the light path while the lower trace a was made with the cell containing the formaldehyde vapor placed in the light path.

No evidence has been uncovered by these observations that any appreciable absorption exists beyond the region studied by Ebers and Nielsen. This supports their assignment of the regions 1165 cm^{-1} and 1278cm^{-1} as due to the frequencies ν_5 and ν_6.

The writer wishes to express his sincere appreciation for help and encouragement to Dr. H. H. Nielsen, Chairman of the Department, who suggested the project and made available the facilities of the Infra-Red Laboratory.

PHYSICAL REVIEW VOLUME 71, NUMBER 8 APRIL 15, 1947

Experimental Evidence of the Viscous Behavior of Grain Boundaries in Metals*

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(Received November 12, 1946)

The mechanical behavior of grain boundaries in metals has been a subject of constant controversy. The present research is designed to examine thoroughly the mechanical behavior of grain boundaries in metals in a quantitative manner. A simple torsional apparatus has been devised for measuring four types of anelastic effects at very low stress levels, namely: internal friction at low frequencies; variation of dynamic rigidity with temperature; creep under constant stress; and stress relaxation at constant strain. All four types of anelastic effects have been studied in 99.991 percent polycrystalline aluminum as well as in single crystal aluminum; these effects are practically absent in single crystal aluminum. The four types of anelastic effects observed in polycrystalline aluminum are completely recoverable and are linear with respect to the applied stress and prior strain. They satisfy the interrelations derived by Zener from Boltzmann's superposition principle within experimental error. These are consistent with the viewpoint that the grain boundaries behave in a viscous manner. The maximum amount of shear stress relaxation in polycrystalline aluminum determined by the four types of anelastic measurements is about 33 percent. This is in good agreement with the theoretical value of 36 percent calculated by assuming the grain boundary to be viscous. The heat of activation associated with the viscous slip along the grain boundaries has been found to be 34,500 calories per mole. The coefficient of viscosity of the grain boundaries in aluminum estimated using this heat of activation, is consistent with that of molten aluminum at the same temperature. Similar anelastic effects have been also observed in polycrystalline magnesium, indicating that the viscous behavior is common to all metals.

INTRODUCTION

IN a polycrystalline material, it is reasonable to think that there is merely a transition layer at the grain boundary, where the atom positions represent a compromise between the crystalline arrangements in the two adjoining grains. However, for the purpose of understanding the mechanisms of deformation and fracture in polycrystalline metals, it is convenient to consider the grain boundary as an entity and to study its mechanical behavior without inquiring into its true nature.

Back in 1912, or earlier, Rosenhain[1] and others suggested that the grain boundaries in metals may be conceived as an intergranular amorphous cement. This assumption is based primarily on the facts that grain boundaries in a metal behave as if they are regions of strength at low temperature and high deformation rate but are regions of weakness at high temperature and low deformation rate. This is precisely the behavior of amorphous or viscous materials. The existence of an actual intergranular cement has been the subject of constant controversy. However, whether this is true or not, it is only necessary

* This research has been supported by the Office of Research and Inventions, U.S.N. (Contract No. N6ori-20-IV) since May 1, 1946.

[1] W. Rosenhain and D. Ewen, J. Inst. Metals 8, 149 (1912). Or see Jeffries and Archer, *The Science of Metals* (McGraw-Hill Book Company, New York, 1924), Chap. IV.

to consider that the grain boundaries behave as if they were viscous, having a coefficient of viscosity decreasing with an increase of temperature. Guided by such a picture, one may explain qualitatively many observed phenomena. A review of such explanations has been made recently by Zener.[2]

It can be easily seen that if the grain boundaries in metals behave in a viscous manner, the so-called anelastic effects, which are effects arising from the strain not being uniquely determined by the stress in the pre-plastic region, should be observed under proper experimental conditions. The measurement of anelastic effects offers, therefore, a powerful tool for the study of the mechanical behavior of grain boundaries in metals. Zener and his collaborators[3] have made a preliminary study of the viscous behavior of grain boundaries in zinc, alpha brass and alpha iron by measurements of internal friction and elastic after-effect. However, only qualitative information has thus far been obtained. The purpose of the present research program is to examine quantitatively the viscous behavior of the grain boundaries in metals and to make a systematic study of the effect of standard metallurgical variables upon this behavior with four types of anelastic measurements in torsion. They are: internal friction at low frequencies (a few cycles per second); variation of dynamic rigidity with temperature; creep under constant stress; and stress relaxation at constant strain.

EXPERIMENTAL METHODS OF MEASURING ANELASTIC EFFECTS

In the measurement of anelastic effects, the applied stress should be so small that the following conditions are fulfilled: (1) There should be no permanent set after the stress is removed and all the effects should be recoverable after a sufficiently long period of time; (2) The observed anelastic effects should be linear with the applied stress or prior strain. Thus the internal friction and the dynamic rigidity should be independent of the amplitude of vibration; the creep per unit elastic strain (or instantaneous strain) should be independent of the magnitude of the elastic strain; and the stress relaxation per unit initial stress should be independent of the magnitude of the initial stress. Such a linearity is necessary for a simple interpretation of the observed anelastic effects. Thus, if the grain boundaries in metals behave in a viscous manner, one can consider that a polycrystalline metal consists of a two-component system. One component behaves in a viscous manner, obeying the relation

$$\dot{e}=as+b\dot{s}, \tag{1}$$

where s is the shear stress component, e the shear strain, and a and b are constants independent of s, e, and $\dot{s}$. The other component is of a true elastic nature, obeying the relation

$$e=s/M, \tag{2}$$

where M is the elastic modulus. These two microscopic relations are linear in stress, strain, and their time derivatives. Therefore, according to the superposition principle, the macroscopic behavior of the metal specimen as a whole must also be linear in these variables.

The torsional method was chosen in the present investigation for the following reasons. (1) The torsional method can be conveniently used for the measurement of all the anelastic effects mentioned before. This renders an easier comparison and correlation between these effects. (2) The torsional method is much simpler experimentally than the other methods when the strain to be measured or the stress applied is very small. One objection to the torsional method is that the strain in the specimen is inhomogeneous. But this will have no consequence in the present problem if the effects observed can be shown to be linear with strain and stress. In all the following measurements, the experimental conditions were so regulated that this linearity has been checked and the discrepancy, if any, lies within the experimental error.

I. Measurement of Internal Friction and Rigidity

The internal friction and rigidity were determined by measuring, respectively, the logarithmic decrement and the frequency of the free torsional vibration of a wire specimen carrying a small

[2] C. Zener, Metals Technology (August, 1946).
[3] A. Barnes and C. Zener, Phys. Rev. **58**, 87L (1940); C. Zener, D. Van Winkle, and H. Nielson, Trans. A.I.M.E. **147**, 98 (1942); W. A. West, Metals Technology (August, 1946).

