

High Pressure Effect on Grain Boundary Migration and Mechanism of Grain Boundary Migration

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Keywords: Grain Boundary Migration, Mobility, Mechanism, Orientation Dependence, Impurity, Compensation Effect

ABSTRACT

Mechanism of grain boundary migration is one of the least known aspects of grain boundary physics. The main reason of it is a lack of solid data of grain boundary migration. The other reason is that the enthalpy of activation and the pre-exponential factor in the mobility equation are not independent of each other. This is because to so-called compensation effect, due to the activation enthalpy is proportional to the logarithm of pre-exponential factor. The thermodynamical theory of compensation effect will be discussed. That is why the new activation parameter - the activation volume - should be used to understand the relations between the experimentally measured magnitudes and atomic mechanism of grain boundary motion.

1. INTRODUCTION

In spite of a large number of papers devoted to the grain boundary migration, the physical mechanisms and fundamentals of this process are the least known aspects of the grain boundary physics. First and foremost is an obvious lack of reliable physical data of mobility of the single grain boundaries with properly determined crystallographic and geometric parameters, what are measured under the action of definite driving force.

As a matter of fact, most previous measurements of grain boundary migration were distorted by the artefacts and offered a fertile field for misleading conclusions and confusion on the dependence of grain boundary mobility of external parameters. [1-2]

Nevertheless, there are some additional reasons of such situation in the grain boundary motion physics.

2. BASIC OF GRAIN BOUNDARY MOTION

Let us consider the basis for the calculations of the grain boundary mobility rate - the equation, what firstly was arrived by Burke and Turnbull [3]:

$$v = bv \frac{\Delta G}{kT} e^{-G^*/kT} = bv \frac{\Delta G}{kT} e^{S^*/k} e^{-H^*/kT} \equiv mp = m_0 e^{-H^*/kT} p \quad (1)$$

Where the driving force ΔG is the difference between the free energies of the atom in two grains, dividing by the grain boundary; p is the driving force for a unit of volume: $p = \Delta G \Omega$, Ω is the molar volume, m is the grain boundary mobility, m_0 is the pre-exponential factor, H^* is the enthalpy of activation.

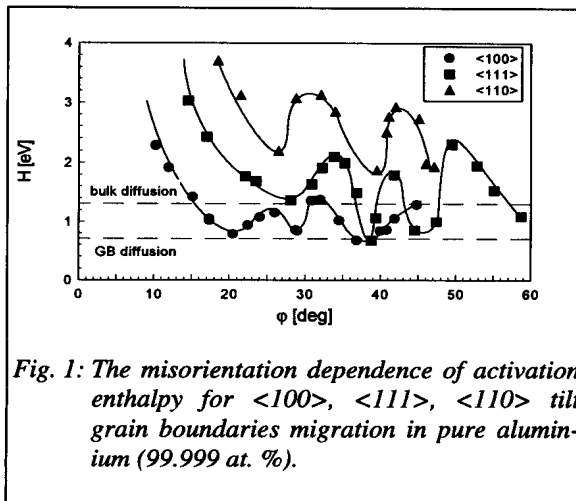
Formally, the Eq. (1) can be represented as:

$$v = \frac{D_0}{b} \frac{\Delta G}{kT} e^{-H_D^*/kT} \quad (2)$$

where H_D^* is the activation enthalpy for diffusion and D_0 is the pre-exponential factor in the equation of diffusion coefficient.

This seemingly difficult task turns out to be relatively simple: to measure the temperature dependence of the migration rate, to determine the enthalpy and entropy (pre-exponential factor) of activation and finally to compare these magnitudes with corresponding characteristics of the known elementary processes in solids, first of all, naturally, grain boundary and bulk diffusion. The similar comparison, what evidently was done firstly for the grain growth in the late 40's, and was done since that time repeatedly both for grain growth and single grain boundary migration, had shown that the activation enthalpy (energy) of mentioned processes far exceeds not only the enthalpy (energy) of grain boundary diffusion, but the bulk one as well. Inasmuch as the purity of materials at that time was, naturally, not very high, the idea was put forward that the observed effects arose from the impurity influence. The success in the chemistry of pure materials demonstrated that the activation energy of grain boundary migration actually depends on the amount of impurities, but not only...

