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CLIMB KINETICS OF DISLOCATION LOOPS IN ALUMINUM

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May 1968

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Inorganic Materials Research Division, Lawrence Radiation Laboratory, and the Department of Mineral Technology, College of Engineering, University of California, Berkeley, California

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ABSTRACT

The annealing kinetics of dislocation loops in quenched aluminum has been studied using transmission electron microscopy techniques. An influence of the vicinity of the foil surface on the rate of climb was confirmed. The apparent activation energy for climb of faulted loops was found to be 1.18±0.02 eV and the pre-exponential factor, $(7\pm3)10^{13}$ Å/s. The stacking-fault energy was estimated as 110 ergs/cm^2 by comparing shrinkage rates of 1/3<111> and 1/2<110> loops. A simple model taking into account rapid diffusion of vacancies along the dislocation is suggested to account for the observed maintainance of circular shape during loop shrinkage.

1. INTRODUCTION

In recent years a number of studies have been reported on the annealing behaviour of dislocation loops in aluminum. Using an electron microscope equipped with a heating stage, Silcox and Whelan (1960) were first to observe the climb of loops in thin foils. It was early recognized that a study of the kinetics of the process could prove valuable for estimating stacking-fault energies and obtaining self-diffusion data. However, until recently, critical data have been missing due to the inherent inaccuracy of in-situ annealing techniques and/or inadequate analysis methods. These limitations have been stressed by Saada (1966) and Dobson et al. (1966), among others. While it was generally assumed that, at least in thin foils, the kinetics of loop climb was controlled by vacancy emission from the dislocation into the lattice, Seidman and Balluffi (1966) showed on theoretical grounds that the process should rather be controlled by the diffusion of vacancies away from the dislocation. The external annealing experiments of Dobson et al. (1967) lend experimental support to this conclusion.

In the present paper experiments carried out concurrently with those of Dobson et al. (1967) on the kinetics of loop shrinkage in aluminum are reported. More accurate measurements of climb rates and annealing temperatures than those achieved in previous investigations were made possible by the combined use of an external oil bath, lower annealing temperatures and magnification calibration at every step of the picture-making. The working range of temperature was extended down to 80°C by resorting to annealing periods of up to 200 hours.

2. EXPERIMENTAL PROCEDURE

Low dislocation density ($10^6/cm^2$) single crystals with a (112) orientation were grown from 99.999% pure polycrystalline aluminum strips 200μ thick. After quenching from 610°C into boiling water and electropolishing, the specimens were stored at 0°C prior to their observation in a Siemens Elmiskop IA. The magnification was determined with an accuracy better than 2% by using a 28,800 lines per inch carbon replica grating. The thin foils were annealed in an oil bath, the cap holding the specimen being unscrewed from the body of the holder and placed in a copper receptacle. A calibrated chromel-alumel thermocouple was maintained in contact with the tip of the cap throughout the annealing. After corrections, the error on the temperature was estimated as less than 0.1°C.

3. CLIMB ANALYSIS

3.1. Single-Faulted Loops

Most loops were observed to become round and then shrink maintaining that shape. However, the original hexagonal shape sometimes reappeared to some extent (Fig. 2). In some instances part of the loop was found to lag behind, giving rise to a sharp corner. This effect was more frequent in some specimens than in others and occasionally almost all loops developed pinning points as shown in Fig. 3. This pinning was tentatively attributed to impurities. Once freed from a pinning point, the loops rapidly recovered their circular shapes.

3.1.1. Emission vs. Diffusion-Controlled Mechanism: For a large enough loop (diameter $\gtrsim$ 1000Å) which lies approximately parallel to the surface

of the foil, the diffusion problem may be reduced to that of an infinite straight cylindrical source of radius r_o in a slab of thickness L and at a distance ℓ from one surface. If the vacancy concentrations are C_1 and C_0' at the source and at the free surface respectively, a standard calculation shows that the steady-state outward vacancy flux per unit length of dislocation is:

$$\phi = \frac{2\pi\left(C_1 - C_0'\right)D_v}{K} \tag{1}$$

where

$$K = \ln\left[\sin\left(\frac{\pi\ell}{L}\right) \cdot \frac{2L}{\pi r_o}\right] ,$$

$$D_v = 2\nu a^2 \exp\left(\frac{-U_m}{kT}\right) \cdot \exp\left(\frac{S_m}{k}\right) ,$$

