the energy involved in reversing in succession two neighbor spins. From (7) the average energy to reverse the first spin is

$$\Delta E_1 = 2JSz. \tag{64}$$

The average energy to reverse the second spin, in the presence of the reversed first spin, is

$$\Delta E_2 = 2J(Sz-1). \tag{65}$$

Thus in (59a) we replace

$$2g\beta H_E = \Delta E_1 + \Delta E_2$$
$$= 2J(2Sz-1), \tag{66}$$

and now the result differs from (29) by the factor

$$\xi_0 = \frac{2Sz}{2Sz-1}. \tag{67}$$

This is equivalent to the exchange-interaction correction of Sec. III, Eq. (40), in the constant-denominator approximation $\eta = 1$.

The η correction cannot be obtained easily from Van Vleck's method. This is because the state with a spin reversed is not an eigenstate of the entire exchange Hamiltonian, but only of the $S_i{}^z S_j{}^z$ portion. Therefore the improvement embodied in (66) replaces the molecular-field approximation by an Ising model. The correct energy denominator, as exhibited by the spin-wave calculation, has an additional fluctuating term.

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Time-Dependent Internal Friction in Aluminum and Magnesium Single Crystals*†

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Magnesium and aluminum single crystals subjected to varying amounts of oscillatory strain of audio frequency have been investigated by measuring the strain amplitude-dependent complex dynamical-mechanical modulus at audio frequencies as a function of temperature and time. If the amplitude of the applied excitation exceeds a critical breakaway strain, an excited mechanical state is manifested in a modification of the amplitude dependence of the complex modulus. Upon cessation of the excitation, the excited state decays. The decay following short excitation times obeys a $t^{\frac{1}{2}}$ law, becoming a $t^{\frac{1}{3}}$ law as excitation approaches saturation. The short excitation decay rate is found to be governed by an activation energy in the range of 7–10 kcal per mole.

The time dependence is considered to be caused by the dispersal and condensation of a pinning atmosphere which has high diffusivity and is easily dispersed by a dislocation segment undergoing pinning interactions with the atmosphere.

INTRODUCTION

THE literature relating to nonlinear mechanical behavior of metal single crystals has increased steadily ever since Read's[1-3] early experiments and his interpretation of the amplitude dependence of internal friction and Young's modulus in terms of the motion of dislocations. It was early recognized that amplitude dependent internal friction measurements also showed marked time dependence.[1-6] At temperatures well below the recrystallization temperature, rapid recovery of internal friction occurs following deformation of metal single crystals (Koester effect, after Nowick[7]) and is attributed to the redistribution of dislocation lines.

The following is a study made of a time-dependent phenomenon in amplitude-dependent internal friction and modulus measurements of aluminum and magnesium single crystals resulting from controlled oscillatory deformations.

EXPERIMENTAL TECHNIQUE

A resonant bar technique is used to measure the decrement and effective Young's modulus of 16 cm long

[1] T. A. Read, Phys. Rev. **58**, 371 (1940).
[2] T. A. Read, Trans. Am. Inst. Mining Met. Petrol. Engrs. **143**, 30 (1941).
[3] T. A. Read and E. P. T. Tyndall, J. Appl. Phys. **17**, 713 (1946).
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[5] A. S. Nowick, Symposium on Plastic Deformation of Crystalline Solids, Office of Naval Research, 1950 (unpublished).
[6] T. A. Read (quoted in discussion to reference 5).
[7] A. S. Nowick, J. Appl. Phys. **25**, 1129 (1954).

single crystals of aluminum and magnesium. By means of a telephone-type electromagnetic exciting and pick-up unit longitudinal fifteen kilocycle standing waves are induced in the bar. Force coupling between bar and electromagnet is provided by thin magnetic disks cemented to the end of the bar. The electromagnetic system is calibrated piezoelectrically.[8]