The pre-exponential factor in the equation of grain boundary mobility exceeds the value, estimated from the single atomic mechanism (Eqs. (1) and (2)) on many orders of magnitude. Unfortunately, the small number of experimental works contents data allowing to analyse at one time the energy and pre-exponential factor. There are practically all measurements where the driving force is created by the surface tension of grain boundary itself [4-7].



The misorientation dependencies of the energy of activation and the pre-exponential factor A_0 of the reduced mobility A ($A = m\sigma$, σ is the grain boundary surface tension) for <100>, <111> and <110> tilt grain boundaries in pure aluminium are presented in Figs. 1 and 2 [1]. The common values for the grain boundary and bulk diffusion in aluminium and for the pre-exponential factor, determined by the single atomic mechanism, are marked off on the diagrams. One can see, that for the <100> tilt grain boundaries only the obtained values correspond with the magnitudes which are typical for the migration at work by the single atom transfer mechanism. The pre-exponential factor for the <111> tilt

boundaries and especially for $\langle 110 \rangle$ tilt boundaries is much superior to the magnitude of A_0 for the single atom mechanism. The energy of activation considerably exceeds also not only the activation energy of grain boundary diffusion but the bulk one.

In Figs. 3-4 are presented the results of precise measurements of $\langle 111 \rangle$ tilt grain boundary mobility in the vicinity of the special misorientation $\Sigma 7$ [6]. It is seen that in this case also the activation enthalpy and particularly the pre-exponential factor significantly exceed these values for the motion by single atom.

Further, the activation energy (enthalpy) and the pre-exponential factor depend on the concentration of impurity in the material. As to the activation energy it increases, as a rule, with impurity increase. It is significant that this rise cannot be described by the impurity drag theory. In Fig. 5 is shown the activation enthalpy as a function of a total concentration of different impurities in the samples of very pure aluminium. [7] One can see that even such small change of total concentration causes the rise of activation enthalpy on 0.3-0.4 eV. Because of this, even a simple comparison the activation values for grain boundary migration with the corresponding ones characteristic for different elementary processes in solids comes up against some obstacles, inasmuch as even small change in impurity content changes drastically the boundary migration activation parameters. However, there is a principle difficulty in such comparison. The point is that the activation energy (enthalpy) and pre-exponential factor in the equation of kinetic coefficient are not independent. They are associated by virtue of the compensation effect.

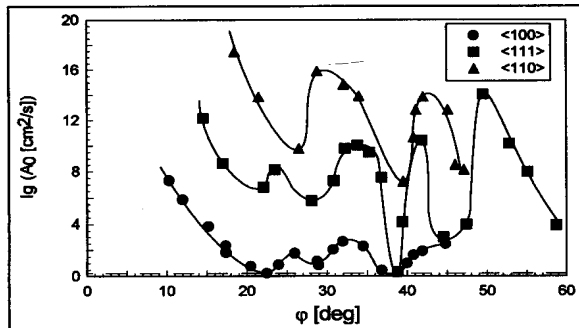


Fig. 2. The misorientation dependence of the pre-exponential factor of grain boundary mobility for $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ tilt grain boundaries in pure aluminium (99.999at. %).

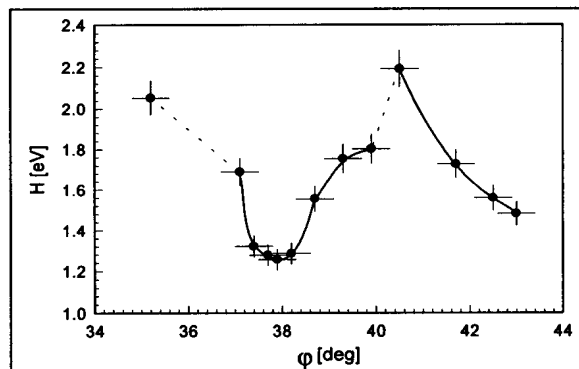


Fig. 3. The misorientation dependence of migration activation energy for $\langle 111 \rangle$ tilt grain boundaries.