ν is the natural frequency of vibration (10^{13}/sec), U_m and S_m are respectively the energy and the entropy of motion of a vacancy and a is the atomic diameter. Rather than making arbitrary assumptions about the value of C_1 (generally assumed to be such that the chemical stress exactly counterbalances the combined effect of the stacking-fault and the dislocation line tension), one can derive an independent expression for ϕ from Friedel's (1964) theory of climb, namely:

$$\phi = cjz\nu \exp\left[\frac{\left(-U_f - U_m\right)}{kT}\right] \exp\left[\frac{\left(S_f + S_m\right)}{k}\right]\left[\exp\left(\frac{F_c B^2}{kT}\right) - \frac{C_1}{C_0}\right] \tag{2}$$

where c_j is the jog concentration per unit length of dislocation, z is of the order of the coordination number, B is the area per atom in the (111) plane, C_0 is the equilibrium vacancy concentration in stress-free material at T and U_f and S_f are respectively the energy and entropy of formation of a vacancy. F_c can be derived from Bacon and Crocker (1965) as:

$$F_c = \left(\frac{3\mu b^2}{8\pi R}\right)\left[\ln\left(\frac{8eR}{r_o}\right) - \frac{9}{8}\right] + \gamma$$

where R is the loop radius, μ the shear modulus, b the Burgers vector and γ the stacking-fault energy. From (1) and (2) one obtains:

$$\phi = \frac{\left(\frac{zc_jD_s}{2a^2}\right)\left[\exp\left(\frac{F_cB^2}{kT}\right) - \frac{C_0'}{C_0}\right]}{\left(1 + \frac{ac_jzK}{4\pi\sqrt{2}}\right)} \qquad (3)$$

where D_s is the self-diffusion coefficient. For the typical case where L = 6000Å, r_o = 2.86Å and ℓ (minimum) = 700Å, K varies between 7.20 and 6.18, hence in order for the effect of diffusion to be observable, ac_j would have to be not much smaller than unity. It is well-known that when the curvature of a Frank loop is analyzed in terms of elementary jogs, the jog concentration varies from zero to one around the circumference of the loop. Equation (3) being highly dependent on the jog concentration, especially for small values of c_j, fails to explain the near-circular shape which is maintained by shrinking loops. Another possibility is that the vacancy emission rate is not proportional to c_j as assumed in (2). For

example, if the vacancies are emitted from the dislocation by a two-step process in which they first escape from a jog onto the line and then into the lattice, the emission rate might become nearly independent of c_j at high jog concentrations because of the increasing probability of recombination with another jog rather than escape into the lattice. The following simple semi-quantitative treatment is proposed. All jogs are assumed to be of unit height, which seems reasonable in view of the repulsion between jogs of like sign. Neighboring jogs in a loop are of the same sign; this leads to a configuration of the type shown in Fig. 1. Vacancies are emitted from A onto AB. Emission from B onto BA is considered at least as difficult as emission directly into the lattice, hence very unlikely. This may be the reason why the rounding of the loops during the early stages of annealing does not occur by conservative climb (i.e. with conservation of the area of the loop). A bound vacancy has equal probability to jump either to the right or to the left, except when it reaches the extremity B of AB, in which case it is assumed that it may stay in B or jump back toward A. The relaxation time for such jumps is:

$$\frac{1}{\tau_1} = \nu \exp\left(\frac{-U_p}{kT}\right)$$

where U_p is the activation energy for rapid diffusion along the line and the entropy terms are left out for simplicity. The life-time of a bound vacancy on AB is then

$$\tau_1 \sum_{n=1}^{\infty} n p_n(AB) \quad ,$$

where $p_n(AB)$ is the probability (geometrical) that the vacancy perform n jumps after being formed before it recombines at A. The relaxation time for a bound vacancy jump from the dislocation into the lattice may be expressed as:

$$\frac{1}{\tau_2} = Z\nu \exp\left(\frac{-U_{d1}}{kT}\right) \tag{4}$$

where Z is of the order of 9 and U_{d1} is the corresponding activation energy. The rate of emission from AB is then:

$$|AB|\phi_e = \nu \exp\left(\frac{-U_{jd}}{kT}\right)\left(\frac{\tau_1}{\tau_2}\right)\sum_{n=1}^{\infty} np_n(AB) \tag{5}$$

where U_{jd} is the activation energy for emission of a vacancy from a jog onto the dislocation. If C_1 is the vacancy concentration in the vicinity of the dislocation and neglecting the probability that a vacancy jump back into the lattice before the probability that it recombines at a jog, the rate of absorption on AB may be written:

$$|AB|\phi_a = Z\nu\left(\frac{AB}{a}\right) C_1\left(\frac{a^3}{\sqrt{2}}\right)\exp\left(\frac{-U_m}{kT}\right)$$

