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PIPE DIFFUSION IN MAGNESIUM OXIDE

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When plastically deformed magnesium oxide is annealed, edge-dislocation dipoles break up into rows of prismatic dislocation loops by pipe diffusion. From the measurements of fluctuations in the separation of two dislocations in the dipole during breakup, an activation energy of $60,600 \pm 5000$ cal/mole for the formation and motion of point defects in the core of a dislocation has been obtained. This value has been compared with the results of a study of pipe diffusion along screw dislocations, in which a prismatic dislocation loop inside the foil is connected to both surfaces of a thin foil by a screw dislocation of the same b-vector. These results give the pipe diffusion coefficient as:

$$D_p \approx 3.0 \times 10^{-3} \exp - \frac{(62,700 \pm 5000)}{RT}$$

I. Introduction

There have been various studies on rapid mass transport along dislocations (pipe diffusion) in metals. For example, Price¹ observed the breaking up of long dislocation dipoles into rows of circular loops in zinc and cadmium at relatively low temperatures. The process occurred without change in the enclosed area of the dipole as viewed

along the direction of the Burgers vector. The breakup was attributed to fast dislocation pipe mass transport. Kroupa and Price² observed the translatory motion of a dislocation loop under a net applied force in zinc and have interpreted the result on the basis of pipe diffusion. Similarly Berghezan et al.³ found that a relatively stable dislocation loop in zinc started shrinking immediately after a nearby dislocation moved into a position so as to connect it to a grain boundary on one side and a free surface on the other side. Recently, Volin et al.⁴⁻⁶ developed a technique for observing rapid self-diffusional mass transport along isolated dislocations in aluminum. They studied the annealing kinetics of voids which were connected to both surfaces of an electron microscope thin foil by dislocations and found that these voids annealed out at considerably faster rates than nearby isolated voids. The phenomenon of pipe diffusion has not been studied in detail in ionic crystals. The breaking up of narrow dislocation dipoles into rows of prismatic dislocation loops on annealing was first observed by Washburn et al.⁷ An approximate quantitative treatment of this was given by Groves and Kelly⁸ and upper limits of activation energy for pipe diffusion were determined. Recently Turnbull⁹ reported a quantitative analysis of self climb of dislocation loops in UO_2 .

The two dislocations of the dipoles in Groves and Kelly's experiments were unresolved so the mechanism of dipole breaking was not clear. In the present experiments the breakup of individual more widely spaced resolvable dipoles has been observed directly as a function of annealing temperature and time. The activation energy

for pipe diffusion along edge dislocations was determined with greater accuracy.

During annealing of plastically deformed magnesium oxide, a mobile screw dislocation occasionally intersects a dislocation loop of the same b-vector. The loop is annihilated entirely by pipe diffusion to the surfaces. The rate of shrinkage of such a dislocation loop was measured at three different temperatures giving an estimate of the activation energy for pipe diffusion along a screw dislocation.

II. Experimental Procedure

A. Material

Magnesium oxide supplied by Muscle Shoals Electrochemical Corp., Tuscumbia, Alabama was used for the experiments. The following are the impurities reported by American Spectrographic Laboratories.

Al - .06%, Fe - .03%
Ca - .03%, Mn - .002%
Cr - .002%, Cu - <.001%
Si - <.005%

B. Specimen Preparation

Material, as supplied, was polycrystalline of very large grain size. Single crystal specimens in the form of thin sheets (~ 0.50 - 0.25 mm thick) were obtained by cleaving along {100}. The surface damage introduced during cleaving was removed and the sheets were

thinned down to ~ 0.1 mm by chemical polishing in hot phosphoric acid (150 - 160°C). At this stage the crystals were bent backwards and forwards (± 5 cm radius) about 200 times until the entire surface was covered with slip bands. Then the chemical thinning was continued after applying masking lacquer around the edges. The final thinning to get electron microscope samples was done by a jet polishing technique.⁷ After cold working the thinning was done from one side, as far as possible, because plastic strain is maximum at the surfaces and zero at the center for bending deformation.

C. Foil Orientation and Electron Microscopy

When a thin sheet of MgO is bent along the [010] axis, dislocation dipoles are introduced on (101)[$\bar{1}01$], ($\bar{1}01$)[101] and on (110)[$\bar{1}10$], ($\bar{1}10$)[110] slip systems.

Dipoles on (101) [$\bar{1}01$] and ($\bar{1}01$)[101] are of primary interest as dipoles on (110)[$\bar{1}10$] and ($\bar{1}10$)[110] are seen edge on. If the bending axis is slightly off from [010], dipoles on (011)[$0\bar{1}1$] and ($0\bar{1}1$)[011] also appear.

All the foils were examined in a Siemens 100 kV electron microscope. A double tilt holder was used. The same area was observed repeatedly after annealing at constant temperature outside the electron microscope and cooling in air. Further details of the annealing procedure have been given elsewhere.¹⁰ Care was taken to keep the same deviation from Bragg angles, during a series of observations. Measurements were made from the electromicrographs with both g_{+ve} and g_{-ve} diffraction conditions.

III. Theories

A. Model for Breakup of Dipoles

We assume that a dipole consists of two long edge dislocations. On heating the separation between the two glide layers on which the dislocations lie is assumed to vary along the dipole according to:

$$y = h + a \sin px, \quad (1)$$

where $p = 2\pi/\lambda$, λ is the wavelength and 'a' is the amplitude of the fluctuation (see Fig. 1). h is the separation between two dislocations in the dipole.