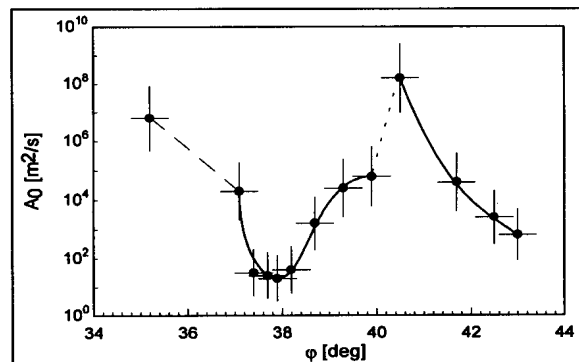


Fig. 4. The misorientation dependence of pre-exponential factor of mobility for $\langle 111 \rangle$ tilt grain boundaries.

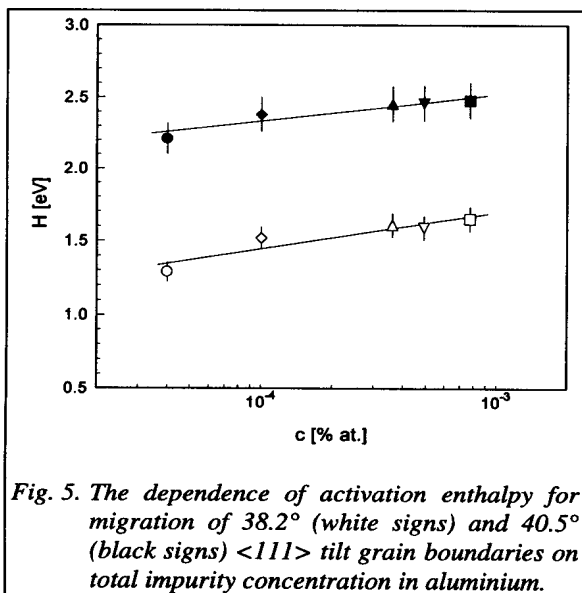


Fig. 5. The dependence of activation enthalpy for migration of 38.2° (white signs) and 40.5° (black signs) $\langle 111 \rangle$ tilt grain boundaries on total impurity concentration in aluminium.

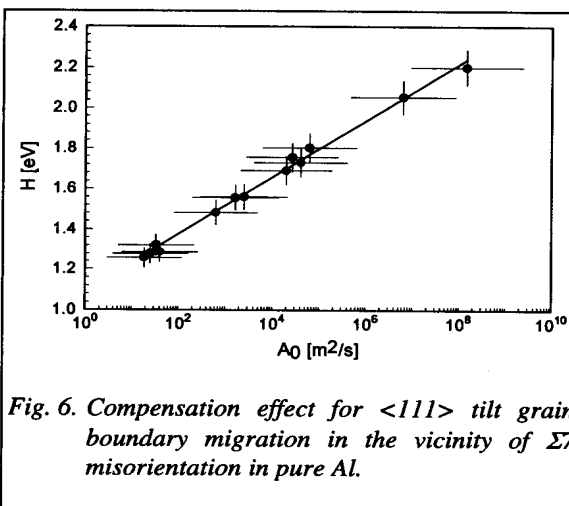


Fig. 6. Compensation effect for $\langle 111 \rangle$ tilt grain boundary migration in the vicinity of $\Sigma 7$ misorientation in pure Al.