All single crystals used in these experiments were grown by the Bridgman method in graphite crucibles. Four magnesium crystals, Mg D-1 to Mg D-4, were donated by the Dow Chemical Company. Zone-refined aluminum specimens, ZR Al-1, ZR Al-2, were made from four nines pure aluminum samples donated by the Aluminum Company of America. The as received crystals are designated as 4–9 Al-1 and 4–9 Al-2. The zone-refined samples were given about 40 zone passes in a carbon boat by W. A. Tiller of the Westinghouse Research Laboratories. Residual resistivity measurements of sections of these specimens have been measured by A. F. Kip of the University of California, Berkeley. These measurements indicate that the zone refining lowered the impurity level only by a factor of 3 to 5. End sections one cm long were subjected to x-ray crystal perfection analysis by L. F. Vassamillet by observing the width and fine structure of the Bragg reflection spots using modified double crystal spectrometry.[9] The dislocation density deduced from these measurements was $4 \times 10^7/cm^2$. No detectable change in the structure of the Bragg spot was noted until temperatures exceeding 200°C were reached. Annealing at 300°C for 5 hours showed strong breakup of the spot into many small lines indicating the onset of polygonization.[10]
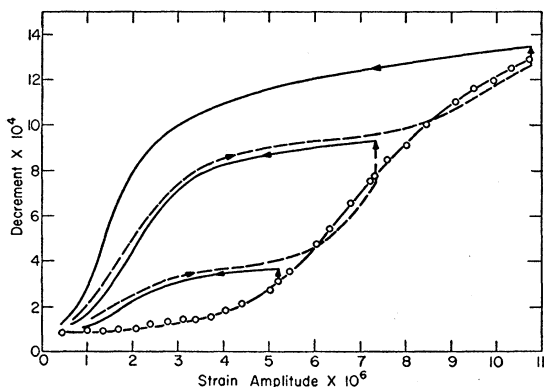

FIG. 1. Time effects in the measurement of decrement as a function of strain amplitude. Vertical lines correspond to oscillation at given amplitude for 20 minutes. Full and dashed curves correspond to measurements made while the strain amplitude was decreasing or increasing, respectively. Sample 4–9 Al-2; $T = 60°C$.

[8] For further details see R. H. Chambers, Carnegie Institute of Technology thesis, 1957 (unpublished).
[9] Lambot, Vassamillet, and Dejace, Acta Met. 1, 711 (1953) and 3, 150 (1955).
[10] L. F. Vassamillet and R. Smoluchowski, J. Appl. Phys. 30, 418 (1959).

TIME-DEPENDENCE DATA

It has been observed in some well-annealed metal single crystals that oscillation of strain amplitude in excess of certain amplitude S_B, termed the breakaway amplitude, disturbed the mechanical state of the crystal. The disturbance is manifested by the failure of the curve of decrement and modulus vs amplitude made by decreasing the amplitude to reproduce the curve made by increasing the amplitude. This type of behavior, analogous to multiple valued B-H curves encountered in magnetic experiments, has been called the hysteresis effect.[3,11] Early in an investigation of this effect in aluminum and magnesium single crystals, it was noted that the size of the hysteresis effect depended upon the speed with which measurements were made. Particularly at high strain amplitudes, hysteresis effects could be induced if measurements were not completed in seconds.

Figure 1 shows an example in which "measurements" at several amplitudes were continued for 20 minutes and the resultant decrement vs strain amplitude curve quickly made for lower values of amplitude. It is seen that there is considerable change from the original plot in which a measurement of the decrement at a given strain amplitude was made "instantaneously" (1 to 2 sec per measurement). Figure 1 also shows that for amplitudes exceeding the amplitude at which the 20-minute "measurement" was made the instantaneous decrement curve is relatively unchanged by the lower amplitude oscillation.

Only by making measurements as quickly as possible, the hysteresis effect could be made to disappear. If a high-amplitude measurement was made too leisurely, however, and hysteresis noted, it was found that the original instantaneous curve could be reproduced several hours later. It became evident that some sort of "excited state" which affected the amplitude de-
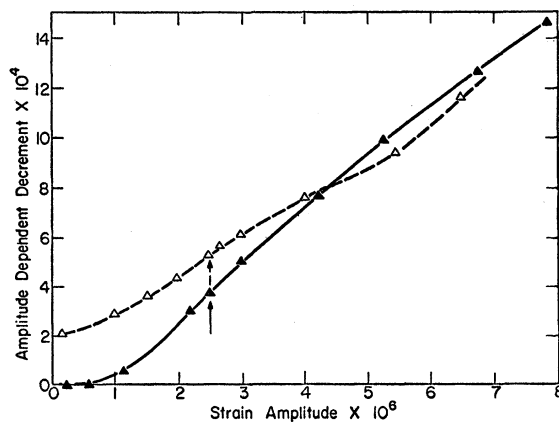

FIG. 2. Amplitude dependent decrement vs strain amplitude at 45°C. Full triangles—before excitation. Open triangles—after excitation for 20 min at $S = 2.5 \times 10^{-6}$. Sample ZR Al-1; $\delta_0 = 7.2 \times 10^{-4}$.

