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INTERNAL-FRICTION STUDY OF ALUMINUM ALLOY CONTAINING 4 WEIGHT PERCENT COPPER

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INTERNAL-FRICTION STUDY OF ALUMINUM ALLOY CONTAINING 4 WEIGHT PERCENT COPPER

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SUMMARY

A study has been made, by means of low-frequency internal-friction measurements in both torsional and flexural vibration, of aluminum (Al) alloy containing 4 weight percent copper (Cu) during aging. Both polycrystalline and single-crystal specimens exhibit an initial internal-friction peak at 173° C (for a frequency of 1 cps) after solution treatment and quenching. This peak shows all the characteristics of a Zener relaxation, including strong anisotropy. It falls on aging in a manner simply related to the decrease in the copper concentration of the matrix. The peak is also sensitive to the reversion of Guinier-Preston (G.P.) [1] zones.

The precipitation of the phase θ' is marked by the appearance of a second peak at 135° C (for a frequency of 1 cps) and by a rise in the high-temperature background internal friction. Both these contributions grow with kinetics similar to those for the precipitation of θ'. The second peak is associated specifically with the presence of the nonequilibrium phase θ'; it is reduced by the transformation from θ' to θ and is absent in specimens containing only the θ phase. The high-temperature background, however, is increased further by this transformation. Possible causes of the second peak and the background changes are discussed.

INTRODUCTION

Internal Friction and Anelasticity

Internal friction is often loosely described as the ability of a solid to damp out vibrations. More strictly, it is a measure of the vibrational energy dissipated by the operation of specific mechanisms within the solid. Internal friction arises even at the smallest stress levels if Hooke's law does not properly describe the static stress-strain curve of the material. The nonelastic behavior which Zener (ref. 1) has called anelasticity arises when the strain in the material is dependent on variables other than stress. A material showing the simplest kind of

anelasticity responds to a suddenly applied stress with an elastic strain followed by an anelastic strain which increases exponentially with time to a limiting value proportional to the applied stress. The rate at which the anelastic strain increases with time (a process called a relaxation) is measured conveniently by the time τ required for the completion of the fraction $1 - e^{-1}$ (about 63 percent) of the total anelastic strain. The magnitude of the anelastic behavior is measured by a quantity called the relaxation strength Δ which is defined as the ratio of the total anelastic strain to the elastic strain.

Important relaxations are produced in many alloys by atom movements which are induced by an applied stress, a process known as stress-induced ordering. Here the relaxation time τ is related intimately to the mean jump time of the affected atoms, and thus τ follows an equation of the form

$$\tau = \tau_o \exp(H/RT) \tag{1}$$

where τ_o and H are constants and R and T are, respectively, the gas constant and the absolute temperature. In some cases the enthalpy (heat) of activation H can be identified directly with an activation energy for diffusion, and the constant τ_o can be related to the preexponential constant D_o in the Arrhenius expression for the diffusion coefficient D.

For a given frequency of vibration f the temperature dependence of the internal friction of a material showing simple anelasticity may be predicted from formal theory (ref. 1) in terms of the parameters Δ and τ

$$\delta/\pi = \Delta \frac{\omega\tau}{1 + (\omega\tau)^2} \tag{2}$$

where δ is the logarithmic decrement, defined subsequently, and $\omega = 2\pi f$. When the internal friction (measured, e.g., by the rate of decay of free vibrations) is plotted against $1/T$ as abscissa, a symmetrical bell-shaped curve is obtained which is referred to as an internal-friction peak. Inspection of equation (2) shows that the peak occurs at the temperature T_p, for which $\omega\tau(T_p)$ is unity. Experimental measurement of the peak at one frequency enables numerical values to be obtained for Δ and τ at the temperature of the peak. If, in addition, a second different frequency is used, H and τ_o may also be obtained by calculation.

Two examples of anelasticity arising from stress-induced ordering are now presented. The first, which may be called the Snoek relaxation, is found in body-centered cubic metals containing interstitial solute atoms. The best known example is that of α-iron containing carbon. The carbon (C) atoms lie at the midpoints of the cube edges of the iron (Fe) lattice and cause a local distortion which is most severe along the cube edge joining the two nearest iron atoms. If the cube edges are taken as a set of axes X, Y, and Z, a given site for a carbon atom belongs to one of three groups, the X-, Y-, or Z-sites, according to which direction is that of greatest distortion when that site is occupied. Because of the very small solid solubility of carbon in α-iron, very few of the total possible sites can be occupied. Under zero stress the carbon atoms are randomly distributed and the total distortion along each of the X-, Y-, and Z-directions is the same. However, if, for example, the X-sites were occupied preferentially, an elongation would occur in the X-direction. Hence, from the thermodynamic reciprocity relations, application of a stress in the X-direction will cause the X-sites to become preferentially occupied through stress-induced movement of some of the carbon atoms. A detailed theory of this relaxation has been worked out in reference 2. The relaxation time is related simply to the mean atomic jump time of carbon atoms, the activation energy of the relaxation is that for the diffusion of carbon in α-iron, and the relaxation strength is directly proportional to the number of carbon atoms in solution, as shown experimentally by Dijkstra (ref. 3). The unique relationship between the concentration of interstitial atoms in solution and the relaxation strength made possible an important study of precipitation which will be mentioned later.

The second example of anelasticity caused by stress-induced ordering is found in several face-centered cubic substitutional solid solutions and is known often as the Zener relaxation. The atomic rearrangement which is responsible for this relaxation is not known fully. LeClaire and Lomer (ref. 4) have treated the relaxation in terms of a stress-induced change of short-range order in different nearest neighbor directions; this treatment appears to be an advance over the original hypothesis of Zener (ref. 5) in which the process was regarded as a stress-induced reorientation of nearest neighbor pairs of solute atoms. The experimental evidence concerning the relaxation is summarized as follows:

(a) There is at present no method for predicting definitely which alloys should show the Zener relaxation. An earlier suggestion of a correlation between the relaxation strength and the size difference of the solvent and solute atoms has not been substantiated.

(b) The relaxation strength is strongly dependent on the composition of the alloy. The experiments of Childs and LeClaire (ref. 6) on α-brasses indicated that the relaxation strength is proportional to the square of the concentration of zinc, while work on silver-zinc (Ag-Zn) alloys (ref. 7) led to the same conclusion.

(c) As a result of the strong concentration dependence, measurements have been made mainly on alloys containing in excess of 10 atomic percent solute.

(d) The half-peak width is generally only a little greater (3 to 20 percent) than that predicted for a relaxation having a single relaxation time (eqs. (1) and (2)).

(e) In the single instance where accurate measurements exist (ref. 8) the activation energy of the relaxation is close but not equal to that for lattice diffusion of either the solvent or solute atoms. Nowick's analysis (ref. 7) shows that differences are to be expected but does not explain the direction of the deviation observed.

(f) Following the procedure suggested by Wert and Marx (ref. 9) it is found for a standard frequency, usually chosen as 1 cps, that the absolute temperature of a Zener peak is directly proportional to the activation energy for the relaxation. The implication of this relationship is that the value of τ_o is very nearly the same for all Zener relaxations. Experimentally determined values of $\log \tau_o$ range from -14.0 to -15.2 (τ_o in seconds), with most values between -14.5 and -15.0. In the absence of a specific model from the relaxation, a relationship between τ_o and the appropriate D_o for diffusion cannot be calculated. However, accurate diffusion measurements in face-centered cubic substitutional solid solutions indicate a fairly constant value of D_o of about 0.3 cm^2/sec. This value of D_o, combined with the values of τ_o given above, indicates that the Zener relaxation is accomplished by relatively few atomic jumps, with one to three atomic jumps as a reasonable estimate.

(g) Nowick and Sladek (ref. 10) observed that the relaxation time for a silver-zinc alloy is decreased greatly by quenching from elevated temperatures. The same behavior was found also by Li (ref. 11) in a copper-aluminum alloy. An explanation has been advanced (ref. 10) in terms of the freezing-in of an excess of lattice defects (most likely single vacancies) which increase the mean atomic jump rate and hence cause the relaxation to occur more rapidly. During a low-temperature anneal the relaxation time of a quenched specimen increases, and measurements of this kind have been used to study the decay of the excess of lattice defects (ref. 12). The decay takes place in two stages, the first being much more rapid and having a slightly different activation energy than the second stage. Possible explanations of this behavior have been advanced in references 12 and 13.

Anelasticity of Precipitation Alloys

Both Dijkstra (ref. 14) and Wert (refs. 15 and 16) have made internal-friction studies of the precipitation of carbon and nitrogen from supersaturated solid solution in α-iron. Using the height of the Snoek internal-friction peak as a direct measure of the concentration of interstitial atoms in solution, quenched specimens were step annealed at one of a series of temperatures, and the height of the peak after each anneal was used to obtain the concentration remaining in solution. Dijkstra's work, dealing principally with the precipitation of nitrogen (N), revealed that certain aging temperatures and degrees of supersaturation led to the precipitation of two phases, one of which was Fe_4N. The other, called N phase 1, was not identified. The kinetics of the precipitation were explained qualitatively by the theory of nucleation and growth. Wert extended further the study of the precipitation of nitrogen and also made a more detailed study of the precipitation of carbon. No indication was obtained in this case of a precipitate other than Fe_3C. The activation energies obtained by plotting the time for a given fractional decrease in initial concentration against $1/T$ gave for both carbon and nitrogen values markedly lower than the precisely known activation energies for diffusion. Wert predicted and showed experimentally that the difference arose because the number of growing particles is not the same at different temperatures. Hardy and Heal (ref. 17) have emphasized the danger of ignoring this fact in calculating activation energies. Wert analyzed his results on the kinetics of precipitation with the semiempirical equation

$$u = \frac{c - c_\infty}{c_o - c_\infty} = 1 - \exp(-t'/\lambda)^m \tag{3}$$

where u is the fractional decrease in supersaturation, c is the concentration of solute remaining in solution after a growth time t', and c_o and c_∞ are, respectively, the initial and equilibrium solute concentrations. Both λ and m are constants. It may be noted that when $t' = \lambda$ the precipitation is 63 percent complete regardless of the value of m. When $t'/\lambda \ll 1$ (the range in which the equation is most strictly followed because of the absence of interference between neighboring particles), equation (3) becomes

$$u = (t'/\lambda)^m \qquad (t' \ll \lambda) \tag{3a}$$

Zener (ref. 18) has shown for the diffusion controlled growth of a precipitate particle in an infinite matrix that the exponent m is related

to the shape of the particle. This analysis can be applied also to a collection of widely dispersed (noninterfering) particles which are nucleated at the same instant. For precipitates in the form of flat disks, cylinders, and spheres, the value of the growth exponent m is, respectively, 5/2, 2, and 3/2. It should be noted, however, that if nucleation and growth are occurring simultaneously the value of m is increased by unity. Thus, for example, the simultaneous nucleation and growth of spheres could be confused with the simple growth of flat disks. Microscopic observations are clearly desirable to avoid possible confusion.

The result of Wert's analysis was that $m = 3/2$ for the precipitation of Fe_3C and 5/2 for N phase 1. No incubation period was detected in these experiments, so the growth time t' was set equal to the aging time, and the shapes of the particles were therefore taken as spheres for Fe_3C and, in agreement with the microscopic observations of Dijkstra, (ref. 14) as disks for N phase 1.

The depletion of both carbon and nitrogen from cold-worked α-iron has been investigated by Harper (ref. 19) who found that for both elements the growth exponent m was changed to 2/3. This provided striking support for a theory of Cottrell (ref. 20) and Bilby (ref. 21) which predicted this exponent on the basis that depletion would occur by the formation of atmospheres of interstitial atoms around dislocations. Dijkstra (ref. 14) had noted earlier that a sample of cold-worked α-iron containing nitrogen showed no microscopically observable precipitate even when the nitrogen internal-friction peak had fallen to the equilibrium value.

Other investigations of precipitation by anelastic methods have been confined so far to aluminum-based alloys, with the exception of the work of Ang, Sivertsen, and Wert (ref. 22) on gold-nickel (Au-Ni) alloys. The equilibrium diagram of this system shows complete solid solubility at high temperatures. At lower temperatures a miscibility gap exists across virtually the whole of the diagram and a high-temperature face-centered cubic solid solution breaks down on slow cooling into two other face-centered cubic solid solutions of different lattice parameters, one rich in gold, the other rich in nickel. Two unstable internal-friction peaks were observed in solution-treated and quenched alloys of several different compositions. For the Au alloy containing 30 atomic percent of Ni the peaks occurred at 250° C and 400° C at a frequency of approximately 1 cps. The peak at 400° C was identified tentatively as a Zener peak and was found to decrease on aging with the kinetics of the decomposition of the quenched phase. In contrast to the high-temperature peak, the height and position of the low-temperature peak were found to be dependent on the quenching temperature, and the peak was not found in specimens quenched from just inside the miscibility gap. Further, this peak annealed out much more rapidly than the 400° C peak and disappeared completely before

resistivity measurements or microscopic examination revealed the start of precipitation. While no explanation for the origin of this peak was advanced, it provides another illustration of the sensitivity of internal friction to the condition of an aging alloy.

In the field of aluminum-based alloys, an investigation (ref. 23) was carried out on Al alloy containing 39 weight percent of Zn. No internal-friction peak was observed in this alloy. Precipitation occurs in a discontinuous manner, and the anelastic behavior was explained in terms of coupled relaxations (ref. 2) across the new interfaces produced by precipitation. Damask and Nowick (ref. 24) did find a peak in the Al alloy containing 20 weight percent of Ag. During aging following solution treatment and quenching the peak underwent four successive changes as follows:

Stage 1.- The relaxation time τ increased rapidly without a detectable change in the peak height. A significant change in τ was detected after 1.5 hours aging at 26° C. This stage was attributed to the annealing out of quenched-in vacancies.

Stage 2.- Stage 2 followed the completion of stage 1 and persisted up to about 2 hours at 165° C. During this stage no change occurred in the peak, and the structure of the alloy consists of clusters of silver atoms in a considerably depleted matrix.

Stage 3.- Stage 3 appears to be associated with the reversion of the silver clusters. The peak increased in height by about 50 percent as the peak migrated to slightly higher temperatures, and a hysteresis was observed between measurements after heating and cooling. This stage is complete after about 2 hours at 205° C.

Stage 4.- Stage 4 commences at about the same time as the intermediate precipitate γ' is detected by X-rays and consists of a fall in the peak height and a slight decrease in the peak temperature.

After rejecting the Zener relaxation as the origin of the peak, a new mechanism was proposed, based on the interaction of an applied stress with the local internal stresses around a precipitate particle. A discussion of this mechanism will be given subsequently, but in passing it may be remarked that some difficulties are encountered in describing the behavior of Al alloy containing 20 weight percent of Ag in terms of this mechanism.

Entwistle (ref. 25) has studied the early stages of aging in a variety of aluminum alloys, using apparatus with a very low level of external energy loss. Two small relaxations were detected after low-temperature (20° to 60° C) aging in the commercial alloy Duralumin, but

these were not found in the pure binary Al alloy containing 4 weight percent of Cu nor in several other binary alloys examined. The simplest alloy showing a relaxation akin to the major one found in Duralumin was a quaternary alloy of aluminum, copper, magnesium, and silicon. While a calculation shows that $\log \tau_0$ has a value associated with a relaxation by single atomic jumps ($\log \tau_0 = -15.0$), the activation energy has the strikingly low value of 13 kcal/mole, which is far too low for normal atom jumps in the substitutional solid solution, and is even lower than might be reasonably expected for diffusion down dislocations. No satisfactory interpretation of this value has yet been offered.

A preliminary study has been made by Kê on the alloys Al containing 0.5 weight percent of Cu (ref. 26) and Al containing 4 weight percent of Cu (ref. 27) using a torsion pendulum. A strongly amplitude-dependent "anomalous" peak was claimed to exist near room temperature in cold-worked Al alloy containing 0.5 weight percent of Cu after cooling from a recovery anneal of 1 hour at 300° C. (The solubility of copper in aluminum at 300° C is 0.45 percent weight.) It has been shown (ref. 2), however, that the effect is difficult to reproduce and that prior cold-working does not seem necessary.

In solution-treated and quenched Al alloy containing 4 weight percent of Cu, Kê obtained evidence for the existence of a peak at 200° C. This peak was not present after the specimen had been furnace cooled from 525° C. Kê concluded that the peak arose from viscous slip along grain boundaries, a phenomenon which he had previously studied extensively (refs. 28 to 30). The disappearance of the peak caused by precipitation during furnace cooling seemed readily explicable on the grounds that precipitation at the boundary prevents slip from occurring, a phenomenon again suggested from Kê's earlier work (ref. 30). In his last known publication on the subject (ref. 31) Kê claimed that upon isothermal aging at 200° C the peak first decreased, then increased, and finally (after about 10 days) fell again. An attempt was made to correlate this behavior with the microscopically observed condition of the grain boundaries. The present work shows that the peak does not originate from grain-boundary slip and hence invalidates the interpretation given to these results by Kê and later by Geisler (ref. 32).

More recently Maringer, Marsh, and Manning (ref. 33) have reported results on the internal friction of Al alloy containing 4.82 weight percent of Cu. Two maximums were found below 200° C in the internal-friction curve obtained on heating the solution-treated and quenched alloy, and both were interpreted as anelastic peaks arising from the stress-induced diffusion of copper atoms in solid solution. Maringer, Marsh, and Manning reported further that after aging a relatively fine-grained specimen of Al alloy containing 4.82 weight percent of Cu at 300° C for 17 hours the curve on heating showed a maximum at 400° C. This maximum was interpreted as the grain-boundary peak.

The present work is concerned with an investigation of the anelastic behavior of the Al alloy containing 4 weight percent of Cu. Since this work is far more extensive than that of previous workers, it is possible to obtain a clearer picture of the various phenomena that take place and to establish their origins. In particular, single crystals as well as polycrystalline specimens were used in order to show which, if any, of the effects observed were due to grain boundaries.

Structural Changes During Aging of Al Alloy Containing 4 Weight Percent of Cu

The purpose of this section is to bring together those findings of other workers on the structural changes during aging of Al alloy containing 4 weight percent of Cu which are of importance in the interpretation of the present results.

The phase in equilibrium with the terminal aluminum-rich solid solution is the intermetallic compound $CuAl_2$(θ phase). The structure of $CuAl_2$ was found by Friauf (ref. 34) to be of tetragonal symmetry with the parameters $a = 6.04A$ and $c = 4.86A$ and with four copper and eight aluminum atoms per unit cell. Bradley and Jones (ref. 35) confirmed these conclusions and gave more precise values of the lattice parameters for $CuAl_2$ containing 47 weight percent of Al. When Al alloy containing 4 weight percent of Cu is aged at temperatures below 300° C simple precipitation of the θ phase does not occur. Instead, one or more of three other structures may be produced, depending on the aging temperature.[1] Current knowledge of these structures (ref. 17) is summarized as follows:

(1) The G.P. [1] zones: It was discovered independently by Guinier and Preston in 1938 that room-temperature aging of single crystals causes the appearance of scattering streaks (non-Braggian reflections) on Laue transmission photographs. The cause of the streaks was given as the modulation in interplanar spacing and scattering power arising from a local enrichment in copper of small areas distributed on the {100} planes of the matrix. These areas are now called G.P. [1] zones. At room temperature the zones are detected after 5 hours of aging and reach a constant condition in a few days, after which no further change has been detected. The thickness of the zones was estimated to be about 2 atom distances (8A) and the diameter after room-temperature aging to be somewhat less than 50A

[1]The views presented here are principally those of Guinier, Preston, Silcock, Heal, and Hardy. However, Geisler's opinion (ref. 36) is that G.P. [1] zones are structurally perfect θ' plates which are too thin to cause normal diffraction.

(ref. 37), although the zones attain larger diameters at higher aging temperatures. Using these figures and the further estimate that 10 percent of the total available copper segregates in zones having one copper atom to four aluminum atoms, Preston (ref. 38) concluded that the fully formed zones were scattered about 200A apart in the matrix. The insensitivity of the lattice parameter to the formation of G.P. [1] zones is the basis for the suggestion that the fraction of the total available copper atoms which segregate to the zones is fairly small.

Use of the more recent X-ray technique of small-angle scattering has supported the general picture given above. Gerold (ref. 39) has made quantitative comparisons of the measured intensity of small-angle scattering with that predicted from a variety of possible models. He concluded that the most satisfactory agreement was obtained with a model containing a single plane of exclusively copper atoms with neighboring closely spaced planes of aluminum atoms and in successive planes a decreasing disturbance of the normal interplanar spacing extending to the 16th plane on either side of the plane of copper atoms.