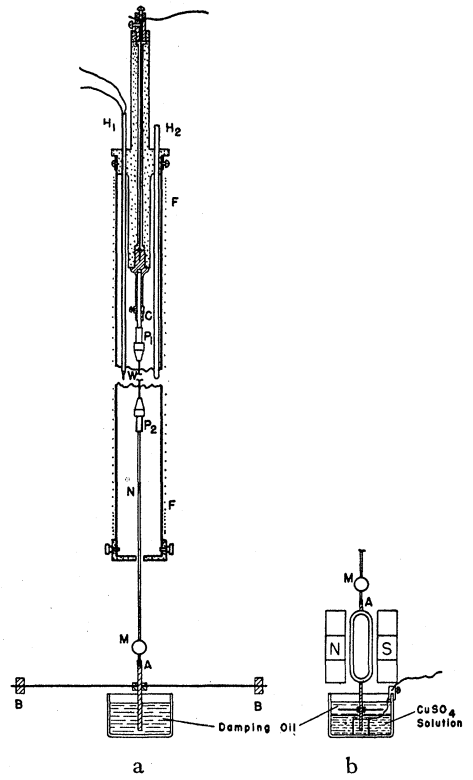

FIG. 1a. Apparatus for measuring internal friction and dynamic rigidity of wire specimen. 1b. Moving coil arrangement for measuring creep under constant stress and stress relaxation at constant strain of wire specimen.

torsional bar. The measure of internal friction herein adopted is the logarithmic decrement divided by π, (Q^{-1}). When the logarithmic decrement is small, the rigidity modulus G of the wire is proportional to the square of the frequency of vibration provided the length and radius of the wire are kept constant.

The arrangement for the measurement is diagrammatically shown in Fig. 1a. W is the test wire of 0.033″ diameter and 12″ length. P_1 and P_2 are two small steel pin vises, to which both ends of the wire are firmly clamped. The handle of the upper pin vise P_1 is clamped tightly inside a steel tubular chuck C. The top of the steel chuck is screwed into a cylindrical transite rod and cemented there rigidly with Insalute adhesive cement. This transite rod minimizes the loss of heat in the test wire outward through conduction. The top of the transite rod is enlarged to rest on the fringed top of the steel wall of an electric furnace as shown in the figure. It can be clamped to prevent rotation by a set of three screws in the furnace wall.

The lower pin vise P_2 is welded to a thick nichrome wire N (B & S gauge No. 12) which is a poor conductor of heat but has a much higher rigidity than the test wire at various temperatures. M is a concave mirror mounted on the nichrome wire. By means of this mirror, a beam of light passing through a narrow slit forms a sharp image on a translucent scale 3 meters away from the mirror. BB is a torsional bar about 8 inches long carrying at each end a cylindrical piece of iron. The total longitudinal load on the test wire, including the lower pin vise, nichrome rod, the mirror, and the torsional bar is about 30 g. An electromagnet is placed at a suitable distance from the iron weight, so that the torsional vibration can be started by tapping a key beside the scale while watching the deflection of the light on the scale. The lower end of the rod is attached to a thicker brass tube and this is dipped into a beaker containing thick machine oil, the depth of immersion being so adjusted that the lateral motion is critically damped. With such an arrangement, measurements can be taken immediately after the torsional vibration is started.

FF is an electrical resistance furnace. It consists of a thin seamless steel tube $1\frac{1}{2}$″ in diameter and 28 inches long, wound with B & S gauge No. 18 nichrome wire. The turns were spaced more closely near both ends of the tube to obtain a uniform temperature along the axis of the furnace. The temperature does not vary more than 2°C over a length of 15 inches at 350°C and the test wire was always placed in this region of uniform temperature. Furthermore, since the ends of the test wire were effectively thermally insulated from outside, the temperature of the wire is uniform throughout its length. The lower end of the furnace was closed by a split transite cap having a central hole just large enough to permit the nichrome rod N to emerge from the furnace without contact.

The temperature was measured by means of a chromel p-alumel thermocouple inserted into the furnace through the hole H_1. The hole H_2 was used to insert short pieces of test wire inside a Pyrex glass tube to be taken out at desired times

for microscopic examination and other purposes. It was also occasionally used to lead a jet of nitrogen or inert gas into the furnace to prevent excessive oxidation of the test wire at high temperatures.

The usual method of timing was followed in measuring the period of vibration. The period of torsional vibration of the test wire was raised to about 1.2 seconds at room temperature by attaching the torsional bar *BB* as described above. Visual observations could therefore be easily made. The logarithmic decrement was determined by observing the consecutive amplitudes of vibration for a suitable length of time. In all the measurements at all temperatures, the maximum amplitude of vibration (on a scale 3 meters away from the mirror) used was less than 8 cm. With a test wire of 0.033″ diameter and 12″ long, this amplitude corresponds to a maximum shearing strain on the surface of the test wire of 2×10^{-5}. When the consecutive amplitudes were plotted on a semi-logarithmic paper against the ordinal number of vibrations, a straight line has always been obtained indicating that, under the experimental conditions used, the logarithmic decrement is independent of the amplitude of oscillation.

II. Measurement of Creep under Constant Stress and Stress Relaxation at Constant Strain

A simple technique has been devised for both kinds of measurements by utilizing the principle of a moving coil galvanometer. The test wire to be examined forms the suspension of a moving coil galvanometer. Since experiments are only conducted at a low stress level, the current passing through the galvanometer is a measure of the shear stress acting on the test wire, the deflection of the galvanometer is a measure of the shear strain. The apparatus used is the same as that used for the measurement of internal friction and rigidity, except that the torsional bar is unscrewed at *A* and a moving coil with appropriate damping arrangement is substituted. This is schematically shown in Fig. 1b. The moving coil was made by winding about 700 turns of B & S gauge No. 38 copper wire on an oval copper frame having average dimensions of $\frac{3}{4}\times2\frac{3}{8}$ inches. The total resistance of the coil is about 150 ohms. The permanent magnet used consists of three horseshoe magnets mounted together. A copper rod was attached to the lower end of the moving coil. This forms one electrode of an electrolytic coil serving as a rotatable current junction. The electrolyte used for the cell is saturated copper sulphate solution and the other electrode of the cell is a copper cylinder surrounding the copper rod. The damping to the torsion of the specimen by the copper sulphate solution is negligibly small and the change of internal resistance of the electrolytic cell due to the expansion of the test wire at high temperatures is also small in comparison with the total resistance in the circuit. The measurements at different temperatures can thus be compared without worrying about the effect due to the expansion of the test wire. A layer of heavy machine oil is floated on the copper sulphate solution and critical damping of the torsional vibration of the system is obtained by attaching a cross bar to the copper rod so that it is immersed in the oil layer. The orientation of the cross bar is parallel to the plane of the observing scale. The lateral motion parallel to the scale is also critically damped by such an arrangement. The total longitudinal load on the wire, including the moving coil and the damping arrangement, is about 30 g.

