Of course these equations follow also from the formalism of Section III. Substitution of $\omega = \exp(-ika)$, $B = k^{\frac{1}{2}}$, $C = 0$, as given for the case of no interaction in the external region (Table I), and R from (62) into (38) leads to $u^J = 1$, i.e., to zero scattering cross section, as it must. However, this result appears as a cancellation of the effect of the resonance levels given in (64) with the effect of the deviation of ω from 1. Obviously the knowledge of the E_λ and γ_λ alone is insufficient to provide us with a picture of the variation of the cross section with energy. In fact, if one tries, e.g., to estimate the scattering cross section at low energies by using for R the first term in its expansion (63) one obtains about $0.1a^2$. This result is not so bad if one has chosen a small value of a. However, if one chooses a large a, as one is entirely at liberty to do formally, this gives a grossly inaccurate picture of the cross section. Only by considering the effect of all levels on R does one obtain the correct zero cross section.

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Stress Relaxation across Grain Boundaries in Metals*

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In order to elucidate further the concept of relaxation of shear stress across grain boundaries in metals, the temperature dependence of internal friction and rigidity modulus of 99.991 percent aluminum have been measured as a function of frequency of torsional vibration and as a function of grain size of the specimen. It has been found that for the same specimen, an increase of frequency of vibration shifts the internal friction curve and the rigidity relaxation curve (Q^{-1} and G/G_U *versus* temperature) to higher temperatures; and when the frequency of vibration is kept constant, a change in grain size of the specimen has the same effect as a change of the frequency of vibration The observed internal friction and rigidity relaxation can be expressed as functions of the parameter (G.S.)$\times f \times \exp(H/RT)$, where (G.S.) is the grain size or average grain diameter of the specimen, f is the frequency of vibration, and H is the heat of activation. It is shown that all these observed phenomena are necessary manifestations of the stress relaxation across grain boundaries arising from the viscous behavior of the grain boundaries in metals, which behavior has been demonstrated by previous anelastic-effect measurements.

1. INTRODUCTION

It has been demonstrated[1] that the grain boundaries in metals behave in a viscous manner in the sense that they cannot sustain a shear stress. Thus, when an over-all stress, however small, is applied to a specimen, the shear stress across all grain boundaries will gradually relax. Because of this relaxation of shear stress, the stress no longer remains a unique function of the strain, and vice versa, in the conventionally elastic region, and this causes all kinds of anelastic effects. The locking effect of the grain edges and corners will insure that the over-all stress relaxation will be of limited extent for a fixed overall strain. The maximum amount of macroscopic shear stress relaxation in 99.991 percent polycrystalline aluminum (average grain diameter = 0.03 cm) determined by four independent types of anelastic-effect measurements (namely, internal friction, temperature variation of rigidity modulus, creep under constant stress and stress relaxation at constant strain) is 33 percent, which agrees fairly well with the theoretical value of 36 percent[2] calculated by assuming the grain boundaries to be viscous.

It has also been shown that the rate of the stress relaxation across grain boundaries is a function of the temperature of measurement and

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[1] T. S. Kê, Phys. Rev. **70**, 105(A) (1946); *ibid.*, **71**, 142(A) and 533 (1947).

[2] C. Zener, Phys. Rev. **60**, 906 (1941).

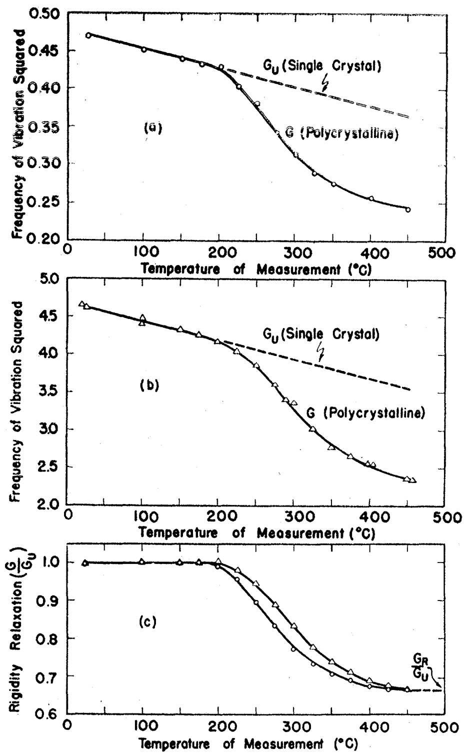

FIG. 1. Effect of frequency of vibration on rigidity and rigidity relaxation in aluminum (average grain diameter =0.02 cm).
(a) frequency of vibration = 0.69 c.p.s. at room temperature;
(b) frequency of vibration = 2.16 c.p.s. at room temperature;
(c) rigidity relaxations for two frequencies of vibration: ⊙, 0.69 c.p.s.; △, 2.16 c.p.s.