(2) The G.P. [2] or θ'' structure: This structure was first discovered by Guinier (ref. 40) in specimens which had been aged at room temperature and then heated for several days at 100° C or for some hours at 150° C. Guinier found that the G.P. [1] streaks developed intensity maximums along their length and resolved ultimately into four diffuse spots. The structure responsible for these spots was termed θ'' by Guinier and later G.P. [2] by Hardy. The appearance of the spots suggests that the G.P. [2] structure forms in thin plates parallel to the {100} planes of the matrix. Guinier suggested that the G.P. [2] structure consists of copper-enriched regions where ordering has occurred, in the sense that copper-enriched planes alternated with impoverished planes in a regular or orderly sequence, the repetition occurring after every fourth plane.

The spacings between successive {100} planes in the c direction of the G.P. [2] unit cell have been given by Gerold (ref. 39) as 1.82A, 2.02A, 2.02A, and 1.82A, the smaller of the two spacings being the distance between a copper-rich plane and a neighboring plane. The sum of these spacings gives the c parameter of G.P. [2] as 7.68A, in agreement with that found by Silcock, Heal, and Hardy (ref. 41) for aging at 165° or 190° C, where G.P. [2] was the first structure detected. On aging at 130° C Silcock, Heal, and Hardy noticed, however, that the c parameter changed progressively on aging, from 8.08A to 7.68A, a result which led them to observe that since G.P. [1] preceded G.P. [2] in the aging sequence, G.P. [1] may serve as a nucleus for G.P. [2]. The question of whether the G.P. [2] structure is simply a more stable ordered array of G.P. [1] zones has apparently not been discussed. Silcock, Heal, and Hardy argue that G.P. [1] is essentially different from G.P. [2] on the grounds of the behavior of the c parameter mentioned above and also because of the

marked difference in the growth characteristics of the two structures (ref. 41).

(3) The θ' phase: The structure of this phase was subject to structure analysis by Preston (ref. 42) after its discovery in 1935 by Wassermann and Weerts (ref. 43). Preston concluded that the structure is slightly tetragonal but otherwise of the calcium fluoride (CaF_2) type, containing aluminum and copper in the proportion 2 to 1. The planes $\{100\}_{\theta'}$ match the planes $\{100\}_{Al}$ with $\langle 100\rangle_{\theta'}$ parallel to $\langle 110\rangle_{Al}$; the boundary across these planes is therefore coherent. Some loss of coherency must occur along the c axis of the θ' structure because of a difference in the interplanar spacing of θ' and the aluminum matrix in this direction. The precipitation of θ' phase in the form of platelets on the $\{100\}$ matrix planes is shown well in the photographs of Calvet, Jacquet, and Guinier (ref. 37).

Preston checked his proposed structure by comparison of the calculated and observed intensities of the diffraction spots and found good though not perfect agreement. Silcock, Heal, and Hardy (ref. 41) pointed out that the intensity discrepancies which do exist, together with the frequent appearance of an unexplained diffraction spot, reduce Preston's proposal to "a very good approximation" of the θ' structure on which they were unable to improve.

The work of Silcock, Heal, and Hardy (ref. 41) has established the general sequence of structures during aging as G.P. [1], G.P. [2], θ', and θ. No more than two neighbors in this sequence are known to coexist, and as the temperature of aging is increased progressively fewer of the structures are detected. Below roughly 165° C, G.P. [1] is the first structure detected, between 165° and 220° C it is G.P. [2], and above 220° C, the phase θ'. The temperature above which θ precipitates directly is probably in the range 350° to 400° C. It has been mentioned earlier that present evidence indicates that G.P. [2] is nucleated directly at temperatures above 165° C. At lower temperatures, where G.P. [1] is formed first, nucleation of G.P. [2] from G.P. [1] appears probable.

With regard to the possibility of the transformation of G.P. [2] to θ', Silcock, Heal, and Hardy have shown that θ' platelets, when formed subsequently to G.P. [2], have an initial thickness greater than that of G.P. [2], a fact suggesting that θ' can be formed by transformation of G.P. [2]. Guinier (ref. 44) has published results which bear on this point. For the three aging temperatures 150°, 180°, and 190° C he has given curves showing the variation in the amount of G.P. [2] and θ' as a function of aging time. The curves show that the amount of G.P. [2] first increases, reaching a maximum with the detection of θ', and then falls steadily as the amount of θ' increases. If the G.P. [2] structure

is not itself transforming to θ', these results require a gradual re-solution of G.P. [2] and a diffusion of copper atoms to other regions where the θ' phase is nucleated. Possibly calorimetric measurements would be of help in settling this question.

The kinetics of the precipitation of the θ' phase are known at various temperatures from (a) the X-ray work of Guinier (ref. 44) and of Silcock, Heal, and Hardy (ref. 41) who measured quantitatively the intensities of θ' spots during aging and (b) from the dilatometric studies of Lankes and Wassermann (ref. 45). A small contraction is associated with the development of the G.P. [1] and G.P. [2] structures, while a much greater expansion accompanies the precipitation of θ'.[2] (An expansion occurs because the predominant effect is the increase in lattice parameter of the matrix as copper is removed from solution.) Where comparison was possible between the X-ray and dilatometric methods, good agreement was obtained (ref. 44).

Guinier has produced convincing evidence that the θ' phase transforms allotropically to the θ phase (ref. 40). When precipitated directly at high temperatures, the crystallographic orientations of the θ particles are random. However, the θ particles produced by high-temperature annealing of the θ' phase show definite orientation relationships to the matrix, which Guinier has shown to be those expected from an allotropic transformation of the oriented θ' phase. There is little information on the kinetics of this transformation. For an aging temperature of 300° C, Calvet, Jacquet, and Guinier (ref. 37) detected θ' phase after 30 seconds, and later the spots became more intense. The θ phase was detected after 1 hour. On further aging the intensity of the θ' spots decreased, being just visible after 8 days and undetectable after 16 days, by which time the θ spots were well defined.

The only other topic requiring mention here is the phenomenon of reversion. As an example of reversion, a specimen aged to an increased hardness at room temperature reverts to the as-quenched hardness if it is annealed for a few minutes at 200° C. The X-ray photographs of Preston (ref. 46) show clearly that, after the anneal, the G.P. [1] zones formed during room-temperature aging have disappeared. The energy required to disperse the G.P. [1] zones has been obtained from specific-heat measurements, by Suzuki, for example (ref. 47). Reversion is expected when the temperature is raised either to a value above that at which particles that have formed become of subcritical size for stability or above that at which the structure is no longer even metastable (ref. 17).

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[2]It is difficult to reconcile these results with Geisler's opinion that G.P. zones are small platelets of θ'.

SYMBOLS

A,B	constants
A_n	amplitude of oscillation after n cycles
A_o	initial amplitude of oscillation
C	$(100)[010]$ shear modulus
ΔC	relaxation strength of the C modulus
C'	$(110)[\bar{1}10]$ shear modulus
$\Delta C'$	relaxation strength of the C' modulus
c	concentration of copper in solution
D	diffusion coefficient
D_o	preexponential constant for D
E	Young's modulus
ΔE	relaxation strength of Young's modulus
f	frequency of vibration
G	shear modulus of the specimen
ΔG	shear relaxation strength
H	enthalpy of activation
K	bulk modulus
ΔK	bulk relaxation strength
m	growth exponent
n	number of cycles
R	gas constant

S_{11}, S_{12}, S_{44} elastic constants of a cubic crystal

T absolute temperature

t time

t' growth time

U_s strain energy

U_T total energy

U_w potential energy of a weight

u fractional decrease in supersaturation

α, β, γ angles between axis of a single-crystal specimen and the three cube axes

Δ relaxation strength

δ logarithmic decrement

λ constant

σ Poisson's ratio

τ relaxation time

τ_0 preexponential constant for τ

ϕ orientation function

ω circular frequency of vibration

Subscripts:

f final

o initial

p peak

R relaxed

S specimen

t	after aging time t
U	unrelaxed
∞	equilibrium

APPARATUS

Torsion Pendulum

With the exception of a few experiments conducted in transverse (flexural) vibration, all the internal-friction results have been obtained with the torsion pendulum. This apparatus came into prominence through the researches of Kê and is the simplest and yet the most useful internal-friction apparatus which has been devised. Though various design modifications have been published (refs. 48 and 49), the present pendulum follows closely the description of Kê (refs. 28 and 50), with the additional feature of permitting tests in a vacuum.

The torsion pendulum requires specimens in the form of wires, usually 8 to 12 inches long and of approximately 0.030-inch diameter. The top end of the wire is clamped by a pin vise fastened rigidly to the top cap of a vertical tube furnace. A steel extension rod projecting from the bottom end of the furnace is fastened to the lower end of the wire by a second pin vise. The specimen, pin vises, and extension rod are located centrally down the vertical furnace tube. A steel crossbar and a concave mirror are attached to the projecting end of the extension rod. The moment of inertia of the crossbar (which may be varied by the addition of suitable weights) is chosen to give natural free torsional oscillations in the easily observable frequency range (i.e., 0.2 to 2.5 cps). Oscillations are excited or stopped by manual operation of a tapping key which makes and breaks the current energizing a pair of electromagnets appropriately placed to attract the ends of the magnetically soft crossbar. The amplitude of oscillation is observed on a galvanometer scale placed several meters from the specimen by means of a beam of light reflected from the concave mirror.

The measure of internal friction used in this report is the logarithmic decrement δ defined as

$$\delta = \frac{1}{n} \log_e \frac{A_o}{A_n} \tag{4}$$

where A_n is the amplitude of oscillation observed on the scale n cycles after the amplitude A_o. A strain amplitude of 10^{-5} in the specimen corresponds to the A_o value of 4 centimeters usually used. The frequency of oscillation f was determined with each internal-friction measurement by timing the period required for the execution of the n cycles.

To reduce the air-damping energy loss in the apparatus, tests were conducted in an atmosphere of helium at 10 millimeters pressure. The pressure dependence of internal friction, both in air and helium, is shown in figure 1 for a specimen of Al alloy containing 4 weight percent Cu vibrating at 1.95 cps at room temperature. The internal friction in helium is appreciably lower than that in air for pressures above 1 millimeter. The use of a high vacuum was found to be undesirable because of the large lag in the thermal response of the specimen upon changing the temperature of the furnace wall. The use of a 10-millimeter pressure of helium proved most effective in eliminating this lag while reducing the internal friction to one-third that observed at atmospheric pressure in air.

Because speed of operation is essential in studies of an aging alloy, the furnace was built with the minimum thermal capacity consistent with a maximum operating temperature of 520° C (i.e., a temperature in the α phase field of Al alloy containing 4 weight percent Cu). Heating rates of 30° C per minute were readily obtainable, and the cooling rate of the furnace was comparably high above roughly 120° C. Despite the fast heating rates used, trouble due to overshooting the temperature desired was avoided by the excellent performance of an electronic temperature controller of the proportioning type working from a control thermocouple placed very close to the noninductive furnace winding. The temperature of the specimen was measured by a second thermocouple placed within the furnace tube and close to the specimen. During the majority of measurements, the total temperature variation of the specimen did not exceed 0.5° C.

The temperature distribution within the furnace was investigated at at a series of temperatures, with the results shown in the following table:

Temperature, °C	Maximum temperature difference, °C, for -	
	Specimen 8 in. long	Specimen 12 in. long
150	1	2
205	2	3
265	2.5	2.5
367	3.5	6.5

Flexure Pendulum

In the course of this work it became desirable to test some of the torsion-pendulum specimens in flexural vibration and at approximately the same strain amplitude and frequency which were used in torsion. A search of the literature revealed nothing suited to this purpose, so a new apparatus, called the flexure pendulum, was designed and built. This apparatus was produced by simple modification of the standard torsion pendulum.

The important factors which must be considered in the design of a flexure pendulum will now be discussed. Observation of the tip of a transversely vibrating wire reveals that the vibration is nonplanar. The wire vibrates in an ellipse which undergoes an alternating change in eccentricity as the major axis of the ellipse alternates between two perpendicular planes. This complicated behavior arises even in an elastically isotropic wire if the specimen has a nearly but not exactly symmetrical cross section. The practical result of present importance is that a nonplanar vibration makes an internal-friction measurement extremely difficult. The easiest method of avoiding this behavior is by the use of a specimen which has considerable asymmetry of cross section, for example, a reed with a large width-to-thickness ratio. However, this solution was of no use in the present case where the object was to test in flexure the wire specimens used in the torsion pendulum.

The most suitable choice of the mode of transverse vibration appeared to be that in which the specimen is clamped at one end as a cantilever. The fundamental frequency of vibration in this mode is the lowest natural frequency attainable in any transverse mode. Even so, the wire specimens to be tested had frequencies too high to be measured visually, and it was therefore necessary to weight the end of the specimen to lower the frequency to the desired value. With the wire held horizontally, the addition of this weight caused an alarmingly large sag in the wire. Holding the wire vertically would, of course, remove the static bending strains imposed by the weight, but at the same time another very serious factor is introduced. For, when vibrating about a vertical axis, the total energy U_T in a position of maximum deflection is the sum of the strain energy U_S stored in the deflected specimen and the potential energy gained by weight U_W (assume a specimen of negligible mass). If ΔU_S is the energy lost during the next cycle of vibration, the observed decrement δ_{obs} is given by

$$\delta_{obs} = \frac{1}{2} \frac{\Delta U_S}{U_S + U_W} \tag{5}$$

However, the decrement of the specimen itself δ_S (as would be measured if gravity were zero) is

$$\delta_S = \frac{1}{2} \frac{\Delta U_S}{U_S} \tag{6}$$

Hence,

$$\delta_{obs} = \frac{U_S}{U_S + U_W} \delta_S \tag{7}$$

Calculation shows that $U_W >> U_S$, and hence vibration about a vertical axis leads to an observed decrement much lower than that of the specimen itself. Measurement of the correct decrement can be obtained if the specimen is held horizontally.

The way in which a planar vibration and a restricted static sag were obtained in horizontally mounted specimens is shown in the diagram of the flexure pendulum (fig. 2). Following the notation of figure 2, two identical specimens H are used. These are parallel and mounted in horizontal pin vises F, one above the other and separated by about 0.75 inch. The loading weight J is constructed of aluminum in two equal parts, and each part has a gripping flange of 2 millimeters width projecting from the inner side. The weight J is secured to the specimens by sandwiching the ends of the specimens between the flanges and tightening up the steel screws joining the two halves together. When viewed end on, there is a slit down the middle of J the width of which is equal to the diameter of the specimens. The static sag of this arrangement is acceptably small because of the much greater vertical bending stiffness of this system compared with that of a single specimen. A planar vibration is obtained in the direction shown because the bending stiffness in the horizontal plane is appreciably lower than that in the vertical plane.

The general form of the apparatus is shown in the lower drawing of figure 2. The torsion pendulum furnace G is mounted horizontally and the pin vises F join a hollow steel tube E which may be secured rigidly to the end of the furnace. The furnace is made vacuum tight by the cover D. The shaded areas are flat rubber gaskets. Windows at C and K permit light from the lamp A to shine through the tube E, the slit in the loading weight J, and the lens L. The low-power microscope N, fitted with a graduated eyepiece, is focused on the real image of the slit formed at M by the lens L. A green filter B reduces the light intensity to a comfortable level and removes chromatic aberration from

the image. Transverse vibrations are excited by means of an electromagnet acting on the steel screws in the loading weight J. This magnet (not shown in fig. 2) was located inside the furnace and was wound with glass-covered silver wire to withstand elevated temperatures. The hot junction of the measurement thermocouple was located between the two specimens.

Logarithmic decrement measurements were made in the same manner as that described for the torsion pendulum by observing one edge of the image of the slit vibrating across the scale of the graduated eyepiece.

To minimize the sag in the specimens, the weight J was reduced to the minimum value consistent with visual determination of the frequency. The particular conditions used are summarized in the following table:

Length of specimens, in.	8.0
Approximate diameter of specimens, in.	0.035
Loading weight, g	3.00
Approximate frequency, cps	3.0
Maximum strain amplitude at start of measurement	10^{-5}
Atmosphere	
Helium at pressure, mm, of	10

Compared with the torsion pendulum, the flexure pendulum has several disadvantages. Twin specimens are required instead of a single specimen, and the error of measurement is larger (±5 percent for the mean of five readings). Eye fatigue became considerable when many measurements were taken, as was done to compensate partially for the poorer precision of a single measurement. The room-temperature damping of solution-treated and quenched Al alloy containing 4 weight percent of Cu (a measure essentially of external energy losses) was considerably higher in the flexure pendulum $\left(\delta_1 = 1.8 \times 10^{-3}\right)$ than in the torsion pendulum $\left(\delta_2 = 0.4 \times 10^{-3}\right)$. However, as tests showed that the value of δ_1 was reproducible, the results obtained from the flexure pendulum were considered to be ready for comparison with those from the torsion pendulum after subtraction of δ_2, $\delta_1 - \delta_2 = 1.4 \times 10^{-3}$.

Heat-Treatment (Quenching) Furnace

A well-insulated electric tube furnace with a 36-inch winding was built for the heat treatment of specimens. The furnace was mounted vertically and directly above a quenching bath, so that upon release a specimen dropped freely from the furnace into the bath.

A desired temperature could be maintained to within 1° C over several weeks by an electronic controller of the proportioning type. The maximum temperature difference over a 12-inch zone in the furnace was 3° C $\left(\pm 1\frac{1}{2}^{\circ}\ C\right)$.

Vacuum Furnace for Alloy Preparation

To insure freedom from gas porosity in the ingots and to help in maintaining the purity of the starting materials, a small furnace was built for melting, alloying, stirring, and casting aluminum alloys in a vacuum.

A steel channel, carrying an Alundum melting crucible and a split steel mold with its top normally downward facing the mouth of the crucible, was mounted vertically inside a stainless-steel furnace tube. The part of this tube containing the crucible was covered on the outside by a demountable electric furnace capable of raising the crucible to 850° C maximum temperature. The cool end of the tube remote from the furnace carried a simple rotary vacuum seal through which passed a steel shaft terminating in a graphite blade which could be lowered into the crucible and revolved to stir the melt. A delivery rod, extending from the cool end of the furnace tube to the mouth of the crucible, enabled a cold addition to be made to the melt. Upon releasing a catch from the outside of the furnace, the addition slid down the delivery rod into the crucible.

Casting was performed by inverting the furnace tube, which was pivoted in a frame. This caused the alloy to pour from the crucible over a graphite-lined runner into the preheated mold. After casting, the furnace was removed from the tube to allow more rapid cooling.

The furnace tube was evacuated by a rotary oil pump, and the pressure attained with the furnace in operation was 0.02 millimeter of mercury.

PREPARATION OF SPECIMENS

Materials

The purity of the starting materials is shown in the following table:

Metal	Purity, percent	Source
Al	99.99+	Aluminum Co. of Am.
		(Analysis, percent: Cu, 0.002; Fe, 0.001
		Si, 0.002; Mg, 0.000
		Na, 0.000; Ca, 0.000)
Cu	99.999	Am. Smelting & Refining Co.

Preparation and Composition of Polycrystalline Wire

The Al alloy containing 4 weight percent Cu was made in the vacuum furnace described previously. The metals were melted together in a new Alundum crucible at a pressure of 0.02 millimeter of mercury, and after thorough stirring the melt was cast into a steel mold yielding an ingot 5 inches long and 5/16 inch in diameter. Ingots were machined to 0.25-inch diameter and then homogenized at 450° C for one day. This treatment and later recrystallization anneals were carried out with the alloy wrapped in aluminum foil.

The ingots were cold-rolled and cold-drawn to wire of 0.062-inch and 0.033-inch diameter. An anneal of 1 hour at 400° C was given each time the cold-working amounted to roughly 50-percent reduction in area. The 0.033-inch-diameter wire was cut into 12-inch lengths for use in the torsion pendulum. The grain size of this wire after the final drawing was approximately 0.1 millimeter, but rapid and considerable grain growth occurred after recrystallization during the first solution treatment of several hours at 525° C. After this solution treatment the grains were larger than the wire diameter (i.e., about 1 millimeter), and the boundaries extended normally across the wire to form a bamboo structure.

A random sample of wire was submitted for chemical analysis, and the report gave the copper content of the wire as 4.08 weight percent.

Preparation of Single Crystals

After several failures, attempts were abandoned to grow long single-crystal wires by the strain-anneal technique. The first attempts to grow single crystals from the melt were also unsatisfactory because of the

porosity caused by gas pickup through the wall of the graphite mold. The more refined technique described below eliminated this trouble and several sound single crystals were obtained.