In the measurement of creep under constant stress, a constant torque was applied and the creep was recorded visually. Measurements can be started one second after the torque is applied. In the measurement of stress relaxation at constant strain, the current through the galvanometer coil was reduced by increasing the resistance in the circuit so as to maintain a constant deflection.

ANELASTIC EFFECTS IN POLYCRYSTALLINE ALUMINUM

In the study of the mechanical behavior of grain boundaries in metals by measurement of anelastic effects, it is of paramount importance that the measurement is done under controlled conditions so that the effects attributable to the grain boundaries can be observed and can be separated from those attributable to other reasons. It is thus desirable to start the investigation with pure metals to avoid possible

effects due to impurities. Aluminum was chosen as the principal working metal for the present investigation for the following reasons: (1) The so-called temperature of recrystallization of aluminum is relatively low, and controllable grain size can be obtained by annealing at moderately low temperatures. (2) Aluminum possesses a high elastic isotropy and thus the mechanical behavior will not change appreciably even if there is a change of crystal orientation during measurement.

I. Internal Friction

The 99.991 percent aluminum was kindly supplied by the Aluminum Company of America in the form of ingots. A piece of about one cubic inch was cut from the ingot without remelting and this was swaged into rods in the Metallurgy Section of this Institute. The rod having a diameter of about 0.15 inch was annealed at 500°C for one hour. This annealed rod was then cold-worked by drawing successively through the holes of a drawing plate always along the same direction to a final size of about 0.033″ diameter without intermediate annealing. This corresponds to a cold work of about 95 percent reduction in area (95 percent RA). After being straightened by pulling, the wire was mounted between the two pin vises shown in Fig. 1a, so that the portion between the two pin vises was exactly 12 inches long. The whole suspension system (except the inertia bar) was fed into the furnace through the top of the furnace, the axis of which was adjusted to be exactly vertical. The inertia bar was then slipped underneath and screwed tight to the damping pin. The wire was annealed in the furnace at 450°C for five hours for stress relief and to give a comparatively stable grain size. The logarithmic decrement and rigidity were determined at and below 450°C down to room temperature and then again from room temperature up to 450°C. The wire was examined microscopically (etched with 0.2 percent hydrofluoric acid) after the measurement and was found to be recrystallized into rather uniform grains having an average grain diameter of about 0.03 cm. A short piece of aluminum wire was placed in a Pyrex glass tube fed into the furnace through the hole H_2 to receive the same heat treatment as the test specimen except that no longitudinal load was applied during annealing. It gave recrystallized grains having the same size as the test specimen.

The variation of internal friction in polycrystalline aluminum with temperature is shown in Fig. 2. The frequency of vibration used is about 0.8 cycle per second at room temperature. It is seen that the internal friction reaches a maximum at a temperature of about 285°C and has a maximum value of about 0.09. The existence of a maximum is just what was expected, accepting the concept of a viscous grain boundary. The internal friction is determined by the product of the distance slipped and the resistance to slip along the grain boundaries. At low temperatures, the viscous slip along the grain boundaries is small and therefore the internal friction is small. At high temperatures, the resistance to slip along the grain boundaries is small, so again the internal friction is small. Only in an intermediate temperature range, when both the slip distance and the resistance to slip are appreciable, will the internal friction be appreciable.

In order to show that this effect observed in thoroughly annealed polycrystalline aluminum has its origin at the grain boundaries rather than in the interior of the grains, the internal friction of a "single-crystal" wire of commercially pure aluminum, consisting at most of a few grains in a wire one foot long, was measured at temperatures up to 450°C. This is also shown in Fig. 2. It is small over the whole temperature range but increases slightly at higher temperatures. However, there is definitely no maximum at around 285°C as in the case of polycrystalline aluminum. Further experiments have shown that the slow increase in internal friction in "single-crystal" aluminum may be due to the handling of the "single-crystal" wire. As the wire was first prepared in an annealing furnace and then mounted between the two pin vises, it is unavoidable that a certain amount of cold work was introduced during the manipulation.

If the internal friction observed in polycrystalline aluminum is entirely due to the viscous slip along the grain boundaries, the internal friction should decrease continuously at high

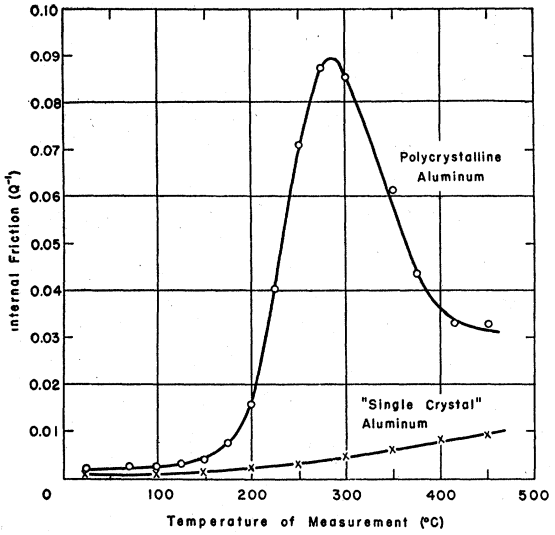

FIG. 2. Variation of internal friction with temperature in polycrystalline and "single crystal" aluminum (frequency of vibration = 0.8 cycles per second at room temperature).

temperatures once the maximum is over. However, as can be seen in Fig. 2, the internal friction did not decrease as rapidly as expected at high temperatures. It has been found that the high temperature side of the internal friction curve is quite sensitive to the amount of pre-anneal cold work, indicating that some other effects connected with the cold work come in at very high temperatures.

Another factor to be considered is the possible effect of the longitudinal load on the wire, which is about 30 g. Since the diameter of the wire is 0.033 inch, this corresponds to a stress of about 94 pounds per square inch. It has been found that the internal friction shown in Fig. 2 remains approximately the same when a longitudinal load three times as large was used, as long as the applied stress is sufficiently low so that the internal friction is independent of the stress levels. The frequency of vibration was, of course, kept the same in both cases.

In summary, it is obvious that the internal friction observed in polycrystalline aluminum as described above cannot be ascribed to thermoelastic origin, because it is very much larger than the internal friction attributable to thermal diffusion.[4] It cannot be ascribed to the self-diffusion in aluminum, as this internal friction observed does not occur in single crystal aluminum. It cannot be due to the diffusion of impurities along the grain boundaries, since the internal friction in less pure (99.2 percent) aluminum has been found to be smaller under similar conditions. Also it is unlikely to be due to the effect of crystal growth, because reasonable stable grains have been obtained by annealing the wires 5 hours at 450°C, and no grain growth can be detected during the time of a single measurement which takes only about $\frac{1}{2}$ minute. It seems thus to be justifiable to say that the internal friction observed in thoroughly annealed polycrystalline, but not in single-crystal aluminum, has its origin at the grain boundaries.

