

## Theory of Grain Boundary Motion\*

R. SMOLUCHOWSKI

*Carnegie Institute of Technology, Pittsburgh, Pennsylvania*

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The mobility of grain boundaries in metals is considered from a point of view similar to that used by Mott in his theory of viscosity of grain boundaries. By introducing a factor dependent on surface tension of the grain boundary and inserting the experimental activation energy, one obtains satisfactory agreement with experiment.

AMONG the various theories and atomic models of grain boundaries, there are two which seem to allow an interpretation of most of the experimental facts. One of them is the dislocation model, proposed sometime ago by Burgers,<sup>1</sup> and recently described in a more quantitative way by Shockley and Read.<sup>2</sup> Briefly, the grain boundary is supposed to be an array of dislocations which allow two grains to meet at any angle. For small angles, the dislocations are far apart (roughly  $1/(\sin\alpha)$  lattice constants) and the theory agrees well with experiment; for larger angles, one expects the model to break down.

The other theory we owe to Mott.<sup>3</sup> It is based on the idea that a grain boundary can be pictured as a sequence of islands of good atomic fit separated by areas of misfit between the two grains. This theory is particularly well suited to large angles where the dislocation model fails. Studies of grain boundary diffusion performed recently<sup>4</sup> for the first time on individual grain boundaries throw important light on the question of applicability of the two theories. They indicate that there is a rather drastic change in the behavior of grain boundaries in columnar copper at around 20 degrees angle between the two grains. For lower angles there is very little if any preferential grain boundary diffusion; for higher angles, on the other hand, the diffusion increases rapidly, reaching a maximum around 45 degrees. This seems to be in agreement with the following interpretation: At small angles, the grain boundary can be pictured as made up of dislocations reasonably far apart and the atomic mobility along such a grain boundary is not much different from that inside of the grain. At angles around 20 degrees, where the dislocations would overlap and lose their identity, the grain boundary is better described in terms of islands of fit and misfit. In such grain boundaries the state of disorder is high, and at low temperatures the diffusion is much faster than the volume diffusion in accord with a lower activation energy.

The present paper is concerned not so much with the mobility of the individual atoms along grain boundaries as with their collective movement associated with the migration of grain boundaries as a whole. On the dislocation model one expects the mobility of a grain boundary to be determined by the mobility of an array of dislocations as it was considered by Shockley. Although a dislocation can move with great ease in its plane of slip, it has to rely on a slow mechanism of atomic diffusion for a motion in a direction perpendicular to that plane. At very small angles of the order of  $10^{-4}$  radian, as, for instance, for mosaic boundaries, the mobility is very high as shown by Guinier.<sup>5</sup> Most experimental determinations of the velocity of motion of true grain boundaries are based on measuring the largest grains, and thus presumably they correspond to grain boundaries with large atomic mobility. It is for that reason that the theory here developed is based on Mott's model.

The basic mechanism of motion of a grain boundary is thus a transfer of a group of atoms from the lattice of one grain to the disordered state at the grain boundary and a transfer of a group of atoms from the disordered boundary layer to the crystalline lattice of the other grain. The two processes are somewhat analogous to melting and solidifying. However, as pointed out by Mott, a literal interpretation of the viscosity of the grain boundary as an extension of a liquid condition to low temperatures is not very tenable in view of the much more rapid temperature dependence of the viscosity of grain boundaries as compared with viscosity of the same metal in liquid state.

In order to make the theory more specific, let us consider a group of  $n$  atoms in the lattice of one grain which forms a layer along the grain boundary. In his theory of viscous slip, Mott assumed that the free energy for disordering such a group of atoms is

$$F = nL(1 - T/T_m),$$

where  $L$  is the heat of fusion and  $T_m$  is the melting point. We shall assume that this free energy depends also upon the specific surface energy  $\sigma$  of the grain boundary in the following manner:

$$F = nL(1 - T/T_m) - \sigma n v T/T_m, \quad (1)$$

<sup>5</sup> A. Guinier and J. Tennevin, *Progress in Metal Physics*, Vol. 2 (1950).

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<sup>1</sup> J. M. Burgers, *Proc. Phys. Soc. (London)* **52**, 23 (1940).

<sup>2</sup> W. Shockley, *Phys. Rev.* **78**, 275 (1950). T. H. van der Merwe, *Proc. Phys. Soc. (London)* **63**, 616 (1950).

<sup>3</sup> N. F. Mott, *Proc. Phys. Soc. (London)* **60**, 391 (1948).

<sup>4</sup> M. R. Achter and R. Smoluchowski, *Phys. Rev.* **76**, 470 (1949); *Proc. Nat. Res. Council Conference on "Lattice Imperfections,"* Pocono Manor, October, 1950. M. R. Achter, *Carnegie Institute of Technology, thesis*, 1950.

TABLE I. Observed and calculated mobilities of grain boundaries.