The molds used consisted of a 0.5-inch-diameter baked graphite rod 13 inches long with a central hole 0.064 inch in diameter drilled to a depth of 12.5 inches from one end. A length of 0.062-inch-diameter polycrystalline wire of Al containing 4 percent Cu was pushed down this hole, and the mold inserted into a long Pyrex tube closed at one end. The lower portion of this tube (containing the mold) was placed in a furnace at 750° C, and the upper open end, projecting from the furnace, was connected to a vacuum pump. In the course of a few minutes the glass flowed to form a tenacious skin over the mold which effectively excluded the atmosphere during the later growth of the crystal. Before removal from the furnace, the bottom of the mold was tapped vigorously against the furnace floor to insure that the molten alloy formed a continuous column inside the mold. The mold was then removed from the furnace and the superfluous length of glass tubing removed with a flame.

Single crystals were obtained by remelting the alloy in a vertical furnace at 750° C and then lowering the mold out of the furnace at a rate of 1.5 in./hr through a steep temperature gradient. Specimens were extracted from the mold by first breaking away the glass covering and then cutting and filing away the graphite. A 1-inch length was cut from each end of the specimens to remove the regions of worst segregation, and after etching and visual examination the specimens were electropolished to approximately 0.040 inch diameter. The electrolyte consisted of one part by volume of perchloric acid to five parts by volume of methyl alcohol. Polishing was conducted below 30° C and with a potential of 8 volts between the specimen and a graphite cathode.

The angles α, β, and γ, between the crystallographic axes (i.e., the cube edges) and the specimen axis were obtained from stereographic projections of X-ray back-reflection photographs. At least both ends of each specimen were X-rayed to verify the single-crystal condition of the specimen when this was indicated by etching. Data on the specimens grown from the melt are given in table I.

It will be noted that, in all cases where a single crystal was obtained, a [100] direction is closely parallel to the specimen axis. This suggests strongly that [100] is a preferred growth direction during freezing.

EXPERIMENTAL PROCEDURE

Except where noted later, specimens were solution-treated at a temperature of 525° C. The first solution treatment of specimens grown from the melt was prolonged as long as conveniently possible to reduce microsegregation. The time varied from a week to a month for different specimens. The period of first solution treatment of polycrystalline specimens was 1 day or longer, a time sufficient to stabilize the grain size. Subsequent solution treatments of all specimens were of overnight duration.

Solution treatments were carried out in the furnace described previously. For support inside the furnace and during quenching, specimens were placed along a flat surface filed down the length of an 1/8-inch-diameter steel rod and held in position there with a few turns of fine Nichrome wire. Specimens were quenched in water at room temperature, removed from the support, dried in acetone, and mounted in the torsion pendulum which was then evacuated to about 0.03 millimeter of mercury. During this period adjustments were made to the optical system to secure the optimum image on the galvanometer scale. Prior to the start of measurements the pump was stopped and a 10-millimeter pressure of helium admitted. No subsequent pressure adjustments were required during most runs, but for prolonged treatments the pendulum was pumped out briefly and the helium renewed once a day.

Runs were started 1/2 to 1 hour after quenching, and all aging treatments were given to specimens while they were mounted in the torsion pendulum. For prolonged aging treatments above 250° C the tensile stress on the wire was reduced between runs by removal of the inertia weights.

Crystals grown from the melt were X-rayed for a second time at the end of the investigation, with the results always the same as those given previously (table I).

EXPERIMENTAL RESULTS

Internal-Friction Behavior Without Intentional Aging - Initial Peak

As brief introduction, a summary is given below of some results for solution-treated and quenched specimens which were not aged except for the period at room temperature between quenching and testing and that unavoidably produced during measurement:

(a) An internal-friction peak exists at 185° C for a frequency of 2 cps. This will be called the "initial peak."

(b) The initial peak is unstable and decreases on aging but not rapidly enough to prevent useful measurements. When measurements are made on cooling from the range of 200° to 230° C, the symmetry of the peak indicates a virtually stable condition during the run.

(c) From about 240° C to at least 330° C the decrement rises sharply as the temperature is raised. The internal-friction contribution responsible for this behavior will be called the "high temperature background."

The feature of particular interest in these results is the initial peak. Inasmuch as temperatures above approximately 210° C are not required to trace out the peak, the minimum aging treatment which was unavoidable in determining the peak while decreasing the temperature therefore consisted of the delay at room temperature, the heating of the specimen to 210° C, which required about 5 minutes, and a stay at this temperature of a further 5 minutes to obtain the first reading. The peak obtained on subsequent cooling to room temperature will be called "the initial peak on first cooling."

The time required to cool from 210° C to the peak temperature, taking measurements at five temperatures on the way, was about 35 minutes, and some $2\frac{1}{2}$ hours were required to complete measurements down to room temperature. In view of the much longer time required to trace out the peak compared with that of the previous aging treatment (heating to 210° C with a stay of 5 minutes), it appeared unlikely that a completely stable condition would prevail during the run. Accordingly, some tests were conducted to assess the stability of the initial peak during the period of first cooling. Specimen 3 (table I) was used, and the results are shown in figure 3. Curve A is the initial peak on first cooling from 211° C. After completion of this run the specimen was rapidly reheated back to 211° C, pausing only for measurements round the top of the peak (curve B). Curve C is the peak on second cooling from 211° C. All measurements were made at a room-temperature frequency of 1.71 cps.[3] The 3-percent difference in peak height between curves A and B was taken as an indication of the stability of the peak during measurement of curve A below the peak temperature (183° C). The 7-percent difference in peak height between curves A and C was taken as an indication of the overall stability of curve A. This difference is in line with the estimate that during

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[3]Throughout this report, the frequencies quoted are those at room temperature (25° C) unless otherwise stated. Frequencies at any other temperature t below 200° C may be obtained from the relationship $f_t = f_{25}\left[1 - 0.00027(t - 25)\right]$.

measurement of that part of curve A above the maximum, the peak height does not fall by more than 10 percent, an estimate made from an inspection of the near symmetry of curve A (on a plot of logarithmic decrement against T^{-1}) and the assumption of a stable condition during measurement of the low-temperature side of the peak. It will be shown later that the height of the initial peak varies directly as the square of the free-copper concentration;[4] thus, during measurement of the peak on first cooling the free-copper concentration does not decrease by more than 5 percent. This result has a most important implication which it is convenient to discuss immediately.

During the period of 1/2 to 1 hour at room temperature between quenching and the beginning of a run, a specimen does not retain the as-quenched condition. From the results of Calvet, Jacquet, and Guinier, reference 37, for example, the Brinell hardness number rises from 56 immediately after quenching to 72 after 10 minutes at 25° C, to 82 after 1 hour, and to 96 after 4 days. The structural changes associated with this hardening are the production of G.P. [1] (ref. 41) and a reduction of the free-copper concentration. However, this structure is not retained on heating the specimen to 200° C for a few minutes, as shown, for example, by the results of Preston (ref. 46). The G.P. [1] zones dissolve and the free-copper concentration reverts to the total concentration of copper in the alloy. As this is the stage at which internal-friction measurements are started, the height of the initial peak on first cooling relates to a condition in which about 95 percent of the total available copper is randomly dispersed in the matrix. This conclusion is based on the assumption that at 210° C reversion is complete. If hardness is taken as a criterion, the observed return to the as-quenched value indicates reversion is truly complete even after the alloy has been fully aged at room temperature (ref. 38); it is to be recalled that internal-friction specimens were aged for only 1/2 to 1 hour prior to test. Further, Guinier was unable to detect G.P. [1] at room temperature directly after a reversion treatment (ref. 44). Finally, internal-friction measurements also confirm the completeness of reversion after room-temperature aging, for no detectable dependence of the height of the peak on first cooling upon the aging time at room temperature was found (up to 2 months of aging).

The stability of the initial peak is of considerable importance when consideration is given to the determination of the activation energy of the peak from two runs at different frequencies. Although the second run yields a somewhat smaller peak than the first, it is to be expected that by normalizing the height of the second curve to that of the first a constant shift should be obtained on a $1/T$ plot if indeed the peak is

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[4]That is, the concentration of copper in the matrix at points remote from any G.P. [1], G.P. [2], θ', or θ structures which may be present.

simply activated. Such a result was obtained, as shown in figure 4, for a solution-treated and quenched polycrystalline specimen. The activation energy of the peak is 28.2 ± 1.5 kcal/mole, and $\log \tau_0 = -14.6 \pm 1$ (when τ_0 is in seconds). The width of the peak at half maximum is 30 percent greater on the low-temperature side than that predicted from equations (1) and (2) for a single relaxation time.

Comparison of figures 3 and 4 reveals that the initial peak height of the polycrystalline specimens is significantly greater than that of specimen 3. Measurement of the initial peaks on first cooling for a variety of polycrystalline specimens and all the specimens shown in table I yielded the results shown graphically in figures 5 and 6. It may be seen that the largest initial peaks were found in polycrystalline wires, that specimens 1 and 3 showed peaks of intermediate size, and that the similarly oriented single crystal specimens 2, 4, and 5 have mutually similar but much smaller peaks. The peak heights found from these experiments are given in table II. The extreme values differ by full order of magnitude, a most striking variation.

Sequence of Internal-Friction Changes During Aging

Initial instability.- The initial peak obtained on first cooling is not claimed as the internal-friction behavior of the as-quenched condition. It is, however, the behavior of the alloy in a condition where 95 percent or more of the total available copper is freely dispersed in solid solution. Evidence that the curve on first cooling does not in fact represent the as-quenched condition is obtained by comparison of the portion of this curve below 150° C with measurements made on first heating the quenched specimen up to this temperature. The measurements on first heating fell considerably above the curve on first cooling, and successive measurements at constant temperature showed that the internal friction was decreasing rapidly. This behavior, observed on first heating a quenched specimen above room temperature, will be called "the initial instability." In figure 7 the solid curve is the initial peak obtained on first cooling. For each point on the broken curve the specimen was re-solution-treated and quenched, and heated in the course of 2 to 4 minutes to the desired temperature and the internal friction measured immediately. The points on the broken curve represent therefore the internal-friction measurements made after the least possible aging. Because of the rapid changes occurring in the internal friction, even the broken curve is no indication of the behavior in the as-quenched condition. A 5-minute anneal at 200° C followed by air-cooling is sufficient to wipe out all trace of the initial instability. After this treatment the curve obtained on heating the specimen to 150° C duplicates exactly that obtained in the usual manner on cooling.

The amount of the initial instability at 70° C (i.e., the difference at 70° C between the broken and full curves of fig. 7) was found to be much greater for the polycrystalline specimen than for single-crystal specimen 5. Specifically, the amount of the initial instability detected at 70° C was 1.3×10^{-3} for the polycrystalline specimen and only 0.084×10^{-3} for specimen 5, a difference of a factor of 15. As the ratio of the peak heights is a factor 10, a correlation is suggested between the height of the initial peak and the amount of initial instability.

Aging below 185° C.- Over periods of several days the only change other than the rapid decay of the initial instability was a progressive decrease in the height of the initial peak. By lowering the frequency of vibration the peak is shifted to lower temperatures (fig. 4), and for the lowest convenient frequency (0.4 cps) the peak temperature is 164° C. For aging temperature above 164° C it is therefore possible to take measurements at the peak temperature without introducing any change as a result of the measurements themselves. Below 164° C changes in the peak height must be inferred mainly from the portion of the low-temperature side of the peak existing below the aging temperature because it is not possible to make prolonged excursions above the aging temperature without the real danger of changing the condition of the specimen. However, it was usually possible to make a brief excursion to about 30° C above the aging temperature without a detectable change in the internal friction on returning to the aging temperature. As one example, during aging at 164° C the internal friction of a polycrystalline specimen vibrating at 0.4 cps fell from 0.0060 at the start of measurements to 0.0021 after 70.5 hours of aging. At the end of this period the temperature dependence was measured on cooling from 164° C. This curve was retraced after a 5-minute anneal at 200° C, and all the results fell nearly on the same smooth curve, indicating a stable condition during all of the measurements. After 70.5 hours at 164° C the initial peak had decreased to a size where it was no longer clearly resolved from the background; the estimated height was 0.001, compared with the starting peak height of 0.0055. Using the square-law relationship the free-copper concentration was reduced to 0.44 of its original value.

For specimens aged at 130° C, even for several days, an excursion to a temperature above 160° C caused an increase in the internal friction with time at the higher temperature. This is a manifestation of a striking phenomenon which will be called restoration of the initial peak, a phenomenon predicted and explained by the theory that the height of the initial peak is related to the free-copper concentration. Restoration of the initial peak is illustrated graphically in figure 8. Curve A is the initial peak observed on first cooling, and the solid part of curve B is the reproducible internal-friction behavior after $9\frac{1}{4}$ hours of

aging at 132° C. Above 160° C the internal friction becomes unstable with time and the broken part of curve B cannot be taken too seriously. After a period of 9 minutes at 200° C the specimen was cooled back to room temperature with the results shown by curve C. This short anneal at 200° C has restored the peak almost to the original value. The subsequent behavior of the restored peak is completely normal; further aging causes it to decrease in the manner expected. The almost complete restoration observed after $9\frac{1}{4}$ hours at 130° C may be contrasted with the complete absence of restoration at 200° C after 70.5 hours of aging at 164° C and with the very limited restoration observed after 15 hours of aging at 150° C.

Restoration of the initial peak is attributed simply to reversion, that is, the re-solution of structures which are no longer even metastable at the reversion temperature either because of their size or structure (ref. 17). The results shown in figure 8 will now be considered in more detail. The work of Silcock, Heal, and Hardy (ref. 41) has shown that, for periods up to 3 days at 130° C, G.P. [1] is the only structure produced. Hence, the fall in the initial peak during $9\frac{1}{4}$ hours of aging at 132° C is due to the decrease in the free-copper concentration resulting from the production of G.P. [1]. Using the square-law relationship it appears that roughly one-quarter of the total available copper has in this time segregated to the G.P. [1] zones. After reversion, the restored peak is somewhat lower than the starting value, but in terms of the free-copper concentration the reversion is 95 percent complete.

The absence of reversion after 70.5 hours at 164° C is to be expected, since the G.P. [2] structure formed at 164° C is also metastable at 200° C. Presumably, the aging treatment was long enough at 164° C for growth of G.P. [2] to a point where reversion due to the existence of particles of a subcritical size is unlikely.

Aging at 203° C.- The temperature dependence of internal friction of specimen 3 during a sequence of aging treatments at 203° C is shown in figure 9.[5] The initial peak obtained on first cooling is omitted from this figure; it is shown in figure 3. After 30 minutes at 203° C the

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[5]The curves shown in fig. 9 and similar ones shown elsewhere (e.g., figs. 14 and 17) were obtained on cooling from the aging temperature. The assumption of a stable specimen condition during such runs was justified by the close agreement between the results on cooling and those on subsequent reheating back to the aging temperature whenever such a comparison was made.

initial peak height has decreased from 0.00311 to 0.00264, and after 4.6 hours, to 0.00146. At the end of this time the free-copper concentration has fallen (in terms of the square law) to 0.69 of its initial value. These measurements, and others made in further tests, showed that during this period the peak temperature remained constant (for a given vibration frequency). After 4.6 hours at 203° C the activation energy of the reduced peak was still the same, within experimental error, as that found originally (28.2 kcal/mole); thus the value of τ_0 also remains constant. The reduction in the free-copper concentration for up to 4.6 hours of aging at 203° C is believed to be caused exclusively by the production of G.P. [2]. The G.P. [1] structure is not formed at this temperature, and the θ' phase has not yet precipitated, as indicated by the absence of other internal-friction effects to be discussed later. Previous X-ray work has placed the upper limit of the temperature range of G.P. [2] formation at between 190° and 220° C (ref. 41); the present results indicate that G.P. [2] is definitely formed at 203° C.

After 11.1 hours at 203° C, the internal-friction curve shows a change of character. The presence of a reduced initial peak is seen from the hump in the curve, but otherwise the peak is obscured by other new contributions to the internal friction. The rise on the high-temperature side of the peak was found from other experiments to be the result of an increased high-temperature background contribution; it was not possible, however, to analyze the curve into a reduced initial peak and a smoothly rising increased background. Subtracting from the curve for 11.1-hour aging any reasonable estimate of the remaining initial peak gives a curve which is clearly a combination of a background smoothly rising to higher temperatures and a broad peak centered at about 120° C. This new internal-friction peak will be called the "second peak." One self-consistent analysis of the curve for 11.1-hour aging is shown in figure 10.

For longer aging times at 203° C the new internal-friction contributions detected after 11.1 hours increase considerably, and after 22 hours there is no direct indication of the existence of a remaining initial peak. The curves for 40.6 and 59 hours show a knee at about 120° C which marks the commencement of a plateau extending to 180° C. The plateau is replaced by a maximum in the curve after 144 hours, by which time the internal-friction changes have become very slow. The curves from 11.1 hours onward are readily explained by the continued growth of the high-temperature background and second peak. Although the second peak is never very well resolved, the plateaus on the later curves and particularly the maximum finally developed after 144 hours are strong evidence for its existence and growth. In formulating this interpretation it has been supposed that the initial peak decreases continually on aging, until it is not significant in the interpretation of the later curves. This is consistent with the theory that the initial peak

decreases as the free-copper concentration is reduced. On making the reasonable assumption that the later curves in figure 9 are composed only of a symmetrical second peak and a smoothly rising background, an approximate separation of the second peak from the observed curve can be made on a trial-and-error basis. Using this procedure the estimated second peak after 144 hours of aging at 203° C is shown in curve B of figure 11. Curve A is the second peak redrawn from figure 10 for comparison, and curve C will be discussed later. The second peak is much broader than the initial peak, and during its growth at 203° C apparently retains an approximately constant shape and peak temperature.

Analysis of observed curves into their various contributions, as shown in figures 10 and 11, cannot be claimed to be correct except in broad outline. However, such an analysis is reliable enough to permit one to arrive at the following conclusions:

(a) On aging at 203° C, the rise in the decrement at temperatures below 120° C is due principally to the growth of the second peak.

(b) On aging at 203° C, the rise in the decrement at temperatures above 200° C is due principally to a rise in the high-temperature background.

It follows from (a) that the activation energy of the second peak may be obtained from the temperature shift with change in frequency of the portion of the curve below 120° C. To this end the curve for 144-hour aging was determined at two frequencies, and the results shown in figure 12 yield an activation energy for the second peak of 21.9 ± 1 kcal/mole, a value significantly lower than that for the initial peak. Using this activation energy the width of the second peak was found to be about three times broader than that for a single relaxation time. The value $\log \tau_0 = -12.5 \pm 0.8$ is obtained by taking the temperature of the fully formed peak as 132 ± 5° C (curve B, fig. 11).

As the peak retains approximately the same shape and peak temperature during growth, a second consequence of conclusion (a) above is that on aging the rise in decrement at some temperature below 120° C may be used as a relative measure of the height of the second peak, and hence a plot of these values against aging time at 203° C gives the kinetics of growth of the second peak (curve B, fig. 13). Similarly, from conclusion (b), the rise in decrement at 203° C may be taken as a measure of the growth of the high-temperature background (curve A, fig. 13). It may be seen that the kinetics of growth of both the second peak and the high-temperature background are strikingly similar and that little change occurs in either one after 100 hours.

Aging at 203° C was found to increase[6] the shear modulus by about 2 percent (as evidenced by an increase in frequency of approximately 1 percent), and the course of the change on aging is plotted in figure 13 (curve C) for comparison with curves A and B. It may appear that the modulus change is completed before completion of the internal-friction changes, but it should be noted that within experimental error the modulus curve could have been drawn to parallel the internal-friction behavior.

Aging at 300° C and above, following aging at 203° C.- The leveling off in the growth of the second peak and background after 100 hours at 203° C (fig. 13) was taken as an indication that a metastable condition has been attained which would be affected only slightly by further treatments of practicable duration at 203° C. To accelerate further changes the aging temperature was raised (after 144 hours at 203° C) to 298° C in the first instance and later to 330° C, with the results shown in figure 14. The curve for 144 hours at 203° C is drawn again in figure 14 for comparison purposes. Bearing in mind that the decrement below 120° C is essentially a measure of the size of the second peak, it will be seen that the second peak decreases progressively upon aging at these higher temperatures. The high-temperature background undergoes a further appreciable rise during the first treatment but then remains practically constant.