II. Modulus of Rigidity

The rigidity of a thoroughly annealed aluminum wire (95 percent RA, 450°C anneal for 5 hours) was determined simultaneously with the measurement of internal friction. As before, the frequency of vibration is about 0.8 cycle per second at room temperature. The variation of rigidity is shown in Fig. 3,* as has been briefly reported before.[5] It is seen from Fig. 3 that the rigidity curve is essentially a straight line at low temperatures, and there is a rapid change in curvature around 200°C. This rapid change was not observed in single-crystal aluminum wire, indicating that the observed rapid decrease of rigidity of thoroughly annealed metals at high temperatures is due to viscous slip along grain boundaries.

Since there is no grain boundary in a single crystal, the rigidity curve of single-crystal aluminum can be considered as the unrelaxed rigidity G_U. Let $G(T)$ be the rigidity in polycrystalline aluminum at the temperature T, then we have

$$G(T)/G_U = (f_p/f_s)^2, \tag{3}$$

[4] C. Zener, Phys. Rev. **53**, 90 (1938).

* Actually, the curves shown in Fig. 3 are f^2-temperature curves, where f is the frequency of vibration. These curves are somewhat different from the G-temperature curves because the length and diameter of the wire change somewhat with temperature and therefore G is not strictly proportional to f^2. However, the error thus introduced will not affect the general shape of the curves and thus the f^2-temperature curve can be taken as G-temperature curve in qualitative discussions.

[5] T. S. Kê, Phys. Rev. **70**, 105A (1946).

where f_p and f_s are, respectively, the frequency of vibration in polycrystalline and single-crystal aluminum at the temperature T. The ratio $G(T)/G_U$ is plotted as a function of the temperature of measurement in Fig. 4. It is seen that the ratio is about unity at temperatures below 200°C, drops suddenly therafter, and approaches a constant value of about 0.67, or less, at high temperatures. As a first approximation, we have $G_R/G_U=0.67$, where G_R is the relaxed rigidity. The fractional amount of the total shearing stress that can be relaxed across the grain boundaries can thus be taken as $1-0.67$, or 0.33.

"If the individual grains are essentially equiaxed, and the grain size distribution is uniform, it is anticipated that only a fraction of the overall stress can be relaxed by grain boundary slip. The situation is analogous to the case of a jig saw puzzle where the over-all configuration possesses rigidity in spite of the fact that no shearing stress exists between adjacent pieces." With such a picture in mind, a formula has been arrived at theoretically by Zener by strain energy consideration for the case of equiaxed grains of uniform size, that[6]

$$E_R/E_U=\tfrac{1}{2}(7+5\sigma)/(7+\sigma-5\sigma^2), \qquad (4)$$

where E_R is the Young's modulus of a polycrystalline specimen in the case where the grain boundaries are slippery and the relaxation of shearing stress across the grain boundaries has been complete, E_U is the Young's modulus where no slip occurs across the grain boundaries, and σ

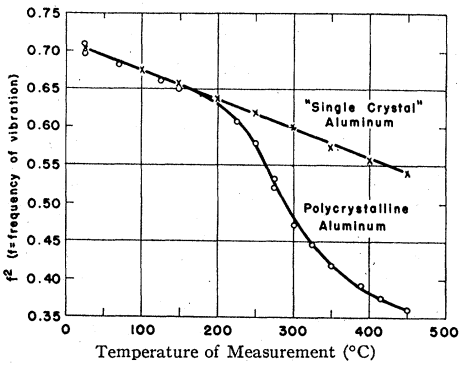

FIG. 3. Variation of "rigidity" with temperature in polycrystalline and "single-crystal" aluminum.

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

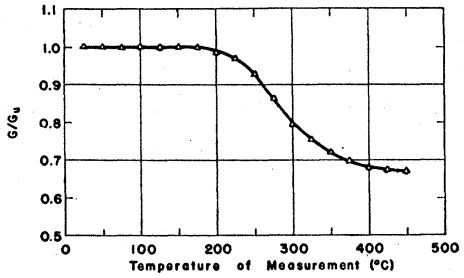

FIG. 4. Relaxation of rigidity in polycrystalline aluminum.

is the Poisson's ratio. The corresponding ratio in rigidity moduli, G_R/G_U, can be shown to be

$$G_R/G_U=2(7+5\sigma)/5(7-4\sigma). \qquad (5)$$

According to Birch,[7] the Poisson's ratio for aluminum (commercial) is 0.355 at 30°C, thus we have

$$G_R/G_U=0.636.$$

This is in good agreement with the experimental value which is about 0.67 as indicated in Fig. 4.

III. Creep at Constant Stress

The viscous grain boundary slip in metals will lead to the relaxation of shearing stress across the grain boundaries and this relaxation will cause an over-all slow yielding or creep of the metal when the applied stress is kept constant. The creep measurement at low stress levels will thus give direct information as to the viscous behavior of the grain boundaries.

The aluminum wire to be examined forms the suspension of a moving coil galvanometer as has been described above. The deflection of the specimen has been found to be proportional to the current passing through the coil when the deflection is small. In all measurements, the maximum deflection used was kept less than 8 cm on a scale 3 meters away from the mirror. This corresponds to a maximum shearing strain on the surface of the test wire of 2×10^{-5}, as has been mentioned above. The creep at the time t is measured by the ratio d_t/d_0 where d_t is the deflection at time t and d_0 the "instantaneous" deflection at $t=0$ when the constant torque was suddenly applied. In the case of single-crystal aluminum wire (99.2 percent pure), there is no

[7] F. Birch, J. App. Phys. 8, 129 (1937).

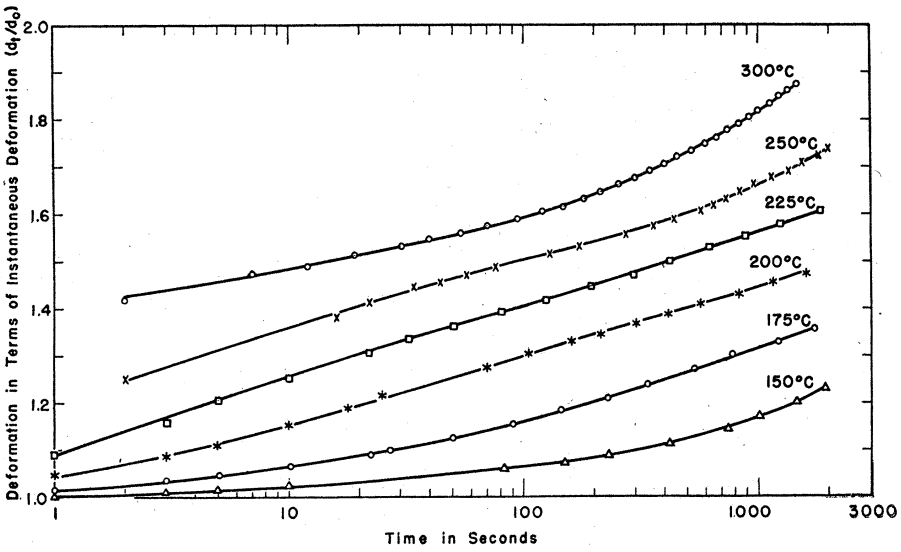

FIG. 5. Creep under constant stress at various temperatures in polycrystalline aluminum.

appreciable creep up to a temperature of about 350°C. This corroborates the viewpoint that the creep observed in polycrystalline aluminum is due to the viscous slip along the grain boundaries.

