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EFFECT OF PRESSURE ON GRAIN BOUNDARY MIGRATION IN ALUMINIUM BICRYSTALS

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Abstract—The temperature and pressure dependencies of ⟨100⟩, ⟨110⟩, and ⟨111⟩ tilt grain boundaries in bicrystals of pure aluminum were measured, and the corresponding activation enthalpies and activation volumes were determined. While the activation enthalpy strongly depended on orientation, in particular close to low Σ coincidence orientation relationships, the activation volume was found independent of orientation except for ⟨110⟩ tilt boundaries. The absolute values of the activation volume for ⟨100⟩ and ⟨111⟩ tilt boundaries were about the same as for bulk self-diffusion, which agrees with previous measurements on polycrystals. The activation volume for migration of ⟨110⟩ tilt boundaries substantially exceeded the activation volume for bulk self-diffusion. It is concluded that at least ⟨110⟩ tilt boundaries migrate by a group mechanism rather than by diffusive jumps of single atoms.

1. INTRODUCTION

Despite long-standing efforts and a large number of papers dedicated to the problem of grain boundary (GB) migration, the physical mechanisms and the fundamentals of this process are still unknown. The main reason for our poor understanding of grain boundary migration is the difficulty to experimentally determine grain boundary mobility. As a matter of fact, most previous measurements of grain boundary mobility were obscured by artifacts and gave rise to misleading conclusions and confusion on the dependence of grain boundary mobility on external parameters [1, 2].

The major problems for proper experimental conduct of grain boundary mobility investigations are:

(a) controlling the driving force for grain boundary migration
(b) the necessity to continuously monitor the shape and displacement of a moving grain boundary
(c) the accuracy and reproducibility of grain boundary crystallography and
(d) composition and purity of the material.

Moreover, it is important to realize that the investigation procedure of grain boundary migration may actually interfere with the grain boundary migration process itself, for instance, locating the grain boundary position on a surface by optical means usually requires the formation of a grain boundary groove, which itself hinders grain boundary migration and seriously affects the measurement of grain boundary mobility.

The basis for all calculations of the grain boundary mobility rate is the theory of absolute reaction rates [3]. The migration rate v of a grain boundary under the action of a driving force ΔG, where $\Delta G \ll RT$ for all relevant driving forces

$$v = b\nu \frac{\Delta G}{RT} \exp(S/R)\exp(-H/RT) \equiv m \cdot \Delta G = m_0 \exp(-H/RT) \cdot \Delta G. \quad (1)$$

The driving force ΔG is the molar free energy gain of the system by detaching atoms from one grain and attaching it to the adjacent grain, b is the displacement of the boundary caused by the transfer of a single atom, ν is the atomic vibration frequency (Debye frequency), S and H denote the entropy and enthalpy of activation, respectively.

From the measurement of the temperature dependence of the grain boundary mobility m the pre-exponential factor m_0 and the enthalpy of activation can be derived. The enthalpy of activation and, to a lesser extent the pre-exponential factor, allow conclusions on the mechanism of grain boundary migration to be drawn. However, the enthalpy of activation and the pre-exponential factor are not independent of each other. As a matter of fact it has been found experimentally in a large variety of systems (physical, chemical, biological etc.) that there is a linear relationship between the activation enthalpy and the pre-exponential factor. This relationship is usually referred to as compensation effect [4, 5]. Therefore,

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from mobility measurements at different temperatures only information on a single activation quantity can be obtained.

At atmospheric pressure the activation enthalpy is essentially identical with the activation energy E. The activation energy of GB migration is usually compared with the energy of diffusion along the GB, although GB migration should be controlled by diffusion across the GB. The activation energy of diffusion *along* GBs changes over a wide range. It depends on the type and misorientation of the GB and varies between 0.3–1.0 of bulk diffusion activation energy [6, 7]. There are no direct measurements of the diffusion *across* GBs. Theoretical considerations show that the quantitative characteristics of this type of GB diffusion should be more close to bulk diffusion than to diffusion along GBs [8, 9].

Moreover, the measured activation energies for GB motion are difficult to interpret. In Figs 1–3 the misorientation dependence of the activation energy of migration is presented for ⟨100⟩ tilt GBs in Al and ⟨10$\bar{1}$0⟩ and ⟨11$\bar{2}$0⟩ tilt GBs in Zn in specimens of different purity as well as for ⟨100⟩, ⟨111⟩, ⟨110⟩ tilt GBs in pure Al [1]. Although the activation energy of migration drops as the purity of metals increases, the activation energy of migration is for most GBs significantly greater than the activation energy of GB diffusion and can even exceed the activation energy for bulk diffusion. Impurity drag theory [10–12] fails to account for this fact, since the energy of activation for joint motion of the GB and impurities cannot exceed the sum of the activation energy of diffusion of the impurity (no matter whether GB or bulk diffusion—see Fig. 3) and the energy of interaction of the GB and the impurities. The latter is usually small (~0.5 eV [13–16]) as evident from segregation behaviour. These results substantiate that the activation energy does not provide sufficient information to identify the mechanism of GB migration.

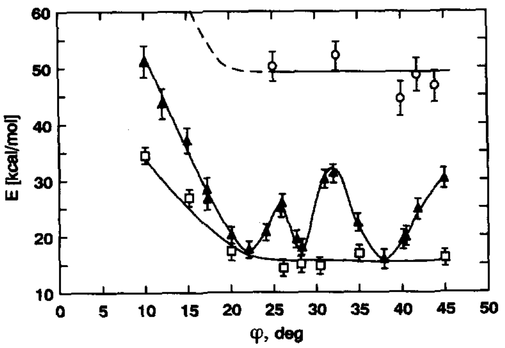

Fig. 1. The dependence of the activation energy of migration for ⟨100⟩ tilt grain boundaries in Al of different purity. (□) 99.9995 at.%; (▲) 99.9992 at.%; (○) 99.98 at.%.

