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EFFECT OF THE SUBSIDIARY MISORIENTATION COMPONENTS ON THE "SPECIAL GRAIN BOUNDARY–GENERAL BOUNDARY" TRANSFORMATION IN THE VICINITY OF THE COINCIDENCE MISORIENTATION OF Σ17 IN TIN

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Abstract—A small-angle twist or second tilt component was introduced to tilt boundaries [001] in tin bicrystals with misorientation angles 28.3°. The method of triple junction was used to measure the temperature dependences of the relative surface tension of the boundaries obtained and to determine the temperature of the "special boundary–general boundary" phase transition. The dependence of the transition temperature on the twist component θ_k and on the second tilt θ_H was found. The temperature of the grain-boundary phase transition, T_c, decreases with growing θ_k and θ_H, but several times slower than under deviation of the misorientation angle on the coincidence misorientation. The tilt component diminishes T_c slower than the twist component does. The results confirm the dislocation model of the "special boundary–general boundary" phase transition, proposed earlier.

Résumé—On a introduit les componentes de torsion θ_k et de deuxième flexion θ_H dan les joints des grains de flexion [001] avec l'angle de misorientation 28,3° en bicristaux d'etain. Une methode des joints triples est utilisé pour mésurer les dependences de tension de surface interganulaire de la temperature et pour déterminer la temperature T_c de transmission de phase "le joint des grains spécial–le joint non spécial". On a mésuré le dépendence de cette temperature T_c des l'angles θ_k et θ_H. T_c descend quand les θ_k et θ_H augmentent, mais quelques fois lentement q'avec augmentation de difference d'angle de misorientation et d'angle de coincidence Σ17. T_c descend avec augmentation d'angle θ_H (deuxième flexion) un peu plus lentement q'avec l'angle de torsion θ_k. Les resultats ont decrete bien avec la modelle des dislocations intergranulaire pour la transmission de phase "le joint des grains special–le joint non spécial".

Zusammenfassung—Es wurden die Dreh-und zweiter Kipp Kleinwinkelkomponenten (θ_k und θ_H) in die Kippkorngrenzen [001] 28,3° in Zinn Zweikristallen eingeführen. Es wurden die Temperaturabhängigkeiten des Verhältnisses von Oberflächenspannungen der Korngrenzen untersucht und die Temperaturen T_c der Phasenumwandlungen "spezielle Korngrenze–nichtspezielle Korngrenze" gemessen. Die Verhältnisse von Kornrenzoberflächenspannungen wurden in der Form der dreifachen Stösse in Dreikristallen gemessen. Es wurden die Abhängigkeiten der T_c von Winkeln θ_k und θ_H gefunden. Die T_c nimmt proporzional dem Wachsen von θ_k und θ_H, aber mehrmal schwacher als mit Wachsen der Winkelabweichung von Zusammenfallen-misorientierung. Die T_c nimmt mit θ_H langsamer als mit θ_k. Diese Ergebnisse bestätigen das Modell der "spezielle–nichtspezielle Korngrenze" Phasenumwandlung, in dem die Versetzungsstruktur der Korngrenzen betrachtet wird.

INTRODUCTION

Already Hart considered thermodynamical properties of phase transitions at grain boundaries [1]. At present phase transitions at grain boundaries receive even closer attention [2]. In particular, a number of stimulating results have been obtained on computer simulation of rearrangement of the grain boundary structure [3–5]. New experimental papers are available which deal with the concentrational phase transitions at boundaries: rearrangement of the boundary structure under action of impurity [6, 7]. The "special boundary–general boundary" transformation is one of most interesting types of phase transitions at grain boundaries. Such a transition was predicted in [19], and was first observed experimentally in the study of nickel diffusion along the boundaries in copper [8]. In paper [9] the then available is experimental data on the structure and properties of grain boundaries were analyzed. It was shown that in the vicinity of the coincidence misorientation there exist intervals of misorientation and temperature angles, within which the boundaries possess a particular structure and properties. For instance, in [9] the number of boundaries with special properties was shown to increase with decreasing temperature. Later in paper [10] it was shown that, indeed, a decrease in temperature gives rise to the number of misorientations, associated with the low surface tension of boundaries.