The extension of the aging temperature to 330° C allows a more extensive examination of the high-temperature background than was previously possible. Figure 15 gives the complete internal-friction curve after the anneal of 15.1 hours at 330° C (the lower part of this curve is shown also in fig. 14). The high-temperature background falls continuously and rapidly as the temperature is lowered, so that it decreases by an order of magnitude between 330° and 200° C. The shape of the background curve suggested that the temperature dependence might be expressed by an empirical equation of the type

$$\delta = A \exp(-B/T) \tag{8}$$

where A and B are constants. This formula was substantiated by the straight line obtained on replotting the results as log δ (internal friction) against $1/T$, as shown in figure 16. The values of the constants A and B were thus determined to be: A = 280 and B = 5,100. Both A and B were found to be affected by aging. The departure from

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[6]Ordinarily a decrease in shear modulus accompanies a rise in internal friction because of an elastic relaxation. In the present case, however, the relaxation effects are too small to be detected by frequency measurements.

linearity in figure 16 is caused by the second peak. Apart from a possible theoretical significance, equation (8) is of practical importance because it can be used with some confidence to obtain by extrapolation the background internal friction at temperatures below 220° C. Subtraction of the extrapolated background from the experimental curve enables the second peak to be separated out more precisely than was previously possible. The shape of the peak obtained by performing this separation (curve C, fig. 11) compares favorably with the earlier, and of necessity less quantitative, estimates of the second peak. Despite the uncertainty in the estimation of peaks A and B in figure 11, the apparent migration of the peak to slightly higher temperatures as aging progresses can probably be taken seriously.

The activation energy for the high-temperature background was obtained as usual from the temperature shift resulting from a change in frequency. The value obtained was approximately 33 kcal/mole.

Aging at 230° C.- The sequence of internal-friction changes during the aging of specimen 2 at 230° C (fig. 17) differs from that of specimen 3 at 203° C in one respect only. At 203° C the initial peak declined considerably in strength before other contributions to the internal friction were detected, while at 230° C the small decrease detected in the initial peak after 0.8 hour was accompanied by the detection of the other contributions. Later remarks justify the conclusion that at 230° C the phase θ' and not the G.P. [2] structure is the first structure formed, as is indeed to be expected from the work of Silcock, Heal, and Hardy (ref. 41). Comparison of figures 9 and 17 indicates that at both 203° and 230° C the later growth of the second peak and the high-temperature background are very similar except for a difference in rate. To emphasize this similarity, the uppermost curves of figures 9 and 17 have been plotted in figure 18 together with the curve obtained from a polycrystalline specimen which had been aged for 110 hours at 200° C to develop fully the second peak. All three curves exhibit a knee of roughly the same height, which is a reasonable indication that the height of the fully formed second peak is about the same in the three specimens. This behavior is in striking contrast to the large differences in the initial-peak heights of these specimens (table II).

The kinetics of growth of the second peak and background are shown in figure 19 for aging at 230° C. Again the curves follow a similar course which is paralleled also by the relative change in shear modulus. Comparison of figures 13 and 19 shows that the important growth occurs in the interval 10 to 100 hours at 203° C and in 1 to 10 hours at 230° C.

Aging at 185° C.- The changes of internal friction and relative shear modulus during isothermal aging at 185° C of a polycrystalline specimen are shown in figure 20. The decrease in the internal friction

first observed is due to a fall in the strength of the initial peak. Other experiments mentioned previously show that during aging the peak temperature remains constant, and hence the first part of curve A in figure 20 gives an indication of the kinetics of the fall of the peak at 185° C. Some care is required in the detailed interpretation of measurements made only at one temperature, for without a knowledge of the temperature dependence of internal friction after various aging times it is not possible to estimate how much of the observed internal friction at the aging temperature arises from the initial peak. This is particularly important when the internal friction has fallen to values near the minimum. Experience has shown, however, that for aging temperatures below 200° C the peak may fall to one-half of the starting value and still be well resolved from the high-temperature background. This corresponds to a fall of 25 percent in the free-copper concentration. Near the minimum of curve A, the initial peak height is estimated to have fallen by a factor of 4, and the free-copper concentration, by a factor of 2, which is in agreement with Guinier's results for the amount of G. P. [2] formed on aging at 180° and 190° C (ref. 44).

After aging for 100 hours at 185° C the internal friction shows a sharp rise, and the temperature dependence below 185° C was then observed to be typical of that caused by the growth of the second peak and background. The activation energy obtained from the shift in the curve of decrement plotted against $1/T$ with frequency after 1,000 hours aging agreed with that previously given (21.9 kcal/mole) for the second peak. The rise in curve A is therefore interpreted as due to the increasing contributions at 185° C from the growth of both the second peak and the background.

The form of curve A (fig. 20) is in qualitative agreement with the curve given by Kê (ref. 31) for aging at 200° C, which is reproduced in figure 21. As mentioned in the Introduction, Kê's interpretation of these phenomena was in terms of a grain-boundary relaxation, which is clearly ruled out by the present work. He also assumed that the rise in internal friction after the minimum in figure 21 is caused by a regrowth of the initial peak. The fact that this latter assumption is incorrect has also been demonstrated.

Effect of Quenching Temperature on Initial Peak

Because of the relatively small size of the initial peaks shown by single-crystal specimens, measurements were confined mainly to polycrystalline specimens on account of the greater sensitivity attainable. However, no difference was detected in the behavior of the two types of specimen.

Quenching from above phase boundary.- For this series of measurements, a polycrystalline specimen was first solution-treated at the highest of the three quenching temperatures used to insure that no grain growth would occur during later re-solution treatments. The three quenching temperatures chosen (570°, 536°, and 501° C) spanned the phase field from just below the solidus to just above the phase boundary. The same frequency was used throughout (0.396 cps), and after each quenching the specimen was heated at the same rate to 190° C. Each heating was interrupted at 100° C for the minimum time required to make an internal-friction measurement. The initial peaks measured on first cooling are shown in figure 22, from which it was concluded that the quenching temperature has no observable effect on the initial peak as determined by the procedure used. The measurements made on first heating to 100° C gave the amount of the initial instability at 100° C (defined as in section entitled "Sequence of Internal-Friction Changes During Aging"). The following values were obtained: 0.00125, 0.00115, and 0.00073, for quenching temperatures of 570°, 536°, and 501° C, respectively. It appears that the lower the quenching temperature, the smaller the amount of initial instability.

Quenching from below phase boundary.- The polycrystalline specimen used for this series of measurements was always solution-treated at the standard temperature of 525° C. It is not the specimen mentioned in the preceding section. After a solution treatment the specimen was lowered to a desired temperature below the phase boundary and left there for a period considered long enough to establish the equilibrium proportion of $\theta(CuAl_2)$ (see table III). The specimen was then quenched and the initial peak measured on first cooling in the usual manner. This procedure was repeated for each of four different temperatures below the phase boundary, and, in addition, the initial peak on quenching directly from 525° C was determined. The results given graphically in figure 23 are summarized below:

(a) The initial peak remains at the same temperature but decreases progressively in strength as the quenching temperature is lowered.

(b) The high-temperature background rises progressively as the quenching temperature is lowered and is particularly prominent after quenching from 427° C. After this treatment, the combined effect of the decrease in the peak and the rise in the background is sufficient to obscure the peak, which is detectable only as an inflection in the curve.

(c) The second peak is not evident in these results.

(d) A correlation exists between the height of the initial peak and the amount of copper remaining in solution. In table III the peak heights are tabulated together with the amount of copper remaining in

solution as calculated from the solubility data given in the "Metals Handbook" (ref. 51). The peak height may be seen to vary more rapidly than the first power of the copper concentration and, as shown in figure 24, a square law fits the behavior within experimental error. The empirical statement of this law is

$$\delta_p = 0.00167c^2 \tag{9}$$

where δ_p is the peak height and c is the atomic percentage of copper in solution. This relationship has been used several times previously in this report to calculate the free-copper concentration remaining after various aging treatments.

Measurements in Flexure

Initial peak.- A consideration of the previous results suggested the particular desirability of determining in flexural vibration the initial peak of a single crystal oriented with ⟨100⟩ parallel to the specimen axis. The flexure pendulum specially developed for this purpose has been described previously. The requirement of twin specimens was no disadvantage in the present case as three single crystals of virtually the desired orientation had been grown (specimens 2, 4, and 5, table I). Of these, specimens 4 and 5 were chosen for the present investigation. The specimens were solution-treated and quenched together from the standard temperature of 525° C and tested on cooling by the same procedure as that used for torsional vibration. The results shown by curve A in figure 25 may be compared directly with the individual tests in torsion (fig. 6), of which curve B is typical. The initial peak heights of these specimens in torsion and flexure are given in table II. The peak in flexure is 13 times larger than the mean peak height in torsion and is the largest of any found in this work.

Measurements in flexure were also made of the initial peak in a pair of polycrystalline specimens. The approximate identity of these specimens was indicated by the separate determination of the initial peak in torsion for each specimen. The results (table II) for the two specimens in torsion differed by 7 percent, the average peak height being 0.00448. On the other hand, the peak height in flexure is 0.0065. Polycrystalline specimens therefore do not exhibit the spectacular difference found for ⟨100⟩ oriented single crystals.

Second peak.- In torsion, the fully formed second peaks in single-crystal specimens 2 and 3 and in a polycrystalline wire are believed to

be roughly equal (fig. 18). Measurements were now made in flexure using specimens 4 and 5 after an aging treatment of 22.5 hours at 230° C, a treatment resulting virtually in complete growth of the second peak (cf. fig. 19). The results of the measurements in flexure are shown in figure 26 together with those from specimen 2 tested in torsion after a similar aging treatment. Using as before the height of the knee in the curve as a gage of the height of the second peak, it is possible to conclude that the height of the second peak is about 50 percent larger in flexure than in torsion.

Internal Friction at High Temperatures

Above 300° C, the solubility of copper in aluminum starts to increase at a significant rate. For example, at 300°, 350°, and 400° C the solubility is, respectively, 0.45, 0.85, and 1.5 weight percent copper. If appreciable re-solution of precipitates occurs during an internal-friction run on heating above 300° C, the apparent internal-friction behavior observed will be modified by the changing solubility. To investigate this, specimen 5 (a single crystal) was solution-treated, quenched, and aged for 35.5 hours at 300° C. After this treatment runs were made on cooling from and heating back to 300° C. The behavior observed is shown by the portion of curve A, figure 27, below 300° C. Above 200° C the high-temperature background contribution was predominant (cf. fig. 15). Upon reaching 300° C the run on reheating was continued to 505° C, a temperature just above the phase boundary, with the results shown in the remainder of curve A. The curve continued to increase up to about 370° C, whereupon the curve passed through a maximum before continuing a rise to higher temperatures. In the region of the maximum, successive measurements at a constant temperature showed the internal friction to be falling with time, and the points shown are mean values obtained by ignoring the time dependence of successive measurements. The maximum in the curve is not interpreted therefore as a peak of anelastic origin but rather as a manifestation of the decreasing background contribution resulting from rapid re-solution of precipitates on reaching temperatures around that of the maximum. This conclusion is supported by the results shown in curve B, figure 27, which were obtained on cooling after the specimen had been held at 505° C for 1.5 hours to insure complete re-solution of any remaining precipitates. In contrast with curve A, this curve falls rapidly and with no sign of a maximum at 380° C. The internal friction below 400° C is much lower than that observed on heating and is so low below 300° C that it appears doubtful that any appreciable precipitation could have occurred on cooling, a conclusion supported by the detection of the initial peak (this is not apparent in curve B because of the scale of the figure).

Above 430° C the results on cooling are higher than those on heating. This is a reflection of the rise in internal friction from 0.140 to 0.221

during the solution treatment at 505° C. Sully and Brook (ref. 52) have reported increases in the high-temperature internal friction of pure aluminum resulting from creep. A similar explanation is offered in the present case because after the completion of measurements the specimen was found to have elongated by 2 percent.

INTERPRETATION AND DISCUSSION OF RESULTS

Initial Peak

A summary of the results to be explained by a theory of the initial peak is given below.

On first cooling:

(a) A wide variation exists in the height of the initial peak exhibited by different specimens tested in torsional vibration.

(b) The initial peak height of ⟨100⟩ oriented single crystals is much greater in flexure than in torsion.

(c) The initial peak height is insensitive to the quenching temperature above the phase boundary.

(d) The height of the initial peak varies as the square of the copper concentration in the matrix.

(e) The activation energy of the peak is 28 ± 1.5 kcal/mole, the log τ_0 value is -14.6 ± 1, and the excess half-peak width is 15 to 30 percent.

On aging:

(f) The initial peak decreases in height but retains the same peak temperature and activation energy. Thus the value of τ_0 must also remain constant.

(g) Apart from the initial instability effect, the decrease in the peak height is the first indication of a structural change in the alloy on aging at temperatures below 200° C. At 230° C the decrease in the peak is accompanied by other changes in the internal friction.

(h) The decline in the height of the peak caused by aging at low temperatures can be restored almost completely by a short anneal at 200° C.

Consideration may be given first to Kê's opinion that the peak was due to grain-boundary slip. This idea is clearly incorrect, since the peak is present in single crystals. Inspection of the results suggested rather that the peak originates from the presence of copper atoms in solid solution; this suggestion is consistent with the facts that the peak has not been detected in pure aluminum and that it decreases in Al alloy containing 4 weight percent Cu whenever specimens are treated in a manner that reduces the free-copper concentration in the matrix. The observed restoration of the initial peak by a treatment known to restore the free-copper concentration is striking evidence for the correctness of a theory relating the existence of the peak to the presence of copper freely dispersed in solid solution. From a closer inspection of the results it is possible to be more specific; all the available evidence points to the Zener relaxation as the origin of the initial peak. This conclusion is reached in view of the following considerations:

(a) The magnitude of the activation energy of the initial peak suggests that relaxation occurs by atom movements in the bulk of the matrix. It is close to the measured and calculated values of the diffusion activation energy of copper in aluminum (28 to 33 kcal/mole) and is higher than might reasonably be expected for atom migration in dislocated regions. Because of the very small copper content (1.7 atomic percent) of the present alloy, the movement of copper atoms in the matrix should be the factor controlling the rate of the relaxation (ref. 7), and a comparison of the activation energy reported here with that for the diffusion of radioactive copper in the alloy would be significant. Unfortunately such diffusion data do not exist.

(b) The value of τ_0 is of the correct magnitude for a Zener relaxation. The significance of this value of τ_0 is the inference that the relaxation is caused by a rearrangement which does not require atoms to jump more than a few atomic distances.

(c) The width of the peak at half maximum relative to that calculated from equations (1) and (2) is called the "relative peak width." If the relaxation process is identical everywhere, the relative peak width is equal to unity. Local variations in structure or in composition will result in a distribution of activation energies and therefore in a spectrum of relaxation times, which is manifest as a broadening of the peak. Usually the observed width is taken from the low-temperature side of the peak only to minimize the complication of apparent peak broadening due to the presence of a high-temperature background. Some of the values so obtained for various initial peaks in Al alloy containing 4 weight percent Cu on first cooling are given as follows:

Specimen and mode of vibration	Relative peak width
Polycrystalline wires in torsion	1.3
⟨100⟩ oriented single-crystal specimens 4 and 5 in flexure	1.3
Specimen 1 in torsion	1.15

These values are typical of other solid solutions which display the Zener relaxation.

(d) The square-law dependence of the initial peak height on the concentration of copper in the matrix is the same as that found for the concentration dependence of the Zener peak in copper-zinc and in silver-zinc alloys. For small concentrations of solute a square law is predicted both from the theories of Zener (ref. 5) and of LeClaire and Lomer (ref. 4). In terms of Zener's "pair reorientation" theory the square law has a simple interpretation, namely, that the height of the peak is proportional to the number of pairs of solute atoms which in turn is proportional to the square of the solute concentration.

(e) A simple explanation of the initial instability in solution-treated and quenched Al alloy containing 4 weight percent of Cu can be advanced by identifying the initial peak with the Zener relaxation. It is well known that quenching from the solution-treatment temperature will trap an excess of lattice defects with the result that the relaxation time is greatly decreased (refs. 10 and 12). The initial peak, observed in a hypothetical experiment where the quenched condition is preserved, would therefore occur at a much lower temperature. According to this explanation the initial instability is due to a migration of the initial peak to higher temperatures during heating, because of the decay of lattice defects. This interpretation is supported by three observations: (1) The magnitude of the initial instability decreases with the quenching temperature even though the initial peak height on first cooling is the same (see section entitled "Quenching from above phase boundary"). This is explained by the decrease in the equilibrium number of defects present as the solution-treatment temperature is lowered. (2) The magnitude of the initial instability for difference specimens is roughly proportional to the height of the initial peak (see section entitled "Initial instability"), as would be expected if the initial instability is caused by the migration of this peak. (3) A close similarity exists between the form of figure 7 and analogous measurements obtained from quenched Ag alloy containing 33 atomic percent of Zn (ref. 12), which is an alloy showing a typical Zener peak. The weight of the evidence presented above, together with the absence of any conflicting results, leads to the conclusion that the initial peak is due to a Zener relaxation. A check on this conclusion would be possible if it were practicable by the use of higher frequency measurements to verify the existence of the peak in the

solid-solution range between the solidus and the phase boundary. Unfortunately, the vibration frequency required is so high (10^6 cps) that the experiment is not possible with existing techniques.

The height of a Zener peak is known to be affected by the degree of order present in the alloy (refs. 16 and 53). However, the observed insensitivity of the initial peak to the quenching temperature above the phase boundary does not permit any conclusions to be drawn regarding the existence of short-range order above the phase boundary. Even if short-range order does exist and is markedly temperature dependent, it may not be possible to retain the condition on quenching.

It is of interest to compare the relaxation strength of the initial peak in polycrystalline Al alloy containing 4 weight percent of Cu (i.e., Al alloy containing 1.7 atomic percent of Cu) with that for the Zener relaxation in silver-zinc and copper-zinc alloys. Experimental data for the last two alloys exist only at higher solute concentrations, but correction may be made to 1.7 atomic percent solute with the aid of the square-law relationship. The results obtained show that the relaxation strength in aluminum-copper alloy is, respectively, 5 and 30 times larger than that calculated for the silver-zinc and copper-zinc alloys.

Attention will be given now to the striking variation in the heights of the initial peaks in various specimens, as measured on first cooling from about 200° C. As pointed out previously, the initial peak measured by this procedure refers to a condition in which at least 95 percent of the total available copper is freely dispersed in solid solution. The widely differing peak heights obtained in torsion and flexure for $\langle 100 \rangle$ oriented single crystals shows that the relaxation strength is strongly anisotropic. The formal theory of anisotropic anelasticity (i.e., one which requires no knowledge of the relaxation mechanism) has been given for cubic crystals (the following considerations are restricted to crystals of cubic symmetry) by Zener (refs. 1 and 5). The general anelastic response of a crystal may be expressed by three relaxation strengths ΔC, $\Delta C'$, and ΔK, defined below. The absolute and relative magnitudes of these constants are of course related to the particular mechanism of relaxation; their determination therefore provides an important clue in a theoretical interpretation of the relaxation in terms of an atomistic model. An outline of the formal theory of anisotropic anelasticity is given below. This is followed by an analysis of the present experimental results.

The deformation of an elastically anisotropic crystal under pure shear stresses may be described in terms of two shear moduli C and C', defined by the equations

$$C = 1/S_{44} \tag{10}$$

$$C' = \frac{1}{2\left(S_{11} - S_{12}\right)} \tag{11}$$

The quantities S_{11}, S_{12}, and S_{44} are the elastic constants which appear for a cubic crystal in the generalized definition of Hooke's law (ref. 1). The modulus C represents the elastic resistance of the crystal to the shearing of (100) planes across one another in the [010] direction, and C', that for shearing of (110) planes in a [$\bar{1}$10] direction.

Further, if a stress system with a hydrostatic component is imposed, the bulk modulus K must be introduced also, as follows:

$$K = \frac{1}{3\left(S_{11} + 2S_{12}\right)} \tag{12}$$

If the crystal behaves anelastically the values of C, C', and K depend on the conditions of measurement. Measurements made under conditions where relaxation does not occur will yield the unrelaxed moduli C_U, C_U', and K_U. Similarly, measurements made under conditions of complete relaxation give the relaxed moduli C_R, C_R', and K_R. The general anelastic response of the crystal is accordingly determined by the three relaxation strengths

$$\Delta C = \left(C_U - C_R\right)\Big/C_R \tag{13}$$

$$\Delta C' = \left(C_U' - C_R'\right)\Big/C_R' \tag{14}$$

$$\Delta K = \left(K_U - K_R\right)\Big/K_R \tag{15}$$

The shear modulus G of a single-crystal wire determined, for example, from the frequency of vibration in the torsion pendulum is given (for either the relaxed or unrelaxed condition) by

$$\frac{1}{G} = \frac{1}{C} + 2\left(\frac{1}{C'} - \frac{1}{C}\right)\phi \tag{16}$$

The orientation function ϕ is defined as

$$\phi = \cos^2\alpha \cos^2\beta + \cos^2\beta \cos^2\gamma + \cos^2\gamma \cos^2\alpha$$

where α, β, and γ are the angles between the specimen axis and the three crystallographic axes (i.e., the cube edges). The relaxation strength ΔG found by internal-friction measurements in the torsion pendulum is then[7]

$$\Delta G = \frac{\frac{\Delta C}{C} + 2\left(\frac{\Delta C'}{C'} - \frac{\Delta C}{C}\right)\phi}{\frac{1}{C} + 2\left(\frac{1}{C'} - \frac{1}{C}\right)\phi} \tag{17}$$

where C and C' may be either the relaxed or unrelaxed quantities (since the relaxation strengths are assumed small).