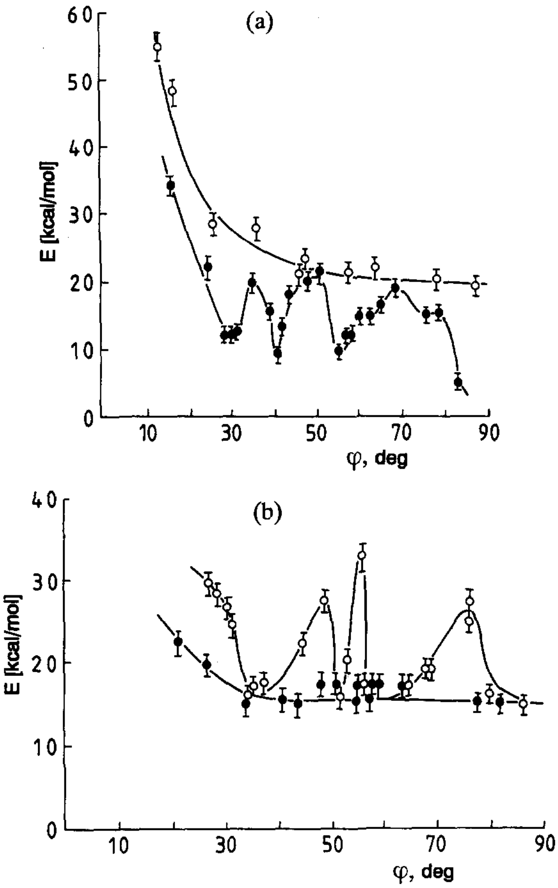

Fig. 2. The dependence of the activation energy of migration on angle of rotation for (a) ⟨10$\bar{1}$0⟩ and (b) ⟨11$\bar{2}$0⟩ tilt grain boundaries in Zn of different purity. (○) 99.995 at.%; (●) 99.9995 at.%.

A more direct measure of the migration mechanism yields the activation volume. The activation volume reflects the difference between the volume of the system in the activated and in the ground state. The activation volume V^* can be obtained from measurements of the pressure dependence of Gibbs free energy of activation according to equation (1)

$$G = H - TS = E + pV^* - TS \tag{2a}$$

$$\frac{\partial \ln v}{\partial p} = \frac{-V^*}{RT} \tag{2b}$$

$$\frac{\partial \ln v}{\partial 1/T} = -\frac{E + pV^*}{R} \equiv -\frac{H}{R}. \tag{2c}$$

For instance, the activation energy for bulk self-diffusion ought to be in the order of an atomic volume. In this case the activated state consists of the vacancy production and the local lattice expansion caused by the diffusing atom in the saddlepoint configuration. The relaxed volume of a vacancy roughly corresponds to a little less than an atomic volume and the lattice expansion during the diffusive jump will be small compared to an atomic volume.

The activation volume for GB diffusion is only a little less than for bulk diffusion (Table 1). This can be easily understood, because the density of GBs is not very different from the bulk density of the crystal (even during melting the density of a metal drops only

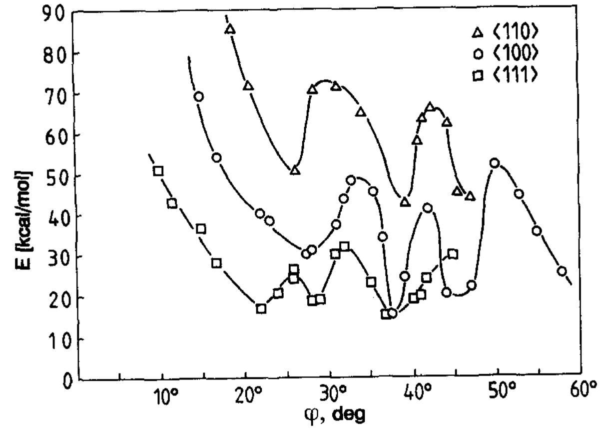

Fig. 3. The misorientation dependence of activation energy for grain boundary motion of ⟨100⟩, ⟨111⟩ and ⟨110⟩ tilt grain boundaries in Al.

a few percent). With regard to grain boundary motion the value of the activation volume is expected to deliver information on essentials of the GB migration mechanism, in particular whether GB migration proceeds by a single or multiple atom mechanism.

Despite the relative ease of interpretation of the activation volume compared to the activation energy, there have been only very few studies on the pressure dependence of grain boundary migration [17–20]. The main reasons for this deficiency are the serious experimental problems that have to be overcome in order to successfully conduct experiments on grain boundary migration at high hydrostatic stresses. To begin with the pressurizing medium, either a gas or a liquid, should be stable up to high temperatures and must be inert to the material of the sample to avoid contamination of the sample. Moreover, the high pressure device must be designed to provide a stable and homogeneous temperature field. The displacement of a grain boundary during annealing at high pressure is given by

$$l = vt = v_0 t \exp(-E/RT)\exp(-pV^*/RT) \qquad (3)$$

where v is the grain boundary velocity, t the annealing time, v_0 the pre-exponential factor, p the pressure and V^* the activation volume of migration. For a fluctuation of temperature δt and pressure δp and an inaccuracy of time measurement δt, the relative error of the grain boundary displacement reads

$$\frac{\Delta l}{l} = \left[\frac{E}{RT^2}\delta T\right] + \left[\frac{V^*}{RT}\delta p\right] + \frac{\delta t}{t}. \qquad (4)$$

Obviously, the uncertainty of the grain boundary displacement measurement will be essentially determined by the stability of pressure and temperature besides the magnitude of the activation energy and activation volume. For instance, if $E \cong 30{,}000$ cal/mol, $T \cong 10^3$ K, $V^* \cong 10\ \mathrm{cm^3/mol}$, $\delta T \cong 1$ K at a pressure of the order of 10^3 bar, this minor fluctuation of temperature is equivalent to change of the pressure by 150 bar. Therefore, a high stability of pressure and temperature is required for an accurate measurement.

Moreover, equation (4) evidences that high values of pressure are necessary to obtain an impact on GB motion by pressure comparable to the measured temperature influence. To compensate the effect on GB mobility by a temperature change of the order of 250°C the hydrostatic stress has to change by the order of 10 kbar. This demonstrates the serious experimental problems, which have to be overcome to properly measure the pressure dependence of grain boundary mobility.

These problems were addressed and overcome in the current study, and the pressure and temperature dependence of grain boundary mobility were measured for ⟨100⟩, ⟨111⟩ and ⟨110⟩ tilt boundaries in aluminium.