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The authors of paper [11] succeeded in constructing the existence region of Σ17 special boundaries in tin. They also studied the experimental dependences of mobility of tilt boundaries [001] in tin in the vicinity of the coincidence misorientation Σ17. It turned out that when special boundaries become of the general type, their ability diminishes abruptly and the migration activation energy E increases. Below T_c the activation energy E strongly depends on the misorientation angle ϕ (more exactly on the difference $\Delta\phi = |\phi - \phi_\Sigma|$ where ϕ_Σ is the coincidence misorientation). Above T_c the activation energy E is almost independent of ϕ. Temperature dependences of the relative surface tension of the same tilt boundaries [001] in tin in the vicinity of the Σ17 coincidence misorientation were also measured in paper [4]. These temperature dependences were found to exhibit a kink at T_c, when the boundary loses its peculiar properties. Additional experiments confirmed the fact that the temperature, T_c, when these kinks and mobility shocks are observed, is determined solely by the angle of the boundary misorientation. It has been concluded, that at T_c an equilibrium phase transition occurs at the boundary which is determined by the boundary structure only. The line of $T_c(\phi)$ was constructed in the "temperature–misorientation angle" coordinates. In this line the special boundaries of Σ17 and general boundaries are in equilibrium. This line was extrapolated to low homologous temperatures T/T_m, where T_m is the temperature of melting. At $T/T_m = 0.22$ and $T/T_m = 0.1$ Balluffi and co-workers studied the structure of boundaries ⟨100⟩ in gold and magnesium oxide, respectively [12, 13]. They determined the intervals of angles near $\phi = 28.07°$ (Σ17), where secondary grain boundary dislocations (SGBD's) are observed at boundaries. These dislocations accommodate the deviation of misorientation angle to the coincidence misorientation. It turned out [11] that the "Σ17 special boundary–general boundary" equilibrium line, extrapolated to low T/T_m, coincides with the line, separating the boundaries with SGBD's from those without SGBD's [12, 13]. Proceeding from this statement, the authors [11] supposed that at high temperatures the grain-boundary transformation is accompanied by the same structural changes, as those observed at low T/T_m. In other words when the boundary loses its peculiar properties with increasing the temperature above T_c, the secondary grain-boundary dislocations vanish in it (delocalize). Using this assumption, the authors [11] carried out a thermodynamical analysis of the data obtained, while describing curve $T_c(\phi)$ by means of the two-dimensional analog of the Klausius–Clapeiron equation. It was supposed that variation in the energy of the special boundary with a misorientation angle can be described by the Frank formula for a SGBD's low-angle wall. Such a model description of transition well agrees with the macroscopic estimates made. It was also shown that the transition temperature diminishes with the impurity (sodium) concentration [20].

The results of studying the boundary structure by electron microscopy show that general boundaries involve the so-called primary grain-boundary dislocations (SGBD) with the period d determined by the Frank formula

$$d_1 = b/2\sin(\phi/2) \qquad (1)$$

here b is the Burgers vector of lattice dislocations. Special boundaries involve not one but two systems of primary dislocations with period $d_1 = d_1(\phi + \Delta\phi)$: primary dislocations with period $d_1 = d(\phi_c)$(both at the boundaries with $\phi = \phi_c$, ϕ_c is the coincidence misorientation), and a SGBD's with period $d_2 = d_2(\Delta\phi)$. Period d_2 is also determined by the Frank formula (1), but it has b_Σ, the SGBD Burgers vector, instead of b, and $\Delta\phi = /\phi_c - \phi/$ instead of ϕ, b_Σ is related with the Burgers vector of lattice dislocations by the relation: $b_\Sigma = b/\sqrt{\Sigma}$. Here Σ is the reciprocal density of coinciding sites. In our case $\Sigma = 17$.