[11] A. Granato and K. Lücke, J. Appl. Phys. 27, 583, 789 (1956)

pendent behavior of the crystal for amplitudes less than the highest amplitudes previously encountered was created by the oscillation and that this state was decaying and finally disappearing in the order of hours.

A typical example of the reproducibility of this excited state is given by the behavior of an aluminum single crystal, which, after remaining in the apparatus for several months, was first measured instantaneously, then oscillated for 20 minutes at a maximum strain amplitude of 7×10^{-6} and rested for 24 hours, measured instantaneously, oscillated again, etc., for a total of fifteen such cycles without significant changes in the instantaneous decrement vs amplitude curve. Further investigation showed that this cycle could be reproduced apparently indefinitely.

Figures 2 through 5 represent the results of a set of time-dependent experiments on the specimen ZR Al-1. The specimen was annealed in $situ$ at 150°C for 100 hours and brought slowly to room temperature; the amplitude independent or initial decrement δ_0 was 4.5×10^{-4}, and the maximum strain amplitude at which the decrement becomes strongly amplitude dependent or the breakaway amplitude S_B is 1.5×10^{-6}. The temperature was increased to 45°C, and measurements were made of the decrement and resonant frequency vs strain amplitude (Figs. 2, 3). The solid triangles represent data taken "instantanesouly," and the open triangles are points taken after the crystal was oscillated at $S = 2.5 \times 10^{-6}$ for 20 minutes, hereafter called the $excitation$ $period$. The decrement at the excitation amplitude increased, and the resonant frequency dropped as indicated by the arrows. At the end of the excitation period, measurements were taken as the amplitude was lowered giving the triangle points; then the amplitude was increased and the rest of the points taken. The large increase in the zero amplitude decrement and frequency change as well as the slight depression of the decrement above the excitation amplitude should be noted.
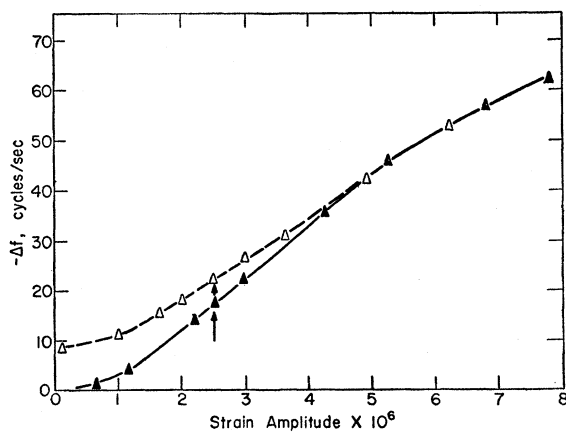

FIG. 4. Amplitude dependent decrement vs strain amplitude at 115°C. Full dots—before excitation. Open triangles—after excitation for 20 min at $S = 2.5 \times 10^{-6}$. Full square—immediately after measurement at $S = 5.0 \times 10^{-6}$. Sample ZR Al-1; $\delta_0 = 16.3 \times 10^{-4}$.

Figures 4 and 5 are corresponding curves taken at 115°C. The zero amplitude decrement and frequency change have become larger; the excited state is evidently decaying rapidly as can be seen by comparing the triangle points with the measurement (designated by the squares) made within several seconds after cessation of the excitation. The depression of the decrement is evident. The large change in the zero amplitude decrement and modulus following excitation was characteristic of the zone-refined material.

The following set of experiments was performed in an attempt to characterize more fully the nature of the excited state and the subsequent decaying state. The specimen was first annealed in the apparatus at 400°C for 24 hours, then slowly (~ 5°C/hr) cooled to room temperature, and finally held at the desired measuring temperature until no change was detected in the amplitude independent or zero amplitude decrement.