There is a force F per unit length, acting on each dislocation due to the other, which tends to make them climb together. We assume that the rate controlling process for climb of the dislocations is oxygen ion transport in the core and that it takes place by a vacancy mechanism. The concentration of vacancies c in the core of each of the dislocations is given by:

$$c = c_0 \exp (Fb^2/kT), \quad (2)$$

where c_0 is the equilibrium concentration of vacancies in the dislocation core at temperature T when no climb force is acting on the dislocation.

The climb force has two components: (i) the attraction between dislocations of opposite sign, and (ii) the line tension of the dislocations which tends to straighten out the waviness.

$$\text{The attraction term} = \frac{Gb^2}{2\pi(1-\nu)y}$$

$$\text{The line tension term} = \frac{Gb^2 \ln(\lambda/4b)}{4\pi(1-\nu)} \frac{(d^2y/dx^2)}{[1-(dy/dx)^2]^{3/2}}$$

The line tension force opposes the force of attraction near the points of closest approach and they act in the same direction at points of greatest separation. Since $(dy/dx)^2 \ll 1$,

$$F \approx \frac{B}{y} - C \frac{d^2 y}{dx^2} ; \quad (3)$$

where $B = \frac{Gb^2}{2\pi(1-\nu)}$, $C = \frac{Gb^2}{4\pi(1-\nu)} \ln\left(\frac{\lambda}{4b}\right)$ and G is the shear modulus of elasticity at the temperature of consideration.

The flux of vacancies across 0 (in Fig. 1) is given by:

$$J_0 = -D_v \left. \frac{\partial c}{\partial x} \right|_0 , \quad (4)$$

where $D_v \approx 1/3 \nu b^2 \exp(-U_m/kT)$. U_m is the activation energy for the motion of vacancies in the core and ν is the atomic vibration frequency in the core.

The number of vacancies migrated across 0 in time dt

$$= A_p J_0 dt , \quad (5)$$

where A_p is the cross sectional area of the core (area of the dislocation pipe).

The number of vacancies migrated across 0 in time dt is also equal to dA_s'/b^2 , where dA_s' is the area of the shaded region in Fig. 1.

$$dA_s' = da/p . \quad (6)$$

So we have

$$A_p J_0 dt = da/pb^2 . \quad (7)$$

Now from Eq. (2)

$$\left(\frac{\partial c}{\partial x}\right)_0 = \frac{c_0 b^2}{kT} \left(\exp \frac{F_0 b^2}{kT} \right) \left(\frac{\partial F}{\partial x}\right)_{\text{Av. at } x=0} \quad (8)$$

evaluated at $x = 0$, point 0 in Fig. 1.

Neglecting the variation of c with x :

$$\left(\frac{\partial F}{\partial x}\right)_{\text{Av. at } x=0} = 1/2 \left[\frac{-B}{h^2} a p + C a p^3 \right], \quad (9)$$

Then from (4), (7), (8) and (9):

$$\frac{da}{dt} = A_p a p^2 b^2 \left[\frac{B}{h^2} - C p^2 \right] \frac{b^2 D_v}{2kT} c_0 \exp \frac{F_0 b^2}{kT}, \quad (10)$$

F_0 is the value of F at $x = 0$

On substituting for D_v and c_0 , we have

$$\frac{da}{dt} = \frac{A_p a p^2 b^6 v n_0}{6kT} \left[\frac{B}{h^2} - C p^2 \right] \exp - \frac{U_f + U_m - F_0 b^2}{kT}, \quad (11)$$

' n_0 ' is the density of atomic sites at the core.

Integrating Eq. (11) from a_1 to a_2 corresponding to time interval

Δt , we have

$$\ln \frac{a_2}{a_1} = \frac{A_p p^2 b^6 v n_0 \Delta t}{6kT} \left[\frac{B}{h^2} - C p^2 \right] \exp - \frac{U_f + U_m - F_0 b^2}{kT}, \quad (12)$$

Assuming that oxygen ion transport in the dislocation core is the rate controlling process then by measuring a_1 , a_2 , p , Δt and T and assuming reasonable values for v and N_o the energy of formation plus migration of oxygen ion vacancies ($U_f + U_m$) can be determined.

B. Model for Shrinkage of a Prismatic Dislocation Loop
Connected to the Foil Surfaces by a Screw Dislocation

Referring to Fig. 2, Δc , the difference in concentration of vacancies in the dislocation core at point 1 and 2 can be written:

$$\Delta c = c_o (e^{\mu/kT} - 1), \quad (13)$$

where μ is the reduced chemical potential of a vacancy in the core due to the line tension of the dislocation.

Assuming the dislocation loop in the middle of the foil, the flux of vacancies along the connecting dislocation, which acts as pipe is:

$$\text{Flux (number/sec)} = \frac{2A D_v N_o}{S\Omega} (e^{\mu/kT} - 1); \quad (14)$$

where D_v and N_o are coefficient of diffusion and fraction of the lattice sites in the core that are vacant when no climb force is acting on the dislocation. Ω is the atomic volume, and $2S$ is the thickness of the foil.

The energy of the dislocation loop (E) can be written:

$$E = 2\pi r \frac{Gb^2}{4\pi(1-\nu)} \ln \frac{or}{r_o} = Kr \ln \frac{or}{r_o}, \quad (15)$$

where r is the radius of the loop, r_o the radius of core, α the core energy factor, ν Poisson's ratio and $K = Gb^2/2(1-\nu)$.

The reduced chemical potential of a vacancy,

$$\mu = \frac{\partial E}{\partial r} \frac{\partial r}{\partial n_v} = K \left[1 + \ln \frac{\alpha r}{r_o} \right] \frac{a_v}{2\pi r}, \quad (16)$$

where a_v is the area of cross section of one vacancy.