To verify the hypothesis on vanishing (delocalization) SGBD's upon the "special boundary–general boundary" transition, one may introduce dislocations into the boundary, which do not refer to the PGBD–SGBD system arising due to grain rotation around axis [001]. The BGBD–SGBD interaction with the introduced system of "new" dislocations will cause a change in temperature, T_c. This temperature

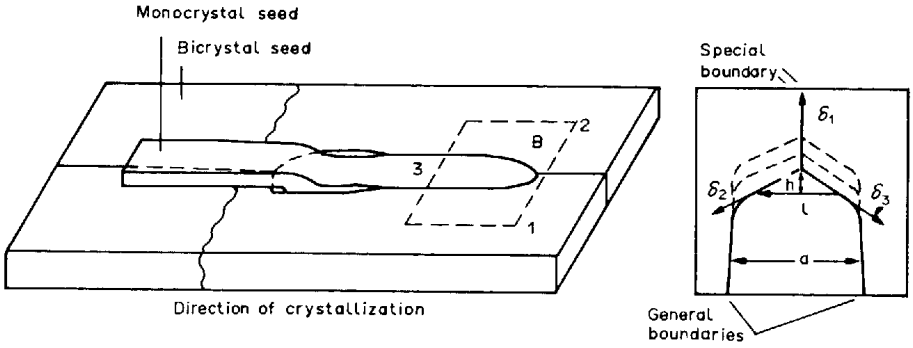

Fig. 1. Diagram of growing tricrystals with triple joints of grain boundaries for measuring the relative tension.

variation will provide information on the mechanism of the grain-boundary transformation.

EXPERIMENTAL

In our experiment we have grown two series of tricrystals of tin with triple joints of grain boundaries. As well as in the experimental paper [11], the triple joints were formed by tilt boundary [001] with the misorientation angle $\phi_1 = 28.3 \pm 0.5^\circ$ and by two equal tilt boundaries with the misorientation angles $\phi_2 = (90\text{-}\phi_1)/2 = 30.9 \pm 0.5^\circ$ (see Fig. 1). But in our experiment, unlike paper [4], the angles of rotation of grains around axis [001] were stable, though an additional small-angle twist component θ_K [Fig. 2(b)] or the "second" tilt component θ_H [Fig. 2(c)] was introduced into boundary I. In this case the position of seed crystal 3 (see Fig. 1) was always invariable upon growing a tricrystal. The value of the twist component varied from 0° to 8° (±0.5°). The values of the tilt component varied from 0° to 9°. The tilt and twist components were introduced separately in two different tricrystal series, but the starting tricrystal was the same for each series. The samples with triple joints were grown by the method of directed crystallization in an atmosphere of high purity argon in a boat made of highly pure graphite of type OB2-0000 tin with a nominal impurity content less than 10^{-4} at.%. Then a sample with a triple joint was cut out of the grown tricrystal by the electrospark cutting technique (Fig. 1). The sample was then subjected to chemical polishing in a HNO_3–40% HF solution. The angle at the triple joint vertex was measured by means of an optical microscope after annealing in a high-temperature attachment to the microscope. The annealing was made in an atmosphere of the high purity argon, the temperature of annealing was accurate to ±0.3°. Other characteristic features and results of test experiments are discussed in detail in paper [11].

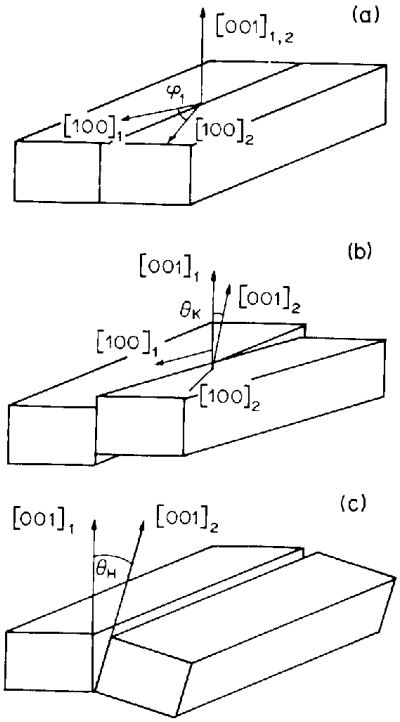

Fig. 2. Diagram of introducing the small-angle torsion component and the second tilt component at the tilt boundary [001] in tin; (a) starting bicrystal; (b) bicrystal with an additional twist component θ_K; (c) bicrystal with an additional second tilt component θ_H.