has a heat of activation. This led to an estimation of the coefficient of viscosity at the grain boundary. The estimated value of the coefficient of viscosity for the grain boundary in 99.991 percent aluminum was found to be consistent with the experimentally determined value of molten aluminum at the same temperature.

The concept of stress relaxation across grain boundaries leads to predications as to the effect of grain size and frequency of vibration on this stress relaxation. In order to elucidate further the concept of stress relaxation across grain boundaries, the temperature dependence of internal friction and rigidity modulus of 99.991 percent aluminum were measured as a function of grain size of the specimen and as a function of frequency of vibration. The apparatus used is practically identical with that described before.[3] The experimental results are reported below.

2. EFFECT OF FREQUENCY OF VIBRATION

Accepting the concept of viscous grain boundary, an increase of the frequency of vibration will shift the internal friction curve (Q^{-1} *versus* temperature) to higher temperatures. This can be shown as follows. Similar to other types of relaxation phenomena, such as relaxation by diffusion (thermal, atomic, magnetic), relaxation of ordered distributions and relaxation of preferential distributions,[4] the internal friction due to stress relaxation across grain boundaries is appreciable only when the period of the applied cyclic stress is comparable to the time of relaxation associated with the stress relaxation across grain boundaries. As has been found in previous experiments,[5] the rate of the stress relaxation across grain boundaries is increased by a rise of temperature. The time of relaxation is thus reduced with an increase of temperature. Therefore when the frequency of vibration is raised, a higher temperature is required to reduce the relaxation time so that it remains comparable to the period of vibration. Exactly similar considerations apply to the case of rigidity relaxation. That is, an increase of the frequency of vibration will shift the rigidity relaxation curve (G/G_U *versus* temperature) to higher temperatures, where G_U is the unrelaxed rigidity, corresponding to the rigidity in the case of single crystal aluminum.

The effect of frequency of torsional vibration on rigidity modulus and internal friction was studied with 99.991 percent aluminum wires having an average grain diameter of 0.02 cm (the

TABLE I. Heat of activation associated with the stress relaxation across grain boundaries in aluminum as determined by four types of anelastic-effect measurements.

Type of measurement	H (calories/mole)
Creep	34,000
Stress relaxation	34,500
Internal friction	32,000
Rigidity	32,000

[3] T. S. Kê, Phys. Rev. **71**, 533 (1947).
[4] A comprehensive account on relaxation phenomena is given in C. Zener, *Elasticity and Anelasticity of Metals*, Institute for the Study of Metals Monograph Series (The University of Chicago Press, to be published).
[5] T. S. Kê, Phys. Rev. **71**, 533 (1947).

specimen was subjected to a cold-working of 70 percent reduction in area and was then annealed at 450°C for two hours). Two frequencies having a ratio of 3.14 were used in the measurement. The higher frequency was obtained by attaching a smaller auxiliary inertia member to the specimen. As visual observation of successive amplitudes of vibration is impossible at the higher frequency, the internal friction was determined by applying the formula

$$Q^{-1}=(\ln n)/\pi\tau_n f, \qquad (1)$$

when τ_n is the time required for the amplitude of vibration to be reduced to a factor $1/n$ of its initial value, and f is the frequency of vibration.

It is seen from Figs. 1 and 2 that the rigidity curve and internal friction curve do shift to higher temperatures when the frequency of vibration is raised.[6] As expected, the maximum internal friction and the ratio G_R/G_U do not change with frequency of vibration, where G_R is the relaxed rigidity.