2. EXPERIMENTAL PROCEDURE

The experiments were carried out on bicrystals of high purity (99.999%) aluminium. Grain boundary motion was investigated under a constant driving force ΔG provided by the surface tension of a curved grain boundary: $\Delta G = \sigma\Omega/a$, where σ is the grain boundary surface tension, Ω the molar volume and a the width of the shrinking grain (Fig. 4). Pure tilt boundaries with ⟨100⟩, ⟨111⟩ and ⟨110⟩ axes of rotation were examined. The angle of misorientation was chosen such that it was either close to a low Σ coincidence rotation (special grain boundary) with $\Sigma5$ (36.9°⟨100⟩), $\Sigma7$ (38.2°⟨111⟩) and $\Sigma9$ (36.9°⟨110⟩), or far from coincidence rotations (random boundaries, see Table 2).

The bicrystals were grown by directional crystallization [21]. The orientation of the crystallo-graphic axes of the crystals was measured by optical means with an accuracy of ±1°, using the characteristic reflection pattern of a laser beam from the specially prepared crystal surface. For this, the samples were etched in a solution of 18 ml HCl, 9 ml HNO_3 and 2 ml HF. Prior to annealing the samples were electrolytically polished to improve the surface quality.

The investigations were conducted at atmospheric pressure and at hydrostatic pressures up to 9 kbar in the temperature range between 350–600°C. The temperature of annealing was kept constant to within ±1°C. At atmospheric pressure the samples were annealed in a high temperature chamber in the field of view of an optical microscope. The position of the moving boundary was determined from grain boundary grooves. Prior to each high pressure annealing the specimen was polished to remove the grooves. The uncertainty of the mobility measurement was <5%. At high pressures, samples with ⟨111⟩ tilt boundaries were annealed at 425°C, samples with ⟨100⟩ boundaries at 450°C and samples with ⟨110⟩ boundaries at 535°C (except samples with 30°⟨111⟩ boundaries, which were subjected to annealing at 560°C). The

Table 1. Parameters of bulk and grain boundary diffusion for some metals

		Bulk diffusion			GB diffusion		
Me	Specimen	H, kcal/mol	D_o, m^3/s	V^*_B/Ω	H_B, kcal/mol	$(\delta D_B)_o$, m^3/s	V^*_{GB}/Ω
Ag self-diffusion [I]	polycrystals	46.0	$8.9 \cdot 10^{-5}$		21.3	$5.76 \cdot 10^{-15}$	
Ag self-diffusion [II]	⟨001⟩ Tilt GB $\varphi = 28°$	45.5	$7.2 \cdot 10^{-5}$		24.2	$2 \cdot 10^{-16}$	
Ag self-diffusion [III]	polycrystals	43.2	$2.78 \cdot 10^{-5}$		15.5	$1.16 \cdot 10^{-16}$	1.09
Ag self-diffusion	single crystal "pure" silver			0.66 [IV] 0.88 [V]			
Al–Zn	polycrystals	29.5 [VI]	$2.45 \cdot 10^{-5}$ [VI]	1.1 [VII]	12.4 [VIII]	$3.1 \cdot 10^{-15}$ [VIII]	0.8–1.08 [IX]
Al–Zn	$\varphi = 32°$ $\varphi = 37°$ ⟨111⟩ tilt GB	31.0 [X]	$1.4 \cdot 10^{-4}$ [X]		12.0 20.0 [XI]		
Al self-diffusion Al–Cu, Al–Ag, Al–Au	single crystal "pure" Al single crystal of Al			1.23–1.35 [XII] 1.16 1.19 1.18 [V]			
Au self-diffusion	polycrystals	41.6 [XIII]	$9.1 \cdot 10^{-6}$ [XIII]	0.67–0.81 [XII]	$3.1 \cdot 10^{-16}$ [XIV]	20.2 [XIV]	
Cd self-diffusion	polycrystals 99.9995 at.%	$Q^{\|} = 18.13$ $Q^{\perp} = 19.0$ [XI]	$D = 1/3$ $(D\| + 2D^{\perp})$ $D_0^{\perp} = 5 \cdot 10^{-6}$ $D_0^{\|} = 1 \cdot 10^{-5}$ [XV]	⊥C 0.53–0.59 ‖C 0.53–0.59 [XVII]	11.0 [XVI]	$3.35 \cdot 10^{-14}$ [XVI]	
Pb self-diffusion	polycrystals 99.95%	25.6 [XVIII]	$1.17 \cdot 10^{-4}$ [XVIII]	single crystal 0.71–0.84 [XIX] 0.57–0.715 [XX]	15.6 [XVIII]	$8.1 \cdot 10^{-14}$ [XVIII]	
Pb self-diffusion	⟨001⟩ tilt and twist GB 99.999 at.%	24.6 [XXIV]	$6.26 \cdot 10^{-5}$ [XXIV]		Twist GB $\varphi = 10°$ [XXV] 8.0 tilt GB $\varphi = 10°$ 9.1 tilt GB $\varphi = 30°$ 4.7		
Sn self-diffusion	polycrystals 99.99%	23.0 [XXI]	$7.8 \cdot 10^{-5}$ [XXI]	single crystal ⊥C 0.304–0.362 ‖C 0.321–0.329 [XXII]	10.0 [XXIII]	$3.22 \cdot 10^{-15}$ [XXIII]	

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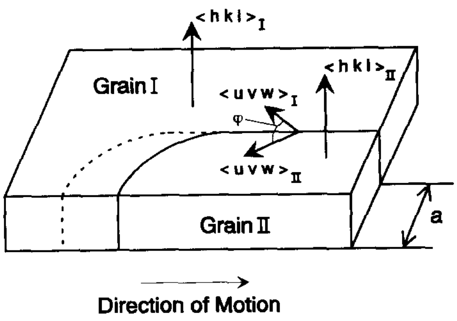

Fig. 4. Bicrystal geometry for grain boundary motion measurements under a constant driving force.

samples were exposed to high pressure by a pressurized argon gas atmosphere. The pressure was kept constant to within ±0.05 kbar in the pressure range up to 4 kbar and within ±0.15 kbar in the pressure range exceeding 4 kbar.

