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STACKING FAULTS IN PLATINUM

by

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A B S T R A C T

Determination by X-ray techniques of stacking-fault densities in platinum was attempted. Heavily deformed platinum was annealed under varying conditions of temperature and time. The X-ray method used for measuring stacking-fault densities was found to lack accuracy for the unequivocal determination of the type of thermal activation process that leads to the loss of stacking faults during annealing. Results suggested that the process may be a first order process with an activation energy of 0.5 ± 0.3 ev. This activation energy is sufficient for extended dislocations to cross each other in platinum, with the formation of jogs. Quenched-in vacancies were found to have no detectable effect on X-ray reflections.

INTRODUCTION

Heidenreich and Shockley [1] described how a total dislocation lying in a close-packed plane can lower its energy by splitting into partial dislocations. Such a process occurring in the {111} of a face-centered cubic crystal produces a stacking fault which consists of a thin layer of close-packed hexagonal structure bounded by the two partial dislocations.

The experimental methods for the direct observation of stacking faults rest on X-ray techniques. Wilson [2] noted that stacking faults in cobalt would affect the intensity and integral breadths of X-ray diffraction lines. More recently, Paterson [3] showed that the pobability of finding a stacking fault could be determined from measurements of the displacement of X-ray diffraction lines from their normal positions. Wagner [4] carried out such an investigation on stacking faults in copper and alpha-brass and reached the conclusions that stacking faults in copper anneal out rapidly at room temperature and that in brass the probability of finding a stacking fault increased with increasing zinc content. Smallman and Westmacott [5] obtained similar results for copper, copper-nickel, copper-tin, copper-aluminum and copper-germanium alloys. Warren and Warekois [6] studied stacking faults in

in cold-worked alpha-brass and Wegner [7] in Nickel.

The basic physical process underlying the loss of stacking faults through annealing has not been adequately investigated. Paterson's [3] analysis of the effect of stacking faults on X-ray diffraction lines was thought to provide a method for the determination of stacking-fault densities. This method would make it possible to observe directly the behavior of stacking faults under various annealing conditions.

In the present study an attempt was made to gain an understanding of the mechanism of the annihilation of stacking faults during annealing and to interpret the results in terms of thermal activation processes.

As a secondary investigation an attempt was made to determine vacancy concentrations in platinum. The analysis proposed by Miller and Russell [8] and by Tucker and Sampson [9] was used in this attempt, since those authors predicted that point imperfections in a crystal should cause a shift of the X-ray diffraction lines.

Platinum was chosen for this investigation for two reasons. First, it simplified the experimental procedure considerably due to the relative stability of lattice defects in platinum at room temperature. Hence, no low-temperature X-ray equipment was required. Secondly, no data on stacking faults in platinum have been published so far.

EQUIPMENT AND PROCEDURE

The specimens used for the measurement of stacking-fault densities were prepared from filings of Commercial Grade A platinum (99.99 % pure). The filings were 325 mesh. All specimens were annealed under vacuum by being sealed in vycor tubes. However, difficulties were encountered with the specimens annealed at 1200°C due to sintering. The specimens annealed at this temperature could not be reduced to powder form again without introducing some degree of cold work. These specimens were, consequently, annealed on porcelain mounts under atmospheric conditions.

A General Electric XRD-5 spectrogoniometer was used. Preliminary alignment of the instrument was made by setting the protractor angle to $2\theta = 0^{\circ}$ and noting the point of maximum intensity on the recorder. Further adjustments were made by reading the intensities at $2\theta = \pm 0.05^{\circ}$. The alignment was then readjusted until readings obtained at those two settings were equal. As the intrument was found to be sensitive to temperature variations the X-ray tube was switched on for at least one hour before alignment was made. Constant temperature was maintained in the room.

The platinum filings were mounted on microscope slides by applying a very thin layer of petroleum jelly over an area of about

$\frac{1}{2}$ cm^2 of the slide. The filings were then spread evenly over the petroleum jelly and very slightly pressed onto it by means of another slide.

The intensities of the diffraction lines were measured by taking counts on the scaler for a period of 20 seconds at each setting. The minimum intensities recorded after the tails of the lines leveled off were of the order of 7000 and, consequently, the maximum probable error was of the order of 1 %. Errors in the positions of the lines due to the instability of the instrument were estimated to be less than $\pm 0.02^{\circ}$. During this investigation it was not found necessary to measure the absolute positions of the lines but only the change in positions. No attempt was made, therefore, to account for the effect of instrumental factors on absolute line positions.

The method proposed by Pike [10] was used in determining changes in the positions of the lines. This method is based on locating the centroid of the line by numerical integration. The centroid of the specimen annealed at 1200°C was chosen as the reference in measuring $\Delta 2\theta$.