Using the result that $\sum_{n=1}^{\infty} np_n(AB)$ is of the order of $\frac{AB}{a}$, the balance outward flux from AB becomes:

$$\phi = \left(\frac{Z\nu}{a}\right)\left\{\exp\left[\frac{\left(-U_{d1} - U_{jd} + U_p + F_c B^2\right)}{kT}\right] - C_1\left(\frac{a^3}{\sqrt{2}}\right)\exp\left(\frac{-U_m}{kT}\right)\right\} \tag{6}$$

It is not clear whether $F_c B^2$ should be introduced in (4) or (5), however this should not influence the final result. A rough energy estimate shows that (6) essentially reduces to (2) except that $c_j a$ is now unity. Short-circuit diffusion would thus merely increase the efficiency of the jogs in the case of low c_j. This in turn makes the process more nearly diffusion-controlled.

3.1.2. Cylindrical Versus Spherical Diffusion: It has been suggested by Dobson *et al.* (1967) and emphasized by Kritzinger *et al.* (1967) that a critical argument favoring a diffusion-controlled mechanism is the increased rate of climb for small loop radii attributed to a change from cylindrical to spherical diffusion. However, their calculation which approximates the loop to a spherical source should lead to an overestimate of the climb rate. Following Seidman and Balluffi (1966) the diffusion geometry may be better represented by a toroidal source (radii R and r_o and concentration C_1 on the surface of the torus) situated at the center of a sphere of radius L/2 large before R, on the surface of which the concentration is C_0. For $r >> R$ the concentration inside the sphere can be approximated by:

$$C(r) = \frac{C_1 L - 2C_0 R^{eff}}{L - 2R^{eff}} - \frac{\left(C_1 - C_0\right) L R^{eff}}{r\left(L - 2R^{eff}\right)}$$

where

$$R^{eff} = \frac{\pi\sqrt{R^2 - r_o^2}}{\ln\left(\frac{8R}{r_o}\right)}$$

hence

$$\left(\frac{dR}{dt}\right)_{sph} \simeq \frac{2\pi DB^2\left(C_1 - C_0\right)}{\ln\left(\frac{8R}{r_o}\right)}$$

as compared to

$$\left(\frac{dR}{dt}\right)_{cyl} = \frac{2\pi DB^2\left(C_1 - C_0\right)}{\ln\left(\frac{2L}{\pi r_o}\right)}$$

For a foil thickness of 6000Å and a loop radius of 100Å one would thus expect an increase of the rate of climb due to a spherical diffusion of only about 30%.

3.1.3. Results: Standard analysis techniques as described for example in Dobson et al. (1966) were used. The rate of climb is equal to $-B^2\phi$. Expanding the exponential in the square bracket of (3) as

$$\left(1 + \frac{\alpha b}{R}\right) \exp\left(\frac{\gamma B^2}{kT}\right)$$

it becomes after integration:

$$R_c = R - \beta b \ln\left(\frac{R + \beta b}{R_o + \beta b}\right) = R_o - At \exp\left(\frac{-U_d}{kT}\right)\left[\exp\left(\frac{\gamma B^2}{kT}\right) - \frac{C_0'}{C_0}\right] \tag{7}$$

where $U_d = U_f + U_m$ and

$$\beta = \frac{\alpha}{1 - \left(\frac{C_0'}{C_0}\right) \exp\left(\frac{-\gamma B^2}{kT}\right)}$$