The creep curves of a 99.991 percent aluminum wire (95 percent RA, 450°C anneal for 5 hours) measured at various temperatures are shown in Fig. 5, in which d_t/d_0 is plotted against logarithm of time. The constant current used to furnish the torque was 1.5 ma in all the measurements. It can be seen that d_t/d_0 increases as a rule with both temperature and time of observation. In order to find if there is a time-temperature relation for the observed creep, let us assume that there is a heat of activation associated with this creep. Then we can express the creep as a function of time and temperature through the heat of activation H:

$$(d_t/d_0) = Af[t \exp(-H/RT)], \qquad (6)$$

where R is the gas constant, T the absolute temperature, and A a constant independent of t and T. If, now, we observe the time required to reach the same d_t/d_0 at different temperatures, then the derivative of d_t/d_0 with respect to $1/T$ is zero, whence we get

$$\frac{d \log_{10} t}{d(1/T)} = \frac{H}{2.3R}. \qquad (7)$$

If such a relationship holds true for all values of d_t/d_0, then the straight lines corresponding to different d_t/d_0 should be all parallel. This has been found to be the case and the average slope is 7400. This gives a heat of activation of 34,000 calories per mole. A composite curve is thus obtained as shown in Fig. 6. It is seen from Figs. 5 and 6 that the creep has a tendency to flatten out when the value of d_t/d_0 is about 1.5, indicating that this is about the limiting value of the over-all creep caused by the viscous slip along the grain boundaries. Further slip along the grain boundaries is probably hindered by the interlocking of the corners between adjacent grains.

The creep curves in Fig. 5 indicate that another effect comes in at higher temperatures. The creep curves at 250°C and higher do not remain constant as they should if the creep is completely caused by grain boundary slip. With the same kind of reasoning as for the case of the internal friction measurement, this new effect at high temperatures may be connected with the cold work.

In order to corroborate the concept of viscous grain boundary slip in which all the microscopic relations are linear with respect to strain and stress, tests have been made showing that the observed creep attributed to grain boundary slip is recoverable (Fig. 7) and d_t/d_0 is independent of the applied stress and prior strain.

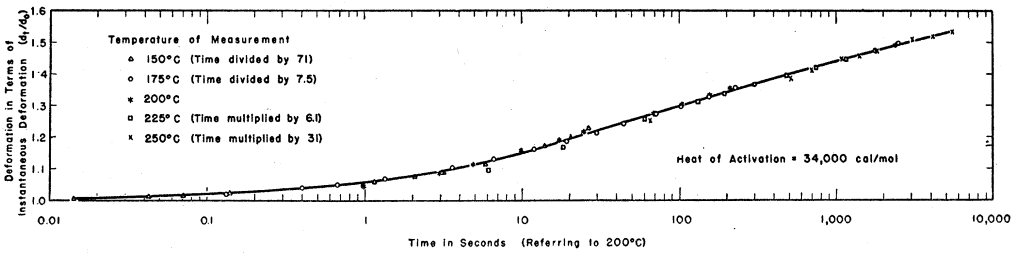

FIG. 6. Composite curve of creep under constant stress at 200°C in polycrystalline aluminum.

IV. Stress Relaxation at Constant Strain

As the torque applied to the specimen is proportional to the current passing through the moving coil, the stress (in terms of the initial stress) at the time t required to keep the specimen at a constant strain is measured by the ratio i_t/i_0, where i_t is the current at time t and i_0 is the initial current at $t=0$. As expected, no appreciable stress relaxation occurs in single-crystal aluminum. The stress relaxation curves of a 99.991 percent aluminum wire (95 percent RA, 450°C anneal for 5 hours) measured at various temperatures are shown in Fig. 8, in which i_t/i_0 is plotted against logarithm of time. The constant deflection maintained in all the measurements was 4 cm. This corresponds to a maximum shearing strain of 10^{-5}.

The heat of activation associated with the observed stress relaxation was determined in a similar manner as has been done in the creep measurements. This is done by finding from the curves in Fig. 8, the time required to reach a given i_t/i_0 at different temperatures and then plotting $\log_{10}t$ against $1/T$. Several d_t/d_0's were picked out and a curve was plotted for each d_t/d_0. These lines have been found to be all parallel. The average slope of these lines is found to be 7500, giving a heat of activation of 34,500 calories/mole, which is very close to that obtained in creep measurements.

It can be seen from Fig. 8 that the stress relaxation has almost been completed after one hour at 225°C, giving an asymptotic value of $i_t/i_0=0.67$. However, at still higher temperatures, the stress starts to relax again, indicating that a new effect enters. This may be connected with the cold work. The composite stress relaxation curve, taking the time at 200°C as unity, is shown in Fig. 9. This common curve tells the complete story of the stress relaxation associated with the grain boundary slip.

BOLTZMANN'S SUPERPOSITION PRINCIPLE AND THE INTER-RELATION BETWEEN VARIOUS ANELASTIC EFFECTS[8]

In order to generalize Hooke's law so that the elastic after-effect can be interpreted, Boltzmann[9] assumed that the fundamental relations between stress and strain are linear in stress and strain and in their time derivatives. The solutions then satisfy the superposition principle. This allowed Boltzmann to consider that the strain is a function also of the past history of the stress. The deformation at any instant can be considered thus as the result of a continuous series of constant forces previously applied. Using the superposition principle as a tool, Boltzmann was able to fit into a precise mathematical formulation all previously observed elastic after-effects and related phenomena. However, the relations derived are valid only when the elastic after-effect and related effects are small. A set of relations was recently derived by Zener[10] which holds independent of the magnitude of the observed effects. The relations correlating the four anelastic effects observed in the present research are as follows:

(1) Between stress relaxation at constant strain and creep under constant stress:

$$\delta(t)f(t)=1+\int_0^t\{\delta(t)-\delta(t-t')\}f(t')dt', \quad (8)$$

where $\delta(t)$ is the creep function and is defined as

[8] T. S. Kê, Phys. Rev. **71**, 142A (1947).
[9] L. Boltzmann, Ann. d. Physik **7**, 624 (1876).
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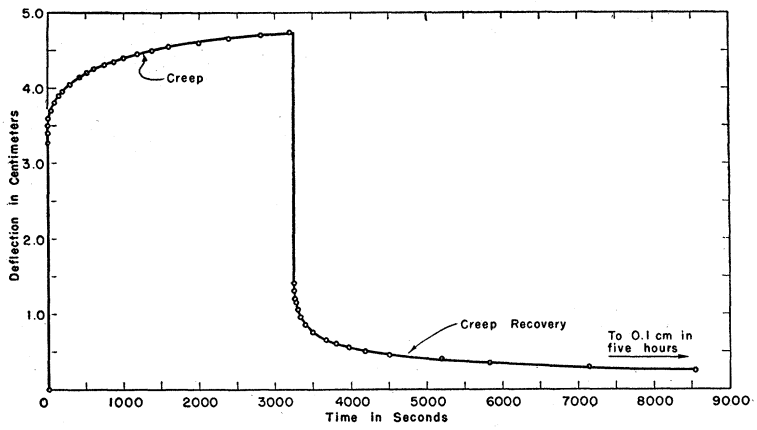


FIG. 7. Creep under constant stress and creep recovery at 175°C in polycrystalline aluminum.

the deformation at the time t when a constant force of magnitude unity was suddenly applied at $t=0$; $f(t)$ is the stress function and is defined as the force which must be applied at the time t in order to keep the deformation at a constant value of unity suddenly applied at $t=0$.

(2) Between dynamic modulus and stress function:

$$M(\omega)=f(t)_{t\cong P/8}, \tag{9}$$

where ω is the angular frequency and P the period of oscillation.

(3) Between internal friction Q^{-1} and stress function:

$$Q^{-1}(\omega)=-(\pi/2)(d\ \ln f/d\ \ln t)_{t\cong P/8}. \tag{10}$$

Now, these relations are derived on the basis of Boltzmann's superposition principle. If they can be experimentally verified and if we can demonstrate that all the effects observed are linear with respect to stress and strain and their time derivatives, then the microscopic relations stated in Eqs. (1) and (2) are adequate. Let us now proceed to compare Eqs. (8), (9), and (10) with experimental data.

I. Dynamic Rigidity and Stress Relaxation at Constant Strain

The relation between dynamic rigidity and stress function is given by

$$G(\omega)=f(t)_{t\cong P/8}.$$

Now, at a constant deformation D, the stress function is

$$f(t)=F(t)/D,$$

where $F(t)$ is the force applied at the time t. In terms of the quantities actually measured in the experiment, we have

$$f(t)=G_U(i_t/i_0),$$

and thus

$$G(P)/G_U=(i_t/i_0)_{t\cong P/8} \tag{11}$$

at a given temperature.

Now consider the case at 200°C. G/G_U at 200°C is, from Fig. 4, 0.985. The period of oscillation at 200°C is 1.26 sec.* Thus from Eq. (11), we obtain $i_t/i_0=0.985$ when $t=\frac{1}{8}(1.26)=0.16$ sec.

Let the conversion factor for converting the time scale at a temperature T to that of 200°C be τ_T, then it can be shown that

$$\log_{10}\tau_T=7500(1/473-1/T). \tag{12}$$

The conversion factors so calculated are summarized in the third column of Table I, from which we can calculate the value of t when $i_t/i_0=G/G_U$. The calculated values of i_t/i_0 in Table I are plotted against the corresponding value of t in the fifth column. These are shown by circles in Fig. 10, where the observed stress relaxation curve, the solid curve, is included for comparison.

II. Internal Friction and Stress Relaxation at Constant Strain

The relation between internal friction and stress relaxation at constant strain is shown in

* This is obtained from the f^2 curve for polycrystalline aluminum in Fig. 3.

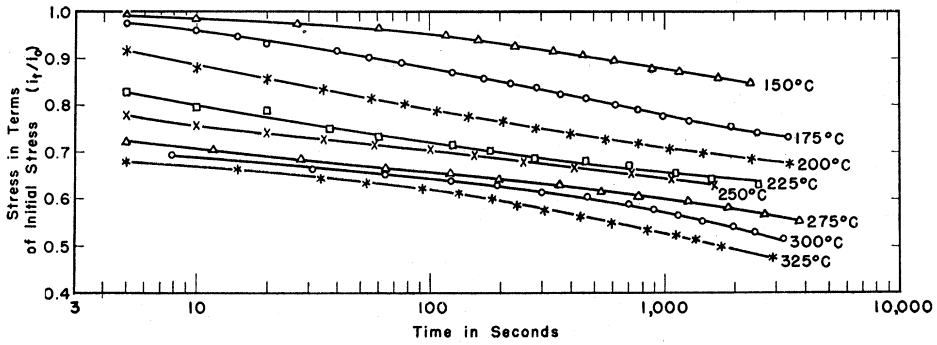


FIG. 8. Stress relaxation at constant strain at various temperatures in polycrystalline aluminum.

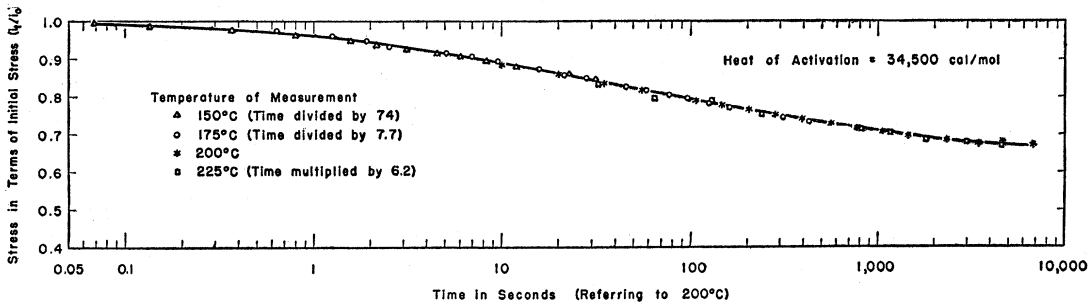


FIG. 9. Composite curve of stress relaxation at constant strain at 200°C in polycrystalline aluminum.

Eq. (10). We have as before,

$$f(t) = G_U(i_t/i_0).$$

Now

$$d \ln f(t) = d \ln G_U(i_t/i_0),$$

hence at a given temperature, we have

$$Q^{-1}(P) = -(\pi/2)\{d \ln(i_t/i_0)/d \ln t\}_{t \cong P/8},$$

because G_U is independent of t at a given temperature. Making use of the time-temperature relation

$$d \ln t/d(1/T) = H/R,$$

we have on integrating and taking the lower temperature limit $T_1 = 200°C$, at which $i_t/i_0 = 0.985$ which is very close to unity,

$$\ln(i_t/i_0) = -0.0092 - 11{,}000 \int_{200°C}^{T} Q^{-1}(T) d(1/T). \tag{13}$$

In order to evaluate the integral on the right-hand side, the internal friction is plotted against $1/T$. The values of i_t/i_0 calculated are shown in Table II.