Line widths were measured at half intensity. The line widths of the cold-worked specimens for which the $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks were not resolved were determined by separating the $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks using the graphical method proposed by Rachinger.[11]

For the investigation of vacancy concentrations specimens were made of 0.003" platinum foil as well as of 325 mesh filings. These were annealed at 1400°C under atmospheric conditions. Quenching was performed by dropping the hot specimens from the vertical tubular furnace in which they were heated, into a water bath. The filings were mounted on a thin slab of porcelain. Annealing and quenching were performed with the specimen in mounted condition. The foil specimen, on the other hand, was mounted only after annealing and quenching.

RESULTS

Paterson's[3] analysis predicts that the presence of stacking faults would cause the following changes in the X-ray reflections of a given plane (hkl) :

(1) If $|h+k+l|$ = 3N, there is a sharp reflection and no line shift (N is a positive integer or 0).

(2) If $|h+k+l|$ = 3N - 1 , there is a brodened reflection and a line shift toward a lower Bragg angle.

(3) If $|h+k+l|$ = 3N + 1, there is a broadened reflection and a line shift toward a higher Bragg angle.

In (2) and (3) the line shift is given by :

(4) $$\Delta 2\theta^\circ = \pm \frac{9_0\sqrt{3}}{\pi^2} \frac{h_3}{l_0^2} \alpha \tan \theta_0$$

where

$h_3 = |h+k+l|$

$l_0^2 = h^2+k^2+l^2$

α = the probability of finding a stacking fault

θ_c = the Bragg angle for the reflection under consideration.

Since the value of $|h+k+l|$ depends not only on the family of planes under consideration but also on the individual plane within the family, it follows that two or all three of the aforementioned effects (equations 1 - 3) may be present simultaneously. The determination of α rests upon the possibility of resolving the various effects. However, in families of the type $\{h00\}$ the reflections of all individual planes shift in the same direction and α can be directly calculated from (4).

Several reflections were investigated. The results are given in Table I.

TABLE I

$2\theta^\circ$ for Cold-Worked Specimen and Specimen Annealed at 1200° C for 20 Minutes. (Cu K_α Radiation)

Reflection	$2\theta^\circ$ Annealed at 1200°C	$2\theta^\circ$ Cold-Worked	$\Delta 2\theta^\circ$
{111}	60.56	60.60	0.04
{420}	122.91	122.83	-0.08
{422}	148.23	148.25	0.02
{222}	86.04	85.95	-0.09
{400}	103.51	103.59	0.08

Fig.1 illustrates the shift in the {400} line, $\Delta 2\theta^{o}$, as a function of the annealing temperature. It also shows the ratios of the {400} line widths of the various annealed specimens to the line widths of the cold worked specimen. The computed stacking-fault densities are given in Table II. The time for all isochronal anneals was 20 minutes.

TABLE II

Stacking-Fault Densities for Specimens Annealed for 20 Minutes (Calculated from {400} Reflection, Cu K_{α} Radiation)

Annealing Temperature ^{o}K	Stacking-Fault Density
1473	0
1173	0
973	0.006
873	0.010
773	0.014
723	0.016
673	0.016
573	0.016
473	0.018
373	0.018
300(room temperature)	0.016

Stacking-fault densities for specimens annealed isothermally at 450°C are given in Table III.

TABLE III

Stacking-Fault Densities for Specimens Annealed Isothermally at 450°C (Calculated from {400} Reflection, Cu K_α Radiation)

Time (seconds)	Stacking-Fault Density
120	0.018
300	0.018
600	0.018
1200	0.016
3000	0.014
6000	0.012

Fig. 2 illustrates the ratio of the {400} line widths of the isothermally annealed specimens to that of the cold-worked specimen, and, $\Delta 2\theta^\circ$ for the isothermal anneals.

DISCUSSION OF RESULTS

A stacking fault is formed by the dissociation of a complete dislocation into partial dislocations. The probability of the presence of a stacking fault is then equivalent to that of the presence of a dislocation. The loss of stacking faults could be expected to be closely associated with the loss of dislocations as the results of annealing treatments.

An interpretation of the results obtained may be made on the basis of the work done by Brindley [12], on the recovery of copper by measurements of the change in the thermoelectric properties of cold-worked and annealed specimens. The results of Brindley's work show that the thermo-e.m.f. is proportional to the density of dislocations present, and his data are in close agreement with a first order recovery process. Assuming that the loss of stacking faults is also governed by a first order process, an equation similar to Brindley's equation may be used, replacing the dependent variable by α, i.e. :

$$\frac{d\alpha}{dt} = -\alpha t^{c} A_{o} e^{-\frac{Q}{KT}} \qquad (5)$$

where

A_o = a constant

c = a constant

Q = the activation energy of the process

K = Boltzmann's constant

T = absolute temperature

t = time

The solution of this differential equation is :

$$\ln \frac{\alpha}{\alpha_o} = - \frac{t^{c+1}}{c+1} A_o e^{-\frac{Q}{KT}}$$

However, since $\frac{\alpha}{\alpha_o} < 1$, this equation can be re-written

$$\ln \left(- \ln \frac{\alpha}{\alpha_o}\right) = (c+1) \ln t + \ln \frac{A_o}{c+1} - \frac{Q}{KT} \qquad (6)$$