For γ not too small $\alpha \sim \beta$ and this was assumed when calculating the corrected radius R_c. This was justified by the good fit to a straight line of the plots R_c vs. t. As expected from 3.1.2, no significant curvature of the lines was observed down to the smallest radii measured ($\sim$100Å) as shown in Fig. 4. Influence of the vicinity of a surface on the rate of climb was confirmed by a 20% overall scatter of (dR_c/dt) for a group of 30 loops as compared to an individual scatter of 3% or less as determined by a least mean squares method. Also the actual values correlated very well with the position of the loops in the foil as indicated by the aspect of their fringes on the micrographs and by stereo-pictures. Averaging the climb rates for the loops close to the center of the foil only, the following values were obtained: $(1.02\pm0.03)10^{-3}$Å/s at 353.3°K, $(0.87\pm0.03)10^{-2}$Å/s at 375.0°K and $(0.79\pm0.03)10^{-1}$Å/s at 398.0°K. This gives an apparent activation energy of (1.18 ± 0.02)eV and a pre-exponential factor $A = (7.3\pm3.5)10^{13}$Å/s. The present results are plotted in Fig. 5 along with those obtained by Dobson et al. (1967).

3.2. Perfect Prismatic Loops

All perfect loops observed (up to 5000Å in diameter) were found to assume a roundish shape after some annealing had taken place and shrink as such. A rotation of the loops was sometimes observed and although no systematic check was performed, it is believed that the loops turned to an orientation near pure edge. This assumption along with that of a circular shape was made in the following analysis. If the surface is a perfect sink, $C_0' = C_0$ and R^2 should be a linear function of time. A plot of R^2 vs. t is shown in Fig. 6. Averaging over the loops which were considered to have

behaved in the most regular manner, a value for $d(R^2)/dt$, at (399±1)°K, of 10.4Å^2/s, was found. Assuming that except for geometrical differences the same climb mechanisms operate for both perfect and faulted loops, the stacking-fault energy is estimated as 110 ergs/cm^2 and the activation energy for self-diffusion as 1.23 eV.

4. DISCUSSION AND CONCLUSION

The controlling effect of diffusion on climb as suggested by Seidman and Balluffi (1966) is confirmed and agrees well with the model for vacancy emission proposed in 3.1.1. The model accounts satisfactorily for the observed aspect of shrinking loops, in particular for the reappearance of a pseudo-hexagonal shape with sides along [110] directions, hence corners where both climb force and jog density should be high. As suggested in 3.1.2, the change from cylindrical to spherical diffusion leads to no observable acceleration of the kinetics of climb. The large effect reported by Kritzinger et al. (1967) is then rather puzzling. It should be noted, however, that their measurements concern annealings inside the microscope and at 182°C, therefore experimental uncertainties cannot be ruled out. It may also be worth noting that according to Fig. 5 in their paper the calculation of M involves the difference between radii 100Å or less apart, which seems questionable considering that under normal conditions, achieving an accuracy on R of ±35Å from cine-techniques may be considered as a good performance.

The parameter A determined in 3.1.3 is related to D_o, the pre-exponential factor in the expression of D_s, by:

$$A = \frac{Z\pi\sqrt{6}\ D_o}{a\left(4\pi\sqrt{2} + ZK\right)}$$

from which D_o is estimated as 0.025 cm^2/s. This is about two orders of magnitude smaller than the value of 1.71 cm^2/s derived from Lundy and Murdock's experiment on radioactive tracers (1962) and which constitutes the only direct measurement available. However, very recently Fradin and Rowland (1967), using NMR techniques in a range of temperatures from 240°C to 550°C, estimated D_o as $(0.035 \pm 0.015)\ cm^2/s$ and the activation energy for self-diffusion as 1.25 eV, both values in excellent agreement with our results. It must be emphasized that the present value of D_o corresponds to $(S_m + S_f) \lesssim k$ as compared to the generally assumed values of $S_m = 2k$ and $S_f = 2.4k$.

γ is estimated at 110 $ergs/cm^2$, which is in good agreement with Dobson et al. (1967) findings; it is felt, however, that this value should be considered with some reserve:

a) The effect of the oxide film at the surface of the foil has been discussed at some length by Harris and Masters (1968) and Eikum and Thomas (1967). The influence of the vicinity of a surface on the rate of climb clearly shows that escape of vacancies at the surface does occur; this is also confirmed by the absence of interaction between loops as long as they did not overlap. Escape of vacancies at cracks in the oxide does not seem likely since the measured rates of climb did not appreciably vary from one part of the foil to another. However, absorption of vacancies at some favourable sites of the metal-oxide interface, as suggested by Vermilyea (1957), may result in a near-equilibrium vacancy concentration at the

interface. In any case, since perfect loops were never seen to grow, an upper limit of 1.10 can be put on C_0'/C_0 so that the faulted loop analysis should remain unaltered. On the contrary, writing the rate of climb for perfect loops as:

$$\frac{d(R^2)}{dt} = -2A' \left[\alpha'b' + R\left(1 - \frac{C_0'}{C_0}\right)\right] \exp\left(\frac{-U_d}{kT}\right) \qquad (8)$$

it appears that the uncertainty will only be removed for small values of R ($\alpha'b'$ = 235Å at 399°K), which unfortunately occupy a reduced region of a R^2 vs. t plot.