In order to obtain a quantitative correlation between the effects of frequency of vibration and the temperature of measurement, let us proceed to determine if there is a heat of activation associated with the stress relaxation across grain boundaries from the above measurements. It has been described previously that there is a time-temperature relationship for the observed creep under constant stress, and stress relaxation at constant strain caused by the stress relaxation across grain boundaries. Thus it has been found that the observed creep and stress relaxation can be expressed as functions of the parameter

$$t\times\exp(-H/RT), \qquad (2)$$

where t is the time of observation and H is the heat of activation associated with the stress relaxation across grain boundaries. In the present case, which is dynamic, we can consider the observed internal friction and rigidity relaxation as functions of the parameter

$$f\times\exp(H/RT), \qquad (3)$$

[6] The cold-working applied to the specimen preceding annealing was 70 percent reduction in area in this experiment instead of 95 percent reduction in area as in previous experiments. As the high temperature branch of the internal friction curve is quite sensitive to the amount of cold-working applied to the specimen prior to annealing, this branch of the internal friction curve is somewhat different from the corresponding curve previously reported.

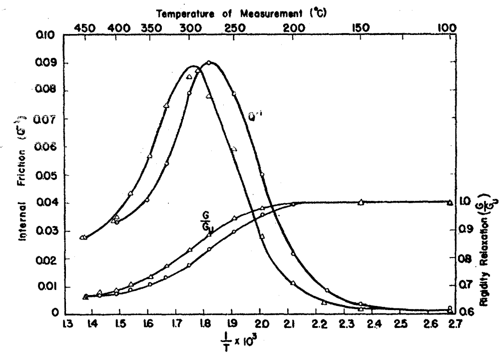

FIG. 2. Effect of frequency of vibration on internal friction and rigidity relaxation in aluminum plotted against $1/T$ (average grain diameter $=0.02$ cm). Frequency of vibration at room temperature: ⊙, 0.69 c.p.s.; △, 2.16 c.p.s.

where f is the frequency of vibration. It can be shown that in order to obtain identical values of Q^{-1} or G/G_U in different measurements with different frequencies of vibration, the frequency of vibration and the temperature of measurement must be related so that

$$d(\ln f)/d(1/T)=-H/R, \qquad (4)$$

or

$$H=R[\ln(f_2/f_1)]/[1/T_1-1/T_2], \qquad (5)$$

when two frequencies f_1 and f_2 are used.

In Fig. 2, the internal friction and rigidity relaxation measured with two frequencies of vibration are plotted as a function of $1/T$. In order to bring the two curves shown to coincidence with each other, the horizontal shift in $1/T$ required in each case is 0.075×10^{-3}. As the two frequencies of vibration used have a constant ratio of 3.14 over the whole temperature range, we have

$$H=32{,}000 \text{ calories per mole}$$

from both internal friction and rigidity measurements.

The values of the heat of activation determined by the four independent types of anelastic-effect measurements are summarized in Table I. It is seen that they agree within the experimental error.

3. EFFECT OF GRAIN SIZE

The concept of viscous grain boundary predicts that a change in grain size of the specimen will have the same effect as a change in the fre-

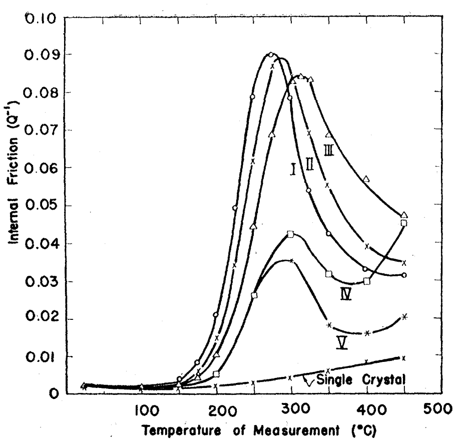

FIG. 3. Effect of grain size on internal friction in aluminum (pre-annealing cold-working = 70 percent reduction in area).

I. ⊙, 450°C annealing for 2 hours, average grain diameter = 0.02 cm;
II. ×, 500°C annealing for 4 hours, average grain diameter = 0.04 cm;
III. △, 550°C annealing for 2½ hours, average grain diameter = 0.07 cm;
IV. □, 600°C annealing for 4 hours, average grain diameter larger than 0.084 cm;
V. ✳, 600°C annealing for 12 hours, average grain diameter larger than 0.084 cm;
(diameter of wire = 0.084 cm).

quency of vibration. This is due to the fact that the relaxation time associated with the stress relaxation across grain boundaries increases with an increase of grain size. This is obvious when we consider the viscous slip along grain boundaries associated with a given over-all stress. With the larger grain size, a larger relative displacement can take place at the grain boundary before it is blocked at the grain edges and corners. A longer time will thus be required to reach the equilibrium state at which further slip is completely blocked. Since the viscous slip along grain boundaries and the stress relaxation across grain boundaries take place simultaneously, it is evident that the times of relaxation associated with both processes increase with an increase of grain size. Thus when the frequency of vibration is kept constant, an increased grain size will shift the internal friction curve and the rigidity relaxation curve to higher temperatures.

