Influence of pressure on the migration of ⟨001⟩ tilt boundaries in tin bicrystals

D. A. Molodov, B. B. Straumal, and L. S. Shvindlerman

Institute of Solid-State Physics, Academy of Sciences of the USSR, Chernogolovka, Moscow Province

(Submitted May 4, 1983; resubmitted November 15, 1983)

Fiz. Tverd. Tela (Leningrad) **26**, 1033–1039 (April 1984)

The dependences of the mobility of individual ⟨001⟩ grain boundaries in tin bicrystals on the hydrostatic pressure were obtained for the first time. The temperature dependences of the mobility were also found. For six boundaries studied, special and nonspecial, values were determined for the activation energy, the preexponential factor in the mobility equation, and a new activation parameter, the activation volume in the boundary migration process. It was found that all the migration activation parameters vary in the same way with the grain misorientation angle, and their minima correspond to special boundaries. The experimental results are discussed as regards various theoretical models of migration.

Of the many aspects of grain boundary migration, the mechanism of the process is surely the one least studied. So far, all the available theoretical constructs have been based on the results of studies of the boundary mobility as a function of temperature and to a lesser extent of the migration driving force. In this sense, there may be con-

 0038-5654/84/04 0629-05 $03.90 © 1984 American Institute of Physics

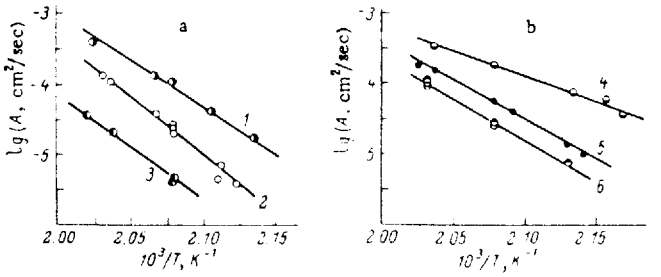

FIG. 1. Temperature dependences of the ⟨001⟩ tilt boundary mobility in tin bicrystals; grain misorientation angles (deg): a) 1) 41.5, 2) 33.5, 3) 25; b) 4) 37, 5) 22.5, 6) 28.

siderable benefit from the use of a new intensive parameter, the hydrostatic pressure in the system. This is because an analysis of the pressure dependence of the grain boundary velocity yields a new activation parameter of the migration process, namely the activation volume V^* which is the difference between the volumes of the system in the ground and activated states. In studying the mobility of individual boundaries of a given type, there is the possibility of determining the orientation dependence of the activation volume, that is, of determining V^* for boundaries having various degrees of ordering. The measurement of this new parameter allows a better-founded approach to the analysis of the migration mechanism.

The above remarks define the plan of the present paper, which gives the results of measuring the mobility of various ⟨001⟩ tilt boundaries in tin bicrystals as a function of temperature and pressure.

1. EXPERIMENTAL METHOD

The motion of pure tilt boundaries with various grain misorientation angles was studied using a constant migration driving force $\Delta F = \sigma\Omega/a$, where σ is the grain boundary surface energy, Ω the atomic volume, and a the width of the disappearing grain.[1] Boundaries were examined both with special grain misorientations (22.5°, 28°, 37° ± 0.5°; the coincidence-site density Σ was respectively 13, 17, 5) and far from coincidence orientations (25°, 33.5°, 41.5 ± 0.5°). The bicrystals were grown from 99.999% pure tin by the horizontal Bridgman method. The orientation was checked optically,[1] the samples being first etched in an $HCl + HNO_3$ mixture for 30–50 sec. The orientation difference was determined with an accuracy of ±0.5°. Immediately before annealing, the samples were electrolytically polished (25% $HClO_4$ with density d = 1.48 g/cm³ at 20 °C and 75% ethyl alcohol) to improve the quality of the surface and eliminate the cold working resulting from the electroerosion treatment.