The tensile modulus E of a single-crystal wire determined, for example, from the frequency of vibration in the flexure pendulum is given by

$$\frac{1}{E} = \frac{1}{3C'} + \frac{1}{9K} - \left(\frac{1}{C'} - \frac{1}{C}\right)\phi \tag{18}$$

and the relaxation strength ΔE determined from internal-friction measurements in the flexure pendulum is

$$\Delta E = \frac{\frac{\Delta K}{K} + \frac{\Delta C'}{3C'} - \left(\frac{\Delta C'}{C'} - \frac{\Delta C}{C}\right)\phi}{\frac{1}{9K} + \frac{1}{3C'} - \left(\frac{1}{C'} - \frac{1}{C}\right)\phi} \tag{19}$$

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[7]From equation (2), the relaxation strength ΔG is $2/\pi$ times the logarithmic decrement at the peak in torsion, while ΔE is the same for the peak measured in flexure.

From equations (17) and (19) it is apparent that the relaxation strength observed in both torsion and flexure will be orientation dependent, unless both ΔC and $\Delta C'$ are zero (i.e., unless relaxation occurs under hydrostatic pressure only). Further, elastic isotropy ($C = C'$) does not imply anelastic isotropy but instead reduces equations (17) and (19) to simpler forms, where the relaxation strength is a linear function of ϕ.

The important case $\phi = 0$ is obtained when the specimen axis is parallel to a $\langle 100 \rangle$ direction. Equations (17) and (19) then reduce to

$$\Delta G_{\langle 100 \rangle} = \Delta C \tag{20}$$

and

$$\Delta E_{\langle 100 \rangle} = \frac{\Delta C'\left(1 + \frac{C'}{3K}\frac{\Delta K}{\Delta C'}\right)}{1 + \frac{C'}{3K}} \tag{21}$$

Equation (21) can be written in the much simpler form

$$\Delta E_{\langle 100 \rangle} \cong \Delta C' \tag{22}$$

when $C'/3K \ll 1$, provided the assumption is made that ΔK is not much greater than $\Delta C'$. No proof of this assumption is possible without appropriate experimental data or knowledge of the correct model of the relaxation.

The elastic constants of Al alloy containing 4 weight percent of Cu have apparently not been measured. The data available for pure aluminum (ref. 54) and Al alloy containing 5 weight percent of Cu (ref. 55) are given in table IV, together with the calculated moduli. Differences between the two materials are quite small, so the values given for Al alloy containing 5 weight percent of Cu have been used for the present 4-percent alloy. The ratio C/C' shows the alloy to be more isotropic elastically than pure aluminum. For Al alloy containing 5 weight percent of Cu the value of $C'/3K$ is 1/37, which may be small enough compared with unity to justify neglecting the bulk-relaxation contribution to flexure for this alloy. Using these moduli, and the experimental results for single-crystal specimens 4 and 5 in torsion and flexure (table II), the values of ΔC and $\Delta C'$ were calculated from equations (17) and (19) with the assumption of a negligible contribution from the bulk relaxation. The results are:

$$\Delta C = 0.00034$$

$$\Delta C' = 0.0058$$

Using these values, and the fact that the alloy is almost isotropic elastically, it is noted that ΔG in torsion increases almost linearly with ϕ from $\Delta G_{\langle 100 \rangle} = 0.00034$ to $\Delta G_{\langle 111 \rangle} = 0.0042$. In flexure ΔE decreases almost linearly with ϕ from $\Delta E_{\langle 100 \rangle} = 0.0058$ to $\Delta E_{\langle 111 \rangle} = 0.00033$.

A rough check on these results is possible using the observed peak height in torsion of specimen 1, a nearly single crystal whose orientation function ϕ was estimated to be 0.18 ± 0.02. The calculated peak height in torsion for this range of ϕ is 0.0035 to 0.0042 (expressed as the logarithmic decrement), and the observed peak height of 0.00356 (table II) is consistent with this calculation.

A $\langle 111 \rangle$ oriented single crystal is expected to show the largest peak in torsion; the logarithmic decrement at the maximum is calculated to be 0.0066. This may be compared with the range 0.0043 to 0.0056 shown by polycrystalline specimens. The existence of a range of peak heights for polycrystalline specimens is to be expected as a result of differences in the distributions of grain sizes and orientations between different specimens. A quantitative comparison of the results for polycrystalline specimens in torsion with those of specimens in flexure is not possible because (a) the different stress systems in torsion and flexure affect the internal-friction contributions from individual grains and (b) the grains mainly responsible for the internal friction in torsion are not those mainly responsible for the internal friction in flexure.

The calculated ratios of $\Delta G_{\langle 111 \rangle}/\Delta G_{\langle 100 \rangle}$ and $\Delta E_{\langle 100 \rangle}/\Delta E_{\langle 111 \rangle}$ are 12.4 and 17.3, respectively. These ratios are much larger than expected from the theory of LeClaire and Lomer (ref. 4) which predicts much more nearly isotropic anelastic behavior for face-centered cubic alloys. For example, the theoretically derived ratio for silver-zinc alloy in torsion is 1.7. The discrepancy suggests either that LeClaire and Lomer's theoretical description of the Zener relaxation is not completely correct or that the initial peak in Al alloy containing 4 weight percent Cu does not arise from a Zener relaxation. However, the current investigations made at Yale University by D. P. Seraphim (unpublished) have revealed that the relaxation strength of the Zener relaxation in silver-zinc alloys is also orientation dependent with $\Delta C' \gg \Delta C$ to a far larger extent than is predicted from the theory. This result strongly supports the supposition that the initial peak in Al alloy containing 4 percent Cu is a Zener relaxation. The results from both alloys therefore show the need for a reappraisal of LeClaire and Lomer's theory.

Second Peak and High-Temperature Background

A comparison of present results with dilatometric (ref. 45) and X-ray measurements (ref. 44) shows that the appearance and growth of the second peak parallels the precipitation of the phase θ'. Good correlation between the different types of data is obtained by assuming that the height of the second peak is proportional to the amount of θ' precipitated. Using the internal friction at 120° C as a relative measure of the height of the second peak (see section entitled "Aging at 203° C") and the assumption of proportionality mentioned above, the kinetics of precipitation of θ' at 203° and 230° C are obtained from figures 13 and 19 using the relationship

$$\text{Percent of } \theta' = 100 \frac{\delta_t - \delta_s}{\delta_f - \delta_s} \tag{23}$$

where δ_t is the decrement at 120° C after an aging time t, and δ_s and δ_f are, respectively, the decrement at 120° C before the appearance of the second peak and after complete growth. The results for 203° C are plotted in figure 28 together with the results of Lankes and Wassermann (ref. 45) and of Guinier (ref. 44) for 200° C. The results for aging at 230° C are shown in figure 29, together with the variation inferred from the dilation curve at 230° C. The agreement between the results is satisfactory considering that the kinetics of precipitation are affected by the type of specimen used and the method of quenching (ref. 41). If equation (23) is assumed to hold exactly, the value of the growth exponent m obtained by analysis of the present data in terms of equation (3) differs somewhat from the value obtained by other techniques. The dilatometric and X-ray results at 200° C yield $m = 1.7$, while the internal-friction results give $m = 1.5$. The dilatometric measurements at 230° C again yield $m = 1.7$, but the noticeably lower value of $m = 1.3$ is obtained from the internal-friction results. As θ' is known to precipitate in the form of platelets, the discrepancy between all of these values of m and the value of 2.5 predicted from Zener's theory (ref. 18) indicates that the assumptions of Zener's analysis are not valid in the present case, as first pointed out by Guinier (ref. 44).

The fall in the second peak on aging at 300° to 330° C after prior full development at 203° C is to be associated with the transformation $\theta' \rightarrow \theta$. The rate of this transformation as indicated by figure 14 is consistent with the observations of Calvet, Jacquet, and Guinier (ref. 37). As there is no sign of the second peak in specimens containing only the θ phase (see, e.g., fig. 23), the second peak is apparently related specifically to the θ' phase.

The present work has produced the following information concerning the second peak:

(a) The peak is produced specifically by precipitation of the phase θ'. The kinetics of growth of the peak indicate that the height of the peak is roughly proportional to the amount of θ' precipitated.

(b) The relaxation strength of the fully formed peak appears to be roughly isotropic for measurements in torsion (see fig. 18). If this conclusion is correct, a larger peak in flexure (fig. 26) can arise only from a substantial bulk relaxation. For a material showing both an isotropic shear relaxation of strength ΔG and a bulk relaxation of strength ΔK, the relaxation strength in flexure ΔE is calculated from equations (17) and (19) as

$$\Delta E = \frac{2}{3}(1 + \sigma)\Delta G + \frac{(1 - 2\sigma)}{3}\Delta K \tag{24}$$

where σ is Poisson's ratio. For $\sigma \cong 1/3$, equation (24) reduces to

$$\Delta E \cong \frac{8}{9}\Delta G + \frac{1}{9}\Delta K \tag{25}$$

The value of ΔG for the fully formed peak is estimated to be 0.0025, and the value of ΔE, to be 0.0037. Substitution into equation (25) gives the result $\Delta K \cong 0.013$. Thus, the second peak may have a substantial bulk-relaxation strength.

(c) The value $\log \tau_0 = -12.5 \pm 0.8$ is calculated from the activation energy and the estimated peak temperature of the fully formed peak. If the slight shift of peak temperature upon aging (fig. 11) is attributed wholly to changes in τ_0, the values obtained are $\log \tau_0 = -12.7$ and -12.0 for the newly formed and overaged peaks (curves A and C, fig. 11), respectively. The relative accuracy of these figures is good enough to infer an increase of half an order of magnitude in τ_0 as aging progresses. If it is assumed instead that τ_0 remains constant throughout, the increase in peak temperature implies an increase of 5 percent in the activation energy. In any case, the quoted values of τ_0 are larger by two orders of magnitude than the value expected for a relaxation which is completed by very few atomic jumps, for example, the Zener relaxation. It therefore seems that about 100 atom jumps are required to complete the relaxation involved in the second peak.

(d) The activation energy of the peak (21.9 ± 1.0 kcal/mole) is considerably lower than that for normal lattice diffusion. Such a value could however be associated with atom movements in dislocated regions, for example, around the interface of a θ' particle.

(e) One of the most striking features of the second peak is its relative peak width, which is about three times that for a single relaxation time. The peak therefore involves a spectrum of relaxation times. Such a spectrum may, in general, be attributed to a distribution of values for both τ_0 and H. The meaning of the existence of a range of τ_0 values is that the number of atomic jumps required to complete the relaxation is not the same throughout the specimen.

In connection with (d) above, the grain-boundary peak in metals provides another example of a broad internal-friction peak. In this case τ_0 is proportional to the linear grain dimension, and a spectrum of τ_0 values arises because the grains are not all of the same size. The grain-boundary relaxation is explained by ascribing to the boundaries the mechanical properties of a viscous layer. A similar interpretation of the second peak, namely, that it arises from viscous slip across θ' interfaces, appears unlikely. In terms of such an interpretation, it would be difficult to explain why the peak decreases and eventually disappears as the boundary becomes more incoherent because of the $\theta' \rightarrow \theta$ transformation. Furthermore, at least in the later stages of θ' development, the θ' platelet forms an intersecting network throughout the matrix, as shown by the micrographs of Calvet, Jacquet, and Guinier (ref. 37). Under these circumstances it would seem likely that coupled relaxations would occur (ref. 2). The concept of coupled relaxations was previously used to explain the monotonically increasing internal friction as a function of temperature for an aluminum-zinc alloy (ref. 23) during precipitation. It is therefore apparent that viscous slip across the new interfaces produced by precipitation provides a more likely explanation for the high-temperature background than for the second peak. On this basis, the rise in the high-temperature background would be expected to follow the course of the θ' precipitation. That this prediction is correct is indicated in figures 13 and 19 by the parallel growth of the second peak and background and by the direct comparison of the isothermal internal-friction and dilatometric curves at both 185° and 200° C (figs. 20 and 21). The rise in the high-temperature background during the $\theta' \rightarrow \theta$ transformation is interpreted readily in terms of the greater amount of slip possible as progressively more of the boundary area becomes incoherent. The rise in the high-temperature background caused by the direct precipitation of the θ phase is shown in figure 23. Finally, the activation energy of the high-temperature background (33 kcal/mole) is not inconsistent with that for grain-boundary relaxation in pure aluminum (32 to 34.5 kcal/mole).

In searching for an explanation of the second peak, speculation was directed toward possible ways in which a stress-induced atomic rearrangement might occur involving the presence of a precipitated phase. This problem has been examined previously by Damask and Nowick (ref. 24) whose views form an essential part of the following discussion. During precipitation the lowering of the total free energy by chemical decomposition is opposed by both surface and strain energy terms. Although final thermodynamic equilibrium is not reached until precipitation of the stable phase is complete, it seems reasonable to apply the usual thermodynamic criterion for the occurrence of anelasticity to a state which is metastable during the period of anelastic measurements. It follows from this criterion that any precipitation causing internal strains will give rise to anelastic relaxation effects, since an applied stress will then change the state of precipitation. Consider for example the case where precipitation causes a bulk expansion. Application of hydrostatic pressure will cause a limited re-solution of precipitate and hence an anelastic change in volume following the instantaneous volume change. If shearing strains are associated with precipitation, application of a pure shear stress will also cause a relaxation. Since pure shear cannot produce a change in volume, the accompanying relaxation will not be associated with a change in the quantity of precipitate but with a redistribution of the precipitate (i.e., with a change in the shape of the precipitate particles). These general considerations apply whether the precipitate is coherent or not. In order to explain the absence of a detectable peak when θ phase is the only precipitate present in Al alloy containing 4 weight percent of Cu, it is necessary to suppose that coherency strains play a major role in determining the magnitude of the relaxation. The mechanism of relaxation by a stress-induced change in the shape of precipitate particles may be used qualitatively to explain the large τ_0 value of the second peak in terms of the large number of atomic jumps required to change the shape of a precipitate particle. Further, the number of jumps required to complete the relaxation would be expected to increase as the particles grow in size, which is consistent with the analysis that suggested an increase in τ_0 with aging. The activation energy for the relaxation would be that for atom jumps across the interface of the precipitate particles, which may reasonably be expected to be considerably lower than that for normal lattice diffusion.

In conclusion, mention will be made of the 2-percent modulus increase which was found to accompany the precipitation of the phase θ'. These results are in good accord with the more accurate high-frequency measurements of Tanaka, Abe, and Hirano (ref. 56). The modulus will be increased somewhat by the rejection of copper from solid solution, but the predominant effect may well be a stiffening of the matrix by a more rigid precipitate, as discussed by Dudzinski (ref. 57).

CONCLUDING REMARKS

A study has been made, by means of low-frequency internal-friction measurements in both torsional and flexural vibration, of aluminum alloy containing 4 weight percent of copper during aging. The results of this study are as follows:

An internal-friction peak showing all the characteristics of a Zener relaxation exists in solution-treated and quenched specimens of Al alloy containing 4 weight percent of Cu. The height of the peak is strongly dependent on the directions of the crystallographic axes with respect to the specimen axis. The basic quantities necessary for a description of the anisotropic behavior of the peak have been calculated from experimental data.

On aging, the peak height decreases as the square of the copper concentration that remains freely dispersed in solid solution, while the two parameters of the Zener relaxation, namely, τ_0 and the activation energy H, remain constant. No new anelastic effects attributable to the presence of G.P. [1] or G.P. [2] zones are detected, but the Zener peak is sensitive to the reversion of G.P. [1] zones.

The growth of a second broader peak and a rise in the background internal friction are associated with the precipitation of the phase θ'. The height of the second peak is at least roughly proportional to the amount of θ' precipitated. The kinetics of growth of this peak and of the high-temperature background are very similar during precipitation of θ', but the different origins of these two effects are reflected by the difference in their activation energies. The peak is associated specifically with the presence of the θ' phase, whereas the background is not. For example, the second peak is reduced by the transformation $\theta' \rightarrow \theta$, and is not found in specimens containing only the θ phase. The high-temperature background, on the other hand, is further increased by the θ' to θ transformation. A possible mechanism for the second peak in torsion is the stress-induced change in shape of the coherent precipitate particles. The changes in the high-temperature-background internal friction are discussed in terms of the possibility of coupled relaxations arising from viscous slip across the new interfaces produced by precipitation.

The height of the initial peak is very sensitive to the free-copper concentration (a square-law variation) and is therefore particularly suited to a study of the decrease of the supersaturation of the matrix during the early stages of aging. This is the only property known to depend in a unique manner on the supersaturation of copper in the matrix. The method is only applicable, however, for temperatures above about 130° C.

Evidence has been obtained for the presence of quenched-in lattice defects (possibly single vacancies) which greatly decrease the mean atomic jump time. The defects decay out rapidly on heating the quenched specimen; specifically, the equilibrium concentration is obtained in less than 5 minutes at 200° C.

Compared with other fundamental techniques (e.g., resistivity, dilatometry, paramagnetic susceptibility measurements, etc.) the internal-friction method is extremely sensitive to the aging process. For example, a change in the initial peak height by a factor of 4 on aging at 150° C may be compared with a contraction in length of 0.005 percent. The growth of the second peak associated with the precipitation of θ' causes the internal friction at 120° C to increase by a factor of 10; the associated increase in length is 0.15 percent.

The successful interpretation of the internal-friction behavior during aging has been made possible only by the comparative wealth of knowledge, particularly from X-ray analysis, which is available for Al alloy containing 4 weight percent of Cu. However, continued study of this alloy in connection with the behavior mentioned above may supplement considerably existing knowledge of the early stages of aging.

Internal-friction studies of other precipitating systems are also expected to be of considerable value. For example, preliminary work on the aluminum-rich aluminum magnesium alloys has shown the existence of an internal-friction peak in the solution-treated and quenched condition, as well as marked changes in the internal-friction behavior on aging. An internal-friction study of these alloys may be particularly significant because the similarity of the atomic scattering powers of aluminum and magnesium decreases considerably the sensitivity of X-ray techniques.

Yale University,
New Haven, Conn., November 27, 1956.

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TABLE I

DATA ON SPECIMENS GROWN FROM MELT

[Finished diam. of specimens, 0.040 in.; finished length of specimens, 8 to 10 in.]

Specimen	Condition	α, deg	β, deg	γ, deg	$\cos^2\alpha + \cos^2\beta + \cos^2\gamma$	θ
1	Nearly single crystal	---	---	---	-----	------
2	Single crystal	4	86	88	1.001	0.006
3	Tricrystal	---	---	---	-----	------
4	Single crystal	4	86	88	1.001	.006
5	Single crystal	2	88	89	1.000	.0015

TABLE II

INITIAL PEAK HEIGHTS ON FIRST COOLING

Specimen	Condition	ϕ	Peak height, logarithmic decrement $\times 10^3$ (a)	
			In torsion	In flexure
1	Nearly single crystal	0.18 ± 0.02	3.56	----
2	Single crystal	.006	.98	----
3	Tricrystal	---------	3.11	----
4	Single crystal	.006	.79	8.9
5	Single crystal	.0015	.56	
-	Polycrystalline	---------	5.6 to 4.3	----
A	Polycrystalline	---------	4.32	6.5
B	Polycrystalline	---------	4.64	

[a]Obtained by subtraction of the room-temperature decrement from the maximum decrement. For specimens 2, 4, and 5 in torsion the estimated high-temperature background contribution was also subtracted from the maximum decrement.