Fig.3 shows a plot of $\ln\left(-\ln\frac{\alpha}{\alpha_o}\right)$ vs. ln t for a constant temperature. Due to the inherent innacuracy of the method used in measuring α it cannot be established with certainty that the process obeys equation (5). However, the experimental points in Fig.3 may suggest a straight line with a slope close to unity. If equation (5) is assumed to be a process of the first order, which would be expected on the basis of Brindley's results then c= 0. The activation energy Q can then be calculated by plotting $\ln\left(-\ln\frac{\alpha}{\alpha_o}\right)$ vs. 1/T as

shown in Fig.4. From the slope of the resulting line the value of Q is found to be 0.45 ev. The possible error in evaluating Q due to the inaccuracy of the data is estimated to be $\pm$ 0.3 ev. The activation energy for the recovery of copper calculated by Brindley [12] was 0.5 ev. It is important, however, to realize that that the inherent inaccuracy of the method used in this investigation makes it impossible to state positively that a first order process with a single activation energy governs the annihilation of stacking faults.

Line widths for the {400} reflections are illustrated in Figs.1 and 2. Williamson and Smallman [13] showed that a relationship exists between line width and dislocation density. However, the method which they propose for claculating dislocation densities has an accuracy of only an order of magnitude. The initial decrease in line width without a corresponding decrease in α is probably due to a rearrangement of dislocations, their number remaining constant.

Another interpretation of the results may be attempted using the analysis of Kuhlmann, Masing and Raffelsiper [14]. These authors showed that the loss of dislocations during recovery could be represented by the following equation :

$$\frac{dn}{dt} = - ce^{-\frac{U_o - \beta\tau}{kT}} \qquad (7)$$

where

c and β = constants

n = the number of dislocations present

t = time

k = Boltzmann's constant

T = absolute temperature

U_o = the thermal activation energy

$\tau = \frac{G b}{\pi L} n$

G being the shear modulus, b the Burgers vector, L the length of a pile-up of dislocations. This approach presupposes that the reduction of the activation energy by stress is a linear function of the stress.

Replacing n by α in (7) it follows that, for an isothermal process

$$(8) \qquad \left(\frac{\alpha}{\alpha_0} - 1\right) \ln B = \ln (At+1)$$

where $B = e^{-\frac{\beta G b \alpha_0}{kT\pi L}}$, $A = C \frac{kT\pi L}{\beta G b} e^{-\frac{U_0}{kT}} e^{\frac{\beta G b \alpha_0}{kT\pi L}}$

For an isothermal process at T = 450°C A is of the order of 1. Therefore for large t $\ln (At+1) \simeq \ln At$. It follows from (8) that

$$\left(\frac{\alpha}{\alpha_0} - 1\right) = \text{constant} \times \ln At$$

or

$$\left(\frac{\alpha}{\alpha_0} - 1\right) = C' \ln t + C''$$

which is a linear function of ln t. Fig.5 shows $\left(\frac{\alpha}{\alpha_0} - 1\right)$ vs. ln t. This approach does not permit the direct evaluation of an activation energy.

Regarding the possible mechanisms by which the annealing of stacking faults may take place, several possibilities can be considered. Dislocation glide per se requires a very small activation energy. However, due to the presence of obstacles, mainly other dislocations, they

come to a halt. Hardening is generally attributed to such a process. Recovery of the original properties could be effected in several ways :

(i) Dislocations climb out of their slip planes to overcome obstacles. This involves primarily the migration of vacancies. According to Bradshaw and Pearson [15] the migration of a vacancy in platinum requires an activation energy of 1.1 ev.

(ii) Screw dislocations can move by cross-slip, a process described in detail by Seeger [16] . The activation energy for this process in platinum is not known but a rough estimate may be obtained by considering the activation energies for cross-slip in aluminum (1.05 ev) and copper (10 ev) [17] . Seeger [18] estimates the stacking-fault energy in copper to be about 40 ergs/cm^2 and in aluminum to be upward of 200 ergs/cm^2. These values were generally confirmed by Thornton and Hirsch [19]. The stacking-fault energy in platinum reported by the latter authors lies between 56 and 110 ergs/cm^2; Seeger [20] also predicts a stacking-fault energy of the same magnitude for platinum. Since the activation energy for cross-slip increases with decreasing stacking-fault energy, as shown by Schoeck and Seeger [17] the activation energy for cross-slip in platinum should lie somewhere between 1.05 and 10 ev.