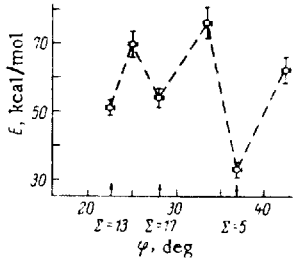

FIG. 2. Activation energy of ⟨001⟩ tilt boundary migration in tin.

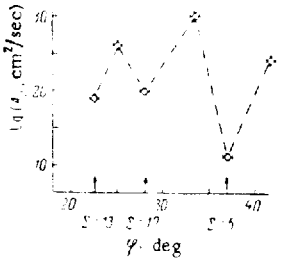

FIG. 3. Preexponential factor in the mobility equation for ⟨001⟩ tilt boundaries in tin.

The investigations were conducted at atmospheric pressure and 185–225 °C, and at hydrostatic pressures up to 16 kbar and 208 °C. At high pressures, the anneals were carried out in a liquid chamber with variable external mechanical support, the working liquid being silicone oil. The pressure was held constant to within ± 0.2 kbar. At atmospheric pressure, the samples were annealed in a high temperature chamber in the field of view of the optical microscope. The position of the moving boundaries was determined from thermal etch grooves,[2] the error in the mobility determination being not more than 5%. The temperature was held constant to within ± 1° by a high-current temperature control.

2. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of the investigated grain boundary mobilities. The mobility A here was found as

$$A = \frac{v}{1\,a} = A_0 \exp\left(-\frac{\Delta G}{kT}\right) = A_0 \exp\left(-\frac{E}{kT}\right)\exp\left(-\frac{PV^*}{kT}\right), \qquad (1)$$

where v is the boundary velocity; A_0 the preexponential factor; ΔG the activation free energy of the migration process; E the migration activation energy; P the pressure; V^* the migration process activation volume. Figures 2 and 3 show the dependence of E and A_0 on the grain misorientation angle φ. From Fig. 4, it is seen that the hydrostatic pressure has a considerable influence on the boundary mobility; the degree of this influence itself depends on the misorientation angle (Fig. 5). The slope of the log A – P lines (Fig. 4) was used to calculate the boundary migration activation volumes (Fig. 6).

It is seen that the orientation dependences found are far from monotonic. A noteworthy point is that minima of all the migration activation parameters E, A_0, and V^* correspond to special misorientations. Moreover, for the special boundaries these parameters increase with the surface density of coincidence sites $\sqrt{\Sigma}$ (Fig. 7).

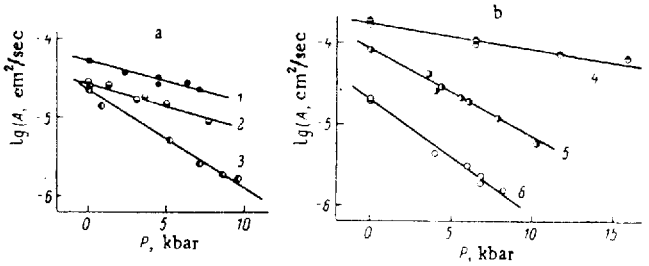

FIG. 4. Dependences of the mobility of ⟨001⟩ tilt boundaries on the hydrostatic pressure in tin bicrystals; grain misorientation angles (deg): a) 1) 22.5, 2) 28, 3) 25; b) 4) 37, 5) 41.5, 6) 33.5.

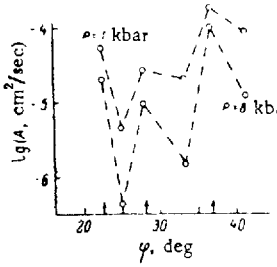

FIG. 5. Mobility of ⟨001⟩ tilt boundaries in tin at atmospheric pressure and 8 kbar.

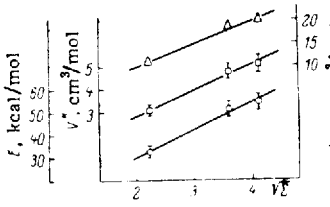

FIG. 7. Dependences of the migration activation parameters for special ⟨001⟩ tilt boundaries in tin on the surface density of coincidence sites.