FIG. 3. Change of resonant frequency vs strain amplitude at 45°C. Full triangles—before excitation. Open triangles—after excitation for 20 min at $S = 2.5 \times 10^{-6}$. Sample ZR Al-1.
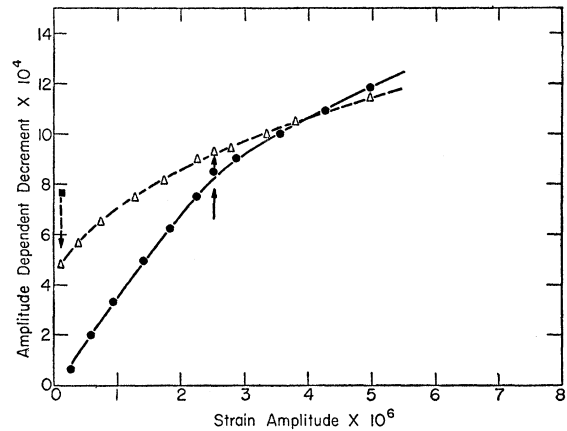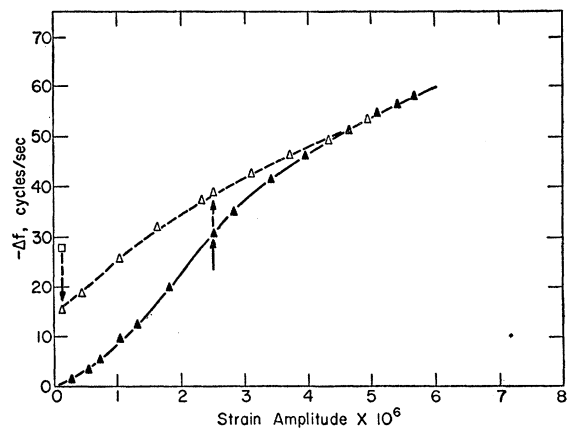

FIG. 5. Change of resonant frequency vs strain amplitude at 115°C. Full triangles—before excitation. Open triangles—after excitation for 20 min at $S = 2.5 \times 10^{-6}$. Open square—immediately after measurement at $S = 5.0 \times 10^{-6}$. Sample ZR Al-1.
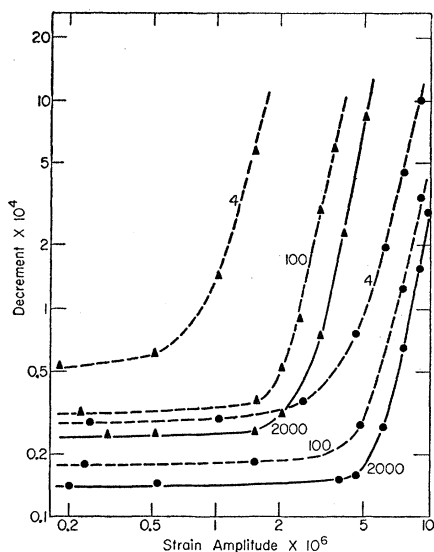
FIG. 6. Instantaneous decrement vs strain amplitude as a function of time. Numbers indicate time in minutes after end of 20 min excitation period. Dots—29°C; triangles—60°C. Sample 4–9 Al-1; $S \approx 10^{-5}$ during excitation.

This treatment resulted in the lowest zero amplitude decrement observed in these experiments. Next, an instantaneous decrement and modulus vs strain amplitude curve was run. At high amplitudes where it was difficult to make a measurement fast enough or when the crystal was mistakenly oscillated for too long a period, measurement of the next higher point was delayed for several hours. Instantaneous curves taken this way were reproducible day after day. The crystal
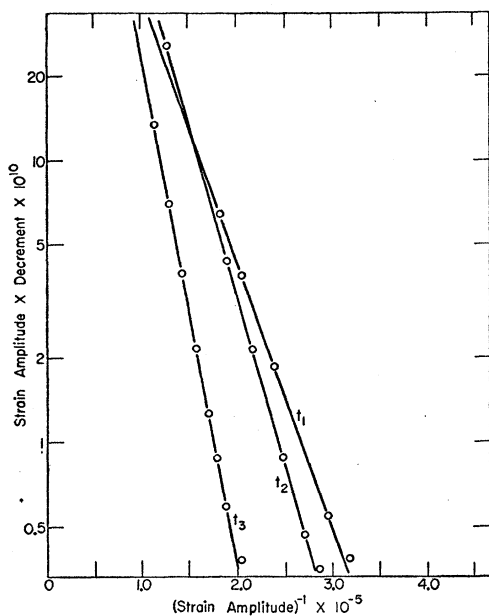