RESULTS

Figure 3 presents temperature dependences of the relative surface tension of boundaries measured by the angle at the triple joint vertex. The data for the boundaries with twist component are shown in Fig. 3(a), and those with the "second" tilt components [Fig. 3(b)]. Each of these dependences shows a discontinuity. In paper [11] such a discontinuity was found to appear when special boundary transforms into a general type one. In case no phase transition takes place at the boundaries denoting the joint, the temperature dependences have the form of horizontal or slightly tilted straight lines [11]. With increasing the additional misorientation components, θ_K and θ_H, the temperature, T_c, at which the discontinuity appears, decreases. Light points in Fig. 4 indicate the dependences of T_c on angle θ_K [Fig. 4(a)] and on θ_H [Fig. 4(b)]. Dark points in the same figure indicate the dependences of T_c on the misorientation angle $\Delta\phi$, according to the data obtained in Ref. [4]. It can be seen that, in principle, an increase in the additional misorientation components, θ_K and θ_H affects T_c in the same way, as the deflection $\Delta\phi$ of the misorientation angle ϕ, from ϕ_Σ (misorientation of coincidence Δ17); $\Delta\phi = |\phi_1 - \phi_\Sigma|$. But a decrease of T_c with increasing θ_K and θ_H occurs several times slower, than with increasing $\Delta\phi$: $dT_c/d\Delta\phi = 12.5$ K/deg; $dT_c/d\theta_H = 2.6$ K/deg, and $dT_c/d\theta_K = 2.4$ K/deg. Figure 5 shows three-dimensional representations of the region, where special boundaries Σ17 are exhibited, in the "temperature–misorientation angle-additional misorientation angle, θ_K and θ_H "coordinates". This region is shaped as a narrow plate normal to the axis of misorientation angles, ϕ. Thus an important conclusion can be made that the additional misorientation components do not too severely distort the shape of the region of special boundaries, defined in experiments at $\theta_{K,H} = 0^\circ$.

DISCUSSION

It has been shown in paper [11] that the angular range of $2\Delta\phi$, within which special properties of grain boundaries are observed, coincides with the range of misorientation on angles, displaying special boundary structure. Inside the latter range there are so-called secondary grain-boundary dislocations (SGBD's) accommodating deflection $\Delta\phi$ of the misorientation angle to the coincidence misorientation.