(iii) Another possible mechanism for the release of a halted dislocation is through the collapse of a Lomer-Cottrell sessile dislocation.The activation energy for this process is not known

and no experimental data are available. However, Stroh [20], on the basis of purely theoretical calculations, arrived at the conclusion that a sessile dislocation would fail by the recombination of imperfect dislocations which are unable to glide. For aluminum this process requires an activation energy of 0.8-2.6 ev, whereas for copper it would require such a high activation energy (about 100 ev) that this mechanism can be ruled out. Stroh [20] shows also that this activation energy increases with stacking-fault width. The stacking-fault width varies inversely as the stacking-fault energy. Since platinum has a stacking-fault energy which is higher than that of copper the activation energy for this process in platinum would have to be greater than 0.8 ev.

(iv) Finally, the movement of a dislocation may be impeded by the intersection of a dislocation with other dislocations. The intersection of moving dislocations would lead to the formation of jogs. Thornton and Hirsch [19] calculated the activation energies for the formation of jogs from experimental data on low-temperature creep. They concluded that these activation energies are a fraction of 1 ev. for all metals (e.g. 0.7 ev.for copper, 0.3 ev. for aluminum). Friedel [21] gives the following formula for an approximate estimate of the activation energy for the formation of a jog :

$$Q_j = \frac{G}{10} b_1^2 b_2$$

where

G = the shear modulus

Q_j = the activation energy for the formation of a jog

b_1 = the Burgers vector of the moving dislocation

b_2 = the Burgers vector of the intersected dislocation.

For platinum this formula yields approximately 0.8 ev. which, within, the limits of accuracy of Friedel's formula, confirms the values obtained by Thornton and Hirsch [19].

If the recovery of stacking faults in platinum is a first order thermal activation process then the activation energy of 0.5 ± 0.3 ev. would suggest that during this process dislocations move through a "forest" of dislocations which are either stationary or moving on intersecting {111} planes. Thornton and Hirsch [19] showed that intersecting partial dislocations first become constricted and then cross each other with the formation of a jog. This process would be possible in platinum with an activation energy of approximately 0.5 ev. The mechanisms which have been proposed for the annihilation of dislocations require, however, activation energies which are higher than 0.5 ev.

No line broadening or line shift could be observed as a result of "quenched-in" vacancies, within the limits of accuracy of the equipment. This was the case in any of the {400}, {422}, and {420} reflections which were investigated.

C O N C L U S I O N S

The investigation led to the following results :

1. Cold-work introduces stacking faults in platinum, which are annihilated by annealing.

2. The inherent innaccuracy of the X-ray method for measuring stacking-fault densities does not permit the unequivocal determination of the nature of the process governing recovery.

3. If recovery is assumed to be a first order process ,an activation energy of 0.5 ± 0.3 ev. is found.

4. Dislocations can move in platinum by intersecting a "forest" of dislocations with the formation of jogs. This requires an activation energy of the same magnitude as that found by assuming a first order process.

5. Quenched-in vacancies produce no detectable effect on the X-ray reflections of platinum.

RECOMMENDATIONS

In view of the inherent inaccuracy of the X-ray method for measuring stacking-fault densities it is suggested that the effect of cold-work on the properties of platinum, such as the modulis of elasticity, hardness, electrical resistivity or thermo-e.m.f. be investigated. The exact nature of the process governing recovery can only be established with certainty with the aid of an experimental method which is more accurate than the X-ray method used in this investigation. This latter method, however, is useful in corroborating other experimental results, inasmuch as it is the only direct evidence of the presence of stacking faults.