3. RESULTS

The temperature and pressure dependence of the reduced grain boundary mobility $A \equiv va = m\sigma\Omega$ of the individual samples are summarized in Figs 5–8. Each solid circle in these figures corresponds to an average of 10 independent measurements. As expected from equations (2b) and (2c) the mobility exhibits an Arrhenius type dependency on temperature and an exponential dependency on hydrostatic pressure. From the slope of the Arrhenius plot the activation energy can be derived, while the slope of the semilogarithmic plot of mobility vs pressure yields the activation volume [equation (2)]. Both activation energy and activation volume depend on misorientation. In Figs 5–7 the results are grouped according to the rotation axis, and from the slope of the Arrhenius plot it becomes obvious that the activation energy is lowest for the Σ5 and Σ7 boundaries and rises with increasing deviation from the exact coincidence orientation, as was shown before for high purity aluminium at ambient pressure [22]. In contrast, the pressure dependence of mobility yields the same slope, e.g. the same activation volume for both ⟨100⟩ and ⟨111⟩ tilt boundaries irrespective of angle of rotation. For ⟨110⟩ boundaries, however, the activation volume rises with increasing departure from the exact low Σ coincidence misorientation. The results become more transparent, when the activation volume is plotted vs the activation energy (Fig. 9). For ⟨100⟩ and ⟨111⟩ tilt boundaries the activation volume does not depend on activation energy. For ⟨110⟩ tilt boundaries, however, the activation volume increases in a linear fashion with increasing activation energy. Also, the activation energies for ⟨110⟩ tilt boundaries are higher than those for ⟨100⟩ and ⟨111⟩ tilt boundaries. Obviously, ⟨110⟩ boundaries behave differently from boundaries with other tilt axes. Finally, Fig. 10 proves, that instead of the activation energy also the pre-exponential factor can be considered, since it is related to the activation energy by the previously mentioned compensation effect.

4. DISCUSSION

Grain boundary migration is the result of a net flux of lattice sites across the grain boundary. This means that the transfer of an atom across the boundary causes a new lattice site to be produced on the grain boundary face of the growing crystal, while a lattice site at the grain boundary face of the shrinking crystal is removed. Thus, this process is fundamentally different from the elementary step of diffusion across the GB, where only an exchange of atoms across the GB takes place without exchange of lattice sites. Nevertheless, in both cases an activation volume close to an atomic volume is to be expected. For diffusion across grain boundaries (for convenience simply referred to as diffusion in the following) the Gibbs free energy of activation G_D is given by

$$G_D = G_f + G_m \tag{5}$$

where G_f refers to the energy of formation of a vacant lattice site in the GB and G_m denotes the free energy change associated with the transfer of the vacancy across the boundary. Correspondingly, according to equation (2a) the respective activation volume is

$$V_D^* = V_f^* + V_m^*. \tag{6}$$

All quantities V^* refer to the grain boundary and not to the bulk but, according to our current understanding of GB structure, as provided for instance by computer simulation, GBs are not much less densely packed than the bulk so that V_D^* ought to be

Table 2. Geometry and activation parameters of migration for investigated GBs in Al-bicrystals

Misorientation			Activation		Pre-exponential factor
Axis	Angle	Σ	Energy (E), kJ/mol	Volume (V^*) cm^3/mol	Log A_0
⟨100⟩	36.9 ± 0.4	5	113.7 ± 7.9	12.0 ± 0.6	4.4
⟨100⟩	31.8 ± 0.4		186.0 ± 11.3	11.9 ± 0.6	10
⟨111⟩	37.1 ± 0.4	7	161.3 ± 9.2	11.0 ± 0.6	8.3
⟨111⟩	32.0 ± 0.5		194.4 ± 10.9	11.9 ± 0.6	10.8
⟨110⟩	38.5 ± 0.5	9	181.4 ± 11.3	16.5 ± 0.6	7.7
⟨110⟩	36.0 ± 1.0		222.4 ± 13.4	22.2 ± 1.0	10.3
⟨110⟩	32.0 ± 1.0		274.6 ± 16.7	32.4 ± 1.7	13.5
⟨110⟩	30.0 ± 1.0		291.3 ± 17.1	36.3 ± 1.8	14.1

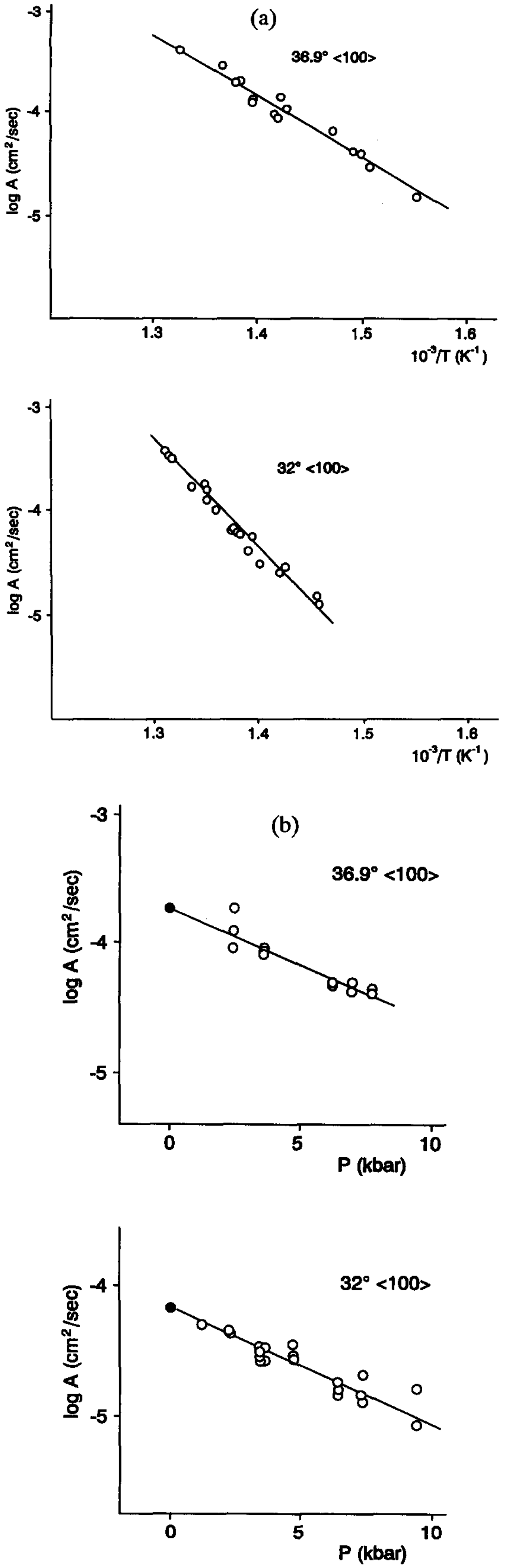

Fig. 5. The temperature (a) and pressure (b) dependencies of grain boundary mobility for ⟨100⟩ tilt boundaries in Al.

