

THE EFFECT OF PRESSURE ON MIGRATION OF  $\langle 001 \rangle$  TILT  
GRAIN BOUNDARIES IN TIN BICRYSTALS

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Of the various aspects of the grain boundary migration problem, the mechanism of the process has been studied very little. So far, all the known theoretical constructions have been based on the temperature dependence of the boundary mobility and, to a lesser extent, the migration driving force. A considerable contribution, in that sense, may be provided by the introduction of a new activation parameter - a hydrostatic pressure of the system. In fact, a study of the pressure dependence of migration velocity makes it possible to determine a new activation parameter of the migration process - the value of the activation volume  $V^*$ , which is the difference between the system's volumes in the original and activated states. When studying the mobility of individual boundaries of a certain type it becomes possible to determine the orientation dependence of activation volume, i.e.,  $V^*$  for boundaries of different degrees of ordering. Measurement of this new parameter will permit analysis of the migration mechanism more fundamentally.

The above, in fact, determines the plan of the present study, which deals with the results of measurements of the mobility of different  $\langle 001 \rangle$  tilt boundaries in tin bicrystals at different temperatures and pressures.

### Experimental

The motion of the pure tilt boundaries with different misorientation angles was studied using the technique of a constant driving force of migration  $\Delta F = \sigma \Omega / a$ , where  $\sigma$  is the surface energy of the grain boundary,  $\Omega$  is the atomic volume, and  $a$  is the width of the grain to be consumed (1). The grain boundaries were studied with both special misorientation angles ( $22,5^\circ$ ;  $28^\circ$ ;  $37^\circ \pm 0,5^\circ$ ), reciprocal coincidence site density  $\Sigma$  being respectively equal to 13, 17, 5) and those far from the coincidence orientations ( $25^\circ$ ;  $33,5^\circ$ ;  $41^\circ \pm 0,5^\circ$ ). The bicrystals were grown from highly pure tin (99,999%) by a directional crystallization technique. Specimen orientation was controlled by the light technique (1); they were preliminarily etched by HCl-HNO<sub>3</sub> (1:1) solution for 30-50 s. The accuracy of orientation determination was  $\pm 0,5^\circ$ . Directly before annealing the specimens were electrolytically polished (25% HClO<sub>4</sub>,  $d = 1,48 \cdot 10^{-2}$  kg/m<sup>3</sup> at 20°C with 75% alcohol added) to improve the surface quality and remove work-hardening after electro-erosion treatment.

The studies were carried out at atmospheric pressure over the temperature interval of 185-225°C and hydrostatic pressure up to  $16 \cdot 10^8$  Pa at 208°C. At high pressures the specimens were annealed in a fluid chamber with variable external mechanical supply and liquid medium (silicone oil). The accuracy of pressure control was about  $\pm 3 \cdot 10^7$  Pa. At atmospheric pressure the specimens were annealed in a high-temperature cell directly in the field of view of the optical microscope. The position of migrating boundaries was fixed with the help of the thermal etching grooves (2); accuracy of determination of mobility did not exceed 5%. The temperature was measured with the help of precise tem-

perature controlling device with an accuracy of 1°.

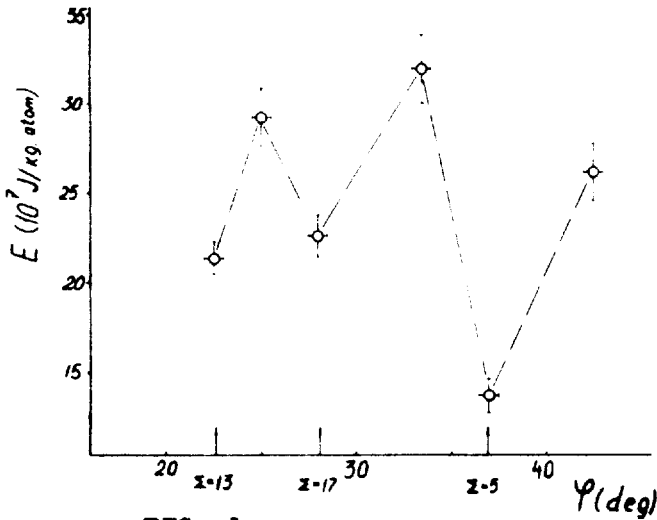


FIG. 1

Activation energy of the migration of <001> tilt boundaries in tin.