It can also be shown that as long as the grain size is smaller than the linear dimensions of the specimen, the maximum internal friction will be independent of grain size. This can be illustrated by the following considerations. Consider the internal friction caused by the stress relaxation across grain boundaries in a unit volume of the specimen. The total surface of a grain is proportional to the square of the grain size, and the volume of a grain is proportional to the cube of the grain size. The total grain boundary surface area per unit volume is thus proportional to the reciprocal of grain size. The internal friction per unit volume is proportional to the energy dissipated per half-cycle. The energy dissipated per half-cycle at a given grain boundary is proportional to the shear displacement, which takes place along the grain boundary during a half-cycle, times the total grain boundary surface area per unit volume. The maximum shear displacement along the grain boundary is proportional to grain size and thus the internal friction maximum is independent of grain size.

By similar considerations, it can be shown that the rigidity relaxation curve (G/G_U *versus* temperature) also shifts toward higher temperatures with an increase of grain size, and the value of the ratio G_R/G_U is independent of grain size.

The considerations described above hold only when the grain size is smaller than the linear dimensions of the specimen. For wire specimens, this means that the grain size should be smaller than the diameter of the wire. When a grain is extended completely across the specimen, we can no longer consider its grain boundaries as isolated viscous regions surrounded by an elastic matrix. The locking effect of the grain edges and corners may not exist and the stress relaxation may be unlimited, as in the case when shear stress is applied to a piece of amorphous substance such as pitch.

In the study of the effect of grain size, the specimen used was 99.991 percent aluminum wire having a diameter of 0.033 inch, and one foot in length. This wire was subjected to a cold-working

TABLE II. Annealing conditions and the corresponding grain size of 99.991 percent aluminum (diameter of wire specimen = 0.084 cm).

Anneal	Average grain diameter (cm)	Curve in Figs. 2 and 3
450°C, 2 hours	0.021_7	I
500°C, 4 hours	0.04_7	II
550°C, 2½ hours	0.07_3	III
600°C, 4 hours	>0.084	IV
600°C, 12 hours	>0.084	V

giving a 70 percent reduction in area prior to annealing. It has been found that in order to remove or to minimize the interfering effect due to the cold-working, the annealing temperature should be 450°C or higher and the annealing time should be 2 hours or longer.** The wire was thus annealed at 450°C for 2 hours, cooled down slowly in air to room temperature and measurements of internal friction and rigidity were made from room temperature up to 450°C, and then down again to room temperature. After the measurement, the test piece placed in the furnace was examined microscopically for grain size. Similar measurements were made after the wire was annealed at 500°C for 4 hours, 550°C for $2\frac{1}{2}$ hours, 600°C for 4 hours and 600°C for 12 hours.

The heat treatment and the corresponding grain size obtained are shown in Table II. The grain size is defined in the conventional way; namely,

$$(\text{G.S.}) = 1/n^{\frac{1}{2}},$$

where n is the mean number of grains per cm^2. The internal friction and rigidity relaxation

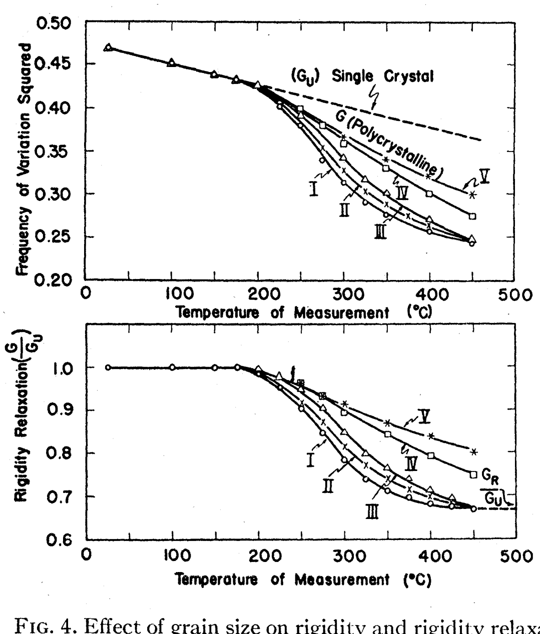

FIG. 4. Effect of grain size on rigidity and rigidity relaxation in aluminum (pre-annealing cold-working = 70 percent reduction in area). Descriptions on curves I–V are the same as shown in Fig. 3.