FIG. 7. Granato-Lücke plot of amplitude dependence as a function of time after start of decay at 60°C. $t_1 = 12$ min, $t_2 = 15$ min, $t_3 = 60$ min. Sample 4–9 Al-1.

was then oscillated for a given time period at a high strain amplitude ($S \sim 10^{-5}$). At selected times after the end of the excitation period, instantaneous measurements were made tracing out the amplitude dependence of the decrement and modulus as the decay proceeded. These measurements were continued until the original instantaneous curve was obtained. In Fig. 6 an example of this type of measurement is shown. The specimen was 4–9 Al-1, and Fig. 6 records just three of ten curves made at the temperatures 29° and 60°C. Very little change was observed beyond 2000 minutes in the decay sequence.

Figure 7 is a plot of $\log S\delta$ vs $1/S$ (Granato-Lücke[11] plot) of part of the decay sequence taken at 60°C and shown in Fig. 6. It is found that the slopes A of all of these curves decrease monotonically, the curve taken
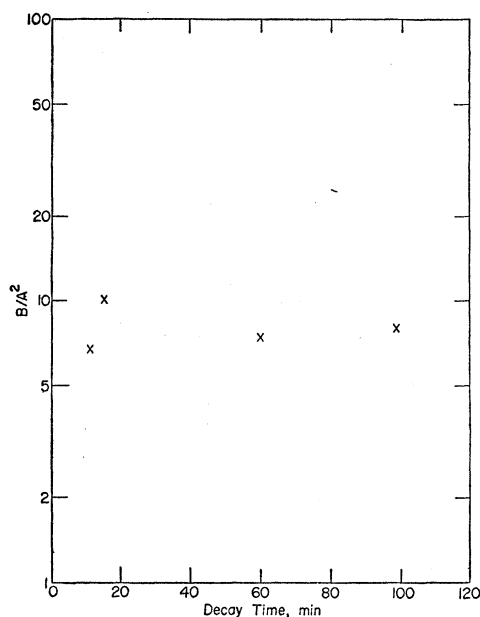

FIG. 8. B/A^2 (as defined) vs time after start of decay at 60°C. Sample 4–9 Al-1.

at 2000 minutes having the largest A. Figure 8 shows that the quantity B/A^2 (B is the intercept of the line with the ordinate) remained approximately constant during the decay sequence.

Figure 9 represents the results of another experiment to determine both the form of the decay law and the effect of different excitation periods on that law. Crystal 4–9 Al-2 received the same annealing in $situ$ as previously mentioned. Constant strain amplitude and temperature were maintained throughout the experiment. A short excitation period of two minutes was first made while recording the rise in decrement and decrease in resonant frequency every 30 seconds. The decrement followed the open circles starting from the zero time point indicated by a small solid circle. Following this excitation period, measurements were made
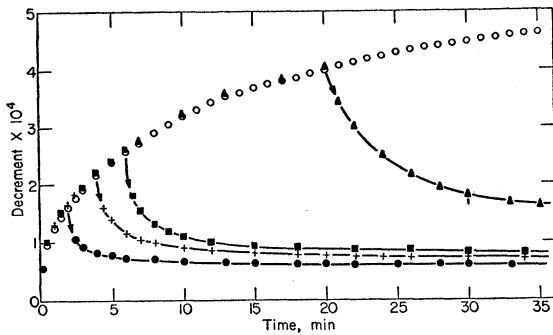
FIG. 9. Decay of decrement as a function of time at 60°C. Constant excitation amplitude. Decay measured at same amplitude. Excitation time: dots—2 min; crosses—4 min; squares—6 min; triangles—20 min. Sample 4–9 Al-2.

instantaneously at frequent intervals. The time constant of the crystal response when the decrement was greater than 10^{-4} was such that rapid measurement could be made. The decay measurements following the two-minute excitation are recorded in Fig. 9 by solid circles. The decay was then followed until the decrement returned to the original value. Following the decay by recording the resonant frequency has been done; but since the decrement is of the order of 100 or 1000 times less sensitive to temperature changes than is the resonant frequency, the easiest measure to use was the decrement. Enough evidence has been obtained during fortunately stable thermal circumstances to show that modulus time dependence parallels that of the decrement.

