from the temperature curves of surface tension [2]; ● – same, from temperature curves of boundary migration velocity. Published data from study of the structure of special twist boundaries $\Sigma 17$ in gold with $T/T_m = 0{\cdot}2$ [12] and in magnesium oxide with $T/T_m = 0{\cdot}1$ [13] is given at the bottom. The closed squares correspond to boundaries on which secondary GBD are observed, open squares to those consisting only of primary GBD, according to the diffraction data.

FIG. 4. Orientation dependences of reduced velocity of [001] tilt boundaries in tin with misorientation from 26 to 29·5° at different temperatures, ° C: *1* – 219; *2* – 213; *3* – 208; *4* – 204. Arrows show size of jump in relative velocity on crossing $\Sigma 17$–$\Sigma 1$ phase equilibrium line.

during which even small changes should shift the breakaway temperature considerably [8, 9, 17]. In fact, in the simplest modification of the theory of [9, 17], breakaway takes place at the moment when the binding force of the impurity with the boundary is equal to the driving force of migration

$$\Delta F = 2cu_0 \exp\left[\frac{u_0}{kT_{ba}}\right], \tag{1}$$

where c is the impurity concentration in the grain interior; u_0 – binding energy of impurity with boundary; T_{ba} – breakaway temperature. Then

$$\delta T_{ba} = \frac{u_0}{k}\left(\ln\frac{\Delta F}{2cu_0}\right)^{-2}\frac{\delta(\Delta F)}{\Delta F}. \tag{2}$$

From (1) and (2) we have

$$\frac{\delta T_{ba}}{T_{ba}} \simeq \frac{kT_{ba}}{\mu_0} \frac{\delta(\Delta F)}{\Delta F}. \tag{3}$$

For typical parameter values ($T_{ba} \sim 10^3$ K, $\Delta F = 10^3$ J/m^3, $u_0 \sim 50$ kJ/mole, $\delta(\Delta F) \sim 10^3$ J/m^3), ($\delta T_{ba}/T_{ba}$)$\sim 0{\cdot}1$, which corresponds to the temperature of breakaway moving by tens of degrees.

The experimental data on the dependence of T_c on driving force for a boundary with $\varphi = 29°$ is given in Fig. 2*e*. In the given range of driving forces ($a_1 : a_2 : a_3 = 2{\cdot}9 : 1{\cdot}5 : 1$) the temperature of the discontinuity is independent (within experimental error) of the driving force. This means that the observed jumps in velocity cannot be explained by breakaway of the boundary from the impurity. In experiments to investigate the breakaway effect, a change in the driving force ($\Delta F \sim 10^3$ Pa) of 1·5 times shifted the temperature by tens of degrees [10].

If the jump in mobility is associated with a phase transition, its value should be independent of the path of intersection of the phase equilibrium line: when $T = \text{const}$ or $\varphi = \text{const}$. The orientational dependences of mobility for four temperatures are shown in Fig. 4. We see that when the phase equilibrium line is intersected by $T = \text{const}$, the mobility also changes by roughly an order of magnitude. This provides additional evidence that we are observing the equilibrium transition of one grain boundary phase to another.

From Fig. 4 it is clear that during the transition of boundaries $\Sigma 17$ into non-special boundaries, the special properties of those boundaries also disappear: the reduced boundary velocities are higher in the range of existence of boundaries $\Sigma 17$ than outside that range.

In our opinion, these results on the temperature dependences of tilt boundary migration velocity in tin provide evidence of the phase transformation of special grain boundaries $\Sigma 17$ into grain boundaries of general type. The sudden change in the reduced migration velocity at the transition point and the absence of critical effects near the point suggest that this is a first-order phase transition. Now let us examine the kinds of structural rearrangements that are involved in this transition.

It has been demonstrated experimentally that grain boundaries posses an ordered structure. At low values of φ, the grain boundaries consist of a wall or network of lattice dislocations. The distance between these dislocations d_1 depends on the period of the so-called O-lattice [11]: $d_1 = b_1/[2 \sin(\varphi/2)]$, b_1 – Burgers vector of lattice dislocations. These dislocations are clearly visible on the electron microscopic pictures, and since the dislocations form an ordered two-dimentional structure, a characteristic set of reflections forms during X-ray or electronic diffraction on them [12–15]. As φ increases, the images of dislocations on the electron microscopic pictures merge, whereas the diffraction pattern do not undergo qualitative change and can be described, as before, by the period of the 0-lattice (see Fig. 5*a*, in which the results from [11], as well as work on twist boundaries in magnesium oxide [12], are given). Grain boundary dislocations (GBD) of this kind are normally called primary, but we shall call grain boundaries which contain only primary GBD boundaries of general type. Since the diffraction patterns from general boundaries do not change fundamentally over the whole range of misorientation angles, they can be assigned to the same grain boundary phase $\Sigma 1$. When $\varphi = 0$ all sites of the lattices coincide, and so $\Sigma = 1$.