The calculated values of i_t/i_0 in Table II are plotted against the corresponding values of t in the fourth column (from Table I). These are shown by crosses in Fig. 10. The observed values of i_t/i_0 listed in Table II are obtained from the composite stress relaxation curve shown in Fig. 9.

III. Creep Under Constant Stress and Stress Relaxation at Constant Strain

The relation between stress relaxation at constant strain and creep under constant stress is shown by Eq. (8). Now $\delta(t) - \delta(t-t')$ is always positive and $f(t')$ is always negative, therefore the integral at the right-hand side is always negative and we have

$$\delta(t) f(t) \leqq 1. \tag{14}$$

It can be shown that the value of the integral is usually much smaller than unity unless the relaxation is complete within a short interval of time as in the case when there is only one single

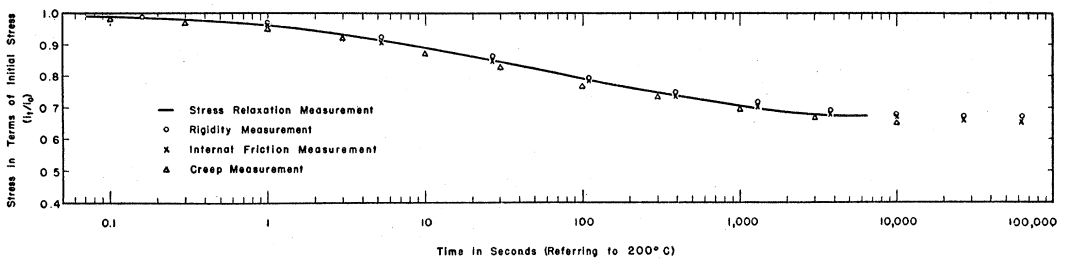


FIG. 10. Stress relaxation across grain boundaries in aluminum at 200°C as determined by four types of anelastic effect measurements (99.991 percent aluminum, 95 percent RA, 450°C anneal for 5 hours; average grain diameter = 0.03 cm).

time of relaxation. In our present case, therefore, we can consider that $\delta(t)f(t)=1$. Now, we have

$$\delta(t)=D(t)/F=D(t)/MD(0),$$
$$f(t)=F(t)/D=MF(t)/F(0). \quad (15)$$

Thus in terms of the quantities actually observed in the experiment, we have

$$\delta(t)f(t)=d_t/d_0\cdot i_t/i_0=1. \quad (16)$$

The values of i_t/i_0 calculated according to this formula are tabulated in Table III. The calculated values of i_t/i_0 in Table III are plotted against the corresponding values of t. These are shown by triangles in Fig. 10.

COEFFICIENT OF VISCOSITY OF GRAIN BOUNDARIES IN ALUMINUM

Having obtained a self-consistent picture that the grain boundaries in polycrystalline aluminum behave in a viscous manner, we are now in a position to compute or, at least, to estimate this coefficient of viscosity and its variation with temperature. Consider a grain boundary with an effective thickness d. Then the coefficient of viscosity may be defined by

$$\eta=s/(v/d), \quad (17)$$

where s is the shearing stress and v is the rate of relative displacement of the two sides of the boundary. Take the case of equiaxed grains as shown in Fig. 11. Let Δx be the distance slipped along the grain boundary during the time τ where τ is the time of relaxation, then

$$v\cong\Delta x/\tau.$$

TABLE I. Conversion table from rigidity relaxation to stress relaxation at 200°C

T (°C)	T (°K)	τ_T	P_T (sec.)	$t=\tau_T P_T/8$ (sec.)	i_t/i_0 (calc.)	i_t/i_0 (obs.)
175	448	1.23×10^{-1}	1.25	1.9×10^{-2}	1.00	——
200	473	1.00	1.26	1.6×10^{-1}	0.985	0.99
225	498	6.25	1.28	1.0	0.97	0.96
250	523	3.23×10	1.32	5.3	0.925	0.915
275	548	1.48×10^{2}	1.38	2.6×10	0.865	0.85
300	573	5.82×10^{2}	1.45	1.1×10^{2}	0.795	0.79
325	598	2.06×10^{3}	1.50	3.9×10^{2}	0.75	0.735
350	623	6.55×10^{3}	1.55	1.3×10^{3}	0.72	0.70
375	648	1.91×10^{4}	1.59	3.8×10^{3}	0.70	0.69
400	673	5.10×10^{4}	1.62	1.0×10^{4}	0.68	——
425	698	1.32×10^{5}	1.65	2.7×10^{4}	0.675	——
450	723	3.02×10^{5}	1.67	6.3×10^{4}	0.67	——

TABLE II. Conversion table from internal friction to stress relaxation at 200°C

T(°C)	Q^{-1}	$\int_{200°C}^{T} Q^{-1}(T)d(1/T)$	t (sec.)	i_t/i_0 (calc.)	i_t/i_0 (obs.)
225	0.040	249×10^{-8}	1.0	0.965	0.96
250	0.071	758×10^{-8}	5.3	0.91	0.915
275	0.088	1368×10^{-8}	2.6×10	0.85	0.85
300	0.086	2053×10^{-8}	1.1×10^{2}	0.79	0.79
325	0.071	2647×10^{-8}	3.9×10^{2}	0.74	0.735
350	0.057	3004×10^{-8}	1.3×10^{3}	0.71	0.70
375	0.044	3327×10^{-8}	3.8×10^{3}	0.685	0.69
400	0.036	3508×10^{-8}	1.0×10^{4}	0.675	——
425	0.032	3697×10^{-8}	2.7×10^{4}	0.66	——
450	0.032	3842×10^{-8}	6.3×10^{4}	0.65	——

TABLE III. Conversion table from creep under constant stress at 200°C to stress relaxation at constant strain at 200°C.

t (sec.)	d_t/d_0	i_t/i_0 (calc.)	i_t/i_0 (obs.)
0.1	1.02	0.98	0.99
0.3	1.03	0.97	0.98
1	1.06	0.95	0.96
3	1.09	0.92	0.93
10	1.15	0.87	0.89
30	1.22	0.82	0.84
100	1.30	0.77	0.79
300	1.36	0.74	0.76
1000	1.44	0.70	0.71
3000	1.50	0.67	0.68