	$Q$ cal/mole	$V_0(\text{obs})$ cm/sec	$V_0(\text{calc})$ cm/sec
Ag	28000	$2 \times 10^3$	$1.5 \times 10^4$
Al	71-85000	$10^{18}-10^{19}$	$1.3 \times 10^{20}$
Brass	55000	$10^8-10^9$	$1.6 \times 10^{10}$

where  $v$  is the area of the layer per atom. Thus the higher the surface energy, the easier it is to disorder the group. This seems to be in accord with the fact that mobility of grain boundaries is strongly dependent upon such crystallographic factors as orientation of the grains and of the grain boundary itself. At the melting point the first term in (1) vanishes; the second term does not vanish, but it is very small, since  $\sigma$  is proportional to the shear modulus  $G$  which itself reaches small values at  $T_m$ . However, in view of the relatively limited temperature range over which experimental data exist, we can put  $\sigma=0$  at  $T=T_m$ . The general character of the underlying assumptions does not seem to justify a more elaborate consideration of that point.

In a stationary grain boundary the number of atoms ordering and disordering on each side of the boundary is the same. However, a driving force, such as

$$\tau_s = 2\sigma/r \quad (2)$$

or

$$\tau_c = \sigma/r, \quad (3)$$

caused by a spherical or cylindrical radius of curvature  $r$  of the grain boundary, can cause its migration. If we say that the force displaces the atoms on the average by a fraction  $f$  of the atomic diameter  $a$ , then the work done is

$$\tau n f a v.$$

The rate of motion of the boundary is then, according to the usual rate theory,

$$V = \nu a \exp(-F + \tau n f a v) / kT - \nu a \exp(-F - \tau n f a v) / kT \\ = 2\nu a \exp(-F/kT) \sinh(\tau n f a v / kT)$$

or approximately

$$V \cong (2\nu \tau a^2 n f v / kT) \exp(-F/kT),$$

where  $\nu$  is the atomic frequency. Inserting the expressions for  $\tau$  and  $F$  we have for a spherical grain of radius  $r$

$$V = V_0 \exp(-Q/kT) \quad (4)$$

with

$$V_0 = (4\nu a^2 \sigma n f v / r kT) \exp[(nL + \sigma n v) / kT_m] \quad (5)$$

and

$$Q = nL. \quad (6)$$

There are several sets of experimental data available which permit a comparison with theory: Alexander and co-workers<sup>6</sup> on silver, Beck and co-workers<sup>7</sup> on alu-

<sup>6</sup> Alexander, Baluffi, Dawson, Kling, and Rossi, Sylvania Electric Products Company Report NYO-663.

<sup>7</sup> Beck, Holzworth, and Hu, Phys. Rev. **73**, 526 (1948).

minum and brass, and Walker<sup>8</sup> and Burke<sup>9</sup> on brass. Their data (in certain cases replotted in the form  $\ln V$  versus  $1/T$ ) give the heats of activation shown in Table I. With  $L=2.73, 2.52$ , and  $3.0$  for Ag, Al, and brass, one obtains from (6) for  $n$  the values 10, 29-35, and 18 atoms, respectively. There is not enough information available to distinguish among the surface energies  $\sigma$  for each of the three metals. It is assumed thus that for all of them  $\sigma=400$  erg/cm<sup>2</sup>, which is a typical value observed for copper by Hollomon and Turnbull.<sup>10</sup> Also there are not enough quantitative data available to consider in detail the influence of grain orientation and boundary orientation on  $\sigma$ . The grain radii in the three sets of measurements were approximately 0.05, 0.05, and 0.005 cm. The factor  $f$ , which plays very little role in the quantitative check of the theory, was arbitrarily put equal to 0.5. The other values were as follows:  $\nu=10^{12}$  sec<sup>-1</sup>,  $a=10^{-8}$  cm, and  $T=500^\circ\text{C}$ , all the experiments being made in proximity of that temperature. The last two columns of Table I permit the comparison of the theoretical and experimental values of  $V_0$ . It should be stressed here that a relatively small change in  $Q$  affects the  $V_0$  a great deal and so, in general, an agreement better than within one or two orders of magnitude should be considered fortuitous. Such factors as stress magnifications, cold work, etc., have not been considered at all.

It is interesting to note the strong dependence of mobility on surface tension  $\sigma$  indicated by formula (4). As shown by numerous investigators,<sup>11</sup> in a given metal grain boundary energies can vary from zero to a maximum value. If, instead of putting  $\sigma=400$  erg/cm<sup>2</sup>, we have assumed  $\sigma=100$  erg/cm<sup>2</sup>, then the  $V_0$  would come out 25 times lower. For twin boundaries, which according to various estimates have an energy of the order of a few percent of the maximum value, the mobility is 1000 times lower. This is in basic agreement with observation.

The theory here developed indicates the need for quantitative studies of mobility of grain boundaries as a function of grain orientation, and for more information on the corresponding orientation dependence of the grain boundary energies. It would be particularly interesting to study the effects at lower angles between the grains where the dislocation model is applicable, and at intermediate angles where the island model becomes more fruitful.

<sup>8</sup> H. L. Walker, University of Illinois Eng. Exp. Stat., Bulletin 359 (1945).

<sup>9</sup> J. E. Burke, Trans. Am. Inst. Mining Met. Engrs. **180**, 73 (1949).

<sup>10</sup> J. H. Hollomon and D. Trumbull, General Electric Company, Report RL-398.

<sup>11</sup> C. G. Dunn and F. Lionetti, J. Metals **1**, 125 (1949). Dunn, Daniels, and Bolton (to be published). K. T. Aust and B. Chalmers, Proc. Roy. Soc. (London) **201**, 210 (1950); **204**, 359 (1950). B. Chalmers, Proc. Roy. Soc. (London) **196**, 64 (1949).