b) Taking for the energy of formation of a vacancy at a jog and emission into the lattice, $U_d + \Delta U$ instead of U_d in Equation (2), would lead to similar remarks as above.

c) The ratio A/A', although probably of the order of unity, is not known with certainty.

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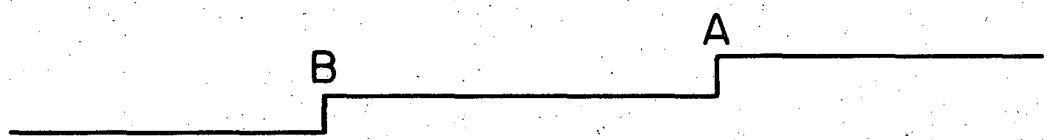

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Fig. 1 Jog configuration.

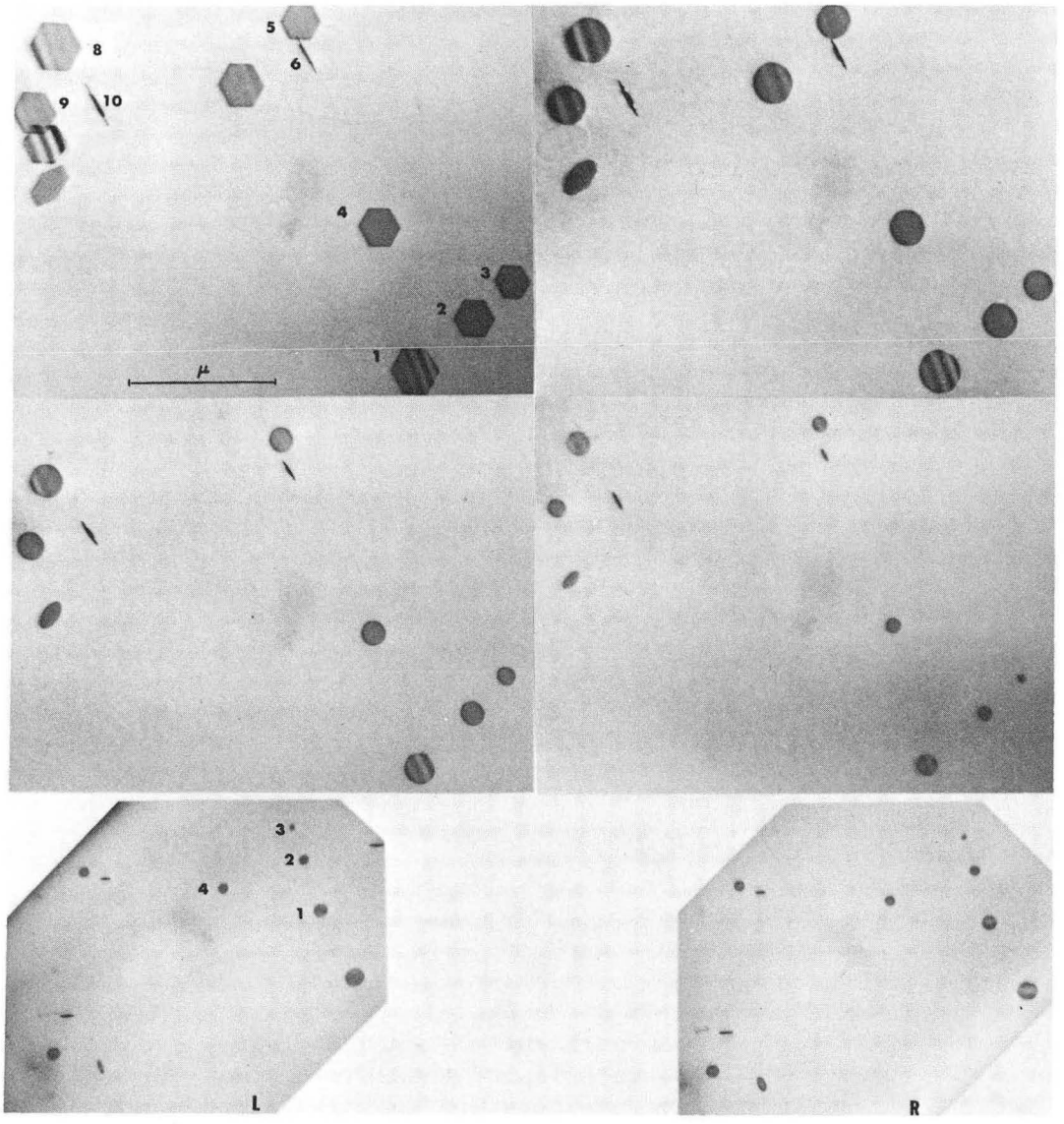

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Fig. 2 Annealing sequence at 101.8°C and corresponding stereo-pair. t = -213, 0, 580, and 1091 minutes.

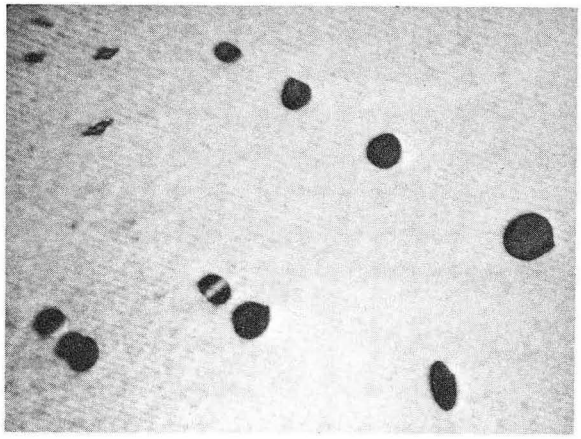

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Fig. 3 Area where the pinning effect was particularly clear. This was attributed to a higher-than-average impurity content in the specimen.