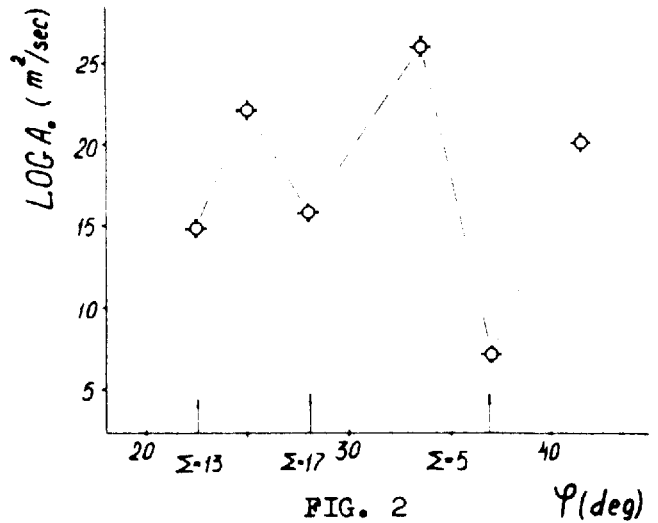
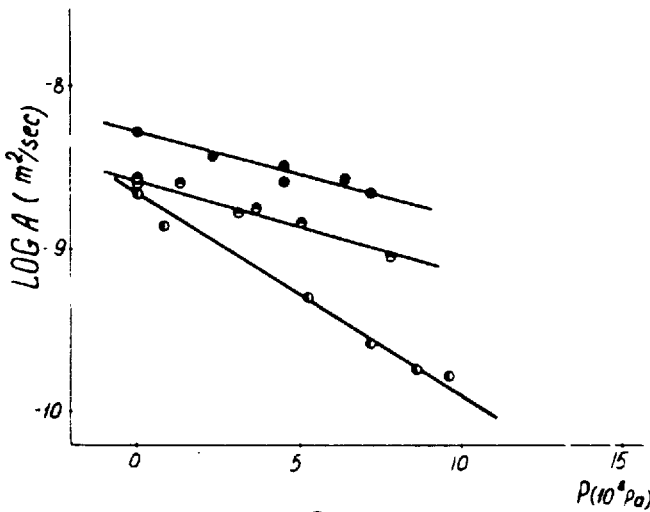
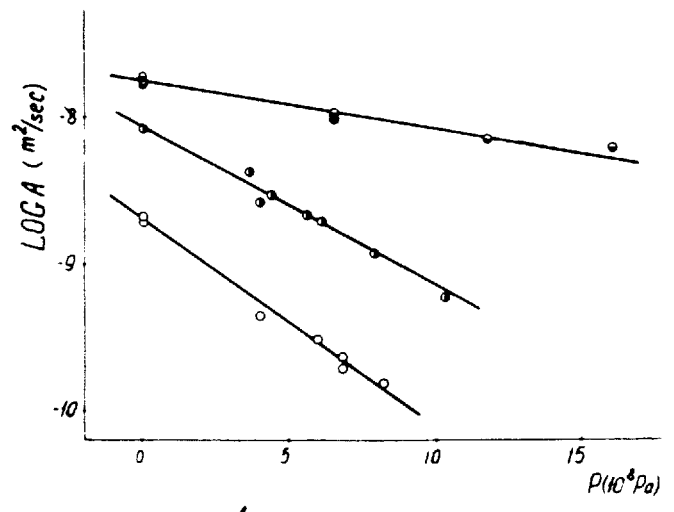