There is found to be a linear relation between E and log A (Fig. 8), called the compensation effect; the compensation temperature (T_c = 236 °C) corresponds, within the experimental error, to the melting point of tin.

The description of grain boundary migration is at present based on the theory of absolute reaction rates. The boundary velocity is then[3] given by

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

where ν is the Debye frequency; ΔF and b are the driving force and the displacement of the boundary in a single atomic transition event. All the various migration mechanisms are customarily divided into two large groups: single-transition mechanisms, where the elementary boundary displacement event is a transition of one atom, and group-transition mechanisms, where it depends on a transition of several atoms. The main fundamental point as yet unresolved is which of these two basic mechanisms in fact occurs. In this paper, a definite opinion is to be expressed. It makes use, as already mentioned, of a further activation parameter, the migration activation volume.

With the single-transition mechanism, the expression for the boundary migration velocity is

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

where b is the displacement of the boundary caused by a transition of one atom (usually assumed to be equal to the lattice parameter), and the mobility in our case is

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

The choice among the transition mechanism models (of which there are quite a few) determines the values of the parameters in the theory: the activation energy and entropy, and the form of the preexponential factor. In analyzing the experimental results, we used three models: one purely diffusional (the boundary displacement resulting from a diffusional transition of an atom from one grain to another), and two modifications of this, the step model (Refs. 4, 5) and the dislocation model.[5]

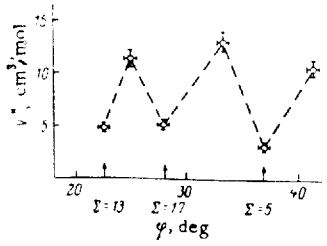

FIG. 6. Activation volumes of ⟨001⟩ tilt boundary migration in tin.

If the elementary migration event is taken to be a diffusional transition of an atom from one grain to another, then ΔG in Eq. (3) is to be interpreted as the self-diffusion free energy ΔG_{SD}. Then, using the published results[6] on self-diffusion of tin, we can find from Eq. (4) the boundary migration parameters E = 25 kcal/mol, $A_0 = b\nu \frac{a\Omega}{kT} e^{\Delta S/k} \simeq 10$ cm²/sec. [If ΔG is taken to be not ΔG_{SD} but ΔG_{GBSD}, the grain-boundary self-diffusion free energy (although the model in question deals with jumps of atoms across the boundary, not along it), the values[6] $D_0 = 6.4 \cdot 10^{-2}$ cm²/sec, E_{GBSD} = 10 kcal/mol give $E = E_{GBSD}$ = 10 kcal/mole, $A_0 \simeq 10^{-1}$ cm²/sec.] The value of σ here is[7] 100 erg/cm². In our experiments, the migration activation energy E ranged from 33 to 77 kcal/mol, and the preexponential factor A_0 from 10^{11} to 10^{30} cm²/sec. In the present case, it is probably reasonable to take as the activation volume V^* the self-diffusion value V^*_{SD}; for tin, this is[8] 5.3 cm³/mol. For special boundaries, therefore, the experimental activation volumes V^* = 3.1–5.1 cm³/mol are close to the theoretical one if this is taken to be the activation volume for bulk self-diffusion; for nonspecial boundaries, V^* = 10.3–12.9 cm³/mol, which is considerably greater than V^*_{SD}.