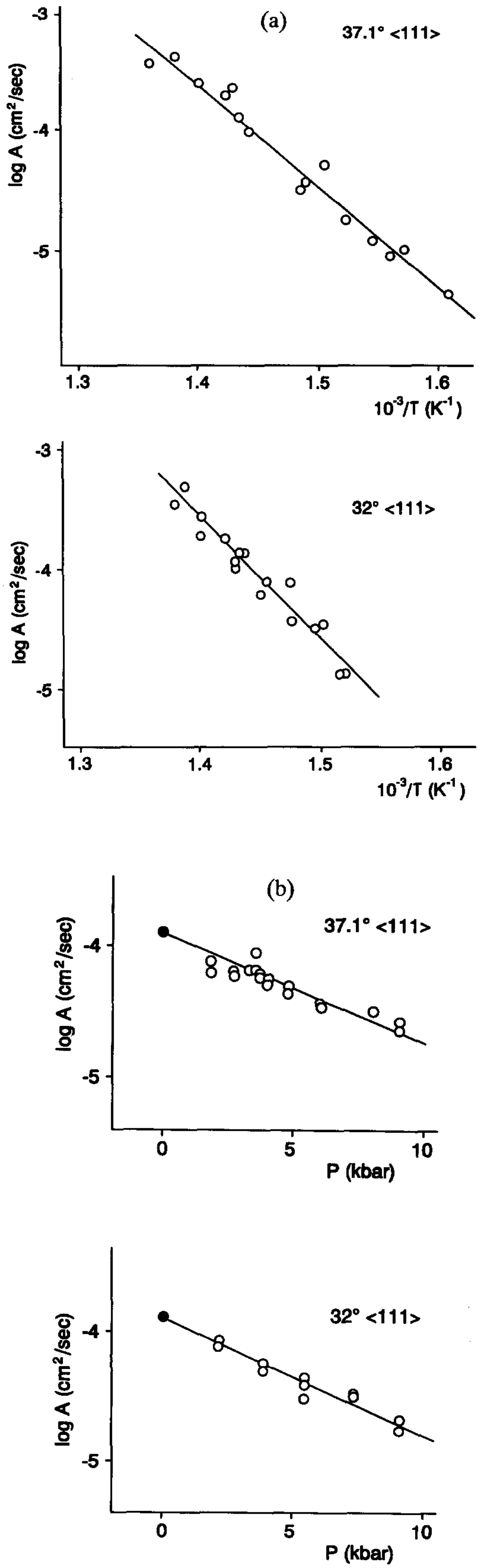

Fig. 6. The temperature (a) and pressure (b) dependencies of grain boundary mobility for ⟨111⟩ tilt boundaries in Al.

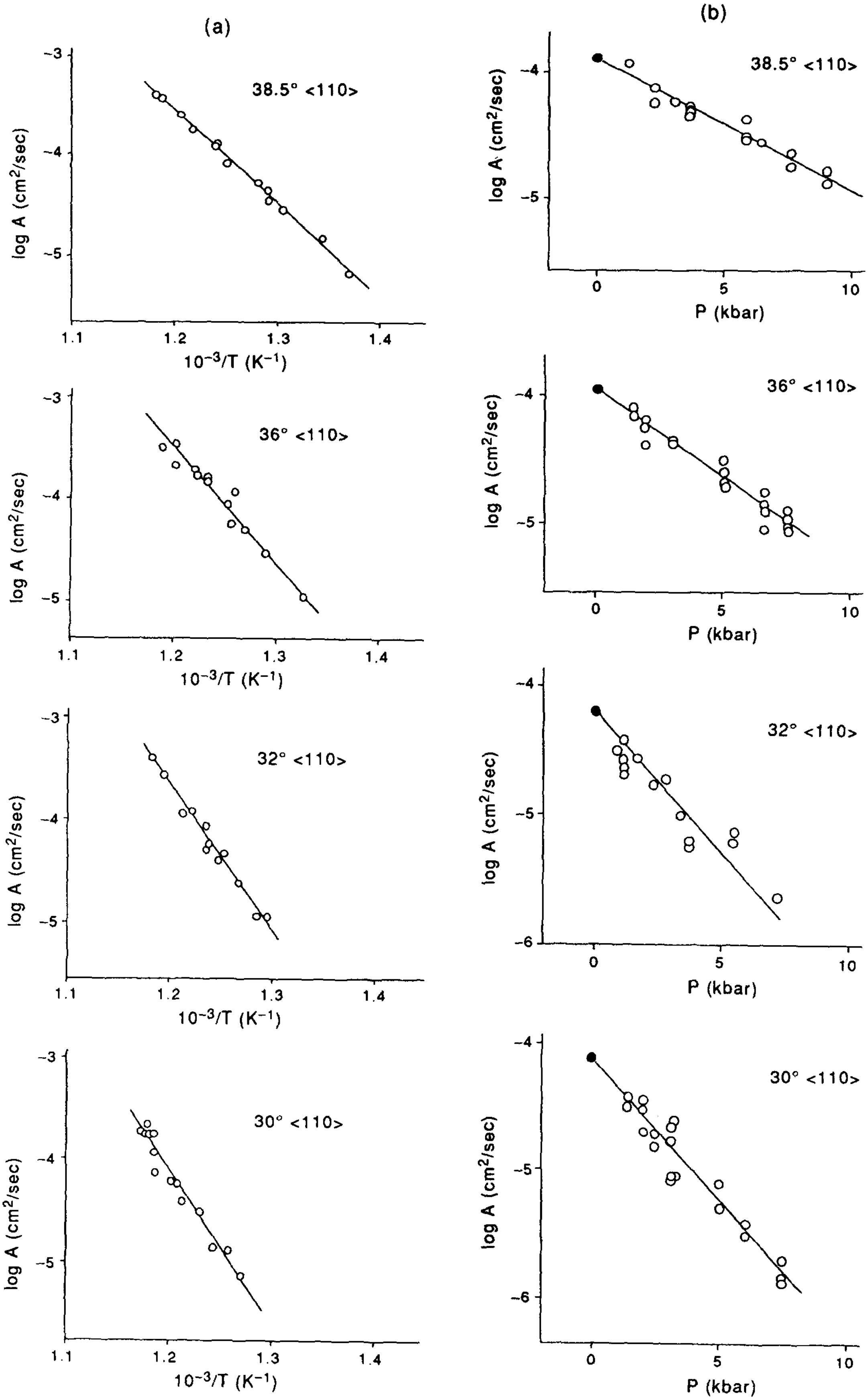

Fig. 7. The temperature (a) and pressure (b) dependencies of grain boundary mobility for ⟨110⟩ tilt boundaries in Al.