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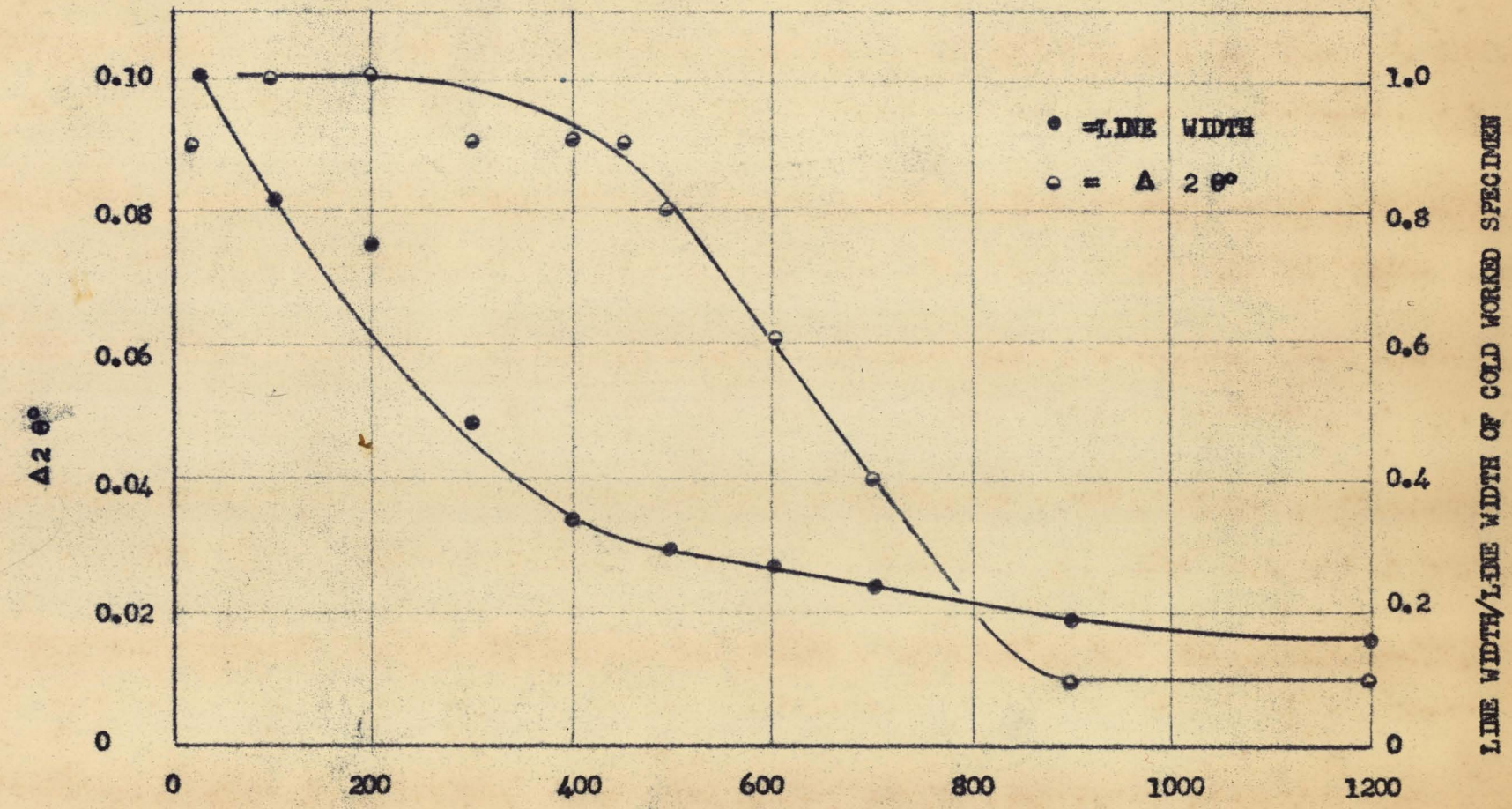
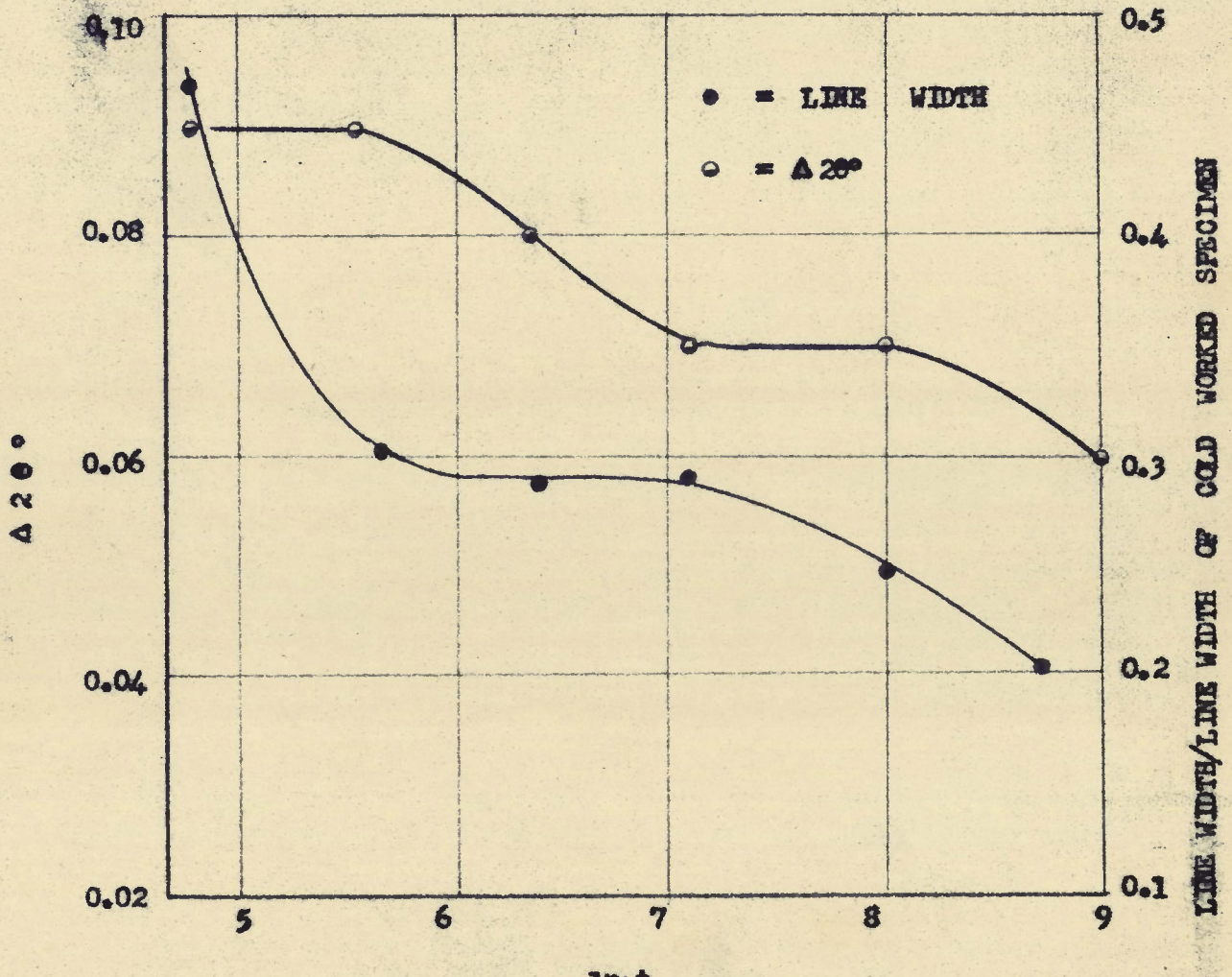
FIGURES