For $\mu/kT \ll 1$, $e^{\mu/kT} - 1 \approx \mu/kT$; therefore, from (14) and (16)

$$\text{flux (number/sec)} = \frac{2A D_p N_o}{S \Omega kT} \frac{K (1 + \ln \alpha r / r_o) a_v}{(2\pi r)} \quad (17)$$

Therefore, the shrinkage rate of a dislocation loop $\left(\frac{dr}{dt}\right)$ is:

$$\frac{dr}{dt} = \frac{2A D_p K (1 + \ln \alpha r / r_o) a_v^2}{S \Omega kT (2\pi r)^2}, \quad (18)$$

where D_p (pipe diffusion coefficient) = $D_{v_o} N_o = D_o^p \exp-(U_m + U_f/kT)$.

Equation (18) can be rewritten as:

$$\frac{r^2 dr}{1 + \ln \alpha r / r_o} = \frac{K'}{T} dt, \quad (19)$$

where

$$K' = \frac{A D_p K a_v^2}{2\pi^2 S K \Omega}$$

By graphical integration of Eq. (19) from r_1 to r_2 (shrinkage of the loop) in time interval Δt , we can find K' , hence $A D_p$. The plot of $r^2/(1 + \ln \alpha r / r_o)$ against r is shown in Fig. 3.

By studying the shrinkage kinetics at different temperatures and from the knowledge of A_p ,¹⁰ the pipe diffusion equation can be determined:

$$D_p = D_0^p \exp - (U_m + U_f)/kT = \exp - E_{act}/kT ,$$

where 'Eact' is the activation energy for the pipe diffusion process.

Results and Discussion

The break-up mechanism of dislocation dipoles is shown schematically in Fig. 4. A wave-like pattern starts from both ends of the dipole in the following way: In an initially uniformly spaced dipole vacancies have a higher chemical potential at the ends than at any other place due to line tension. Therefore, on annealing, vacancies at the left of the line MN in Fig. 4 tend to migrate toward the right. This process increases the spacing at 'a' which results in starting a drift of vacancies also from b to a. This further increases the spacing at a and starts to decrease it at b. The reduced spacing at b then starts a flow of vacancies from b to c. The process repeats toward the middle of the dipole. Thus, a wave pattern is set up which eventually results in breakup of the dipole into a string of loops. As the annealing time increases, the amplitude of the spacing fluctuations increases and the first loop pinches off at 'b', then the next one at 'd' and so on. See dipoles B, D and E in Fig. 5 and dipoles C, D and E in Fig. 6. If the two dislocations in the dipole are not uniformly spaced initially, the effect of non-uniform spacing may cause breakup

to start also at interior points. (See dipole A in Fig. 5 and dipoles AB and D in Fig. 6.)

After breakup wavelength (λ) can be measured because it is equal to the spacing of the resulting dislocation loops. It is determined by h . $\lambda \approx 1000\text{\AA}$, $h \approx 167\text{\AA}$ and $a_2/a_1 \approx 8$ for dipole at C in Fig. 6. Δt from 1 \rightarrow 2 (Fig. 6) is 3600 secs and $T = 1200^\circ\text{K}$. Taking the area of the dislocation pipe (A_p) as $10b^2$ (Ref. 10) and N_o as $\frac{1}{3}$ the value of activation energy for pipe diffusion $U_f + U_m$ (from Eq. 12) is $60,500 \pm 5000$ cal/mole. The uncertainty in the value of activation energy arises from errors of temperature measurement and measurements of the positions of dislocation lines from the electron microscope plates as well as uncertainties of the assumed values of some of the preexponential quantities. The value of a_2/a_1 at A in Fig. 6 is approximately 7.5. Taking the same value of λ as for dipole at C, since h is approximately the same, the same value of activation energy is obtained. $F_o b^2 \approx 4.0 (b/h)$ eV. For $h \approx 167\text{\AA}$, $F_o b^2 \approx 1600$ cal/mole. The term $F_o b^2$ becomes more and more important as h decreases. The quantity $U_f + U_m$ is the activation energy for diffusion along the core of an edge dislocation, pipe diffusion along a screw dislocation was studied by observing the shrinkage of the loop shown in Figs. 7.

After different annealing treatments the size of this prismatic edge dislocation loop, $b = \frac{1}{2} [101]$, which was connected to both surfaces of the foil by a screw dislocation of the same b -vector is given in Table I. Using Eq. (19) and the plot in Fig. 3 ($r^2/(1 + \ln r/r_o)$ vs r), the pipe diffusion coefficient was calculated for three temperatures

(1640°K, 1553°K and 1440°K). Results are also given in Table I. From these data, the pipe diffusion coefficient was determined to be $D_p = 3.0 \times 10^{-3} \exp - \left(\frac{62,700 \pm 5000}{RT} \right)$. The slightly higher activation energy for pipe diffusion along a screw dislocation may or may not be significant. However, it is in agreement with Canon and Stark's¹¹ results on nickel. They diffused Ni⁶³ along both pure tilt and pure twist boundaries with the same $b = \frac{1}{2} \langle 110 \rangle$ and observed a little faster diffusion and a lower activation energy for diffusion along edge dislocations compared to that along screw dislocations.