It should be recorded that in many cases the compensation temperature coincides with the temperature of first order phase transformation in the system. The discussed linear dependence commonly was observed in a row of uniform objects. The definition „uniform objects“ means in this case that the atomic mechanism of the elementary kinetic act in these objects is the same. It was shown in [9] that if the certain systems in the mentioned above row is similar in some sense, so there is a parameter λ , which varies by a small amount on transition from one system to another¹,

3. COMPENSATION EFFECT IN GRAIN BOUNDARY MIGRATION

The compensation effect is designated the linear dependence between the energy of activation and the logarithm of the pre-exponential factor in the equation of kinetic coefficient (diffusion, coefficient, mobility etc.), observed in activation processes. Such behaviour of the activation parameters compensates the change of each by itself. Compensation effect (CEF) was repeatedly observed on the different activation processes in dissimilar systems but most often in interface and grain boundaries. In Fig. 6 as an example is shown a compensation effect for $\langle 111 \rangle$ tilt grain boundary migration in the vicinity of the special misorientation $\Sigma 7$ in pure aluminium [6]. The description of the compensation effect in the activation processes in different, particularly, grain boundary systems is given in [8]. The phenomenological and model approaches to the analysis of this fascinating phenomenon and the relations between the mentioned effect and non-equilibrium thermodynamics are discussed [8].

As is easy to see, the consequence of the specific linear dependence between the activation energy and the logarithm of the pre-exponential factor in the kinetic coefficient equation is the existence of so called temperature of compensation T_c , at which the kinetic coefficients, in particular, the grain boundary mobility, are equal and the kinetic lines in Arrhenius co-ordinates intersect at one point.

¹ The nature of this parameter is of no special concern: it could be composition, misorientation angle of the grains, surface tension and so on.

and secondly the Arrhenius law is fulfilled, the linear relationship between activation energy and pre-exponential factor in the kinetic coefficient equation is found to be observed:

$$\ln m_0 = \frac{S^*(\lambda)|_{\lambda=0} - E^*(\lambda)|_{\lambda=0}/T_c}{k} + \frac{E^*}{kT_c} \quad (3)$$

where

$$T_c = \left(\frac{dE^*}{dS^*} \right)_{\lambda=0} \quad (4)$$

is the compensation temperature.

Inasmuch as the Arrhenius dependence is usually explained in terms of atomic transition across a „potential barrier“, we can consider the state „at the barrier“ as a special „barrier phase“ with its own thermodynamic function and equation of state [9]. The compensation temperature then determines the hypothetical temperature of equilibrium between normal and barrier phases.

In [8] was studied how the compensation effect is consistent with the principles of non-equilibrium thermodynamics, in particular, with the principle of maximal rate of the free energy of the system reduction. In discussed case when grain boundary moves under the constant driving force ΔG the rate of reduction the system free energy G is

$$\frac{dG}{dt} = -v\Delta G = -m \frac{\Delta G^2}{kT} = -m_0 \frac{\Delta G^2}{kT} e^{-\frac{G^*}{kT}} \quad (5)$$

and from the extremum existence conduction with respect to parameter λ (the sense of this parameter was discussed above) one can see, that:

$$\frac{d}{d\lambda}(G^*)_{\lambda=\lambda_0} = 0 \quad (6)$$

Where λ_0 is the point of extremum.

Finally authors [8] come to the relation (4):

$$T_c = \left(\frac{dE^*}{dS^*} \right)_{\lambda=\lambda_0}$$

A number of empirical rules concerning the activation processes were explained on the basis of the concept of a compensation effect [8].

The main consequence what is in particularly importance for us is that from mobility measurements at different temperatures only information on a single activation quantity can be obtained.