By extending the excitation periods to longer times and recording the corresponding decays, the remainder of Fig. 9 was obtained. In all cases the excitation curves tend to saturate; runs of three hours and longer show very little measurable rate of change in the rise of the
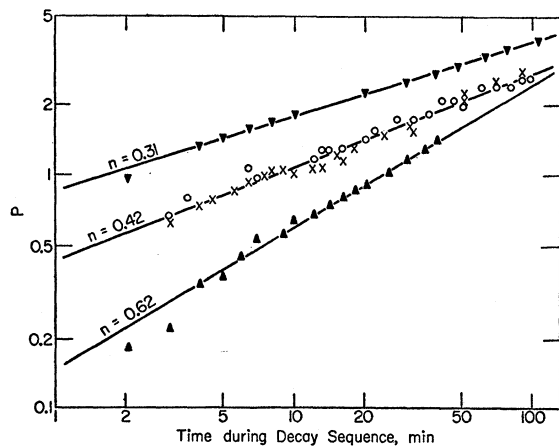

FIG. 10. Quantity P (as defined) vs time of decay. Triangles (upper plot)—excitation time 5 min, $T=40°C$. Sample 4–9 Al-1. Triangles (lower plot)—excitation time 150 min, $T=40°C$. Sample 4–9 Al-1. Open dots—excitation time 20 min, $T=30°C$. Sample Mg D-1. Crosses—excitation time 20 min. $T=30°C$, Sample Mg D-2.
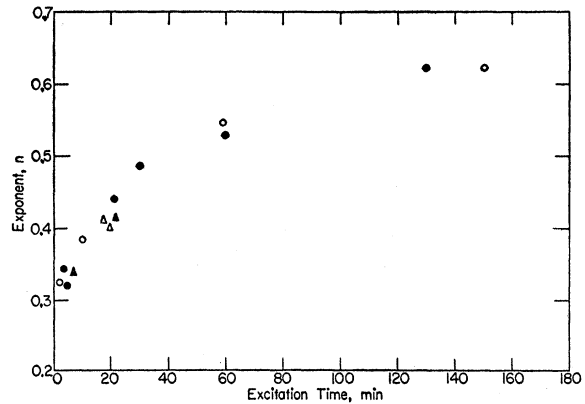

FIG. 11. Exponent n [Eq. (1)] as a function of excitation time. Dots—$T=40°C$, $S=1.5\times10^{-6}$ (open—Sample 4–9 Al-1, full—Sample 4–9 Al-2). Triangles—$T=30°C$, $S=1.5\times10^{-6}$ (open—Sample Mg D-1, full—Sample Mg D-2).

decrement. The reproducibility of the rise in decrement for longer excitation periods should be noted.

Figure 10 is a plot of the quantity P defined as $P=-\ln(\delta-\delta_0)/(\delta_1-\delta_0)$ vs time during the decay sequence. δ_0 is the initial decrement; δ_1 is the maximum decrement reached at the end of the excitation period. It is seen that such a plot shows good straight lines indicating that the decay follows the relation

$$\delta-\delta_0=(\delta_1-\delta_0)\exp(-\beta t^n). \qquad (1)$$

Figure 11 indicates that the power n of the time dependence is a function of the length of the excitation period ranging from about $\frac{1}{3}$ for short five-minute excitations to about $\frac{2}{3}$ for periods extending to saturation.

Figures 12 and 13 show that β in (1) is inversely proportional to the strain amplitude and directly proportional to the quantity

$$(D/RT)^{\frac{1}{2}} \quad \text{where} \quad D=D_0e^{-Q/R} ,$$

for the decay following short excitation times. The Q for the decay process appears to be 7 to 10 kcal/mole
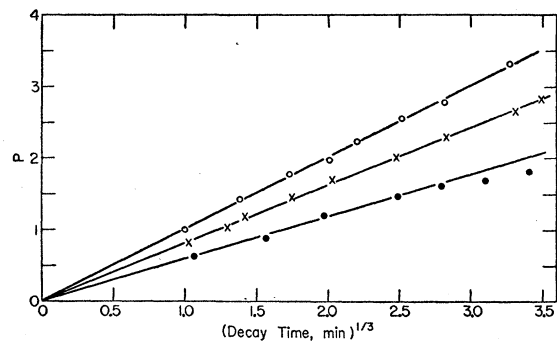