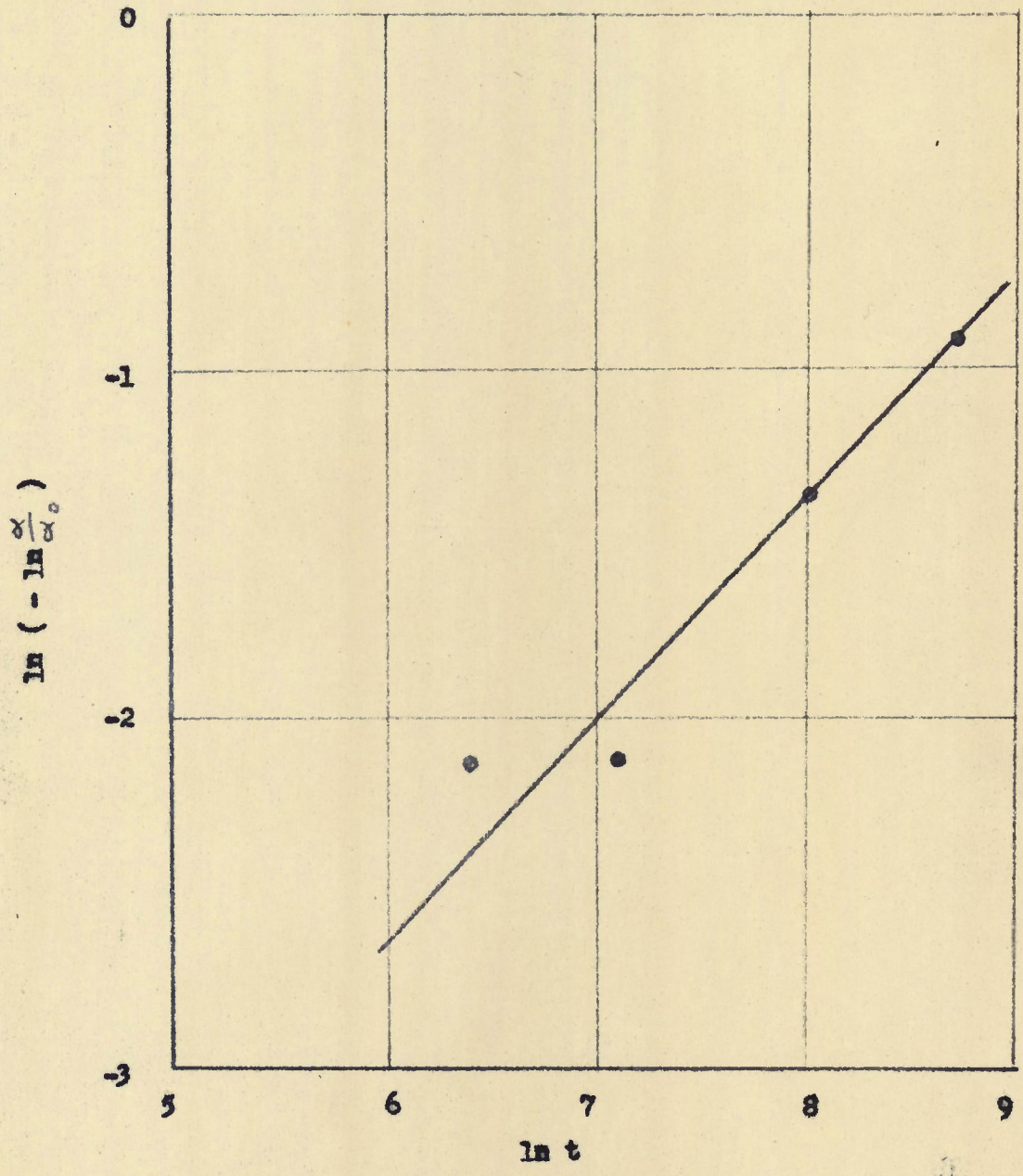
Δ 2 θ° {400} AND LINE WIDTHS FOR ISOCHRONAL ANNEALS (20 MINUTES)