The activation energy for pipe diffusion along edge dislocations ($b = \frac{1}{2} [101]$), obtained from breaking up of dislocation dipoles, is in good agreement with that previously obtained from self climb rate measurements of dislocation loops,¹² $b = \frac{1}{2} [101]$. The results are also consistent with the upper limit of activation energy for pipe diffusion along edge dislocations ($71,400 \pm 4600$ cal/mole) obtained by Groves and Kelly⁸ also from observations on breaking up of dislocation dipoles. This upper limit was a very rough approximation of the true value because break up of individual dipoles was not followed and the dipoles which result from plastic deformation have a wide range of spacings. Therefore, the estimates of the total time of breakup are rather uncertain.

The relatively low value for the pre-exponential term (D_0^p) possibly can be attributed to a lower value of the frequency of atomic vibration within the relatively loose structure of the core. In fcc metals the reported values of the pre-exponential factor vary from 1 to 10^{-3} (Ref. 13).

By measuring the shrinkage rate of dislocation loops at various temperatures, the authors¹⁴ determined an activation energy of $110,000 \pm 4200$ cal/mole for bulk self diffusion. This activation energy probably should also be related to anion self diffusion. As the larger ion it is probably rate controlling. The anion and cation ionic radii are: O^{--} (1.32Å) and Mg^{++} (0.66Å). Taking this value for the activation energy for self bulk diffusion, the ratio of the activation energy for pipe diffusion to that for bulk diffusion is about 0.55, which is about the same as for fcc metals.¹⁵ It seems reasonable that both in self pipe diffusion and bulk diffusion in MgO, the rate of diffusion is controlled by oxygen ion transport.

Conclusions

- (i) The value of activation energy for pipe diffusion along edge dislocations in MgO is $60,600 \pm 5000$ cal/mole.
- (ii) The values of activation energy along screw dislocations and pre-exponential factor are $62,700 \pm 5000$ cal/mole and 3.0×10^{-3} cm²/sec, respectively.
- (iii) The oxygen ion is probably the rate controlling in the diffusion process.

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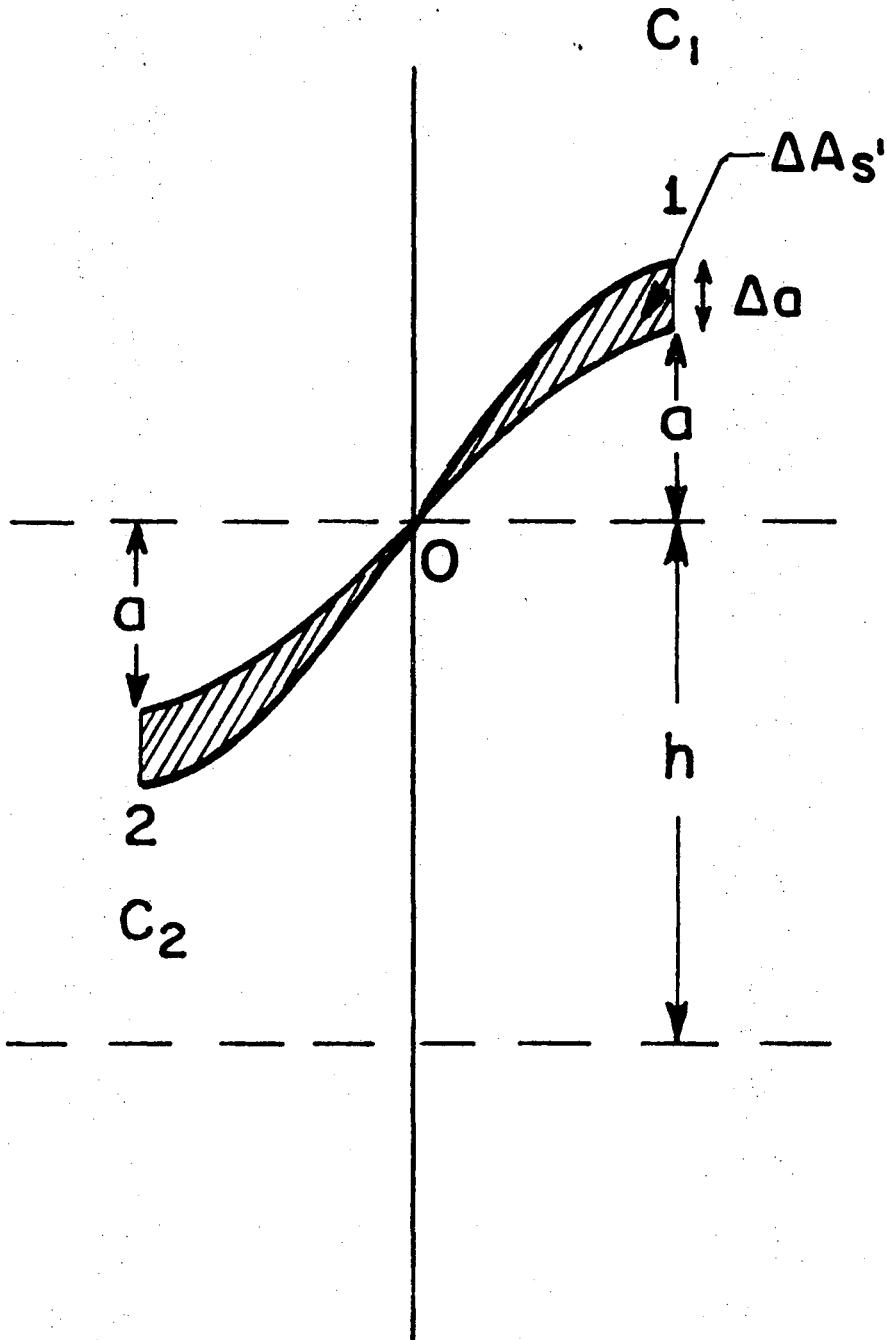
TABLE 1