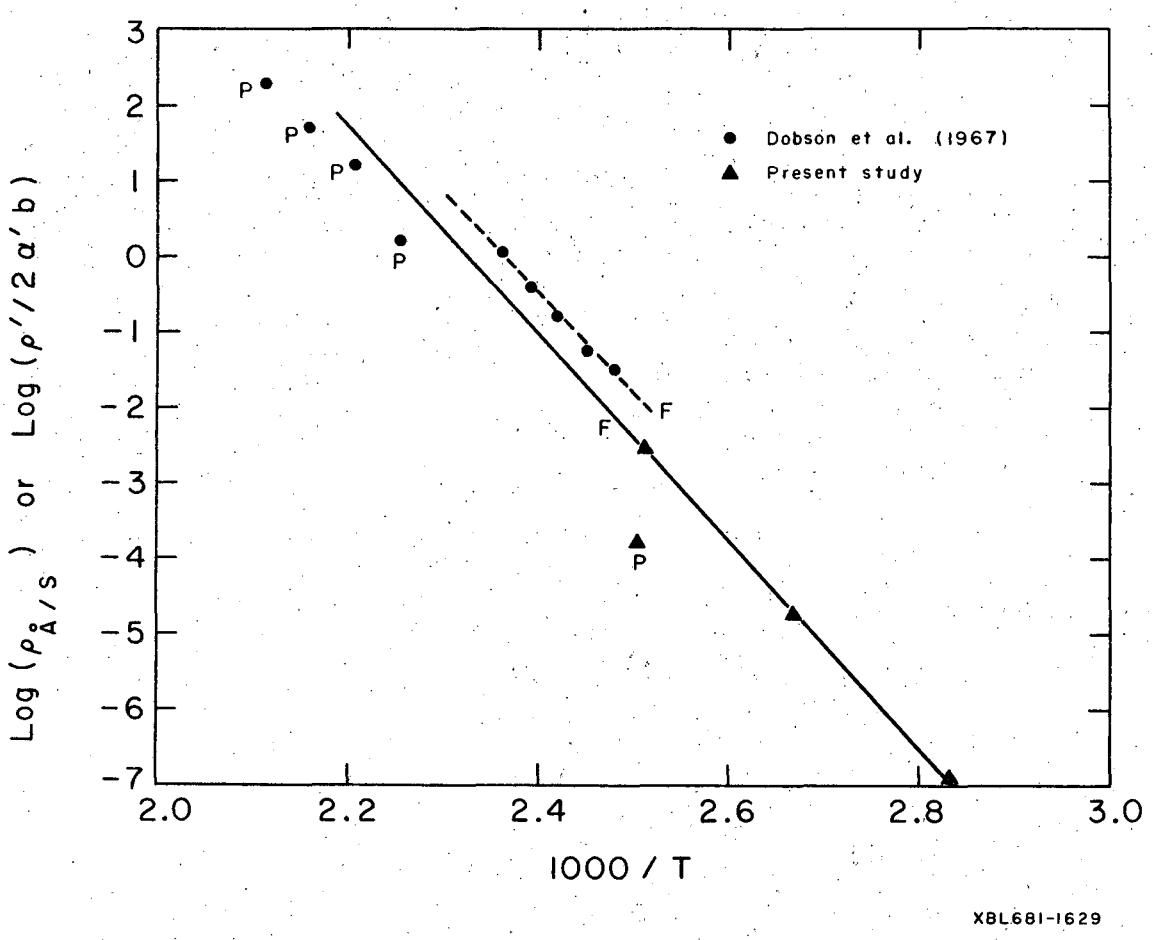

Fig. 4 Annealing curves before and after line tension correction.