FIG. 12. Influence of strain amplitude on the time dependence of quantity P (as defined). Isothermal decay sequence measured at different strain amplitudes following 10 min excitation. Relative strain amplitudes: Open dots—$S=15$; crosses—$S=20$; full dots—$S=25$. Sample 4–9 Al-1.
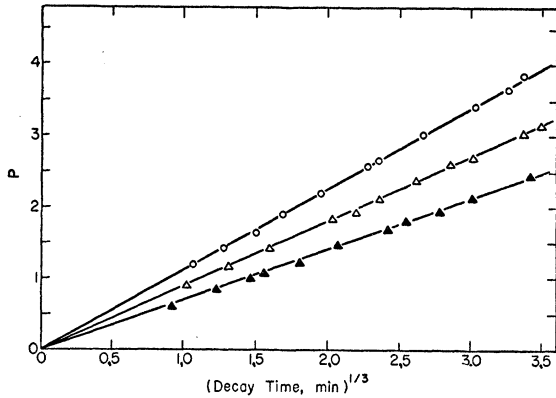
FIG. 13. Influence of temperature on the time dependence of quantity P (as defined). Decay at each temperature measured at same strain amplitude after having been excited for 10 min. Open dots—$T=82°C$; open triangles—$T=60°C$; full triangles—$T=42°C$.

although this number is obtained from only four temperatures, three of which are included in Fig. 13.

DISCUSSION OF DATA

Oscillatory strain of amplitude S_E will be called the *excitation amplitude* if it is applied to a specimen for a time greater than the time (one to two seconds) necessary to make an instantaneous measurement. The following observations characterize the occurrence of time dependence noted during and following excitation.

A. Independent of the previous annealing history or temperature, as long as breakaway strain amplitude, S_B, can be observed, there is no change observed in the instantaneous curve of either modulus or decrement *vs* strain amplitude, if the excitation strain amplitude S_E is less than the S_B.

B. There is no influence of excitation on the modulus measured instantaneously at amplitudes greater than the excitation amplitude S_E. On the other hand, above S_E there does exist a slight depression of the decrement compared with the instantaneous curve measured in the same aplitude region before excitation.

C. If S_E is greater than S_B, the instantaneous curve of both decrement and modulus measured below S_B is increased, the increase being larger in crystals with smaller impurity concentrations.

D. The ratio of amplitude-dependent decrement to the fractional change in Young's modulus remains constant during excitation.

E. Excitation at very high amplitudes (the order of 10^{-5}) produces instantaneous amplitude-dependent curves that resemble instantaneous curves taken at a higher temperature.

F. There is little or no time nor amplitude dependence in freshly strained crystals. The time dependence begins to occur as the crystals begins to show strong amplitude dependence and hence a marked S_B. The

return of time dependence is thus accelerated by high-temperature anneal.

G. If there is no time dependence, there is no hysteresis effect; and if there is no hysteresis effect, there is no time dependence.

The decay following excitation at high amplitude is characterized by a sequence of Granato-Lücke plots[11] which show that the slope A of the straight lines in such plots increases monotonically with time while the quantity B/A^2 remains constant in time. Furthermore, the dependence of A on time during the decay following short excitation follows a $t^{\frac{1}{4}}$ law, approaching a $t^{\frac{1}{3}}$ law as excitation approaches saturation. Limited observations indicate that the decay rate following short excitations is increased by an increase in temperature as if the decay rate were governed by a diffusion activation energy in the range of 7–10 kcal per mole.

INTERPRETATION OF DATA

The Granato-Lücke[11] breakaway model is used to interpret the time-dependent data. This model assumes that the dislocation network in the single crystal consists of equal length sections of dislocations pinned down by point type imperfections at intervals along the network sections. Their model further assumes that amplitude dependence of the decrement and modulus results from the hysteretic depinning and repinning of the dislocation sections as the applied oscillating strain amplitude exceeds the critical amplitude S_B.

The model further deduces the following relation between amplitude-dependent decrement, $\Delta\delta$, and modulus, ΔM, as a function of maximum resolved shear stress, S,

$$\Delta MS = \Delta\delta S = Be^{-A/S}, \qquad (2)$$

where the constant A in their model is proportional to the concentration of pinning points on the network sections, and the function B/A^2 is proportional to the product ΛL_N^3 where Λ is the total length of dislocation line involved in the breakaway and L_N is the network length. The above product becomes equal to the fourth moment of the distribution of network lengths if such a distribution is considered to exist.