Plate No.	Radius in A
B ₁	700
B ₂	595
B ₃	573
B ₄	539
B ₅	438

Temperature	D _P (cm ² /sec)
1640°K	1.5x10 ⁻¹¹
1553°K	5.1x10 ⁻¹²
1440°K	1.05x10 ⁻¹²

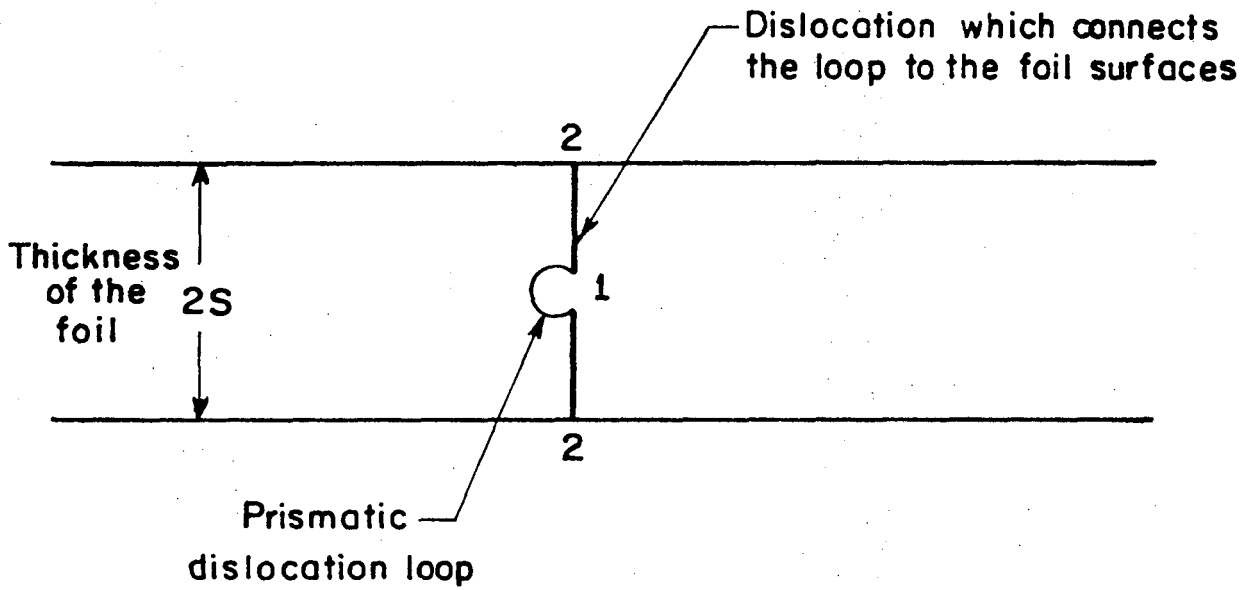
FIGURE CAPTIONS

- Fig. 1. Spacing fluctuation due to pipe diffusion.
- Fig. 2. Model for shrinkage of dislocation loop.
- Fig. 3. Plot of $\frac{r^2}{0.6 + \ln r}$ against r .
- Fig. 4. Schematic illustration of dipole breaking by pipe diffusion as the time of annealing is increased.
- Fig. 5. Breaking of dislocation dipoles, $b = \frac{1}{2}[101]$, on annealing.
- Fig. 6. Breaking dislocation dipoles. Annealing treatment: 1 \rightarrow 2, 60 min. at 927°C.
- Fig. 7. Shrinkage of dislocation loop, $b = \frac{1}{2}[101]$, due to pipe diffusion along screw dislocation of the same b-vector which is connected to both surfaces of the foil. Annealing treatments: $B_1 \rightarrow B_2$, 10 min. at 1367°C; $B_2 \rightarrow B_3$, 15 min at 1116°C; $B_3 \rightarrow B_4$, 30 min at 1116°C; $B_4 \rightarrow B_5$, 26 min. at 1280°C; $B_5 \rightarrow B_6$, 40 min. at 1280°C.