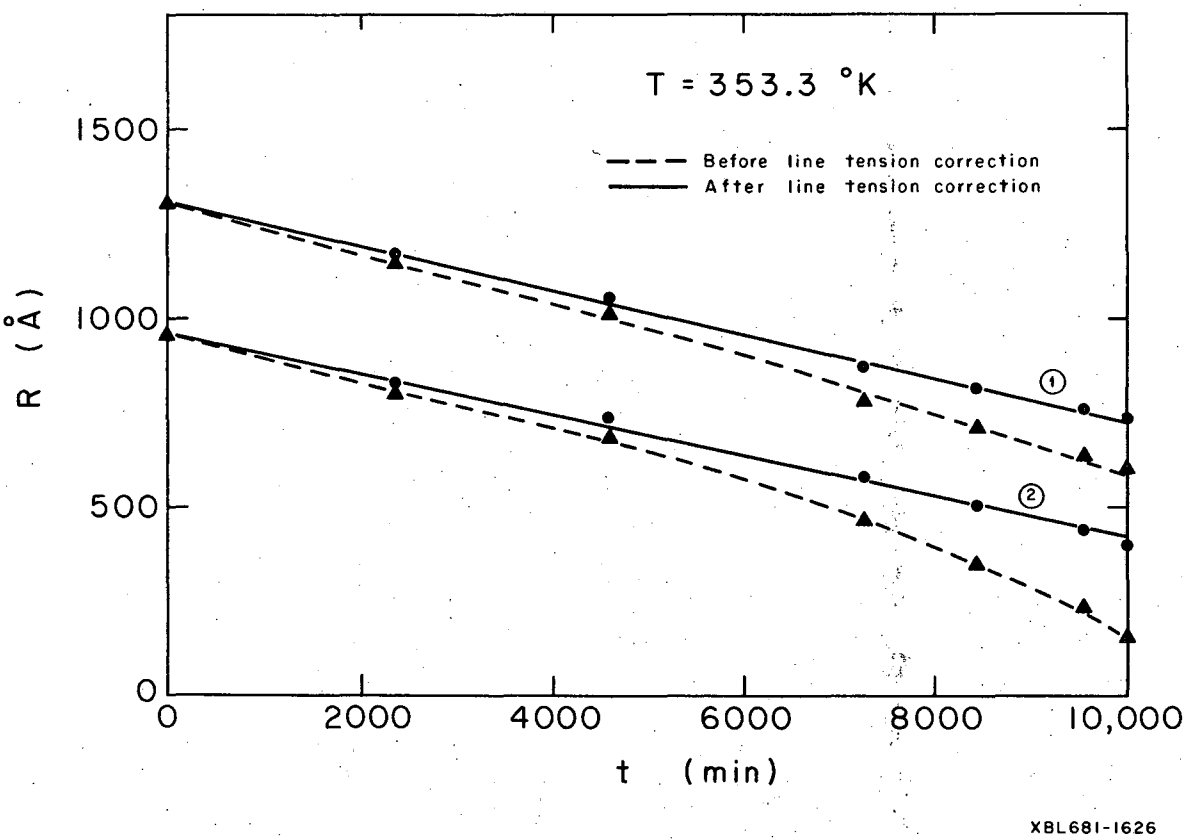

Fig. 5 Plot of $\ln(\rho)$ and $\ln\left(\frac{\rho'}{2\alpha' b}\right)$ against $\frac{1}{T}$.