Let us next discuss the step mechanism of boundary migration.[4,5] Here, the boundary moves by the attachment of atoms to steps formed by close-packed planes separating from the grain surfaces. According to the detailed Gleiter medel,[4] the boundary migration velocity is

$$v = \nu b \frac{\Delta F}{kT} \psi \exp\left(-\frac{\Delta G}{kT}\right). \tag{5}$$

The activation free energy here is the sum of terms describing the transition of an atom from one grain to another; ψ is written as

$$\psi = \frac{b}{\lambda}\left[1 + \frac{b}{\lambda}\left(\frac{1}{f_1} + \frac{1}{f_2}\right)\right]^{-1},$$

where λ is the boundary thickness, f_1 and f_2 the numbers of steps per unit area of the two inner surfaces of the grain

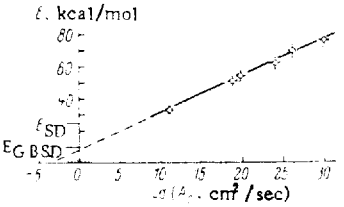

FIG. 8. Dependences of the migration activation energy on the preexponential factor in the mobility equation for ⟨001⟩ tilt boundaries in tin; the dashed part is the range of A_0 values corresponding to single-transition models.

TABLE I. Analysis of Experimental Results by Group Models of Grain-Boundary Migration

φ, deg	Mott model[9]				Model proposed here		
	$n_E = \frac{E}{L_m}$	$n_{\Delta S} = \frac{\Delta S T_m}{L_m}$	$n_{V^*} = \frac{V^*}{\Delta V_m}$	$\Delta V = \frac{V^*}{n_E}$	$n_E = \frac{E\lambda}{\gamma\varepsilon}$	$n_{\Delta S} = \frac{\ln A_0 \lambda kT_k}{\gamma\varepsilon}$	$\Delta V = \frac{V^*}{n_E}$
Σ = 13:							
22.5	31	27	10	0.15	20	17	0.24
25	41	37	25	0.28	28	24	0.41
Σ=17:							
28	32	29	11	0.16	21	18	0.24
33.5	45	43	28	0.29	31	28	0.42
Σ=5:							
37	20	17	7	0.16	13	10	0.24
41.5	37	35	22	0.28	25	22	0.42

boundary. Another expression for the velocity of a boundary moving by the step mechanism[5] is

$$v = d^2 \nu l_S \frac{\Delta F}{kT} \exp\left(-\frac{\Delta G}{kT}\right), \tag{6}$$

where d is the atomic diameter and l_S the step length per unit area of the boundary. If ΔG in Eqs. (5) and (6) is taken to be the diffusion activation free energy, and if we take the activation entropy to be a maximum and equal to the entropy of melting $\Delta S = 2k$, we get from Eq. (5) for $\psi_{max} = 1$, $A_0 = 3 \cdot 10^{-2}$ cm²/sec, and from Eq. (6) for $d = 10^{-8}$ cm, $l_S = 10^6$ cm/cm², $A_0 = 2 \cdot 10^{-1}$ cm²/sec.

The dislocation mechanism of grain boundary migration postulates the movement of grain-boundary dislocations as the elementary event. The boundary velocity is then[5]

$$v = d\rho h \nu \alpha \frac{\Delta F}{kT} \exp\left(-\frac{\Delta G}{kT}\right), \tag{7}$$

where ρ is the dislocation density; h the height of the jogs in the dislocation core; $\alpha = d/b \sin\varphi$; b is the Burgers vector of the grain-boundary dislocations; φ is the angle between the direction of this vector and the boundary plane. Assuming, as above, that the entropy of the process is at its maximum, $\Delta S = 2k$, we get for the mobility preexponential $A_0 = 10^{-2}$ cm²/sec (when $h = d = 10^{-8}$ cm, $\rho = 10^6$ cm^{-1}, $\alpha = 10$).

The following provisional conclusions thus follow from the above analysis. First, the migration activation energy is much greater than the bulk self-diffusion activation energy, let alone the grain-boundary one. Second, the migration activation volume for special boundaries is close to the bulk self-diffusion activation volume; for nonspecial boundaries, it is considerably greater. Last, the preexponential factor in our experiments is many orders of magnitude greater than the theoretically possible value. As an illustration, Fig. 4 shows the theoretical values of the boundary migration parameters given by the single-transition models considered. Such models are evidently unable to account for the observed values of the migration parameters.