4. HIGH PRESSURE EFFECT ON GRAIN BOUNDARY MIGRATION

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:

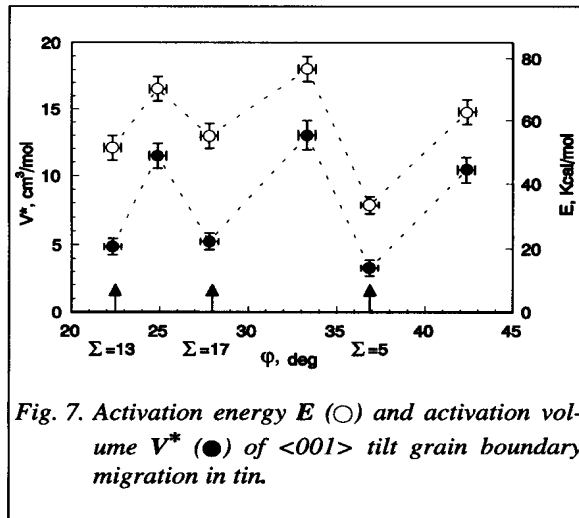
$$G^* = H^* - TS^* = E^* + pV^* - TS^* \quad (7)$$

$$\frac{\partial \ln v}{\partial p} = -\frac{V^*}{RT} \quad (8)$$

$$\frac{\partial \ln v}{\partial 1/T} = -\frac{E^* + pV^*}{R} = -\frac{H^*}{R} \quad (9)$$

Despite the relative ease of interpretation of the activation volume compared, there have been only very few studies on the pressure dependence of grain boundary migration. The main reason 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 pressure. Hahn and Gleiter [10] studied grain growth in pure Cd under high pressure (up to 28 kbar).

The activation volume of grain growth V_{gg}^* [12] was found to be 0.49 of the molar volume Ω , what is in reasonable agreement with the activation volume of self diffusion (0.53-0.59 Ω). The most interesting from our point of view is the pressure influence on the motion of different in structural sense grain boundaries. Unfortunately, there were only two experimental works on the pressure dependence of single grain boundary motion.



Special <001> tilt grain boundaries $\Sigma 13$ ($\approx 22.5^\circ$), $\Sigma 17$ ($\approx 28^\circ$) and $\Sigma 5$ ($\approx 37^\circ$) and random grain boundaries with angle of misorientation $\approx 25^\circ$, 33.5° and 41.5° were studied in tin [11]. The grain boundary migration rate was measured at atmospheric pressure in the temperature range $185^\circ\text{C} - 225^\circ\text{C}$ 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. 7. 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 grain boundaries is 1.5- 2 times larger than the energy of activation for bulk self diffusion and almost by an order of

magnitude larger than grain boundary self diffusion. The activation volumes for special grain boundaries amount to $0.6-0.96 V_{SD}^*$. However, for non-special grain boundaries the activation volumes exceed by a factor of 2 - 2.5, which seemingly contradicts the considerations given above. The last (but not least) investigation what was undertaken in order to clear this problem was carried out on special and non-special $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ tilt grain boundaries in bicrystals of pure aluminium [12]. Grain boundary motion was investigated under a constant driving force. ΔG provided by the surface tension of a curved grain boundary. The angle was chosen such that it was either close to a low Σ coincidence rotation-special grain boundary with $\Sigma 5$ ($36.9^\circ \langle 100 \rangle$), $\Sigma 7$ ($38.2^\circ \langle 111 \rangle$) and $\Sigma 9$ ($36.9^\circ \langle 110 \rangle$) or far from coincidence rotations (non-special boundaries) [12].

The results, obtained in [12], become more transparent, when the activation volume is plotted vs. the activation energy (Fig. 8). For $\langle 100 \rangle$ and $\langle 111 \rangle$ tilt boundaries the activation volume does not depend on activation energy. For $\langle 110 \rangle$ tilt boundaries, however, the activation volume is linearly proportional to the activation energy. Finally, Fig. 9 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.

The activation volume for $\langle 100 \rangle$ and $\langle 111 \rangle$ tilt boundaries is identical and independent of misorientation angle, quite in contrast to the behaviour of the activation energy. The absolute value of about $12 \text{ cm}^3/\text{mol}$ corresponds to slightly more than one atomic volume in aluminium and is, therefore, close to the activation volume for bulk self diffusion.