TABLE III

CONDITIONS USED IN EXPERIMENTS ON QUENCHING FROM

BELOW PHASE BOUNDARY

[Time allowed for solution treatment between runs > 12 hr]

Annealing temperature, °C	Time allowed for equilibrium,	Calculated atomic percent copper in matrix	Peak height (logarithmic decrement) (a)	Temperature of peak, °C	Frequency at room temperature, cps
525	> 24	1.78	5.30×10^{-3}	176	0.900
488	40	1.60	4.38	176	.911
477	80	1.45	3.31	174	.894
464	50	1.26	2.74	175	.897
427	35	.87	.7 to 1.7	---	.897

[a]Given as maximum decrement minus room-temperature decrement for all results except the last, where a range of possible values was determined from inspection of curve.

TABLE IV

ELASTIC CONSTANTS AND MODULI OF PURE ALUMINUM AND ALUMINUM ALLOY CONTAINING 5 WEIGHT PERCENT COPPER

Elastic constants				
Material	S_{11}, $cm^2/dyne$	S_{12}, $cm^2/dyne$	S_{44}, $cm^2/dyne$	Source of data
Al	15.9×10^{13}	-5.8×10^{13}	35.2×10^{13}	Ref. 54
Al alloy (5 percent Cu)	15	-6.9	37	Ref. 55
Calculated elastic moduli				
Material	C, $dynes/cm^2$	C', $dynes/cm^2$	K, $dynes/cm^2$	Anisotropy ratio C/C'
Al	0.284×10^{-12}	0.230×10^{-12}	0.77×10^{-12}	1.23
Al alloy (5 percent Cu)	.27	.228	2.78	1.18

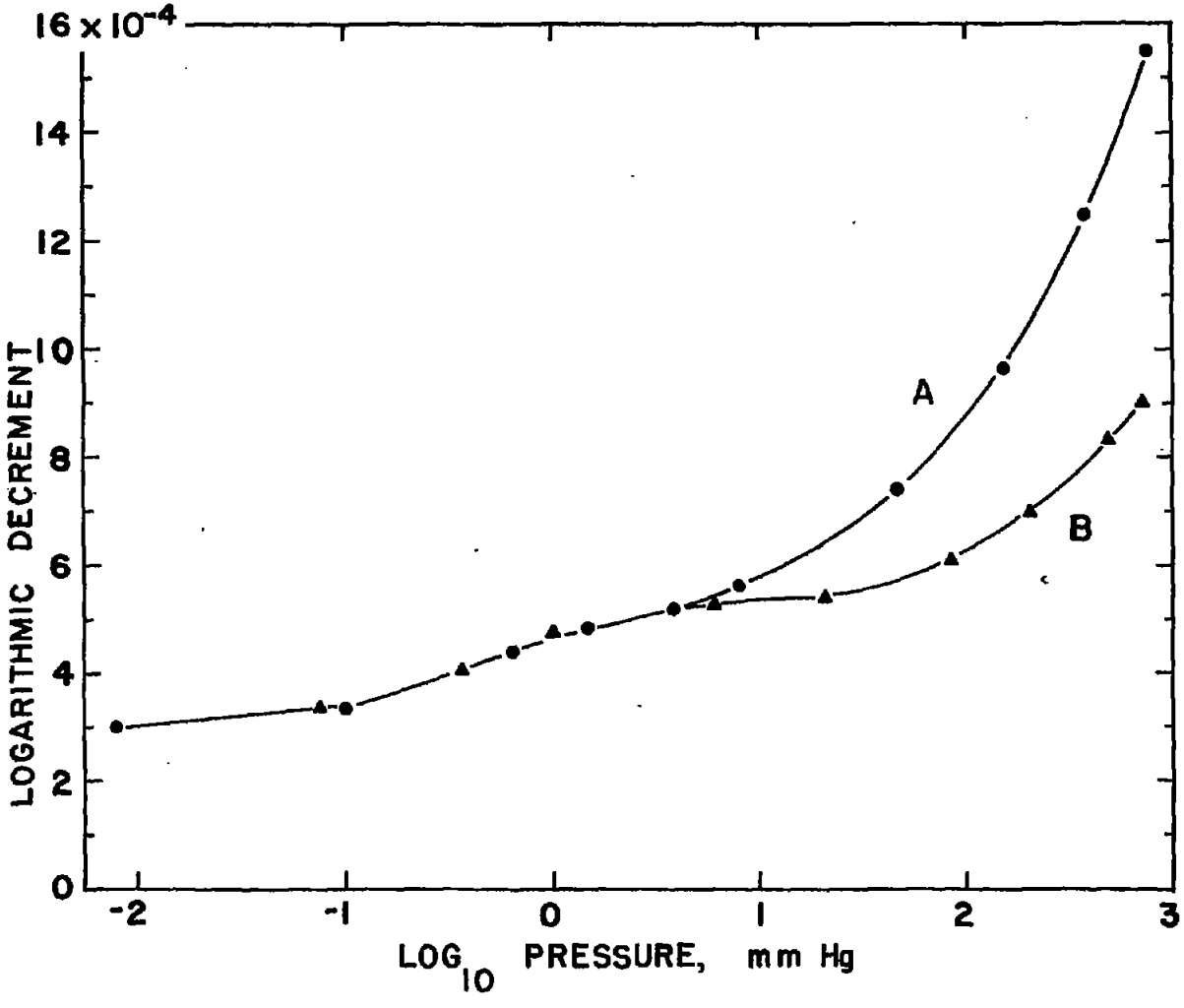

Figure 1.- The pressure dependence of internal friction in air (A) and helium (B) for a specimen of Al alloy containing 4 weight percent of Cu tested at room temperature in torsional vibration at 1.95 cps.

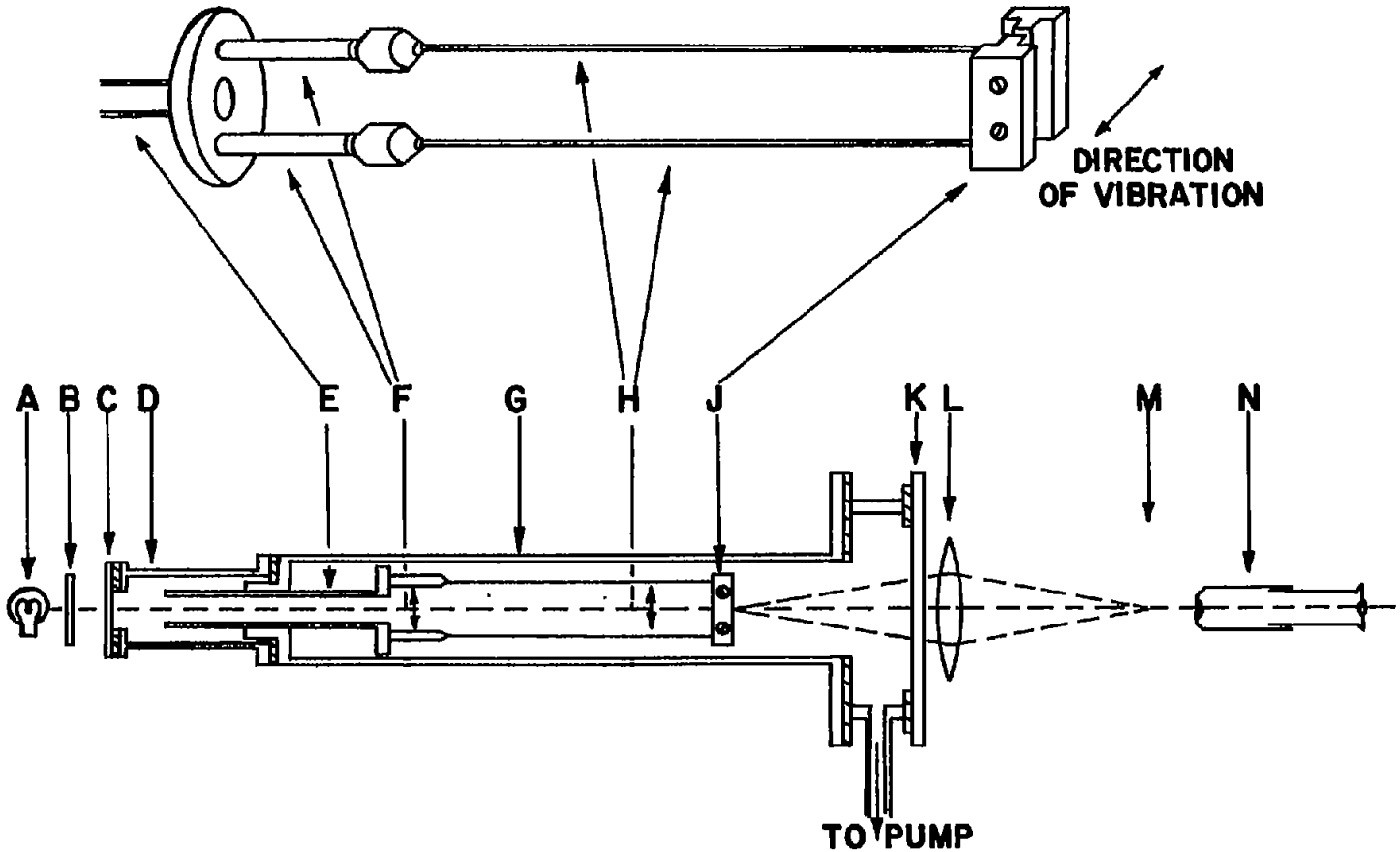

Figure 2.- Flexure pendulum. (A) Galvanometer lamp; (B) green filter; (C) light inlet window; (D) vacuum cover for furnace; (E) hollow stainless-steel tube; (F) pin vises; (G) furnace; (H) specimens; (J) loading weight; (K) light exit window; (L) 8-inch focal-length lens; (M) plane of image of slit in J; (N) microscope with graduated eyepiece; shaded areas indicate flat rubber gaskets. The electromagnet used for exciting vibrations and the measurement thermocouple are placed alongside the specimens and are omitted from the figure for clarity.

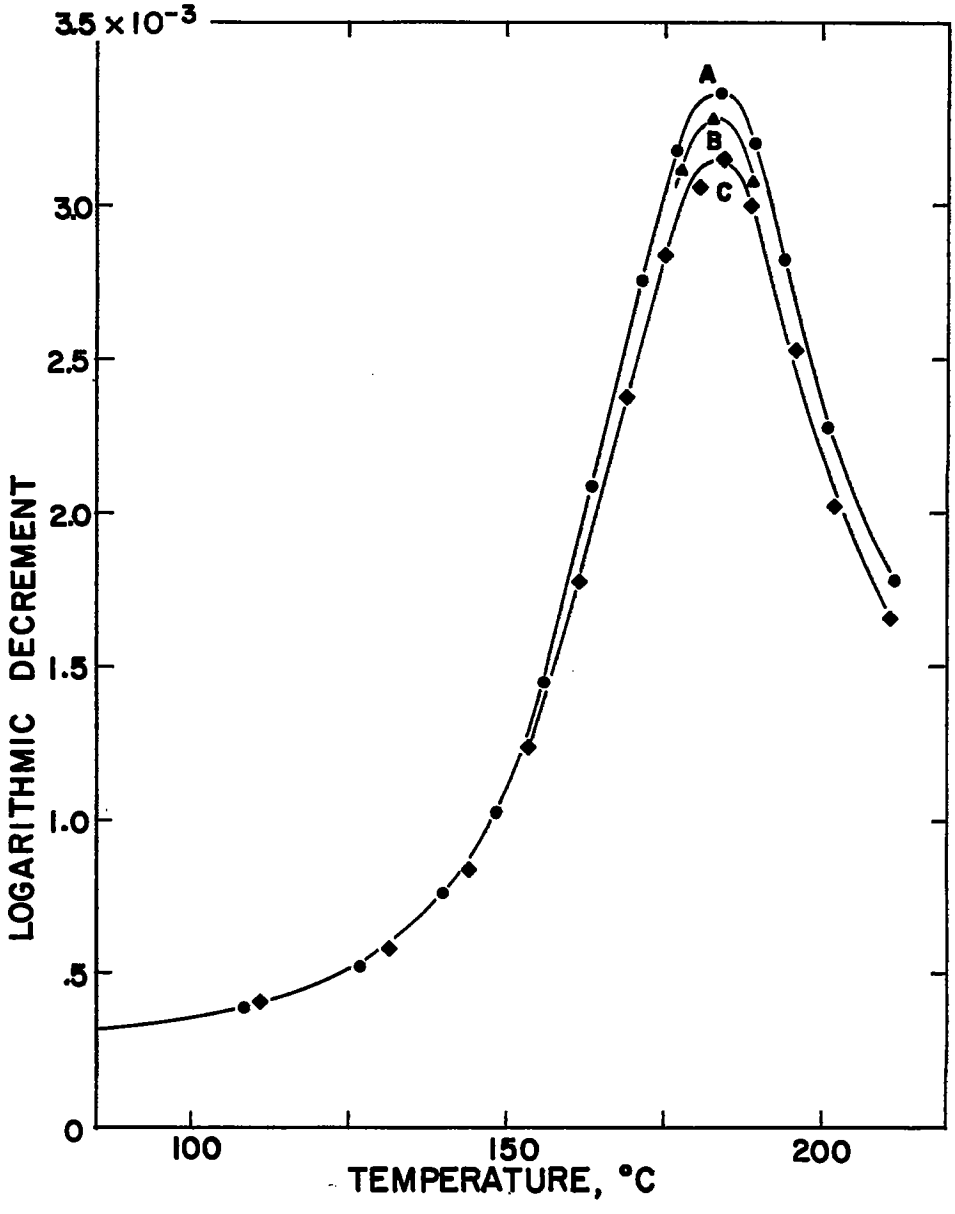

Figure 3.- Internal-friction behavior of solution-treated and quenched specimen 3, tested in torsion at 1.71 cps. After 50-minute aging at room temperature the specimen was heated to 211° C in 6 minutes. Curve A indicates initial peak on cooling after 6 minutes at 211° C; peak height, 0.00310. Curve B indicates initial peak on reheating from room temperature to 211° C; peak height, 0.00300. Curve C indicates initial peak on cooling after a further 5 minutes at 211° C; peak height, 0.00288. Peak heights given as the maximum decrement minus the room-temperature decrement.

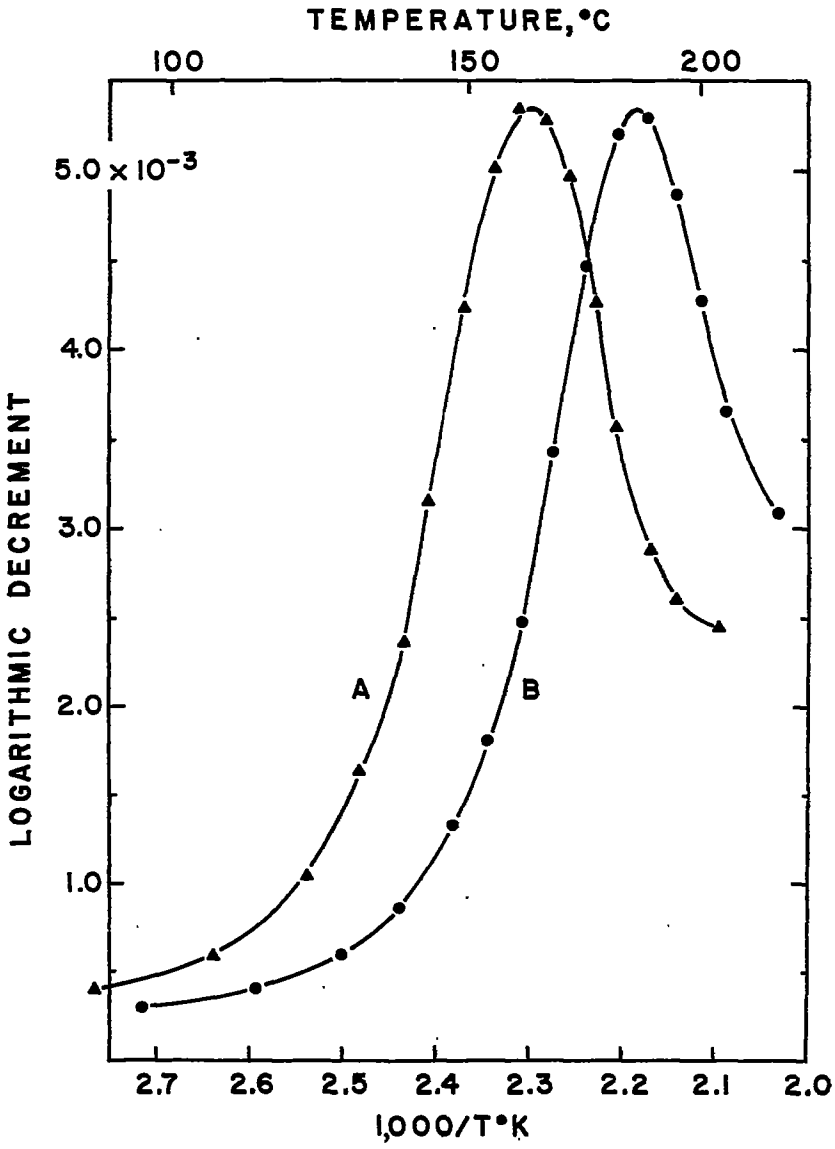

Figure 4.- Initial peak in polycrystalline Al alloy containing 4 weight percent of Cu determined at two frequencies by successive runs on cooling. Curve A is initial peak for a frequency of 0.360 cps at the peak temperature; the room-temperature decrement has been subtracted from the experimental results. Curve B is for a frequency of 1.95 cps at the peak temperature. A decrement of 0.00066 was first subtracted from the experimental results to compensate for the larger room-temperature decrement found at this frequency. The peak so obtained was then normalized to curve A by increasing all values by 4.6 percent. The result is curve B.

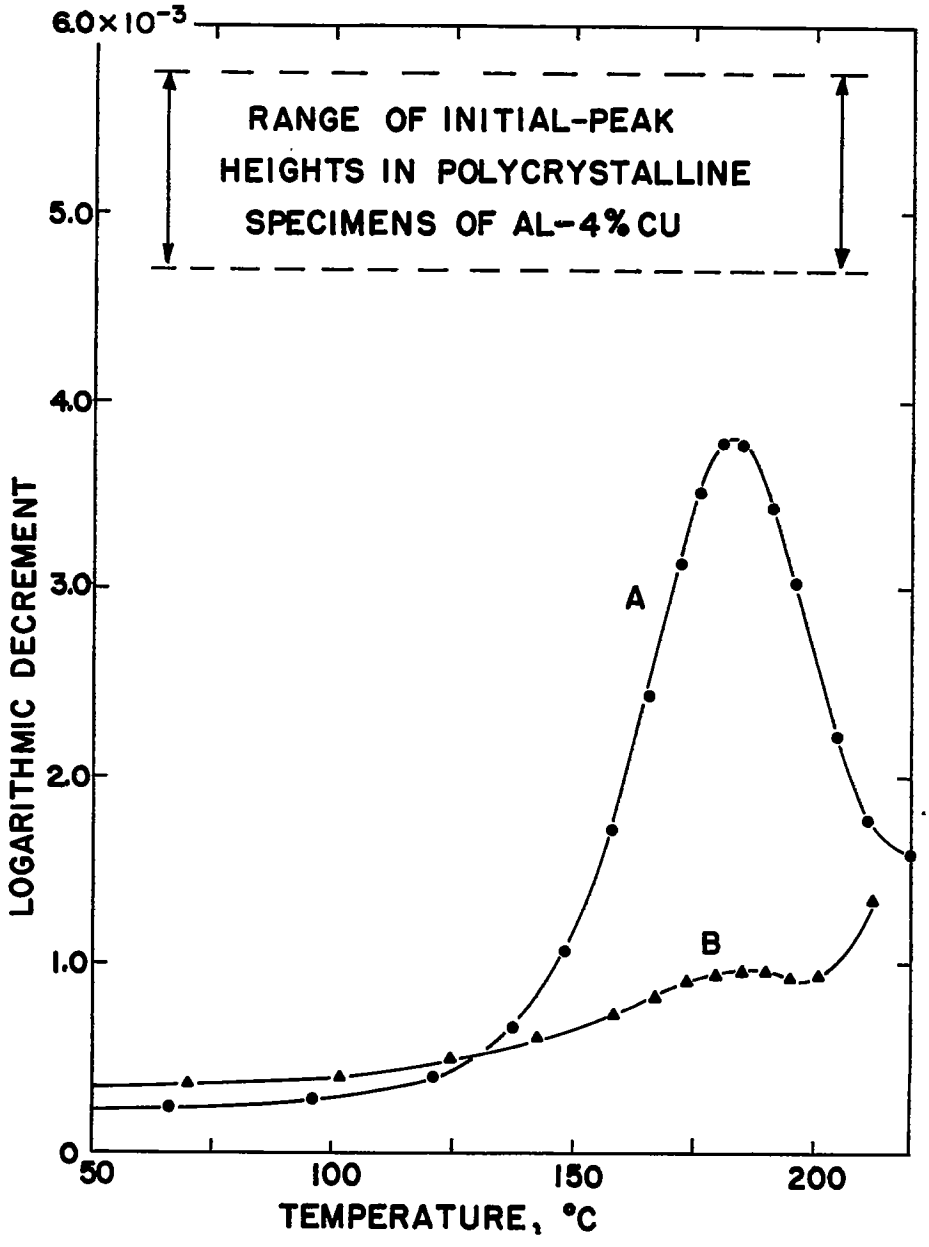

Figure 5.- Initial peaks on first cooling for specimens of Al alloy containing 4 percent Cu tested in torsion. Curve A shows specimen 1 vibrating at 1.71 cps; curve B shows specimen 5 vibrating at 1.41 cps. By inclusion of the range of peak heights found in polycrystalline specimens (without subtraction of the room-temperature decrement) this figure serves also as a graphical illustration of large differences found in peak heights on first cooling for various types of specimens.