For some values of the angle $\varphi = \varphi_c$, the sites of the O-lattice coincide with the sites of the lattices of two contiguous crystals. In that case a lattice with $\Sigma > 1$ arises. Boundaries with misorientation angles φ_c possess lower energy than those of general type [16], and their properties differ greatly from those of boundaries of general type [17]. These are called special boundaries. Although the geometric coincidence of sites of the two lattices is destroyed however small the deviation from φ_c, the structure of special boundaries is so favourable in energy terms that their special properties are preserved in the

range of angles $2\Delta\varphi$. In that range, the structure of special boundaries consists of segments with structure $\varphi=\varphi_c$, which are separated by secondary GBD. These dislocations accommodate the deviation $\Delta\varphi$, their Burgers vectors b_Σ are defined by the so-called complete pattern shift and are equal to $b_\Sigma = b_1\sqrt{\Sigma}$. The distance between these dislocations can be found with the help of the O_2-lattice from a formula in which b_Σ is put in place of b_1, and $\Delta\varphi$ (deviation from φ_c, see Fig. 5*a*) in place of φ.

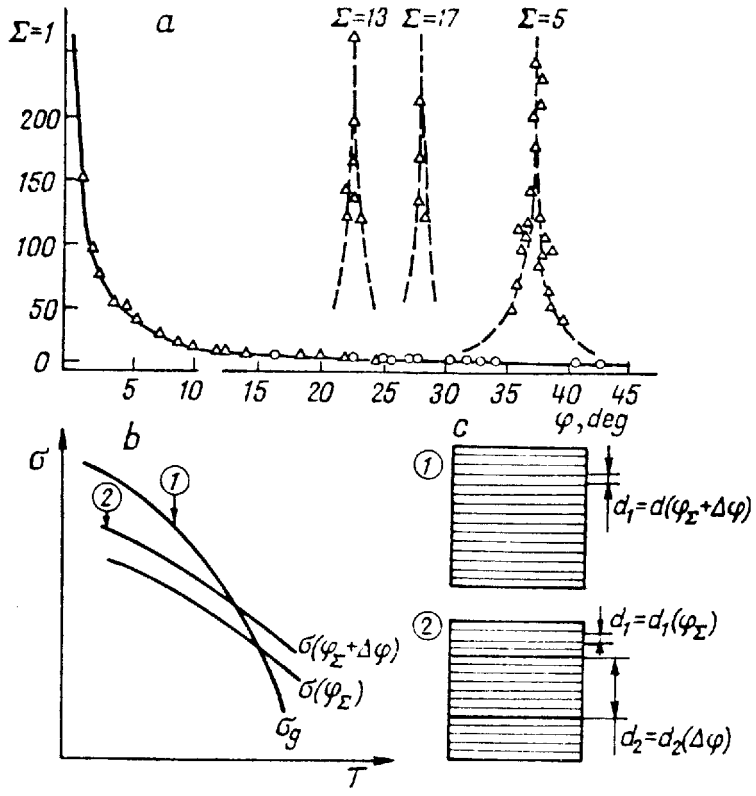

FIG. 5

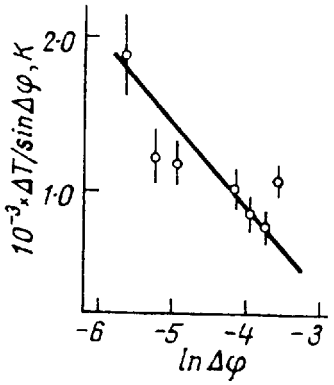

FIG. 6

FIG. 5. *a* — Dependences of distance between primary d_1 and secondary d_2 grain boundary dislocations on misorientation angle φ from data of [12]: —— — d_1; — — — d_2; *b* — change in surface tension and temperature of special boundary–boundary of general type transformation T_c when walls of secondary grain boundary dislocations are introduced into special grain boundaries to accommodate the deviation from special misorientation φ_c; *c* — possible structures of grain boundaries with misorientation angle $\varphi=\varphi_c+\Delta\varphi$.

FIG. 6. Correspondence between shape of $\Sigma17$–$\Sigma1$ equilibrium line (points taken from results of Fig. 3) and dislocation model of transition point T_c (solid line). φ — misorientation, $\Delta T = 220°C - T_c$.