** The effect of prior-annealing cold-working upon the viscous behavior of the grain boundaries in a recrystallized material will be reported later.

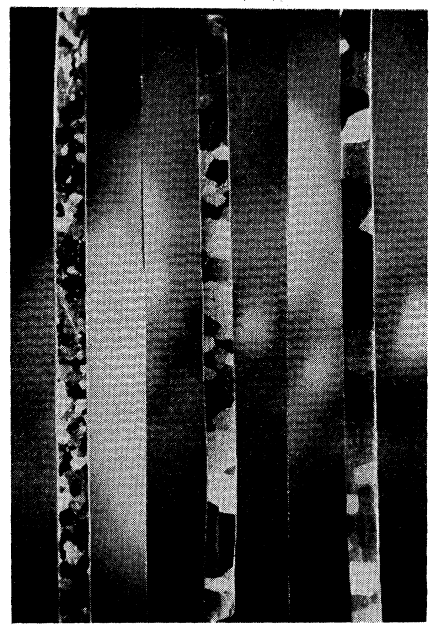

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FIG. 5. Micrographs of 99.991 percent aluminum specimen with different grain size. Pre-annealing cold-working = 70 percent reduction in area.

(a) (G.S.) = 0.02 cm; (450°C annealing for 2 hours).
(b) (G.S.) = 0.04 cm; (500°C annealing for 4 hours).
(c) (G.S.) = 0.07 cm; (550°C annealing for $2\frac{1}{2}$ hours).
Diameter of wire = 0.084 cm.
Magnification: 5×.

curves corresponding to these grain sizes are shown, respectively, in Figs. 3 and 4. It is seen that curves I, II, and III are just what was expected, a shift toward higher temperatures with an increase of grain size. The internal friction maxima (see Fig. 3) and the ratio G_R/G_U (see Fig. 4) from curves I and II are approximately the same. In curve III, a few grains of the specimen have already extended completely across the wire, and the internal friction maximum is somewhat smaller than those in curves I and II. The micrographs of the three grain sizes corresponding to curves I, II, and III are shown in Fig. 5. Corresponding to curves IV and V, most of the grains are extended completely across the specimen, the internal friction maximum becomes much smaller, and the rigidity curves decrease continuously without a sign of flattening out (Fig. 4). Under such conditions, the internal friction and rigidity modulus are independent of stress only at extremely small stress levels corresponding to a maximum shearing strain of about

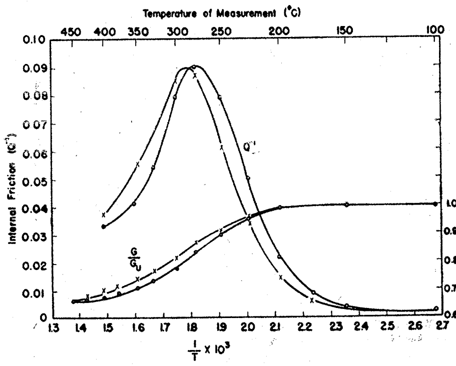

FIG. 6. Effect of grain size on internal friction and rigidity relaxation in aluminum plotted against $1/T$ (frequency of vibration $= 0.69$ c.p.s. at room temperature). Average grain diameter: ⊙, 0.02 cm; ×, 0.04 cm.

5×10^{-7}. The internal friction (*versus* temperature) in "single-crystal" aluminum, as has been previously reported, is included in Fig. 3 for reference.