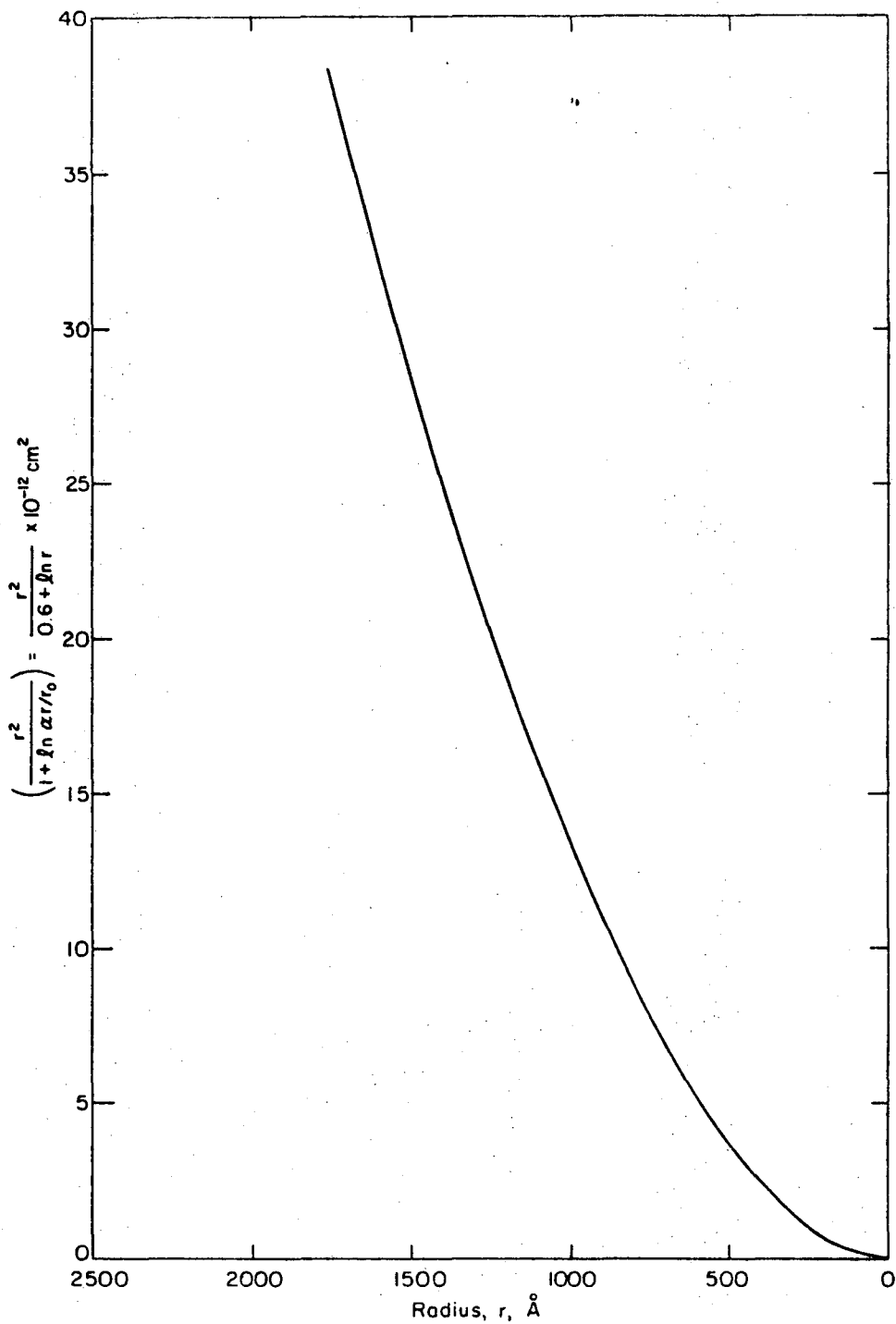
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Fig. 1



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Fig. 2



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Fig. 3

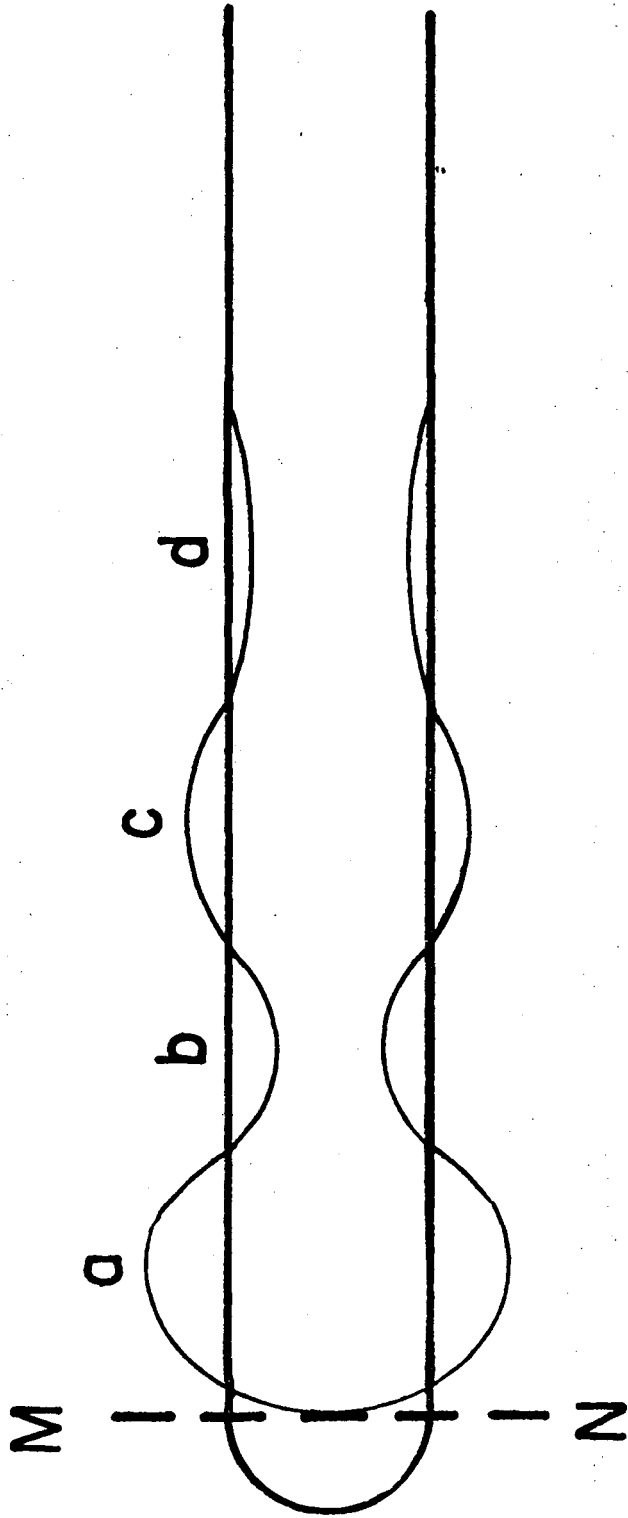
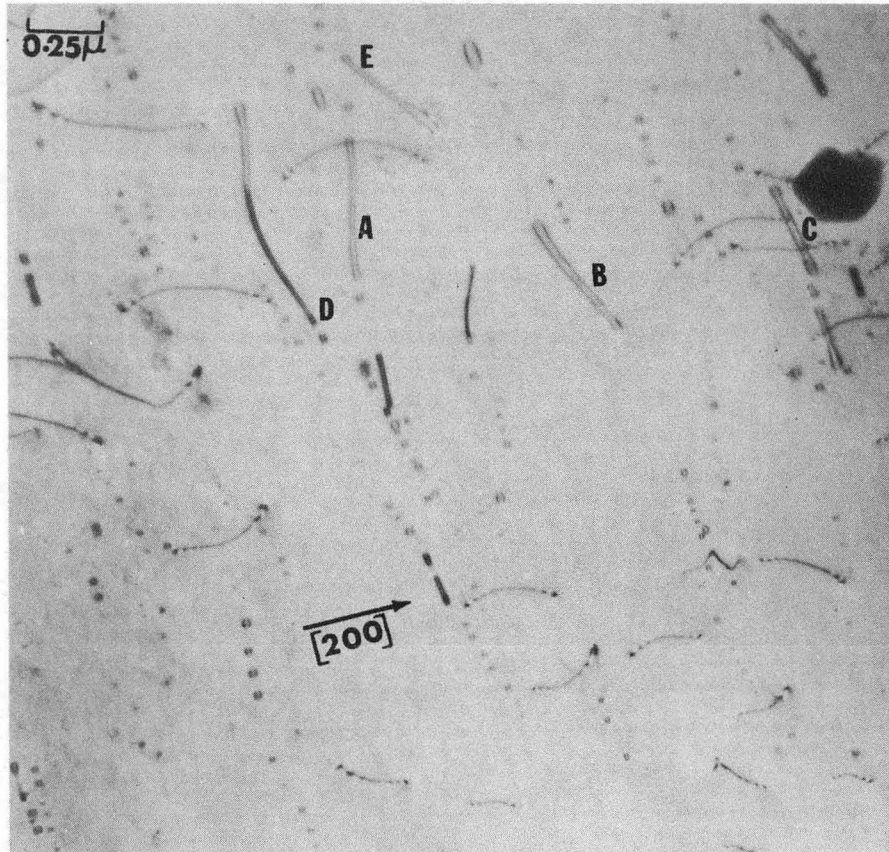