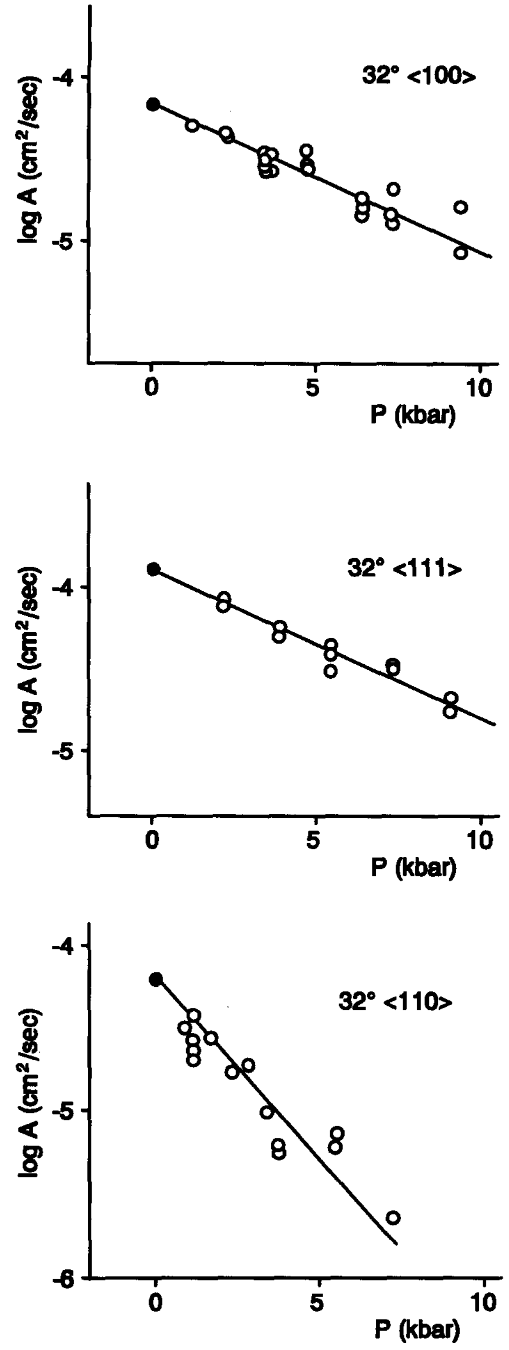

Fig. 8. The pressure dependencies of GB mobility for tilt grain boundaries with different rotation axes but same angle of misorientation.

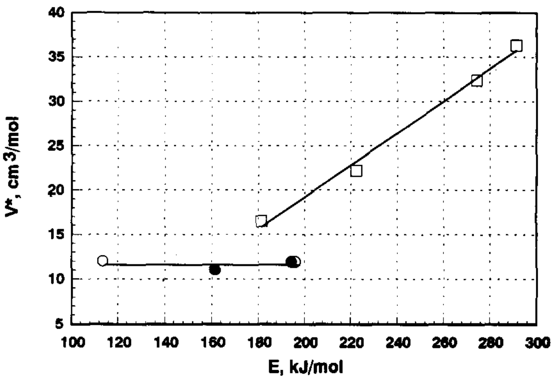

Fig. 9. The activation volume V^* as a function of the activation energy E of tilt grain boundary migration. (○) ⟨100⟩; (●) ⟨111⟩; (□) ⟨110⟩ tilt grain boundaries.

comparable to the activation volume of bulk self diffusion V^*_{SD}.

For GB migration the activated state requires the generation of a lattice site in the boundary and concurrently a jump of an atom into this site. Therefore, the activation volume for GB migration ought to be comparable to V^*_D and, accordingly, to V^*_{SD}. In Equation (6) V_f is the partial molar volume of the vacancies. Its magnitude depends on the degree of relaxation of the lattice around the vacancy. Without relaxation V_f would equal the molar volume Ω. The lattice relaxation causes $V_f \leq \Omega$. This effect is particularly strong in the b.c.c. lattice and other not close-packed crystal structures.

The second term, V^*_m is the partial molar volume associated with the activated state. At the saddle point configuration the diffusing atom has to locally expand the lattice, thus, V^*_m is probably positive but of small magnitude. For example, in gold $V^*_m = 0.15$ [17]. For GB diffusion or GB migration V^*_m should be close to zero practically, since the GB is more open than the bulk crystal and thus, atomic migration requires little lattice expansion. Also, since bonding in the GB is not as strong as in the bulk, the magnitude of V^*_f, the partial molar volume of the vacancy generated in the GB, should be less than in the crystal interior. Of course, V^*_f and V^*_m are expected to depend on GB structure and thus on GB misorientation. For random GBs V^*_f should be smaller than for highly ordered and densely packed special GBs.

As a result the activation volume for migration in randomly textured polycrystals ought to roughly correspond to, but not exceed, the activation volume for bulk self diffusion. Owing to the substantial experimental difficulties associated with the determi-

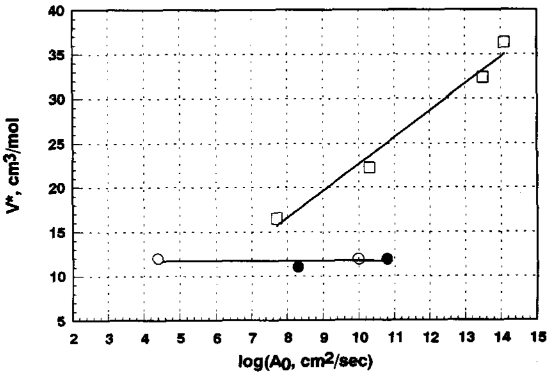

Fig. 10. The activation volume V^* vs the pre-exponential factor of grain boundary mobility [see equation (1)] (○) ⟨100⟩; (●) ⟨111⟩; (□) ⟨110⟩ tilt grain boundaries.