The strain is given by

$$e \cong \Delta x/AB,$$

where AB is the length of one side of the grain and is approximately equal to the average grain diameter (*G.S.*). Consider the region in the immediate vicinity of the boundary, we have

$$e = s/G_U,$$

where G_U is the unrelaxed rigidity. As these two strains must be equal, we get

$$\Delta x/(G.S.) = s/G_U,$$

and thus

$$v \cong s(G.S.)/G_U\tau,$$

whence we may estimate η from the following formula,

$$\eta = G_U\tau d/(G.S.). \tag{18}$$

We shall now estimate the coefficient of viscosity at 285°C where the internal friction is a maximum. The rigidity G_U of aluminum at room temperature is about 2.4×10^{11} dynes/cm². From Fig. 3 it can be shown that the rigidity G_U at 285°C is about 2.0×10^{11} dynes/cm². The average grain diameter of the aluminum wire used in the present study is about 0.03 cm. The thickness of the grain boundary is not known from experimental work. However, it is known that the forces between atoms in solids are of short range type, extending with appreciable intensity only over a few atomic distances.[11] In our present estimation, it is reasonable to consider d as of the order of magnitude of one atomic distance; thus for aluminum, we can take $d \cong 4$A. Thus we have

$$\eta_{285°C} = 2.7\times10^5\tau_{285°C}. \tag{19}$$

The natural period of oscillation at 285°C is 1.4 second. This is the period at which the internal friction is a maximum, when the time of relaxation τ associated with the grain boundary slip is comparable with the period of oscillation. Now we may consider that

$$\tau_{285°C} = P/8 = 0.18 \text{ sec.}, \tag{20}$$

thus

$$\eta_{285°C} = 4.8\times10^4 \text{ poise}. \tag{21}$$

The temperature dependence of τ can be determined through the heat of activation H. Thus we have

$$\tau_T \exp(-H/RT) = k, \tag{22}$$

where $H = 34{,}500$ calories/mole, and k is a constant which can be determined by the condition that at 285°C, $\tau = 0.18$ sec., thus

$$\tau_T = 9.2\times10^{-15}\exp(H/RT) \tag{23}$$

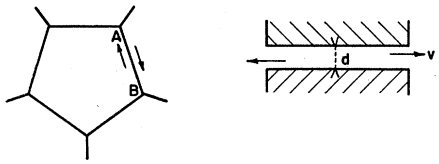
and

$$\eta_T = 1.2\times10^{-20}G_U\exp(17{,}250/T). \tag{24}$$

The values of η at different temperatures calculated according to this formula are shown in Table IV. It is seen that the coefficient of viscosity at the melting point of aluminum, 659.7°C, is 0.18 poise. And at 670°C, the coefficient of viscosity is 0.14 poise. This is of the same order of magnitude as the coefficient of viscosity of molten aluminum determined experimentally by Polyak and Sergee,[12] which has a value of 0.065 poise at 670°C.

TABLE IV. Estimated coefficient of viscosity of grain boundaries in aluminum as a function of temperature.

T (°C)	T (°K)	G_U (dynes/cm²)	η (poise)
25	298	2.4×10^{11}	2.2×10^{16}
100	373	2.3×10^{11}	2.1×10^{11}
200	473	2.1×10^{11}	1.3×10^{7}
285	558	2.0×10^{11}	4.8×10^{4}
350	623	1.9×10^{11}	2.0×10^{3}
450	723	1.8×10^{11}	43.0
550	823	1.7×10^{11}	2.2
660	933	1.5×10^{11}	0.18
670	943	1.5×10^{11}	0.14



a b

FIG. 11a. Equiaxed grains. 11b. Viscous slip along grain boundary.

CONCLUDING REMARKS

It is shown above that the four types of anelastic effects observed in polycrystalline

[11] See F. Seitz, *The Physics of Metals* (McGraw-Hill Book Co., New York, 1943), p. 108.

[12] E. V. Polyak and S. V. Sergee, Comptes rendus Acad. Sci. U.S.S.R. **30**, 137 (1941).

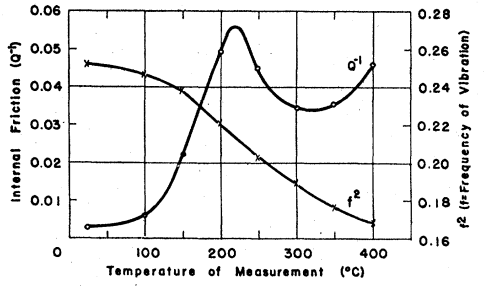


FIG. 12. Variation of internal friction and rigidity in polycrystalline magnesium (frequency of vibration = 0.5 cycles per second at room temperature).

aluminum have their origin at the grain boundaries. These effects are linear with respect to stress and strain and satisfy the inter-relations derived on the basis of the superposition principle within experimental error. We can infer that the microscopic mechanism causing these effects should obey relations which are linear in stress and strain components. The proposed microscopic mechanism is that the grain boundaries in metals behave in a viscous manner. The microscopic relations concerned with such a microscopic mechanism are linear in stress, strain, and their time derivatives.

The concept of a viscous grain boundary is quantitatively substantiated by the following findings:

(1) The maximum amount of shearing stress relaxation is polycrystalline determined by the four types of anelastic measurements is about 33 percent. This is in good agreement with the theoretical value of 36 percent calculated by assuming the grain boundary to be viscous.

(2) The estimated value of the coefficient of viscosity for the grain boundary is of the same order of magnitude as the experimentally determined value of the molten metal at the same temperature.

In order to show that the anelastic effects reported above are not peculiar to polycrystalline aluminum, similar measurements have been done for polycrystalline magnesium. The 99.97 percent magnesium used in the investigation was kindly supplied by the Dow Chemical Company in $\frac{1}{8}''$-rod, extruded at a die temperature of 260°–282°C at a speed of 5 ft/min. The rod was annealed at 450°C for one hour. An average grain diameter of about 0.02 cm was obtained by such a heat treatment. The internal friction and dynamic rigidity of this rod were measured at and below 400°C down to room temperature. The apparatus used for measurement is similar to that shown in Fig. 1a, except that the clamps used for holding the specimen are more rigid and the rotational inertia of the torsional bar is much larger. The frequency of torsional vibration is, in the present case, about 0.5 cycle per second at room temperature. The variation of internal friction and rigidity with temperature is shown in Fig. 12. It is seen that these curves vary in a similar manner as in the corresponding case of aluminum, indicating that the viscous behavior of grain boundaries is common to all metals.

ACKNOWLEDGMENT

The author wishes to express his deep appreciation of the active interest taken in this problem by Dr. Clarence M. Zener, without whose stimulating suggestions and discussions this investigation could not have been carried out. Thanks are also due to Dr. Cyril S. Smith, Director of the Institute, for discussions on metallurgical problems and suggestions especially during the preparation of the manuscript. Acknowledgment for help is here made to almost every member of the Institute.