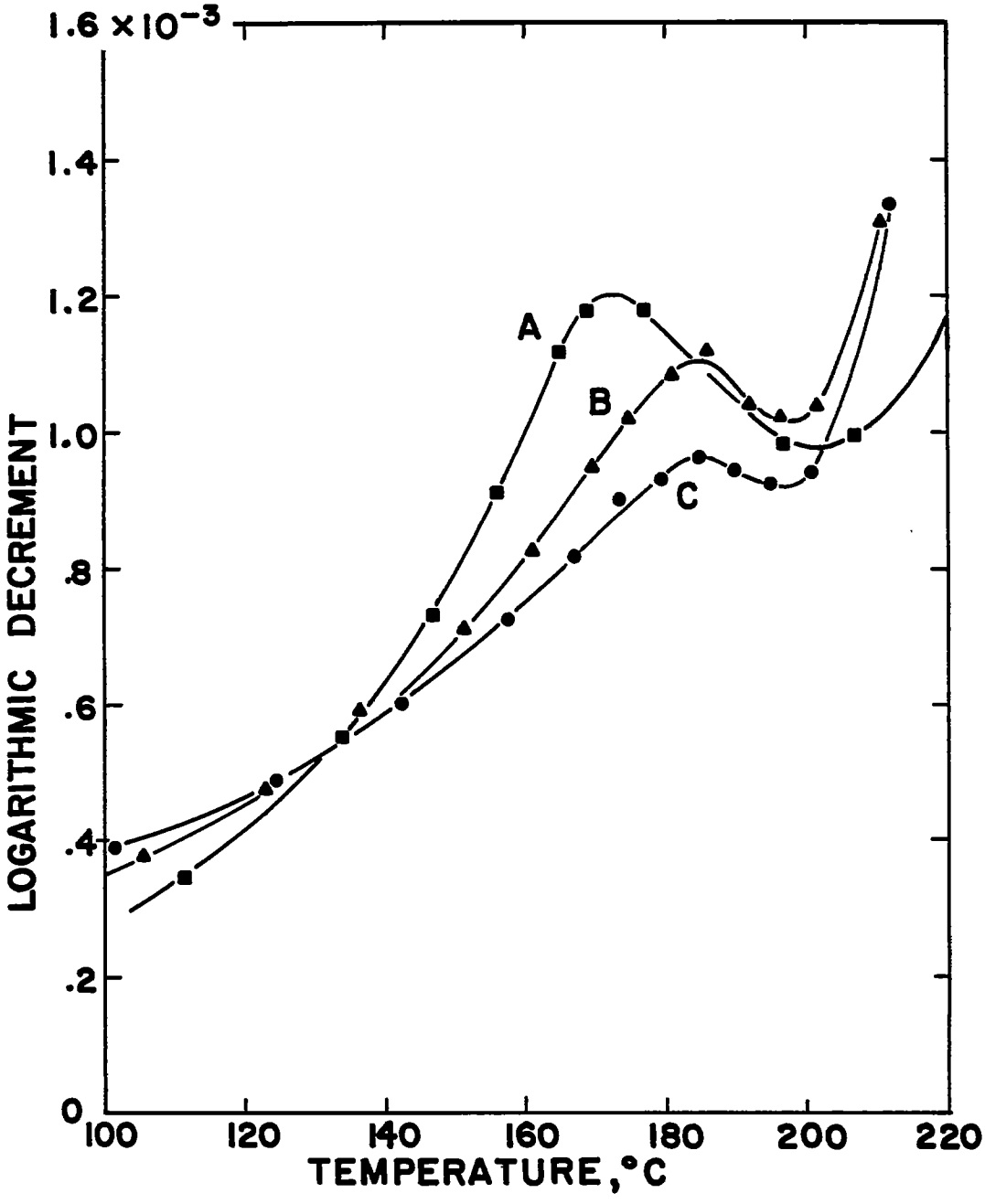

Figure 6.- Initial peaks on first cooling for similarly oriented single crystals tested in torsion. A ⟨100⟩ direction is nearly parallel to axis of each specimen. Curve A shows specimen 2 vibrating at 0.80 cps; curve B shows specimen 4 vibrating at 1.64 cps; curve C shows specimen 5 vibrating at 1.41 cps.

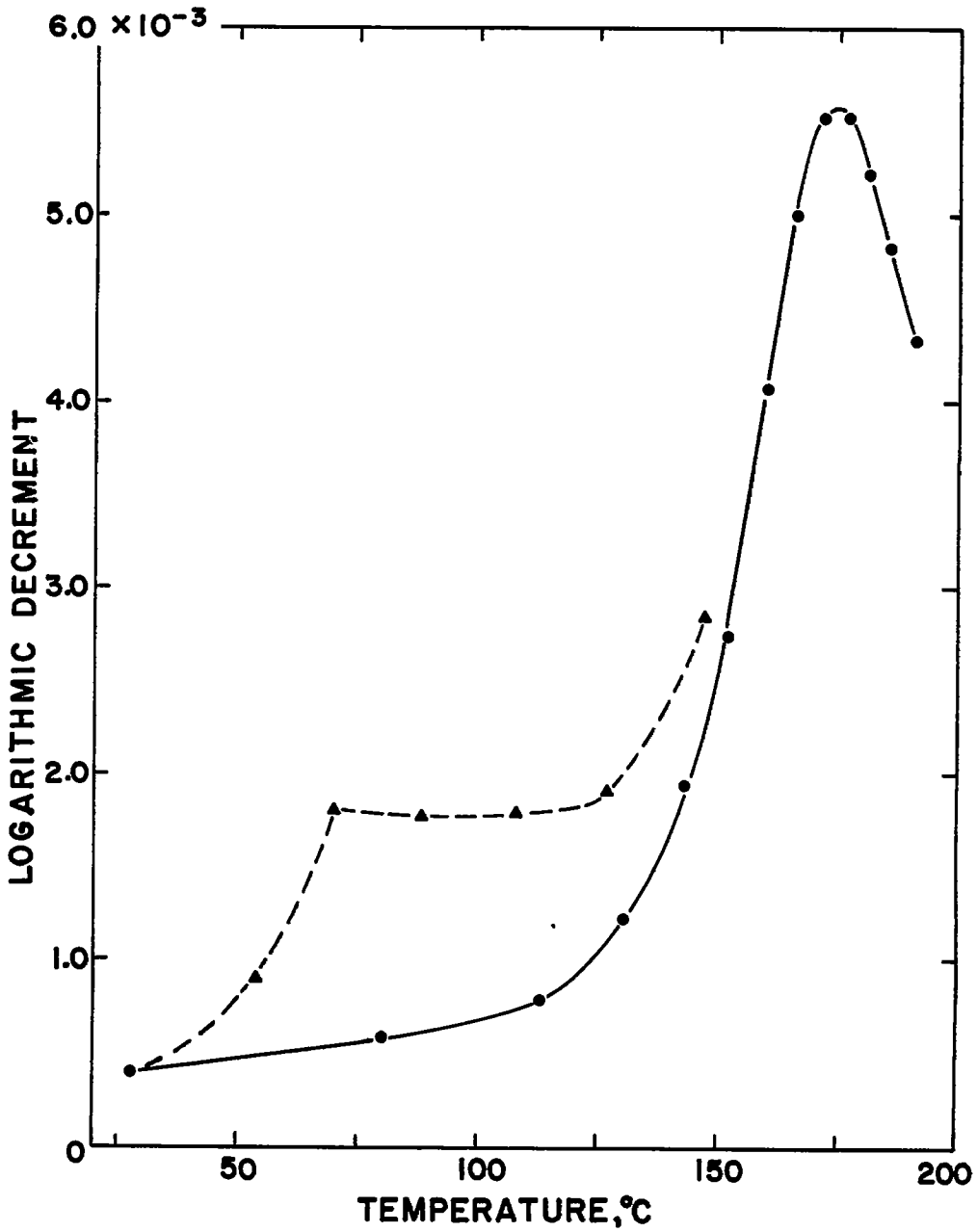

Figure 7.- Initial instability in polycrystalline Al alloy containing 4 percent of Cu tested in torsion at 0.90 cps. Solid curve indicates initial peak on first cooling. For each point on the dashed curve the specimen was re-solution-treated and quenched, heated in the course of 2 to 4 minutes to the temperature shown, and the internal friction measured immediately.

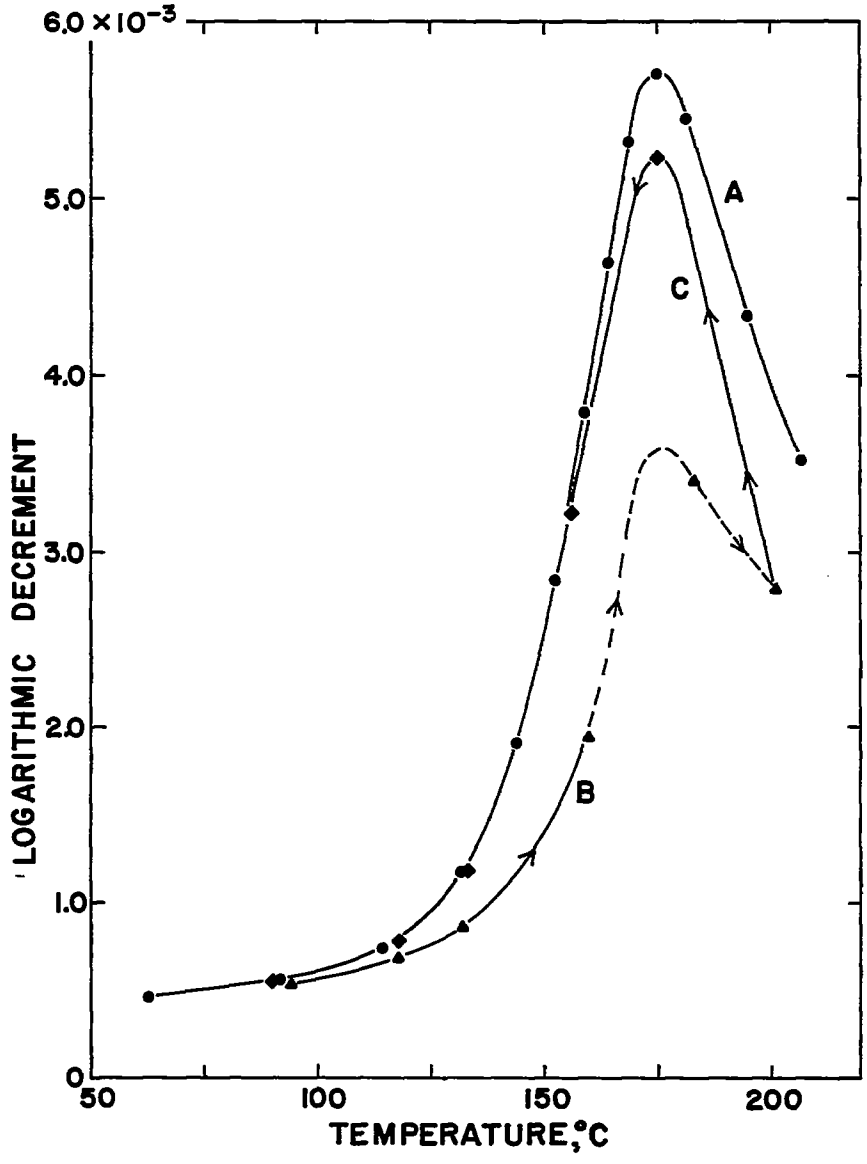

Figure 8.- Restoration of the initial peak in polycrystalline Al alloy containing 4 percent of Cu, tested in torsion at 0.90 cps. Curve A shows initial peak on first cooling; curve B shows initial peak on heating to 200° C from room temperature after 9 $\frac{1}{4}$ hours aging at 132° C; curve C shows initial peak on cooling after a stay of 9 minutes at 200° C. The dashed line of curve B indicates the range in which changes were taking place so rapidly that the internal friction was unstable.

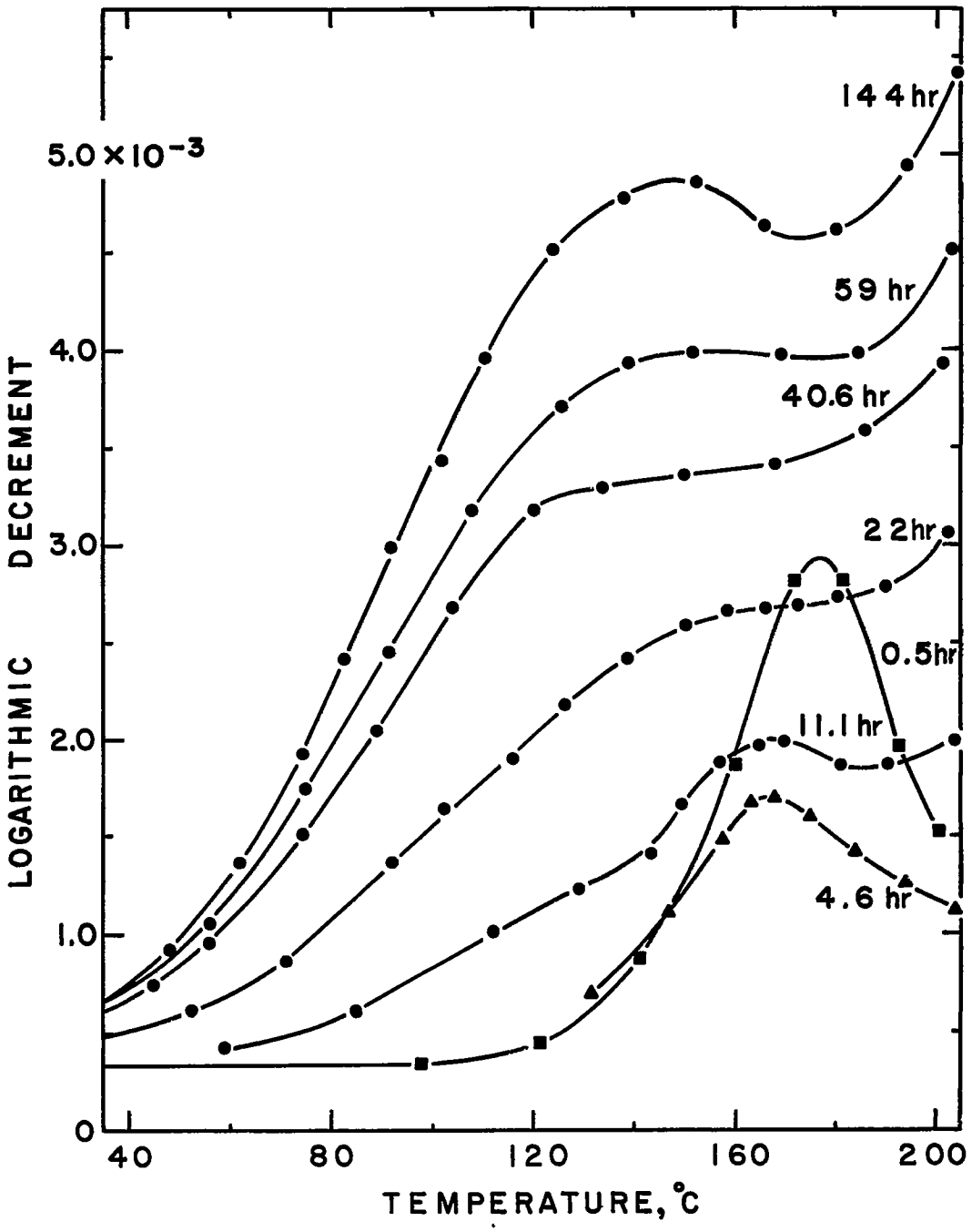

Figure 9.- Temperature dependence of internal friction of specimen 3 after aging at 203° C for times indicated. Measurements were made in torsional vibration at 0.5 cps except for 0.5-hour curve, which was obtained at 1.3 cps.

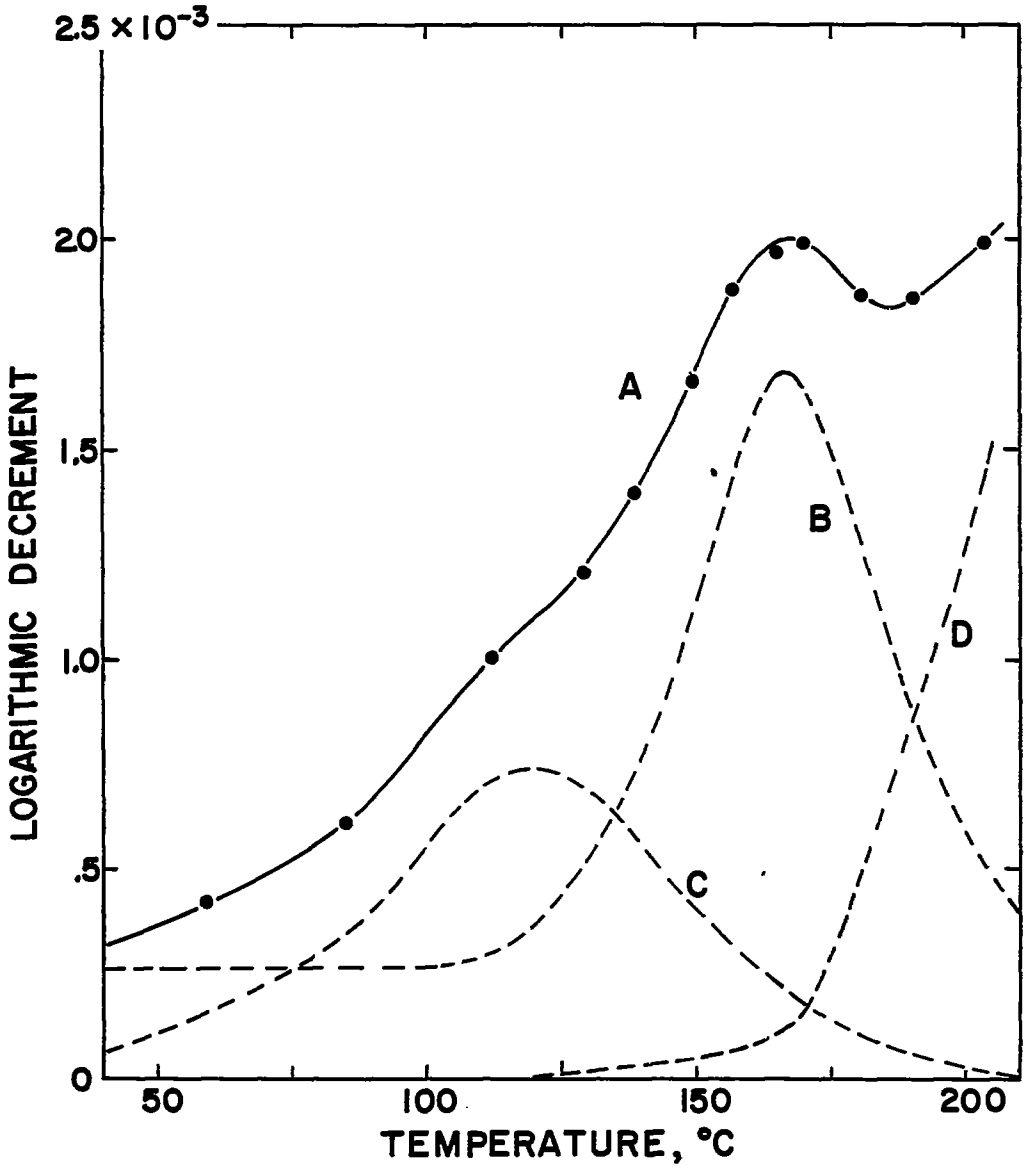

Figure 10.- A possible analysis of contributions to internal friction of specimen 3 after 11.1 hours aging at 203° C. Curve A shows temperature dependence observed after 11.1 hours at 203° C in torsional vibration at 0.5 cps; curve B shows estimated reduced initial peak superimposed on a decrement of 0.00025 which is attributable to a constant external-energy loss; curve C shows estimated second peak; curve D shows estimated high-temperature background. The analysis is self-consistent in the sense that sum of ordinates of curves B, C, and D at any temperature is equal to ordinate of curve A at that temperature.