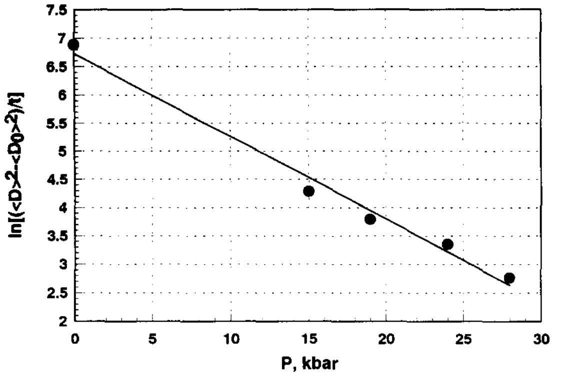

Fig. 11. The pressure dependence of the quantity $A = m\sigma$ during grain growth [see equations (9) and (10)].

nation of the activation volume of GB motion, only few literature data are available to test our hypothesis.

Hahn and Gleiter [17] studied grain growth in pure Cd (99.9999%) under high pressure (up to 28 kbar) and at annealing temperatures 180–260°C. The activation volume was not calculated by Hahn and Gleiter, but can be derived from their data under the assumption of ideal grain growth kinetics.

For normal growth

$$\frac{d\langle D\rangle}{dt} = m\frac{4\sigma}{\langle R\rangle} \tag{7}$$

where $\langle D\rangle$,$\langle R\rangle$ are the average grain diameter and radius of curvature, respectively, A is the grain boundary mobility, σ is the average surface tension of the grain boundaries. With the definition $A = m\sigma$

$$A = A_0\,\mathrm{e}^{-H/RT} \tag{8}$$

where H is the enthalpy of activation for grain growth, i.e. for grain boundary migration. By integration of (7) one obtains

$$\langle D\rangle^2 - \langle D_0\rangle^2 \sim At \tag{9}$$

and correspondingly the activation volume V^*_{GG} of grain growth (or GB migration)

$$V^*_{GG} = -RT\left[\frac{\partial \ln A'}{\partial p}\right]_T$$

$$= -RT\left[\frac{\partial \ln\left[\dfrac{\langle D\rangle^2 - \langle D_o\rangle^2}{t}\right]}{\partial p}\right]_T. \tag{10}$$

In Fig. 11 the rate of grain growth in Cd is given as a function of pressure calculated from the data of Ref. [17]). It yields an activation volume for grain boundary migration $V^*_{GG} = 6.39\,\mathrm{cm^3/mol}$, or $V^*_{GG}/\Omega = 0.49$. The ratio V^*_{SD}/Ω for the bulk self diffusion in Cd ranges from 0.53 to 0.59 [23] and is practically independent of crystallographic orientation. Obviously there is a reasonable agreement between V^*_{GG}/Ω and V^*_{SD}/Ω.

Loikowski [18] studied grain growth in Al (99.99%) under a pressure up to 25 kbar at 400°C. The initial grain size was 4.2 μm. The activation volume V^*_{GG} ranged from 0.65 to 0.8 Ω and depended on the thermomechanical history, i.e. on crystallographic texture of the polycrystals. The values of the activation volume for self diffusion in Al given in literature are contradictory and range from 0.52 to 0.97 Ω [24] or from 1.23 to 1.35 Ω [25]. Although the latter reference seems to provide more accurate data, in any event $V^*_{GG} \leqslant V^*_{SD}$.

There was only a single previous report on the pressure dependence of GB motion [19, 20]. Special $\langle 001\rangle$ tilt GBs Σ13 ($\varphi = 22.5°$), Σ17 ($\varphi = 28°$) and Σ5 ($\varphi = 37°$) and random $\langle 001\rangle$ tilt GBs with angle of misorientation $\varphi = 25$, 33.5 and 41.5° were studied in tin. The GB migration rate was measured at atmospheric pressure in the temperature range 185–225°C and at hydrostatic pressure up to 16 kbar at 208°C. The orientation dependencies of activation energy and activation volume of migration are given in Fig. 12. When the measured values are compared with the activation energy and activation volume of self diffusion, large discrepancies become apparent. The activation energy for the migration of special GBs is 1.5–2 times larger than the energy of activation for *bulk* self diffusion and almost by an order of magnitude larger than for GB self diffusion. The activation volumes for special GBs amount to 0.6–0.96 V^*_{SD}. However, for non-special GBs the activation volumes exceed V^*_{SD} by a factor of 2–2.5, which seemingly contradicts the considerations given above.

The current investigation provides a more specific approach to the problem and allows a more sophisticated interpretation of the GB migration process. Three results of the current study are most noteworthy and deserve a more detailed consideration.

(a) The orientation dependence of activation volume is different from the orientation dependence of activation energy.

(b) For $\langle 100\rangle$ and $\langle 111\rangle$ tilt boundaries the activation volume does not depend on the angle of rotation, while the activation energy does.

(c) The absolute value of the activation volume can exceed the activation volume for bulk self diffusion.

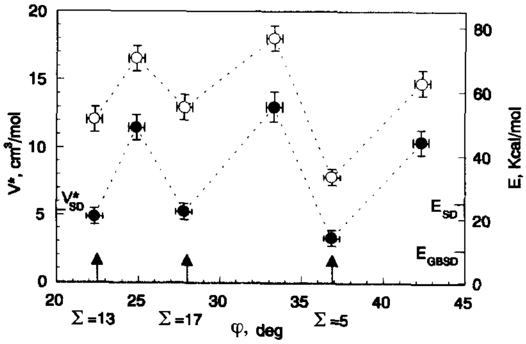

Fig. 12. Activation energy (○) and activation volume (●) of $\langle 001\rangle$ tilt grain boundary migration in tin.