Thus, the structure of special boundaries differs fundamentally from that of boundaries of general type. Thus, each Σ can be said to have its own grain-boundary phase: $\Sigma5$, $\Sigma13$, $\Sigma17$ and so on. Therefore for some value of φ, close to the special value $\varphi=\varphi_c+\Delta\varphi$, two different boundary structures can be realized (see Fig. 5*c*): only from primary dislocations with period $d_1=d_1(\varphi_c+\Delta\varphi)$ or from segments with the periodicity of primary dislocations $d_1=d_1(\varphi_c)=b_1/[2\sin(\varphi_c/2)]$ separated by secondary GBD with period $d_2=d_2(\Delta\varphi)=b_\Sigma/[2\sin(\Delta\varphi/2)]$.

As $\Delta\varphi$ increases, the energy of the wall of secondary GBD grows and, for a certain $\Delta\varphi$, the type of boundary structure changes. In our view, this change should be in the nature of a first-order phase transition. A special boundary–general boundary transition should also take place with change of temperature, since the free energy of less ordered boundaries of general type falls faster with tempera-

ture than the free energy of special boundaries (see the diagram in Fig. 5*b*). The diagram in Fig. 5*b* shows that the temperature of the phase transition T_c falls with rise of $\Delta\varphi$, when the energy of the wall of secondary GBD grows. Let us find the equation for its change.

We consider the equilibrium of two grain boundary phases in a one-component system. At the transition point, the chemical atomic potentials μ_1^s and μ_2^s in the two phases are equal: $\mu_1^s=\mu_2^s$. The curve of grain boundary phase equilibrium is determined by the surface analogue of the Causius–Clapeyron equation. If the chosen variables are σ and T, then

$$\left(\frac{d\sigma}{dT}\right)_e=-\frac{\Delta(\partial\mu^s/\partial T)_\sigma}{\Delta(\partial\mu^s/\partial\sigma)_T};$$

$$\left(\frac{d\sigma}{dT}\right)_e=\frac{\Delta S^s}{\Delta A}.$$

Thus, a first-order phase transition in the boundary is accompanied by a sudden change in entropy ΔS^s and specific area ΔA occupied in the boundary by a model of material. If we are considering boundaries with different angles φ, then

$$\frac{d\sigma}{dT}=\left(\frac{d\sigma}{d\varphi}\frac{d\varphi}{dT}\right)_e=\left(\frac{d\sigma}{d\varphi}\right)_e\left(\frac{d\varphi}{dT}\right)_e.$$

Then the equilibrium temperature of the phase transition changes with the misorientation angle as

$$\left(\frac{dT}{d\varphi}\right)_e=-\frac{\Delta A}{\Delta S^s}\left(\frac{d\sigma}{d\varphi}\right).$$

When the misorientation angle of a special angle changes by $\Delta\varphi$, a wall of secondary GBD with period d_2 appears on the boundary. The surface tension of tilt boundaries grows by

$$\Delta\sigma=\left(\frac{Gb_\Sigma}{4\pi(1-\nu)}\right)\sin\Delta\varphi\left(1+\ln\frac{b_\Sigma}{2\pi r_0}-\ln\Delta\varphi\right),$$

where r_0 is the cut-off radius, G and ν — elastic moduli. Then

$$\Delta T\cong-\frac{A}{\Delta S^s}\left[\frac{Gb_\Sigma\sin\Delta\varphi}{4\pi(1-\nu)}\left(1+\ln\frac{b_\Sigma}{2\pi r_0}-\ln\Delta\varphi\right)\right].$$

Figure 6 shows the dependence of T_c on φ (cf. Fig. 3) constructed in coordinates $(\Delta T/\sin\Delta\varphi)$–$(\ln\Delta\varphi)$. The value of r_0 can be found from the intercept on the abscissa axis: $r_0=5b_\Sigma$. We find that the width of the core of secondary grain boundary dislocations is several times larger than their Burgers vector. This agrees ideas concerning the very wide cores of grain boundary dislocations proposed in [18]. The angle $\Delta\varphi^*$ for which the cores of grain boundary dislocations overlap can be estimated from the condition $d_2=2r_0$. Then $\Delta\varphi^*\approx6°$.

The value of $A/\Delta S^s$ can be found from the slope of the straight line in Fig. 6. When $G=18$ GPa [19], $\nu=0{\cdot}330$ [19] and $b_\Sigma=a/\sqrt{17}=7{\cdot}8\times10^{-2}$ nm we have $\Delta S^s/A=3\times10^{-4}$ J/m²·K. The value of $\Delta S^s/\Delta A$ can be estimated from general thermodynamic considerations: $\Delta S=L/T_0$. For the melting of tin $L_m/T_0=14$ J/mole·K [19], $\Delta A=\Delta V_m\cdot V_{\text{mole}}/a=7\times10^2$ m²/mole [19]. We obtain $\Delta S^s/A=4\times10^{-4}$ J/m²·K. Thus, the value $\Delta S^s/\Delta A$ that we have obtained in our experiments for the $\Sigma17$–$\Sigma1$ transition agrees with estimates for a typical "volume" phase transition.

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