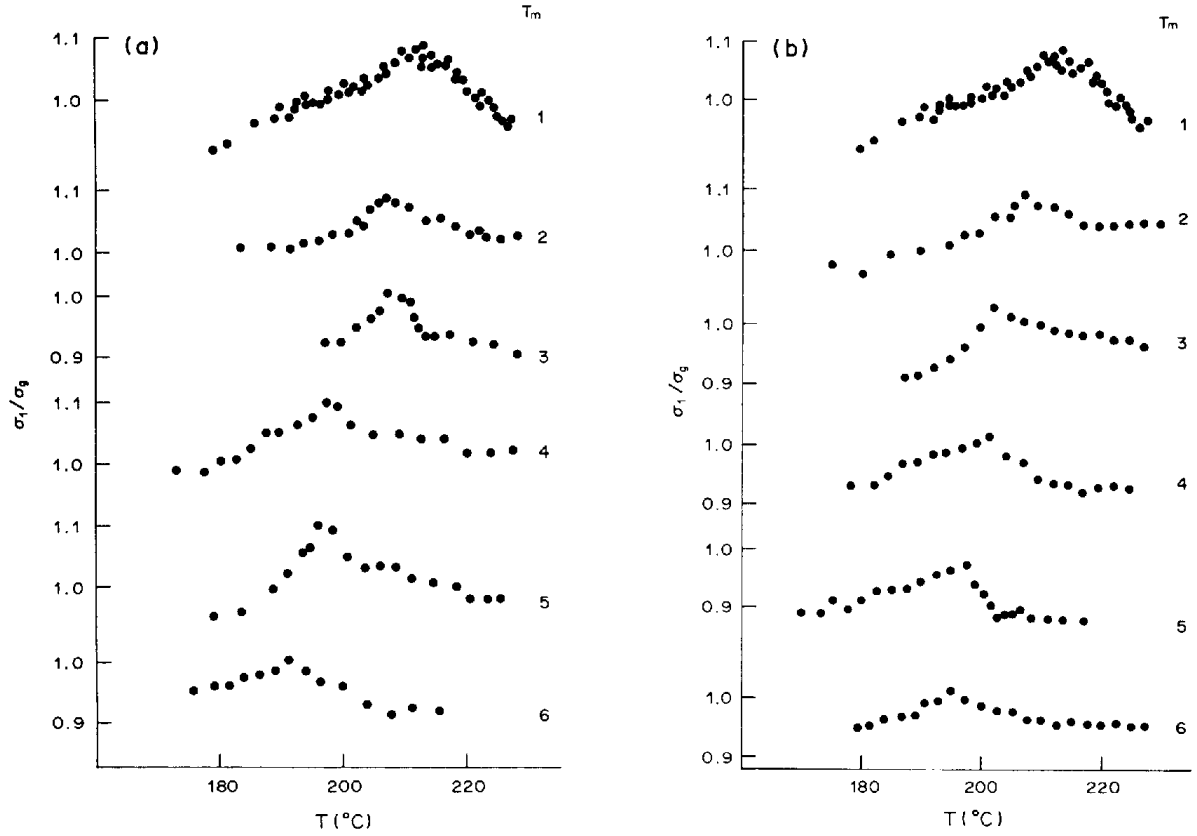

Fig. 3. Temperature dependences of the relative surface tension for the tilt boundary [001] with the misorientation angle $\phi = 28.3°$ and additional misorientation component: (a) twist θ_k 1–0°; 2–1.5°; 3–3.5°; 4–6°; 5–7°; 6–8°; (b) second tilt θ_H 1–0°; 2–3°; 3–4°; 4–5°; 5–6.5°; 6–9°.

Distance d_2 between these dislocations depends on $\Delta\phi$ as

$$d_2 = b_\Sigma/[2\sin(\Delta\phi/2)]. \quad (2)$$

Distance d_2 strongly varies within the range of special boundaries in the vicinity of the coincidence misorientation. Beyond this range the grain boundary structure is also periodic but the grain-boundary recurrence period is in this case determined by the misorientation angle [see equation (1)]. The value of d_1 slightly depends on the misorientation angle at $\phi \geqslant 10$–15°. This elucidates the fact why within the region of special boundaries the properties of the latter are strongly ϕ-dependent, and beyond this region they only slightly vary with the misorientation angle.

Suppose the "special boundary–general boundary" transformation occurs as a first order phase transition, then one may observe equilibrium of two grain-boundary phases at the point of transition. The temperature of the grain-boundary phase transition is described by the equation, an analog of the three-di-

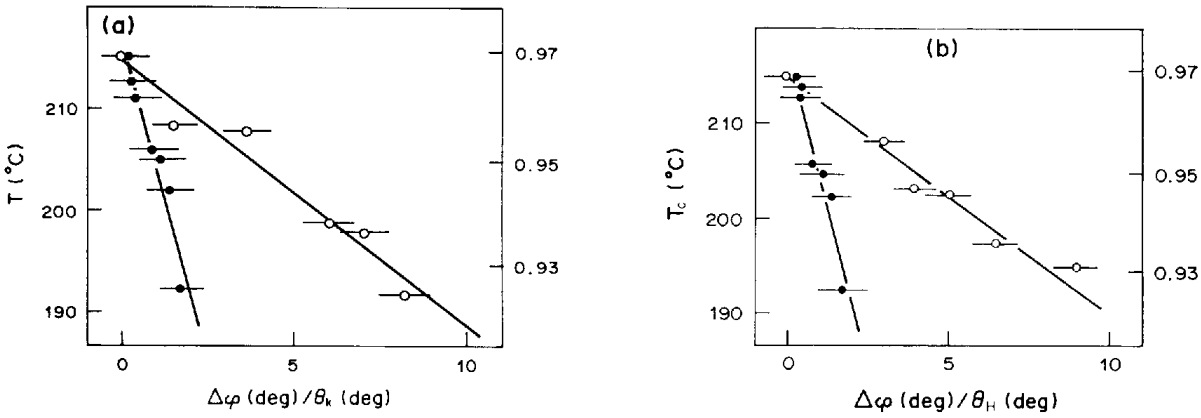

Fig. 4. Dependences of T_c of the Σ17 special boundary–general boundary transition on the misorientation angle ϕ (dark points) and on the additional misorientation component (light points); (a) twist θ_k; (b) second tilt θ_H.