Let us now turn to group mechanisms of boundary migration. In the Mott classical model of group transitions,[9] it is assumed that the elementary boundary migration event consists in the melting of a group of n atoms in the crystal on one side of the boundary and its crystallization in the adjacent crystal. This specific treatment gives immediately the migration activation energy, entropy, and volume:

$$\left.\begin{aligned} E &= nE_1 = nL_m, \\ \Delta S &= n\Delta S_1 = \frac{nL_m}{T_m}, \\ V^* &= n\Delta V_m. \end{aligned}\right\} \tag{8}$$

where n is the number of atoms taking part in the transition; L_m is the latent heat of fusion; T_m is the melting point; ΔV_m is the change in volume on melting. The boundary mobility equation is then

$$v = n^2 b \nu \frac{\Delta F}{kT} e^{\frac{nL_m}{kT m_e} - \frac{nL_m}{kT} - \frac{P n \Delta V_m}{kT}}. \tag{9}$$

The factor n^2 occurs because in the elementary transition event not only the displacement of the boundary but also the driving force is proportional to the number of atoms in the group. It is seen that Mott's equation gives the compensation effect, i.e., a linear relation between the migration activation energy and the logarithm of the preexponential factor if $\ln\left(n^2 b \nu \frac{\Delta F}{kT}\right)$ is neglected; the slope of the line is kT_m. Figure 4 shows that this dependence is indeed observed, and the compensation temperature found, $T_c = 236$ °C, is almost the same as the melting point of tin, $T_m = 232$ °C.

The values of n can be calculated from Eq. (9), the experimental values of the migration parameters, and the reference-book values of L_m, T_m, and ΔV_m. The results are summarized in Table I for $L_m = 1.69$ kcal/mol (Ref. 6) and $\Delta V_m = 0.46$ cm³/mol (Ref. 10). It is seen that the values of n found from the activation entropy and energy are in good agreement, but those of $n = V^*/\Delta V_m$ differ from these quite considerably. It should be noted here that the Mott model is based on the assumption that atoms pass from grain to grain by melting, and the criterion should probably be the migration activation volume V^*, that is, the ratio $\Delta V = V^*/n_E$ (where n_E is the number of atoms in the group), found by calculation from the activation energy, should coincide with $\Delta V_m = 0.46$ cm³/mol. In our case, $\Delta V = V^*/n_E$ is considerably different from ΔV_m.

This appears to us to be the main deficiency of the Mott model. The hypothesis of melting of a group of atoms, which is a natural one for the liquid boundary model, does not fit with current ideas of grain-boundary structure. Our experimental results will now be discussed on the basis of a different model of group transitions.

Let us assume that the boundary moves by the passage of a structural element (a group of n atoms) from one grain to the boundary and of a similar one from the boundary into another grain. The local thickening of the boundary when the number of atoms in it increases by n is the activation free energy of the elementary migration event. A specification as in the Mott model enables us to determine the migration activation parameters

$$\left.\begin{aligned} \Delta G &= \frac{n\sigma\Omega}{\lambda}, \\ E &= \frac{n\sigma_0\Omega}{\lambda}, \\ \Delta S &= -\frac{n\frac{\partial\sigma}{\partial T}\Omega}{\lambda}, \end{aligned}\right\} \qquad (10)$$

where σ_0 is the surface tension σ of the boundary at 0 K, and λ is the thickness of the boundary. The temperature dependence of the surface tension is written as

$$\sigma = \sigma_0(1 - \alpha T + \beta T^2 - \ldots). \qquad (11)$$

This model likewise gives a compensation effect if only the linear term is retained in the expansion (11). The slope of the straight line is here k/α, and so $1/\alpha = T_c$. To find σ_0, we used the expansion (11)[1)] and the measured grain-boundary surface tension in tin, $\sigma_{220\,^\circ C} = 100$ erg/cm^2 (Ref. 7), $\sigma_{160\,^\circ C} = 160$ erg/cm^2 (Ref. 11), whence $\sigma_0 = 658$ erg/cm^2.