In contrast, the activation volume for $\langle 110 \rangle$ tilt boundaries increases with increasing the activation energy (Fig. 8). These results can be interpreted as proof for evidence for a group mechanism of grain boundary migration for $\langle 110 \rangle$ tilt boundaries. It gives the impression that $\langle 100 \rangle$ and $\langle 111 \rangle$ tilt boundaries move by the single atom migration mechanism. However, the pre-exponential factor in the mobility equation for these grain boundaries exceeds the value what correspond to the characteristic one of the single atom movement mechanism on 5-10 orders of magnitude (!).

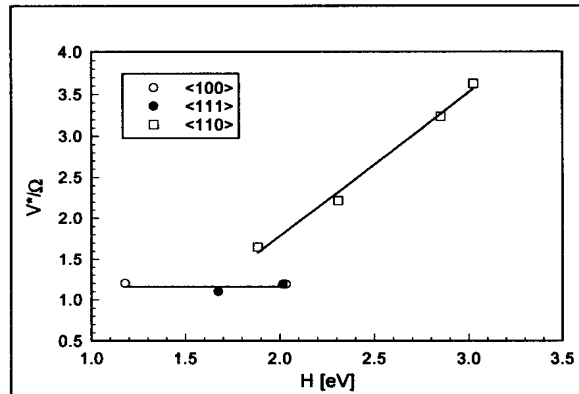


Fig. 8. The normalised activation volume V^*/Ω vs. the activation enthalpy of grain boundary mobility for tilt grain boundaries with different rotation axes in Al.

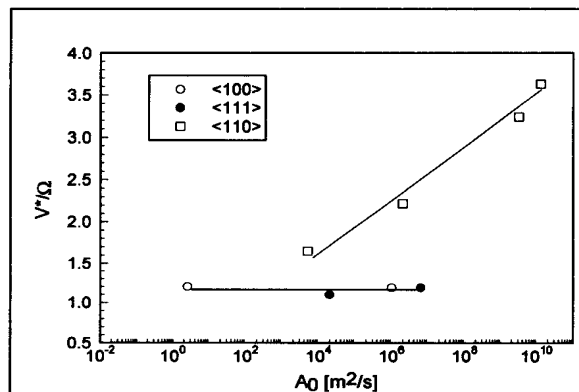


Fig. 9. The normalised activation volume V^*/Ω vs. the pre-exponential factor of grain boundary mobility for tilt grain boundaries with different rotation axes in Al.

5. INSTEAD OF CONCLUSIONS

The compensation effect opens up possibilities to find the point on the diagram with co-ordinates quantitatively associated the single atom motion.

In Fig. 10 are presented the compensation lines for $\langle 111 \rangle$ tilt boundaries in pure aluminium with different total impurity content [7]. These lines are extrapolated to the ordinate correspond the single atomic mechanism of grain boundary migration ($A_0 \sim 10^{-4}$ - 10^{-6} m²/s). One can see that the lines come to almost one point what support the idea of it physical significance. The activation energy relevant this point is about 0.5 eV, what reasonable correlates with the range of activation energy of processes in grain boundary, e.g. self diffusion.

In Fig. 11 are shown the result of approach discussed above applied to the compensation relationships of different types of tilt grain boundaries in pure aluminium. It can be seen that in this case as well as for $\langle 111 \rangle$ tilt grain boundaries the compensation lines come to the point with the co-ordinate corresponding (in our current understanding) the grain boundary motion by single atom transfer.

No doubt, even in absolute pure material mobility for different grain boundaries moving by the same mechanism of motion does not have to be uniform. But so long range extrapolation can not distinguish this difference. It is believed that such agreement can not be accidental and reflects the fundamental physical properties of system and process.