FIG. 2

Preexponential factor in the mobility equation for the <001> tilt boundaries in tin.



a



b

FIG. 3

Dependencies of mobility of the <001> tilt boundaries of hydrostatic pressure in tin bicrystals. Misorientation angles; a) ● -22,5°; ● -28°; ● -25° b) ● -37°; ● -41,5°; ○ -33,5°

Results and Discussion

The boundaries' mobility value  $A$  in our case was determined as

$$A = \frac{V}{l/a} = A_0 \exp\left(-\frac{G}{kT}\right) = A_0 \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{pV^*}{kT}\right), \quad (1)$$

where  $V$  is the migration velocity,  $A_0$  is the preexponential factor,  $G$  is the free activation energy of the migration process,  $E$  is the activation energy of the migration process,  $p$  is the pressure, and  $V^*$  is the activation volume of migration. Fig. 1 and 2 show the change of activation energy  $E$  and preexponential factor  $A_0$  depending on the misorientation angle  $\varphi$ . Fig. 3 shows that hydrostatic pressure considerably affects the boundary mobility, and thereby the degree of this effect depends, in turn, on the misorientation angle (Fig. 4). The slope of the  $A$ - $P$  straight line was used to determine the activation volumes of the boundary migration (Fig. 4).

It is noteworthy, that the special misorientations correspond to the minima of all the activation migration parameters  $E, A_0, V^*$ . Besides, for the special boundaries these parameters increase with the surface density of coinciding sites  $\sqrt{\Sigma}$ .

A linear dependence was revealed between  $E$  and  $\log A_0$  (Fig.5). This is so called compensation effect. The compensation temperature corresponds in our case to the tin melting point.

Nowadays, the description of grain boundary migration is based on absolute rate theory. The rate of migration in this case (3) is determined by the expression

$$V = b \nu \frac{\Delta F}{kT} \exp\left(-\frac{G}{kT}\right), \tag{2}$$

where  $\nu$  is the Debye frequency,  $\Delta F$  and  $b$  are the driving force and boundary displacement due to an elemental act of atomic transition. It is generally accepted to divide all the mechanisms into two major groups: those of individual transitions, where the elemental act of the boundary displacement is a transition of a single atom and those involving group transitions, where the elementary act of the boundary displacement is determined by the transition of several atoms. The principal question, which is not solved so far, is which of the two main migration mechanisms is effective in fact. The present study tries to give a definite opinion on that point. Its feature, as mentioned above, is the determination of one more activation parameter - activation migration volume.

For the mechanism of individual transitions the expression of the migration rate is as follows:

$$V = b \nu \frac{\Delta F}{kT} \exp\left(-\frac{G}{kT}\right) = b \nu \frac{\Delta F}{kT} \exp\left(\frac{S}{k}\right) \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{PV^*}{kT}\right), \tag{3}$$

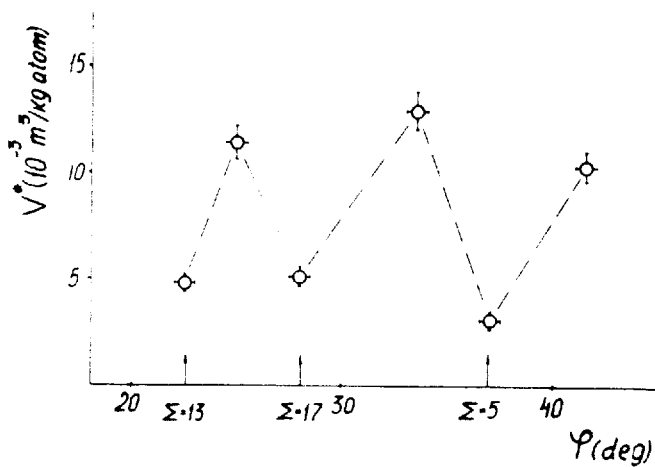


FIG. 4  
Activation volumes of the migration of  $\langle 001 \rangle$  tilt boundaries in tin.