It can be easily seen that (2) may be written

$$\Delta M(t) = \Delta\delta(t) \doteq Be^{-KC(t)/S}, \qquad (3)$$

where $C(t)$ is the concentration of pinning points on the dislocation network sections at time t and K is a constant. If $C(o)$ is the concentration of pinning points remaining immediately after cessation of excitation, then

$C(t) = C(o) + C'(t)$ where $C'(t)$ is a function such that

$$C(o) = 0,$$

and

$$C(\infty) = \text{constant}.$$

Then (3) becomes,

$$\delta - \delta_0 \equiv \Delta\delta(t) = Be^{-KC(t)/S} = Be^{-KC(o)/S} \cdot e^{-KC'(t)/S}, \quad (4)$$

or

$$\Delta\delta(t)/\Delta\delta(o) = e^{-KC'(t)/S},$$

where

$$\delta_1 - \delta_0 \equiv \Delta\delta(o) = e^{-KC(o)/S}.$$

Now $C'(t) \propto (D/kT)^{\frac{2}{3}} t^{\frac{2}{3}}$ if the Cottrell-Bilby[12] strain aging relation is used; this relation is valid for describing the diffusion of impurities into dislocation lines from a cylindrically symmetrical atmosphere for early stages of aging. On the other hand, $C'(t) \propto (D/kT)^{\frac{1}{2}} t^{\frac{1}{2}}$ if a planar atmosphere is assumed.[13]

The following are two hypotheses that are useful in explaining the above data: (1) Breakaway is necessary to produce the time dependence, and (2) The disturbance produced by breakaway is such as to increase the number of long dislocation loop lengths over the number that should exist in equilibrium at a given temperature and set of impurity parameters. The number of long loop lengths can be increased by either decreasing the number of pinning points on the line or by redistributing those present on the line, or both. It can be seen from Figs. 6 and 7 that the original amplitude-dependent decrement curve, and therefore by the Granato-Lücke model, the original distribution of loop lengths is recovered when the breakaway process is stopped. From Fig. 8 it can be seen that during excitation and decay the fourth moment[11] of the distribution is unchanged. Observations B and C follow from hypothesis 1 because network lengths with either highly bound pinning points or a high concentration of pinning points will not have experienced breakaway and thus show no change in the response to increases in strain amplitude while network lengths with either loosely bound pinning points or lower concentration of pinning points will have experienced breakaway and hence by hypothesis 2 become progressively more likely to undergo breakaway for lower values of strain amplitude.

Since the pinning energies are generally only several times kT, it is probable that pinning is statistical in nature, that is, a particular pinning atom will spend its time jumping between the dislocation line and the

surrounding Cottrell atmosphere, and therefore the loop length distribution on each network length is always randomized.[14] Different network lengths, therefore, must be considered to have different concentrations of pinning points instead of different distributions of pinning points. From the above, then, the excitation time dependence can be considered to be due to the thinning of the Cottrell[15] atmosphere surrounding the longest network lengths in the distribution of network lengths. The decay following excitation results from the condensation of the atmosphere by diffusion back to the dislocation. The occurrence of the $t^{\frac{2}{3}}$ law [see Eqs. (1) and (4)] following excitations to saturation is suggestive of the Cottrell-Bilby strain aging relation.[12] This in turn suggests that the excitation to saturation has produced a thinning of the atmosphere which is extensive and possesses cylindrical symmetry, while the occurrences of the $t^{\frac{1}{2}}$ law following short excitation indicates a planar distribution of the atmosphere and subsequent diffusion of this planar atmosphere back to the dislocations.[13]

The very low activation energy for diffusion, 7 to 10 kcal/mole, indicates the atmosphere may be composed of nitrogen, hydrogen, carbon, or perhaps vacancies. The difficulty with the assumption of a gas atom is that a mobile imperfection probably produces little dilatation and, hence, will have a very small binding energy to a dislocation. A vacancy is in a unique position of being both mobile and able to produce a relatively strong interaction with a dislocation. It is believed, however, that vacancies are readily absorbed at jogs and thus removed from the pinning population in metals like aluminum and magnesium.

From the above arguments, the cause of the time dependence is considered to be a pinning atmosphere which has high diffusivity and can be dispersed easily by a dislocation segment undergoing pinning interactions with its atmosphere.

ACKNOWLEDGMENTS

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