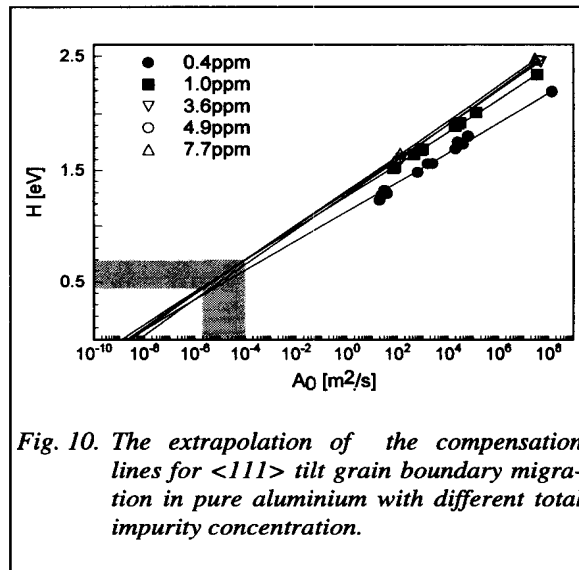


Fig. 10. The extrapolation of the compensation lines for $\langle 111 \rangle$ tilt grain boundary migration in pure aluminium with different total impurity concentration.

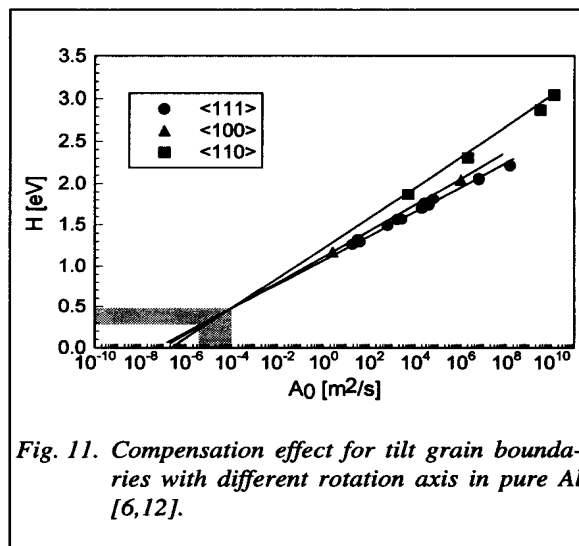


Fig. 11. Compensation effect for tilt grain boundaries with different rotation axis in pure Al [6,12].

REFERENCES

1. G. Gottstein and L. S. Shvindlerman, *Scripta metall. mater.* **27**, 1515 (1992).
2. G. Gottstein and L. S. Shvindlerman, *Scripta metall. mater.* **27**, 1521 (1992).
3. J. E. Burke and D. Turnbull, in *Progress in Metal Physics* (edited by B. Chalmers), Vol. 3. Pergamon Press, New York (1952).
4. E. M. Fridman, Ch. V. Kopezki, L. S. Shvindlerman, *Z. Metallkde.* **66**, 533 (1975).
5. V. Yu. Aristov, V. L. Mirochnik, L. S. Shvindlerman, *Sov. Phys. Solid State* **18**, 137 (1976).
6. D. A. Molodov, U. Czubayko, G. Gottstein, L. S. Shvindlerman, *Scripta metall. mater.* **32**, 529 (1995).
7. D. A. Molodov, U. Czubayko, G. Gottstein, L. S. Shvindlerman, to be published.
8. G. Gottstein, L. S. Shvindlerman, to be published
9. E. L. Maxsimova, B. B. Straumal, V. E. Fradkov, L. S. Shvindlerman, *Phys. Met. Metall.*, **56**, 133 (1983).
10. H. Hahn, H. Gleiter, *Scripta metall.* **14**, 3 (1979).
11. D. A. Molodov, B. B. Straumal, L. S. Shvindlerman, *Scripta metall.* **18**, 207 (1984).
12. D. A. Molodov, J. Swiderski, G. Gottstein, W. Lojkowski, L. S. Shvindlerman, *Acta metall. mater.* **42**, 3397 (1994).