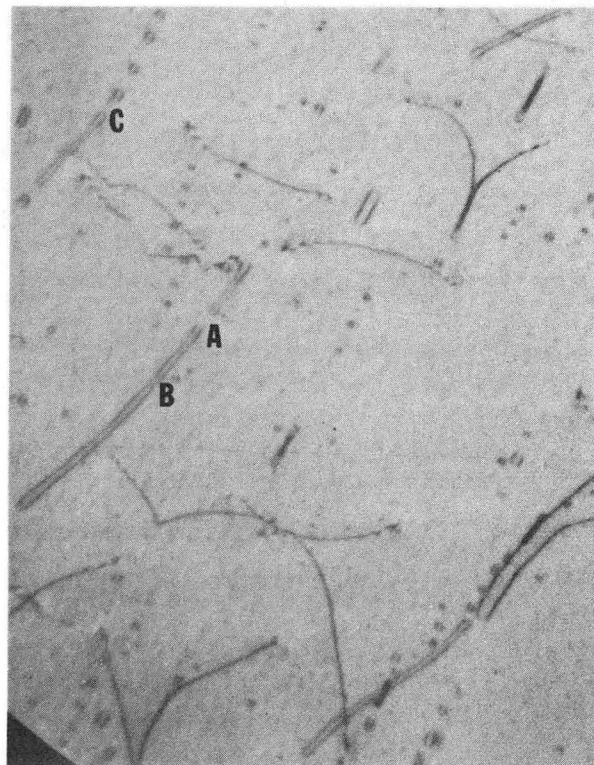
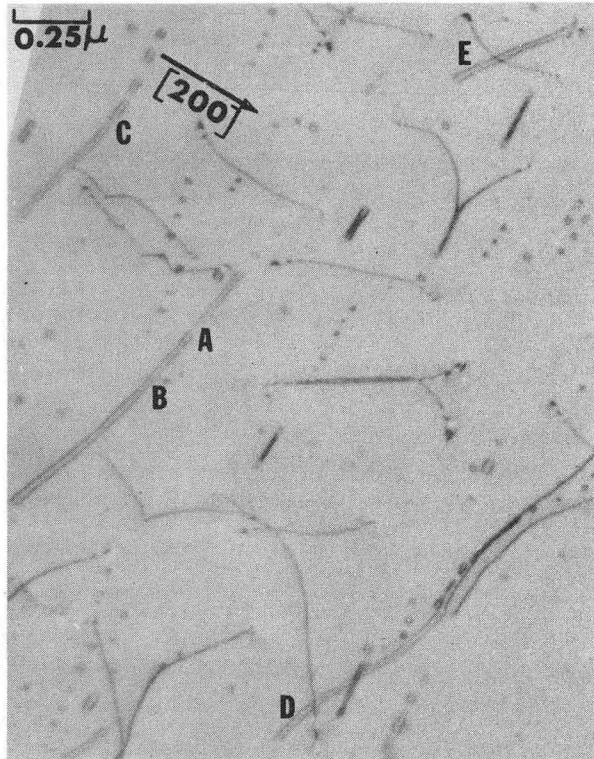
Fig. 4