As has been mentioned above, the concept of viscous grain boundary predicts that a change in grain size of the specimen has the same effect as a change in the frequency of vibration. We should therefore be able to consider the observed internal friction and rigidity relaxation as functions of the parameter

$$(\mathrm{G.S.})\times\exp(H/RT), \qquad (6)$$

where (G.S.) is the grain size or average grain diameter of the specimen and H is the heat of activation. In order to test whether this is true, the observed internal friction and rigidity relaxation for two different grain sizes (from curves I and II in Figs. 3 and 4) are plotted in Fig. 6 against $1/T$. If there is a heat of activation over the temperature range studied, these two sets of curves should be superposed on each other by a horizontal shift of $1/T$. This has been found to be the case, and the horizontal shift $(1/T_1-1/T_2)$ required in each set of curves is 0.050×10^{-3}. Following similar procedures as used in treating the effect of the frequency of vibration, the heat of activation should be given by

$$H=R\ln[(\mathrm{G.S.})_2/(\mathrm{G.S.})_1]/(1/T_1-1/T_2). \qquad (7)$$

Taking H as 32,000 calories per mole, as determined according to Eq. (5), we get from Eq. (7) that $[(\mathrm{G.S.})_2/(\mathrm{G.S.})_1]=2.2$, which is consistent with the value obtained by grain size measurements given in Table II.

We can now test our statement that the observed internal friction and rigidity relaxation are functions of (G.S.), f and T only through the parameter

$$(\mathrm{G.S.})\times f\times\exp(H/RT). \qquad (8)$$

This should be true if the concept of viscous grain boundary is correct. In Fig. 7, the observed internal friction and rigidity relaxation correspond-

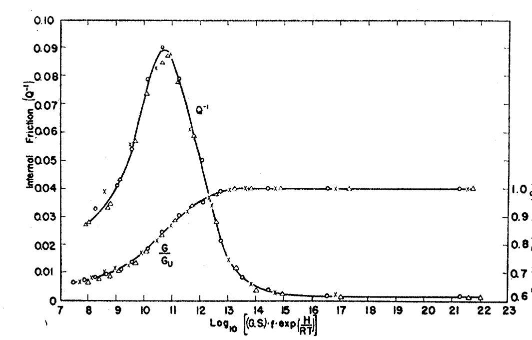

FIG. 7. Internal friction and rigidity relaxation in aluminum as functions of the parameter $(\mathrm{G.S.})\times f\times\exp(H/RT)$, $H=32{,}000$ calories per mole.
⊙, $(\mathrm{G.S.})=0.02$ cm, f_{RT} (frequency of vibration at room temperature) $=0.69$ c.p.s.;
×, $(\mathrm{G.S.})=0.04$ cm, $f_{RT}=0.69$ c.p.s.;
△, $(\mathrm{G.S.})=0.02$ cm, $f_{RT}=2.16$ c.p.s.

ing to two grain sizes and two frequencies of vibration were plotted against the common logarithm of this parameter, using the heat of activation of 32,000 calories per mole. It is seen that the observed data form essentially a smooth curve, showing that the generalized statement given in (8) holds for the range of grain size studied. This gives an additional corroboration of the concept of viscous grain boundaries in metals.

In conclusion, the author is deeply indebted to Dr. Clarence M. Zener for enlightening discussions.

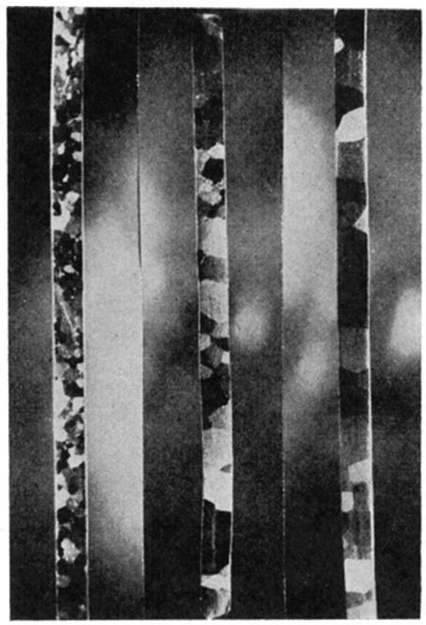

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FIG. 5. Micrographs of 99.991 percent aluminum specimen with different grain size. Pre-annealing cold-working = 70 percent reduction in area.

(a) (G.S.) = 0.02 cm; (450°C annealing for 2 hours).
(b) (G.S.) = 0.04 cm; (500°C annealing for 4 hours).
(c) (G.S.) = 0.07 cm; (550°C annealing for $2\frac{1}{2}$ hours).
Diameter of wire = 0.084 cm.
Magnification: 5×.