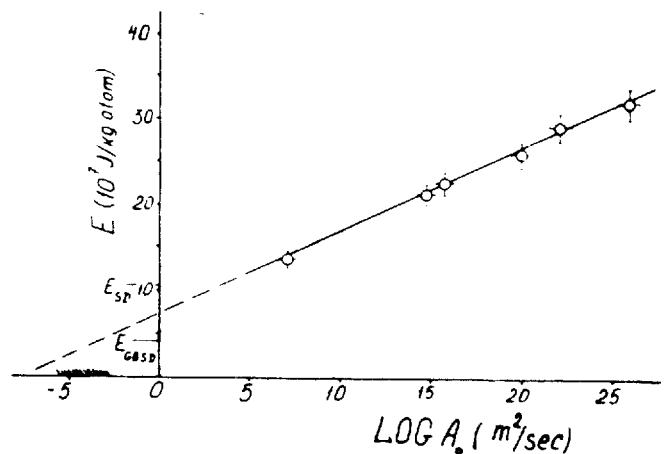


FIG. 5  
Dependence of the migration activation energy of the special  $\langle 001 \rangle$  tilt boundaries in tin on the preexponential factor in the mobility equation for tin. The area is dashed, corresponding to the models of individual atomic transition.

where  $b$  is the boundary displacement due to transition of a single atom (usually  $b$  is taken as equal to one lattice parameter), while mobility determined in our case is equal to:

$$A = b \nu \frac{b\Omega}{kT} \exp\left(\frac{S}{k}\right) \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{PV^*}{kT}\right) = A_0 \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{PV^*}{kT}\right) \tag{4}$$

$\Omega$  is the atomic volume. The choice of model of the transition mechanism (whose number is quite large) determines the values of theoretical parameters such as energy and entropy of activation, and form of preexponential factor. When analyzing the experimental results we used three models - a purely diffusional migration model (boundary migration occurs due to diffusional motion of atoms from grain to grain) and two modifications, a step model (4,5) and dislocation model (5).

When considering the elementary migration act to be the diffusion transition of atom from grain to grain, then the value of  $G$  in eq.(3) should be equal to the free energy of self-diffusion  $G_{SD}$ . Then, using the literature data on self-diffusion for tin (6-8) from (4) one can determine the boundary migration parameters  $E=10,4 \cdot 10^7$  J/kg.atom,  $V^*=5,3 \cdot 10^{-29}$  m<sup>3</sup>/kg.atom,  $A_0=10^{-3}$  m<sup>2</sup>/s. In our case the values  $E$  and  $A_0$  are significantly higher. Only the values of  $V^*$  for special boundaries are close to the theoretical ones.

Analogous results can be obtained with the aid of a step model (4,5) and a dislocation model (5).

Thus, the above analysis leads to conclusions as follows: Firstly, the value of activation energy of migration is much higher than that of bulk self-diffusion (and, of course, than that of grain boundary diffusion). Secondly, the activation volume of migration of special boundaries is close to that of bulk self-diffusion, while for non-special boundaries it considerably exceeds the lattice one. And, finally, the value of the preexponential factor in our experiments is by many orders more than the theoretically conceivable value. (To illustrate this, in fig. 4 the theoretical parameters of the grain boundary migration are given, obtained from the models of individual transitions considered). Apparently, the models of individual transitions are not capable of explaining the experimental values of the migration parameters.

Let us now consider the group mechanisms of boundary migration. In a classical model of group transition by Mott (9) it is assumed that the elementary migration act of boundary migration consists of a melting of the group of atoms from one side of the boundary and its crystallization in the adjacent crystal. However, the assumption about the melting of the atomic group, natural for the model of a liquid boundary, does not correspond to modern ideas about the grain boundary structure. Below, our experimental results are discussed on the basis of another model of the group transition.