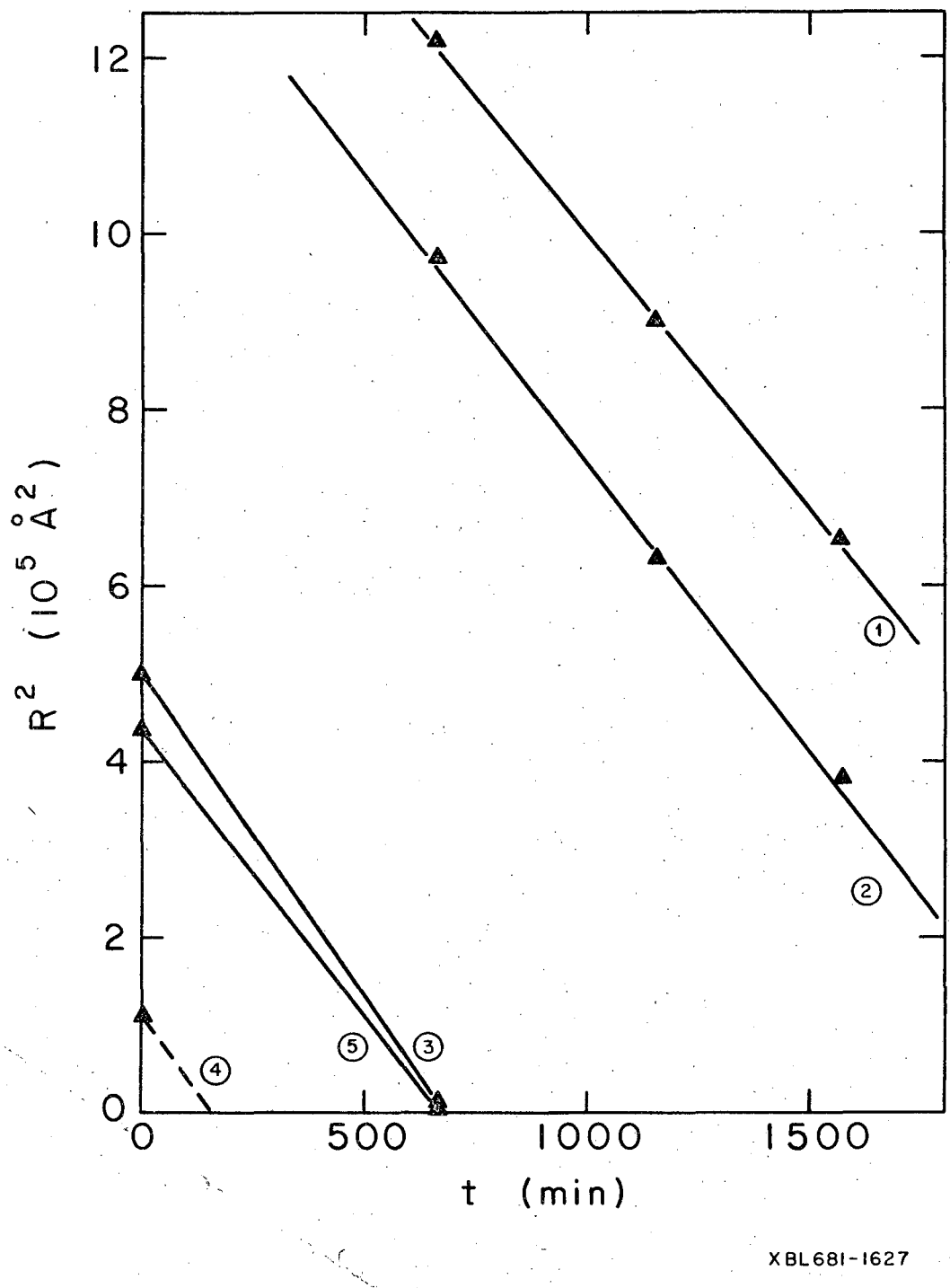

Fig. 6 Plot of R^2 against t for some perfect loops.

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