This gives the quite reasonable value $\partial\sigma/\partial T \simeq -1$ erg·cm^{-2}·deg^{-1}.

From the relations (10) and the experimental values of E and A_0, we can determine the number of atoms in the elementary group (Table I). It is seen that a calculation from independent parameters such as the activation energy and the preexponential factor in the mobility equation gives concordant values of n. With these n values, we easily find the change $\Delta V = V^*/n$ in the atomic volume between the crystal and the boundary (Table I). It is noteworthy that for all special boundaries the ΔV values are the same (0.24 cm^3/mol^2), and they differ by a factor of almost two from those for nonspecial boundaries (0.41–0.42 cm^3/mol); this convincingly demonstrates the structural affinity of all boundaries corresponding to special misorientations and the structural difference between them and ordinary boundaries.

The main conclusion we wish to draw from this work is that the results cannot be explained according to ideas about single-transition mechanisms in the movement of grain boundaries. An important point is that this conclusion is based on measuring not only the activation energy and the preexponential factor but also the migration activation volume.

[1)]The quadratic term βT^2 in the expansion (11) is found to be $\sim 0.2\,\alpha T$ even at the melting point, and may therefore be neglected when analyzing the compensation effect.

[2)]This is further illustrated by Fig. 8, which shows that E, log A_0, and V^* for special boundaries increase in the same way with the surface density $\sqrt{\Sigma}$ of coincidence sites.

[1]V. Yu. Aristov, Ch. V. Kopetskii, D. A. Molodov, and L. S. Shvindlerman, Fiz. Tverd. Tela (Leningrad) 22, 3247 (1980) [Sov. Phys. Solid State 22, 1900 (1980)].

[2]V. Yu. Aristov, Author's Abstract of Thesis for Candidate's Degree [in Russian], Institute of Steel and Alloys, Moscow (1978).

[3]J. E. Burke and D. Turnbull, Prog. Met. Phys. 3, 290 (1952).

[4]H. Gleiter, Acta Metall. 17, 853 (1969).

[5]D. A. Smith and C. M. F. Rae, Metal Sci. 13, 101 (1979).

[6]C. J. Smithells, Metals Reference Book, 5th ed., Butterworths, London (1976).

[7]D. McLean, Grain Boundaries in Metals, Clarendon Press, Oxford (1957).

[8]K. L. DeVries, G. S. Baker, and P. Gibbs, Bull. Am. Phys. Soc. 6, 164 (1961).

[9]N. F. Mott, Proc. Phys. Soc. London 60, 391 (1948), Sec. 4.

[10]I. K. Kikoin (ed.), Tables of Physical Quantities (Handbook) [in Russian], Atomizdat, Moscow (1976).

[11]J. N. Butler and B. H. Bloom, Surf. Sci. 4, 1 (1966).

Translated by J. B. Sykes

Damage profile in molybdenum irradiated with 5–20 keV phosphorus ions

V. F. Reutov and S. P. Vagin

(Submitted August 5, 1983; resubmitted November 17, 1983)

Fiz. Tverd. Tela (Leningrad) 26, 1040–1043 (April 1984)

Transmission electron microscopy was used to study the radiation damage behavior of molybdenum along the track of phosphorus ions with energies in the range 5–20 keV. It was found that in all cases clusters of interstitial atoms were formed, and above 10 keV vacancy-type defects were observed in the surface layer. The threshold energy for the vacancy clusters seen in the transmission electron microscope and formed in displacement cascades was estimated, together with the mean length of the replacement sequence in molybdenum.

Particular attention has recently been given to the study of ion damage profiles in metals. This is due not only to progress in ion metallurgy techniques but also to the need to understand the fundamentals of radiation damage physics. The latter include the formation of displacement cascades on which vacancy clusters then develop[1,2] and the formation of chains of focused collisions (dynamic crowdions) which are now thought to be the cause of effective separation of vacnacies and interstitial atoms in the cascades, as well as the formation of inter-

0038-5654/84/04 0633-03 $03.90

© 1984 American Institute of Physics