We assume that the boundary moves due to the transition of some structural element (group of  $n$  atoms) from one grain into the boundary and transition of the same structural element from the boundary into another grain. Locally the boundary widens by increasing the number of atoms in it by the free activation energy of the elemental migration act. In such a way we can determine the activation migration parameters.

$$\begin{aligned} G &= \frac{n \sigma \Omega}{\lambda} \\ E &= - \frac{n \sigma_0 \Omega}{\lambda} \\ S &= - \frac{n \Omega \partial \sigma / \partial T}{\lambda} \end{aligned} \quad (5)$$

where  $\sigma_0$  is the surface tension of the boundary  $\sigma$  at 0°K and  $\lambda$  is the boundary width. Temperature dependence of the surface tension we represent in the following form:

$$\sigma = \sigma_0 (1 - \alpha T + \beta T^2 - \dots) \quad (6)$$

The compensation effect (Fig. 5) can be described with the aid of (6), when only the linear term is taken in the expansion (6). (The quadratic term in (6)  $\beta T^2$  proved to be about  $\sim 0,2 \alpha T$  even at the melting point). The slope angle in this case will be equal to  $k/\alpha$  and, thus,  $1/\alpha = T_c$ . In order to obtain  $\sigma_0$  we used expansion (11) and experimental data on surface tension for grains in tin  $\sigma_{220^\circ\text{C}} = 10^{-1}$  J/m<sup>2</sup> (7),  $\sigma_{160^\circ\text{C}} = 1.6 \cdot 10^{-1}$  J/m<sup>2</sup> (10), therefore  $\sigma = 6,6 \cdot 10^{-1}$  J/m<sup>2</sup>. Hence we obtain quite a reasonable value of  $\partial \sigma / \partial T = 10^{-2}$  J/m<sup>2</sup> K. Using equation (5) and experimental values of  $E$  and  $A_0$  one can

determine the number of atoms in the elemental group (see table). It is seen that calculation based on independent parameters, which are activation energy and preexponential factor in the mobility equation, gives a close value of  $n$ . With the help of the values of  $n$  obtained one can easily determine the change of atomic volume during the crystal boundary transition  $\Delta V = V^*/n$  (see table). It is noticeable that for all the special boundaries the values of  $\Delta V$  are equal  $-0,24 \cdot 10^{-3} \text{ m}^3/\text{kg. atom}$  and differ almost as much as two times from  $\Delta V$  of non-special boundaries, equal to  $(0,41-0,42) \cdot 10^{-3} \text{ m}^3/\text{kg. atom}$ , convincingly proving the structural similarity of all the boundaries corresponding to special misorientations and their difference in structure from the non-special boundaries.

TABLE

The analysis of our experimental results with aid of group mechanism of grain boundary migration

	$\varphi, \text{deg}$	$n_E = \frac{E \lambda}{\sigma_0 \Omega}$	$n_S = \frac{\ln A_0 \lambda k T_c}{\sigma_0 \Omega}$	$\Delta V = \frac{V^*}{n_E} \left( 10^{-3} \frac{\text{m}^3}{\text{kg. atom}} \right)$
$\Sigma = 13$	$\varphi = 22,5^\circ$	20	17	0,24
	$\varphi = 25^\circ$	28	24	0,41
$\Sigma = 17$	$\varphi = 28^\circ$	21	18	0,24
	$\varphi = 33,5^\circ$	31	28	0,42
$\Sigma = 5$	$\varphi = 37^\circ$	13	10	0,24
	$\varphi = 41,5^\circ$	25	22	0,42

The major conclusion, which we should like to draw from the study presented, is that the results obtained can not be explained on the basis of ideas of the individual mechanism of atomic transition during the boundary motion. It is significant that this conclusion is based not only on the measurement of activation energy and preexponential factor, but also of the activation volume of migration.

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