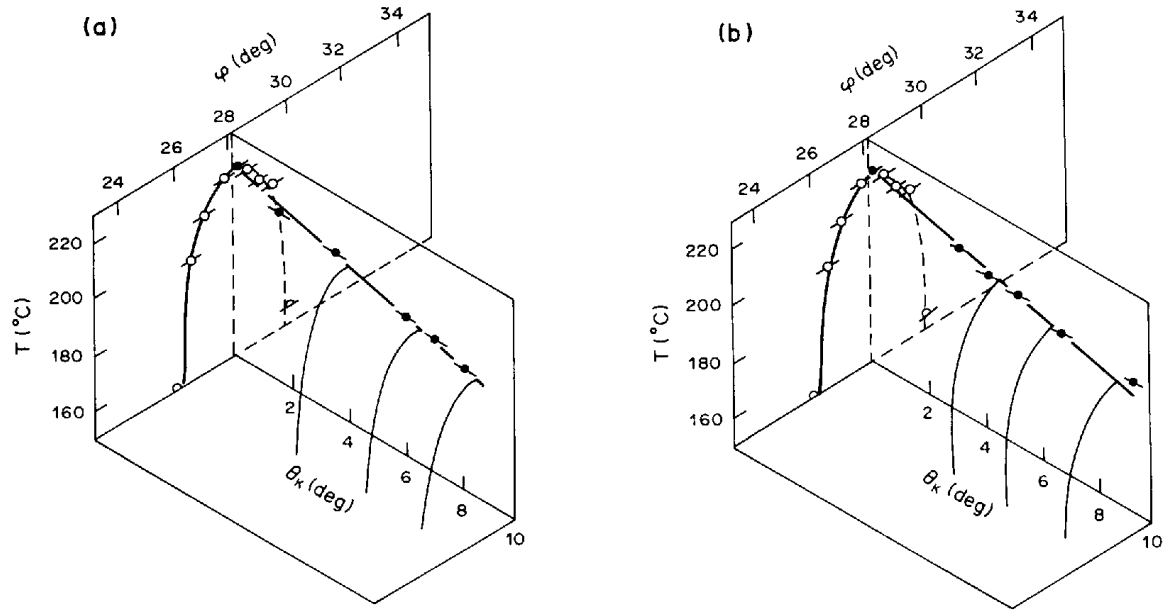

Fig. 5. Three-dimensional image of the region of existence of Σ17 special boundaries in the "T-misorientation angle ϕ-additional misorientation component" coordinates: (a) twist θ_k; (b) second tilt θ_H.

mensional Klausius–Clapeiron equation for surfaces [11]

$$\left(\frac{dT}{d\phi}\right)_l = \frac{A}{\Delta S^s}\left(\frac{d\sigma}{d\phi}\right)_l. \quad (3)$$

Here ΔS^s is the change of entropy upon transition, *and A is the specific area per mole of substance in the* boundary. Under change of the misorientation angle by $\Delta\phi$ the surface tension of the boundary at a temperature below that of transition changes by the value of ΔE, which equals the energy of the SGBD wall

$$\Delta E = \left(\frac{\sigma b \Sigma}{4\pi(1-\nu)}\right) \times \sin\Delta\phi\left(1 + \ln\frac{b\Sigma}{2\pi r_0} - \ln\Delta\phi\right). \quad (4)$$

Here r_0 is the cut-off radius, and G and ν are elastic moduli. No boundaries are observed in the structure when the temperature exceeds that of the secondary grain-boundary dislocation transition, and in the first approximation its surface tension can be assumed to be independent on the misorientation angle. Then in equation (3) $\Delta\sigma = \Delta\sigma = \Delta E$ and

$$\Delta T = -\frac{\Delta A}{\Delta S^s}\left[\frac{\sigma b \sin\Delta\phi}{4\pi(1-\nu)} \times\left(1 + \ln\frac{b\Sigma}{2\pi r_0} - \ln\Delta\phi\right)\right]. \quad (5)$$

The quantity $A/\Delta S^S$, obtained by equation (5) was shown [4] to coincide with the estimate of $A/\Delta S^S$ made for a typical first order bulk phase transition (melting) for a thin layer.