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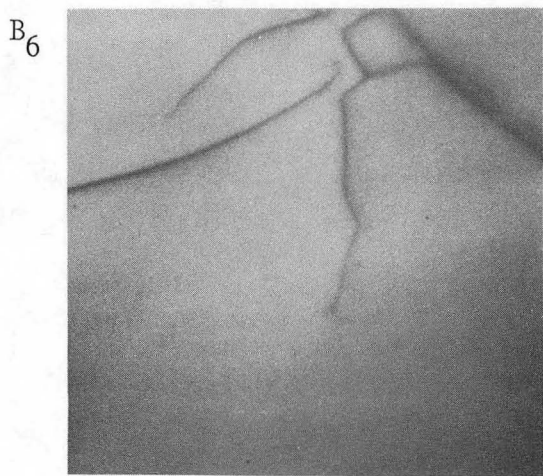
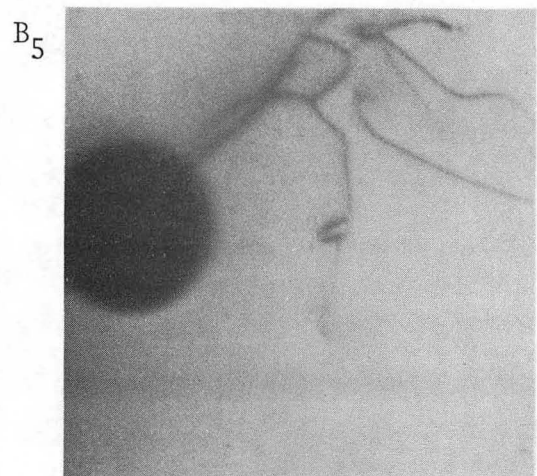
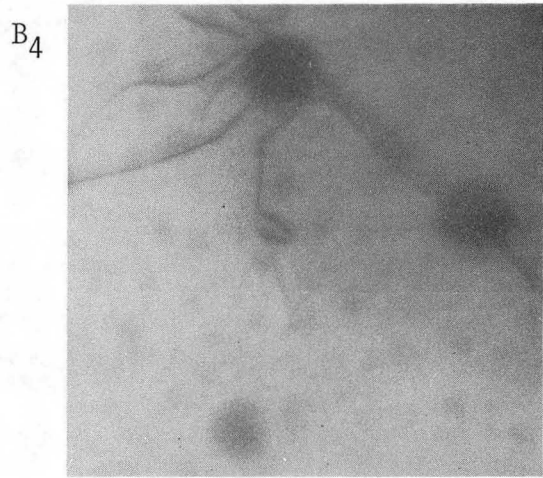
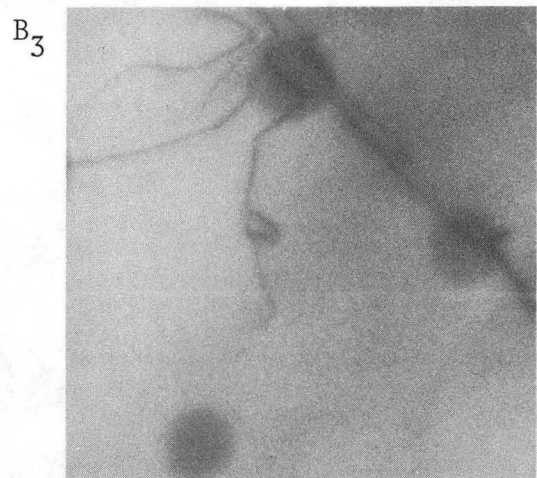
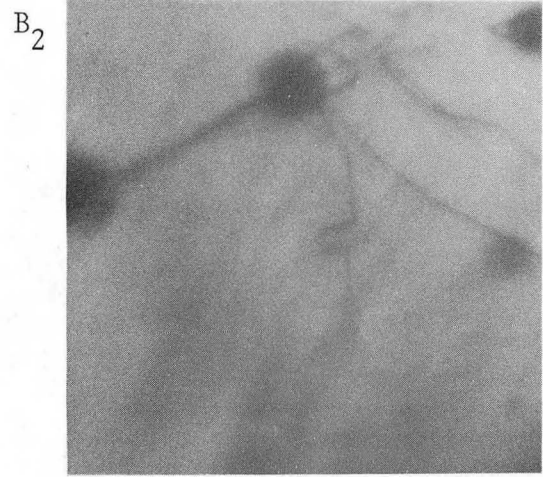
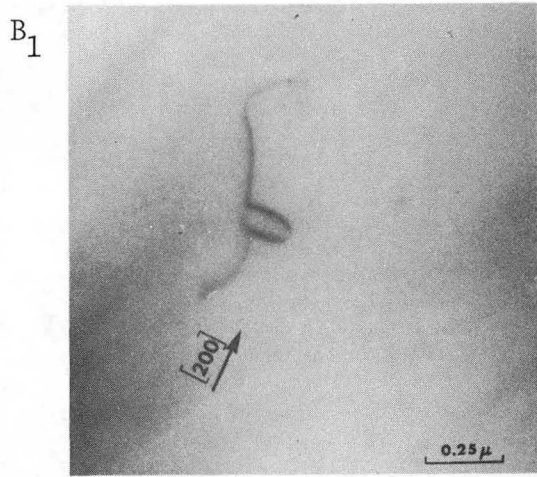
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Fig. 5



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Fig. 6



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Fig. 7

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