FIGURE 1



Δ $2\theta^{\circ}_{\{400\}}$ AND LINE WIDTH FOR ISOTHERMAL ANNEALS

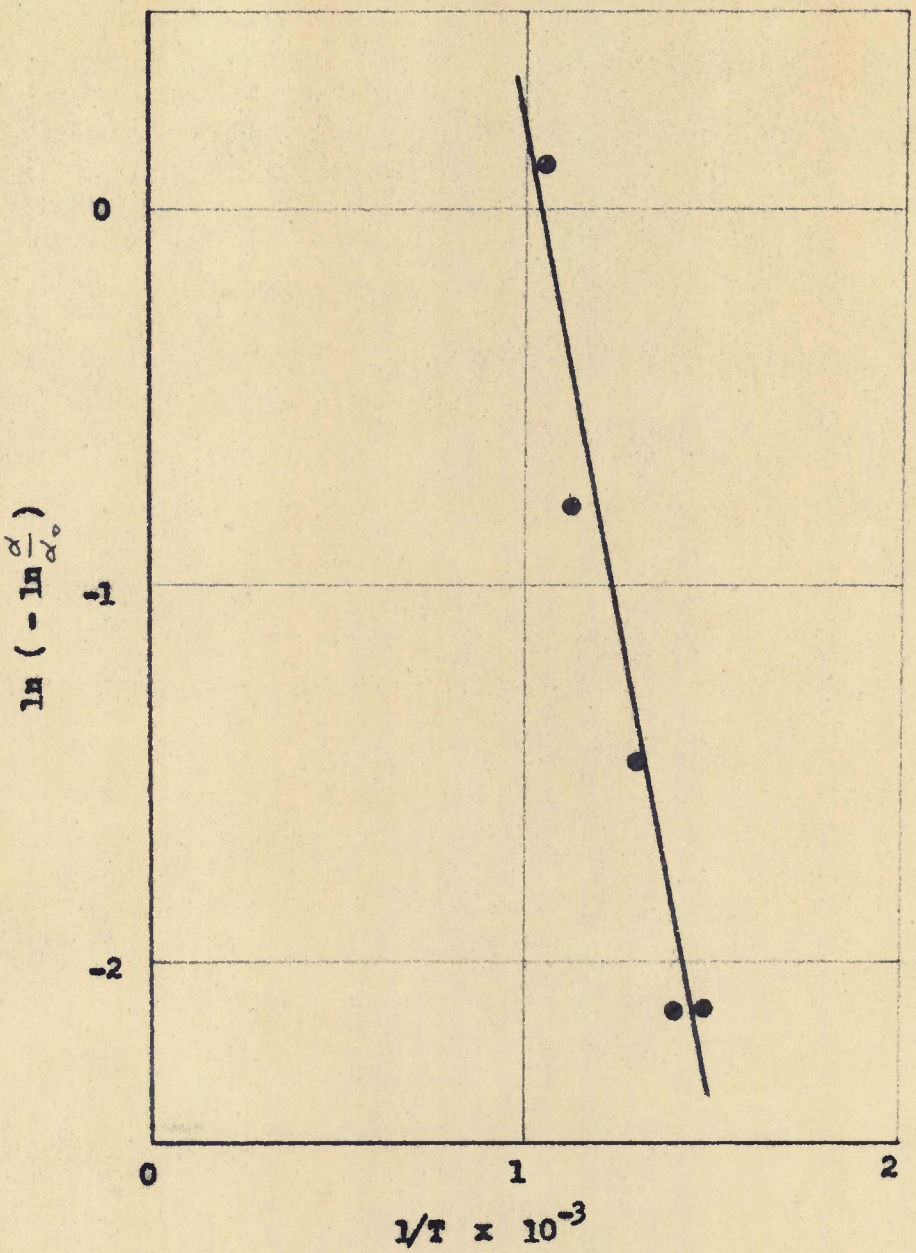
FIGURE 2



ln (- ln $\frac{\alpha}{\alpha_0}$) vs. ln t FOR ISOTHERMAL ANNEALS AT 450° C

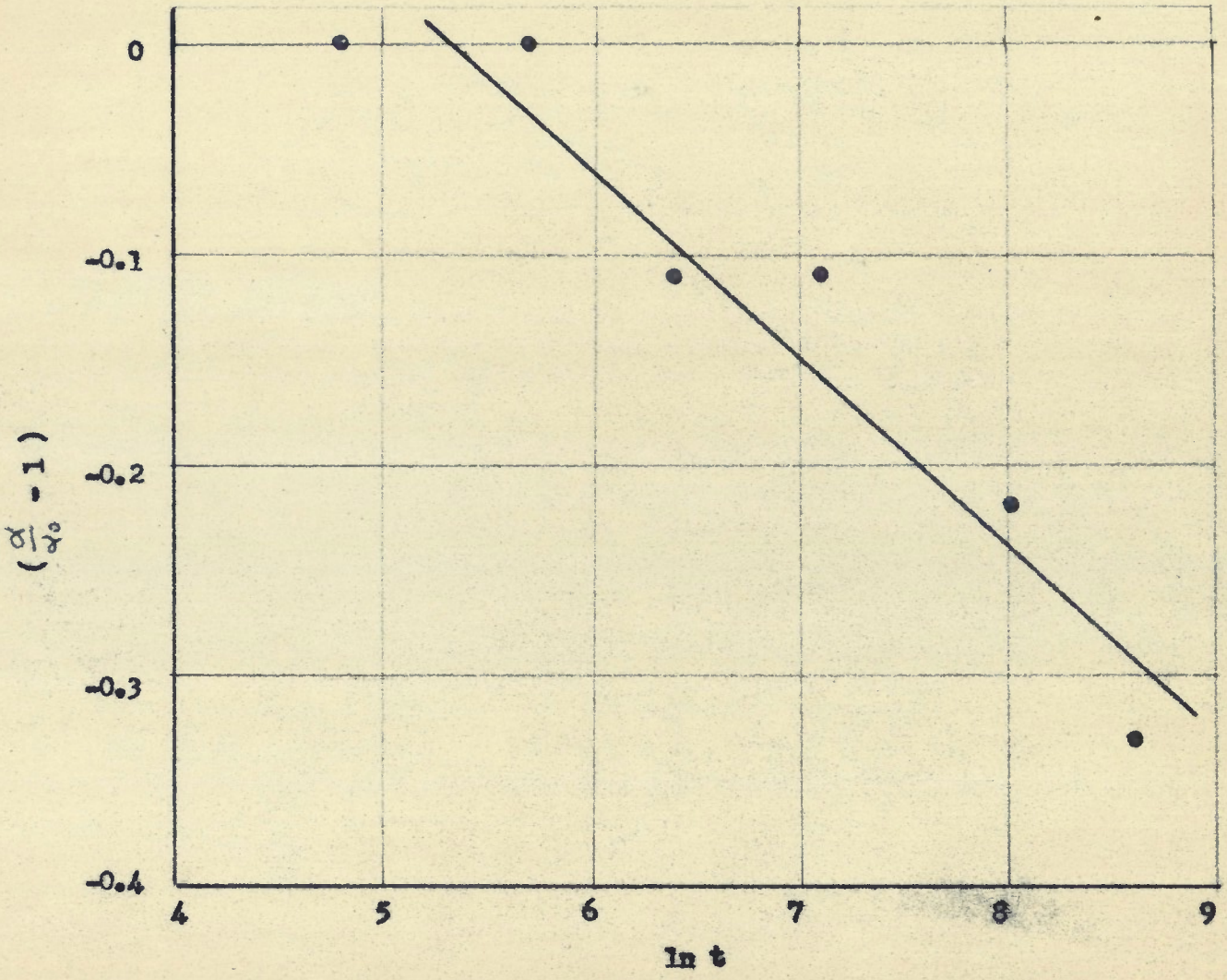
({400} REFLECTION)

FIGURE 3



$\ln\left(-\ln\frac{\alpha}{\alpha_0}\right)$ vs. 1/T FOR ISOCHRONAL ANNEALING

FIGURE 4



$(\frac{\alpha}{\alpha_0} - 1)$ vs. ln t FOR ISOTHERMAL ANNEALS AT 450° C

FIGURE 5

A C K N O W L E D G M E N T

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