The model of the grain-boundary phase transition based on the SGBDs delocalization predicts thus correctly the basic quantitative characteristic features of transition: (1) above T_c the properties of boundaries only slightly depend on ϕ, and below T_c the dependence is strong; (2) the temperature of transition decreases with increasing $\Delta\phi$. At the same time the coincidence of $A/\Delta S^S$, obtained by equation *(5) from the ϕ-dependence of T_c, with the estimate* obtained for melting a two-dimensional tin layer does not provide convincing evidence in favour of the SGBD model. It is for getting another independent proof that we have carried out this investigation.

What comes about with the boundary structure on introducing a small-angle torsion component? At the boundary there appears a small-angle torsion component? At the boundary there appears a small-angle net of screw dislocations, compensating noncoincidence of planes (001) within the boundary plane. The data on lattice dislocations in tin [14, 15] make it possible to conclude that this net consists of a wall of dislocations parallel to axis [001] and of a wall normal to this axis. The distance between the dislocations of each net is determined by equation (1), the Burgers vector of the dislocations being equal to the lattice period.

When the "second tilt" component is introduced, as is shown in Fig. 2(c), planes (001) outcoming at the boundary do not coincide. This noncoincidence can partially be eliminated by relaxation, and misfit dislocations of Van-der-Merve may appear at the boundary [16]. The distance between these dislocations at the given ϕ and θ_H is determined by the formula [17]

$$h = \frac{d_0}{\cos\phi}\left(1 + \frac{1}{\theta_H \mathrm{tg}\phi}\right). \quad (6)$$

Here d_0 is the interplanar distance equal to the lattice period in our case. The electron-microscope contrast

at the dislocations of noncoincidence and screw dislocations nets at the boundaries has been observed, for instance, in paper [18]. How do these defects affect the "special boundary–general boundary" transformation? If the screw dislocation net or the wall of dimensional noncoincidence dislocations did not interact with SGBD at the special boundary, T_c would not change on introducing small-angle components of torsion or of the "second tilt". Our results show that such an interaction exists: T_c decreases with increasing θ_H and θ_k. An increase in θ_H and θ_k changes T_c qualitatively, as well as an increase in $\Delta\phi$ does. This decrease in T_c is likely to be due to an increase in the energy of the SGBDs wall [see equation (3)]. One may assume that the SGBD wall's energy grows due to point defects arising at the sites of intersection of SGBDs with the screw dislocations of the small-angle net or with the misfit dislocations. Then T_c will decrease in proportion to the amount of such intersections. A comparison of formulas (1) and (6) shows that at a fixed value of $\theta_H = \theta_k$ the distance between the dislocations of dimensional noncoincidence is less than that between the screw dislocations (provided $b_1 = d_0$). At $\theta_H = \theta_k = 8$–$10°$ this difference makes up about 10%. Therefore, it follows from the SGBD model that T_c should decrease slower with increasing θ_H that it does with increasing θ_k which has been proved by the experiment.

The decrease in the temperature of the "special boundary–general boundary" transformation, observed with increasing the additional misorientation angles, confirms the model of this grain-boundary phase transition. The model is based on vanishing of the secondary grain-boundary dislocations, accommodating the deflection of the special boundary misorientation angle to the coincidence misorientation. The secondary grain-boundary dislocations are really only the perturbations in the spacing of primary dislocations. We must stress here the deep analogy between commensurate and incommensurate phases in the surface adsorbed layers and special and general grain boundaries firstly declared in [8]. There is also the analogy between the secondary grain boundary dislocations and domain walls in weak-incommensurate structures [8]. The theoretical and experimental works show the very close behavior of "commensurate–incommensurate" transitions on surfaces and "special-general" transitions on grain boundaries [9, 21–25]. It seems that these "weak" defects of structure really play an important role in processes at two-dimensional defects in solids.

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