Owing to its sensitivity to even minor amounts of impurities, the activation energy is less suited for an investigation of the mechanism of grain boundary migration. However, it is conspicuous that the activation energy for ⟨110⟩ tilt boundaries exceeds considerably the activation energy for bulk self diffusion, which is difficult to interpret in terms of solute drag, since the solute drag theory predicts activation energies close to bulk self diffusion. In fact, the activation energy for migration of ⟨100⟩ and ⟨111⟩ tilt boundaries with off coincidence orientation relationships corresponds approximately to bulk self diffusion. On the other hand, for ⟨110⟩ boundaries only grain boundaries close to special orientations follow along the same line with an activation energy close to bulk self diffusion. With increasing departure from a low Σ coincidence orientation, however, the activation energy for migration of ⟨110⟩ tilt boundaries drastically increases and attains values 50% higher than the activation energy for bulk self diffusion. It is difficult to justify such high activation energies in terms of our current theoretical understanding of grain boundary mobility including solute drag theory (see Introduction).

The activation volume for ⟨100⟩ and ⟨111⟩ tilt boundaries is identical and independent of angle of rotation, quite in contrast to the behaviour of the activation energy. The absolute value of about $12\,\mathrm{cm}^3/\mathrm{mol}$ corresponds to slightly more than one atomic volume in aluminium and is, therefore, close to the activation volume for bulk self diffusion. As mentioned before, the activation volume is the difference between the volume of the activated and the ground state.

For self-diffusion this is essentially the volume of a vacancy, which has to be provided for the elementary diffusive step. The finding of an activation volume for grain boundary migration close to that of self diffusion means that the bulk diffusion process controls the boundary migration rate as to be expected for a boundary dragging along solute atoms. On the other hand the intrinsic grain boundary mobility, e.g. in the absence of impurities, is not likely to yield activation volumes very different from a single atomic volume, since a diffusive jump across the boundary by detaching an atom from the shrinking crystal and attaching it to the growing one requires the generation of a lattice site at the internal surface of the growing crystal. If large structural vacancies do not exist in the boundary, then the creation of a lattice site in the boundary requires a volume change close to an atomic volume. In fact, computations of grain boundary structure at 0 K do not predict large excess volumes in grain boundaries, at least not in special boundaries. The results on ⟨100⟩ and ⟨111⟩ tilt boundaries are, therefore, quite in line with our current understanding of grain boundary motion by the transfer of single atoms across the boundary while destroying lattice sites on the shrinking and generating lattice sites on the growing crystal side. Since the activation volume is of the same order as for bulk self diffusion, impurity drag should not substantially affect the results.

In contrast, the activation volume for ⟨110⟩ tilt boundaries increases with increasing departure from the exact low Σ coincidence orientation relationship, as is also the case for the activation energy. Correspondingly, the activation volume for ⟨110⟩ boundaries increases with increasing activation energy, actually in a linear fashion. For a deviation of 8° from a $\Sigma 9$ orientation relationship the activation volume amounts to $36\,\mathrm{cm}^3/\mathrm{mol}$ equivalent to more than three atomic volumes. Such large activation volumes cannot be justified in terms of individual atomic jump mechanisms of grain boundary migration. Rather such values evidence that more than a single atom is involved in the fundamental process of grain boundary migration in these boundaries.

Migration mechanisms, based on groups of atoms, can either consist of the concomitant migration of groups or a cooperative motion (chain transfer) by a serial motion of atoms. Group mechanisms of grain boundary migration have been proposed by several authors in the past, without any proof of evidence, though. In his island model of grain boundary structure, Mott proposed that little patches of perfect crystal structure will detach from one crystal and attach at the other side of the boundary [26]. Such a model of grain boundary migration, however, is not compatible with our current knowledge of grain boundary structure obtained by computer simulation or high resolution microscopy. Grain boundaries are very narrow with little excess volume and do not give room for floating crystal patches across the boundary. In recent computer simulation studies on a $\Sigma 5$ twist boundary Jhan and Bristowe [27] found that concurrent shuffling of groups of atoms may take place during migration. Such concurrent shuffling is compatible with our experimental results and the computed atomistic configuration of grain boundary structure.

The current study demonstrates that the mechanism of grain boundary migration may actually depend on grain boundary structure, in particular on rotation axis. As already indicated by the activation energy, but unambiguously evidenced by the activation volume, ⟨110⟩ tilt boundaries do migrate by a group mechanism. From the current experimental results it cannot be ruled out that also ⟨100⟩ and ⟨111⟩ tilt boundaries involve more than a single atom in the elementary step of boundary migration, but the results are also compatible with the transfer of individual lattice sites from one grain to the other. If a group mechanism should hold also for these boundaries, then it is obviously different from the process of boundary migration in ⟨110⟩ crystals.

From the comparison of the experimentally determined and theoretically predicted absolute value of grain boundary migration rate Haessner and Hofmann [28] concluded that grain boundary migration in general must proceed by a group mechanism. The current investigation cannot confirm the general validity of this statement, since the results on ⟨100⟩ and ⟨111⟩ boundaries in terms of activation energy and activation volume are compatible with single atom migration mechanisms, but for ⟨110⟩ tilt boundaries their conclusions are definitely substantiated.

5. CONCLUSIONS

The temperature and pressure dependence of the migration rate of tilt grain boundaries in aluminium bicrystals with ⟨100⟩, ⟨111⟩ and ⟨110⟩ rotation axes were investigated. The following results were obtained.

1. From the temperature dependence of the grain boundary mobility the activation energy and from the pressure dependence the activation volume were determined.
2. For ⟨100⟩ and ⟨111⟩ tilt boundaries the activation energy increases with departure from special orientations, while the activation volume is independent of the angle of rotation. For ⟨110⟩ boundaries the activation energy also increases with deviation from low Σ coincidence rotations, but the absolute value of activation energy is very high, exceeding the activation energy for self diffusion in the bulk. For these boundaries also the activation volume increases with departure from low Σ coincidence rotations.
3. These results are interpreted as proof of evidence for a group mechanism of grain boundary migration for ⟨110⟩ tilt boundaries.
4. For ⟨100⟩ and ⟨111⟩ tilt boundaries the results are compatible with models of grain boundary migration based on the motion of single atoms. It cannot be ruled out, however, that also for these boundaries the migration proceeds by the concurrent shuffling of groups of atoms. Further investigations and, in particular, molecular dynamics simulation studies will be necessary to clarify this issue.
5. Results on the pressure dependence of grain growth rate suggest a polycrystal behaviour similar to ⟨100⟩ and ⟨111⟩ tilt boundaries and, therefore, seem to indicate a single atom mechanism for GB migration. The current results prove that the mechanism depends on GB crystallography and, therefore, the controlling mechanism of GB motion in polycrystals will depend on crystallographic texture.

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