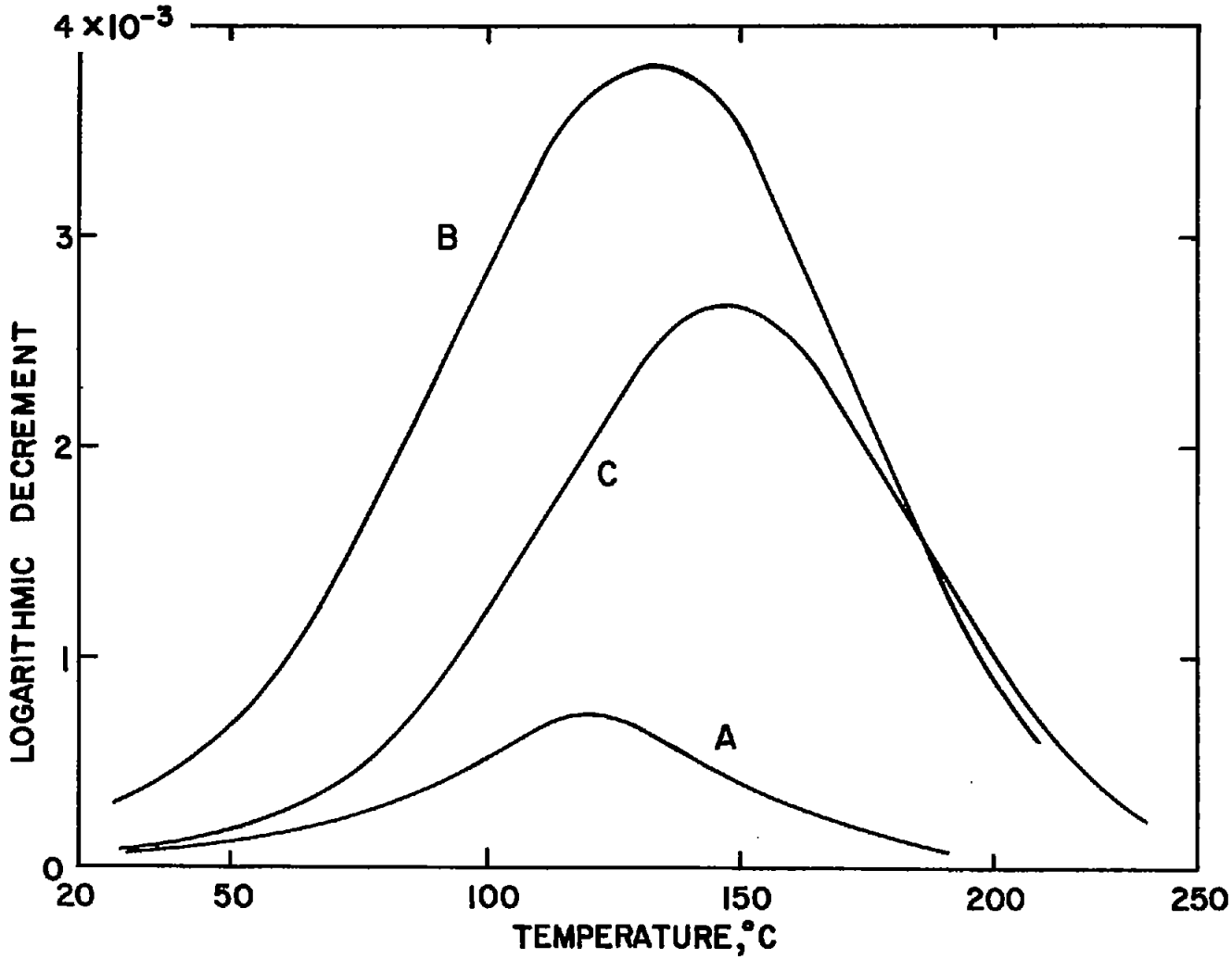

Figure 11.- The estimated second peak in specimen 3 after various aging treatments. Peaks are for torsional vibration at a frequency of 0.5 cps. Curve A indicates peak after 11.1 hours at 203° C; curve B indicates peak after 144 hours at 203° C; curve C indicates peak after 144 hours at 203° C, plus 15.7 hours at 298° C, plus 15.1 hours at 330° C.

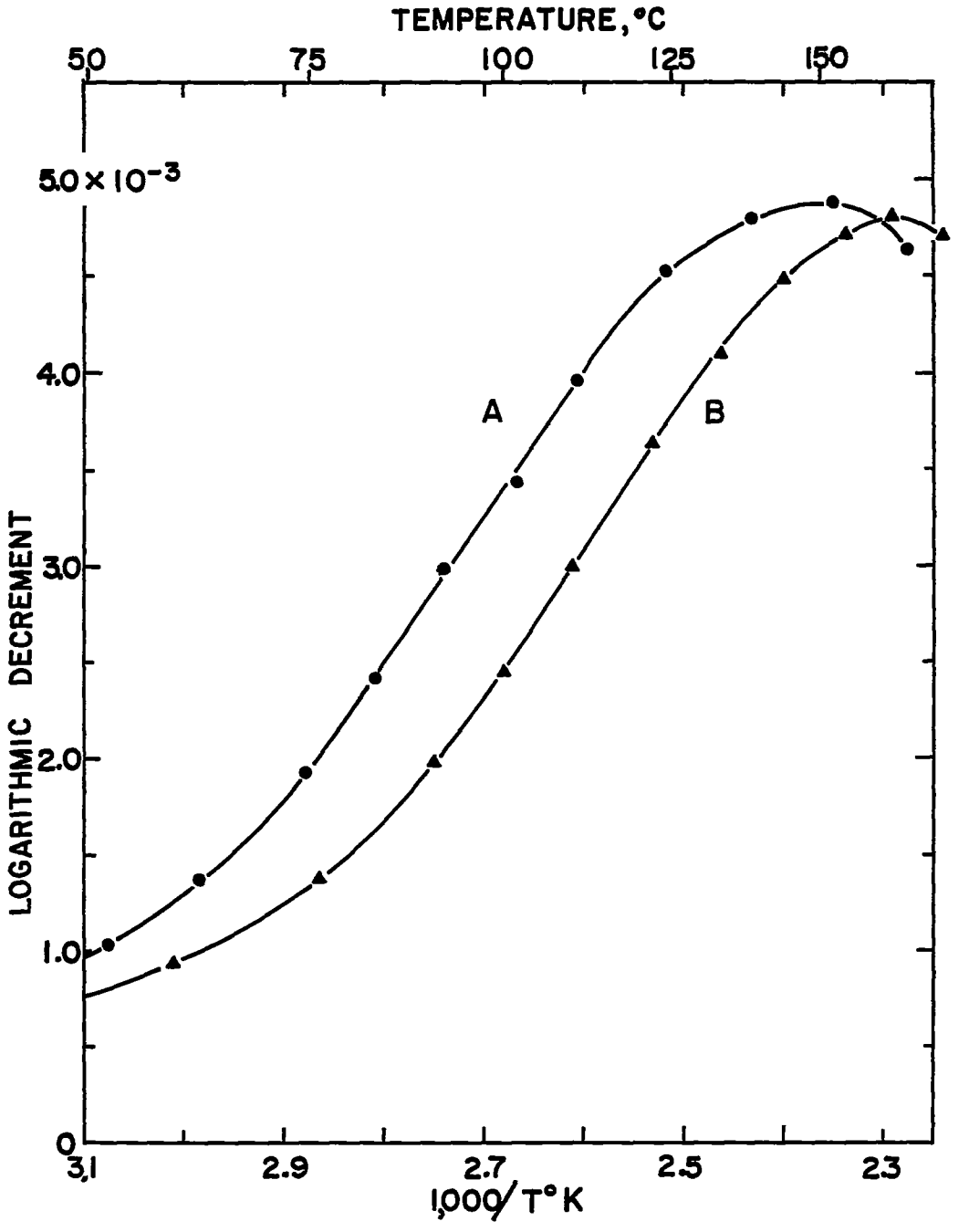

Figure 12.- Temperature dependence of the internal friction of specimen 3 after 144-hour aging at 203° C, for two frequencies of torsional vibration. Curve A is for frequency 0.550 cps; curve B is for frequency 2.04 cps.

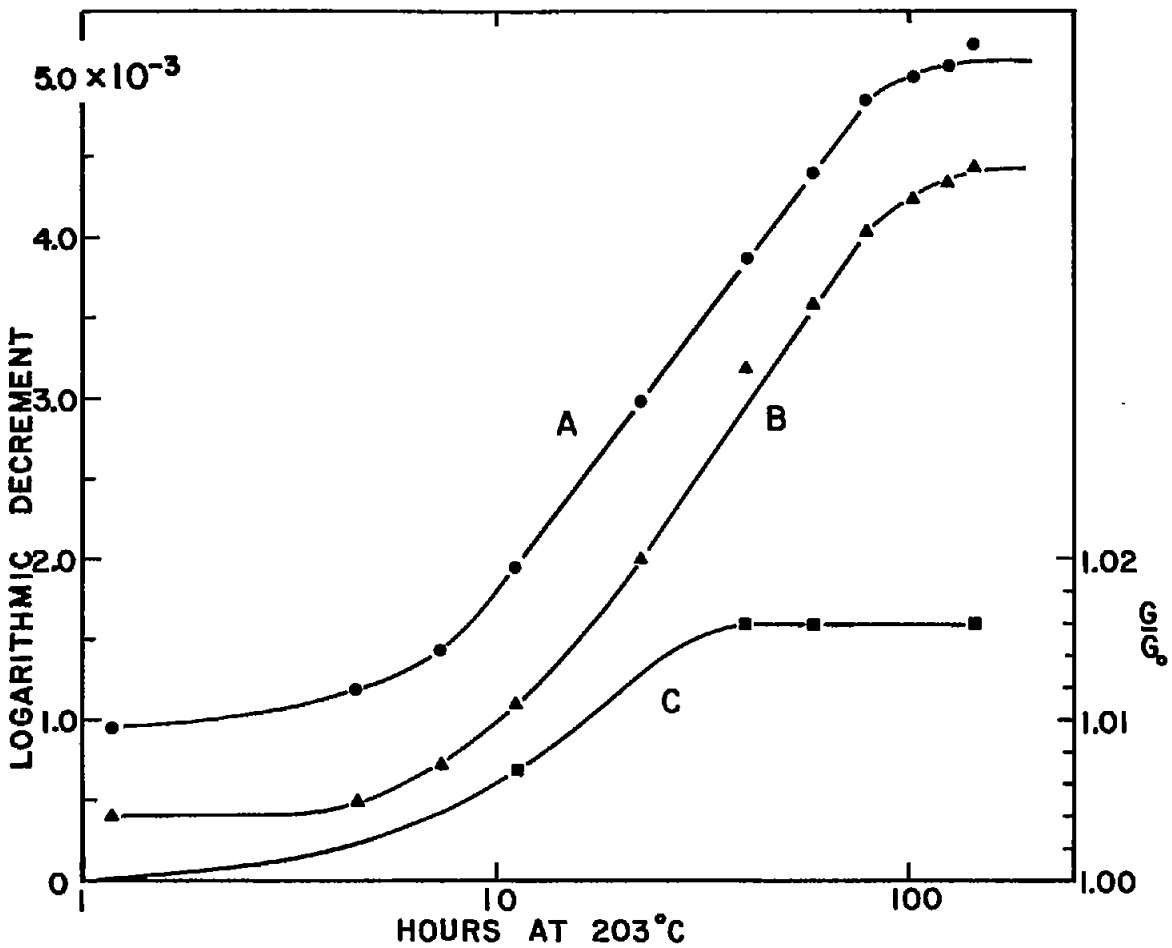

Figure 13.- Changes in isothermal internal friction and shear modulus of specimen 3 with aging time at 203° C. Results are for torsional vibration at 0.5 cps; change in shear modulus G is expressed by ratio G/G_o, where G_o is modulus at start of aging. Curve A indicates internal friction at 203° C; curve B indicates internal friction at 120° C; curve C indicates relative change in shear modulus G/G_o.

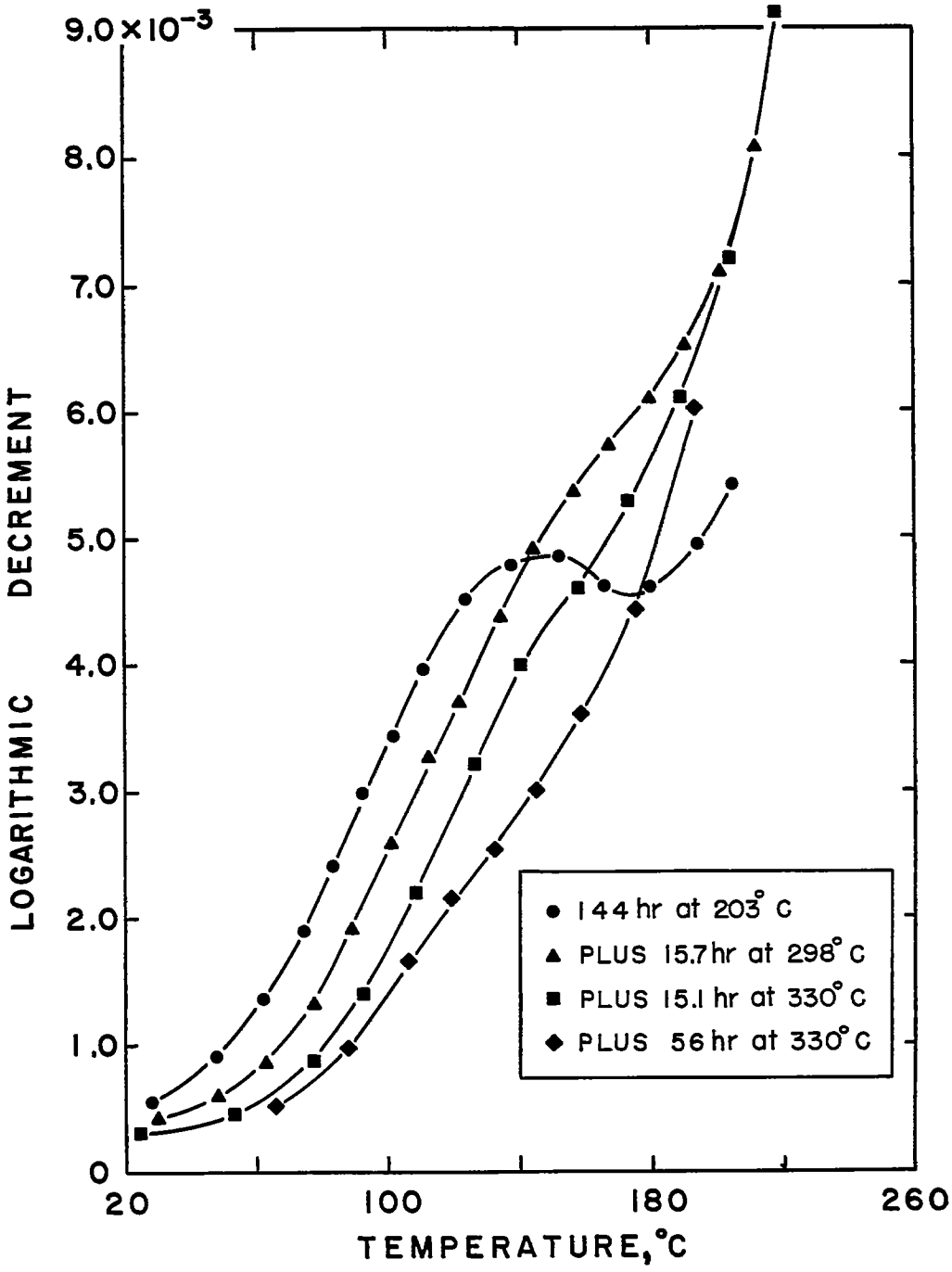

Figure 14.- Temperature dependence of internal friction of specimen 3 after cumulative treatments. Measurements were made in torsional vibration at 0.5 cps.

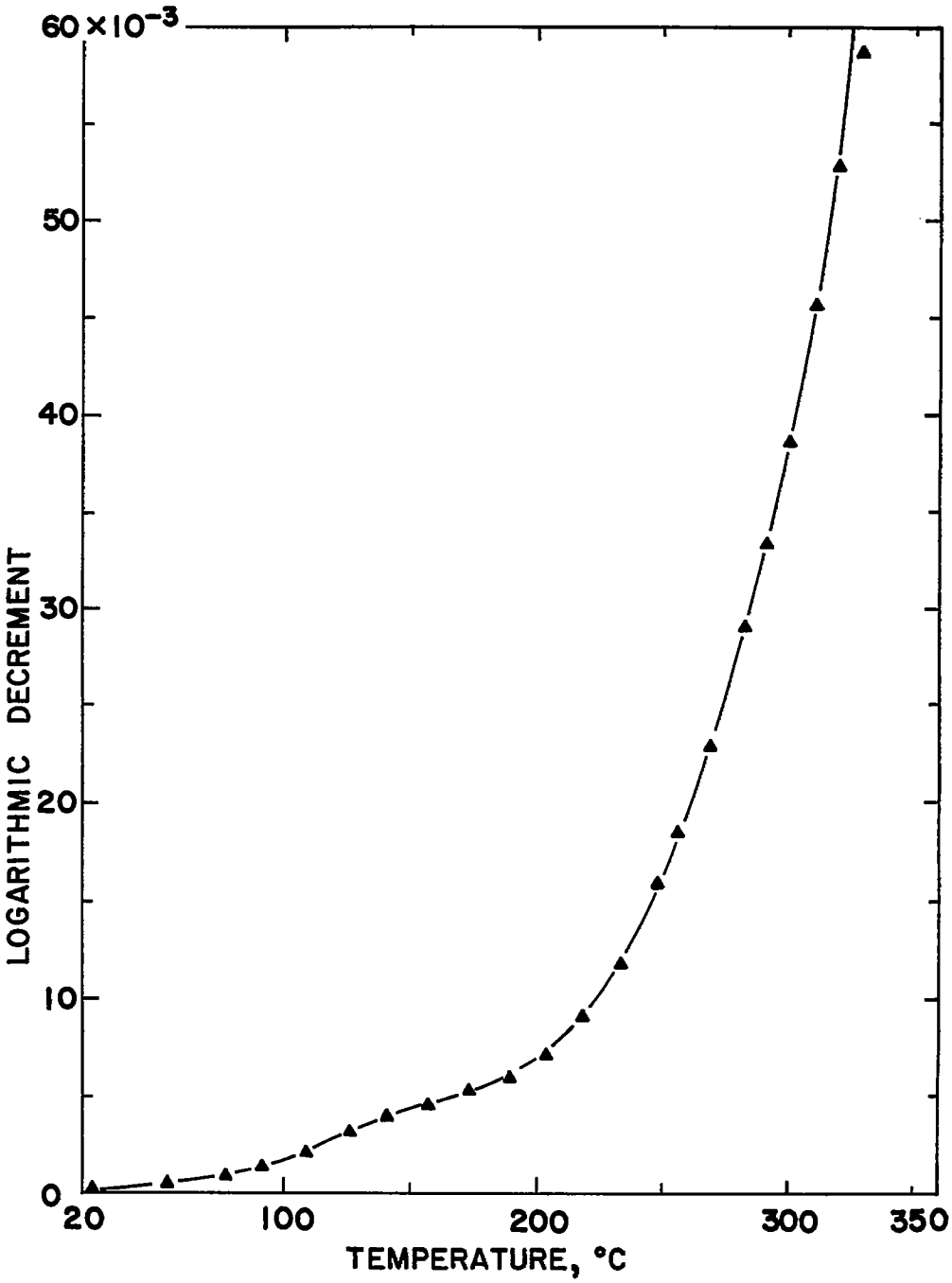

Figure 15.- Temperature dependence of the internal friction of specimen 3 after the following cumulative aging treatment: 144 hours at 203° C, plus 15.7 hours at 298° C, plus 15.1 hours at 330° C. Measurements were made in torsional vibration at 0.5 cps.

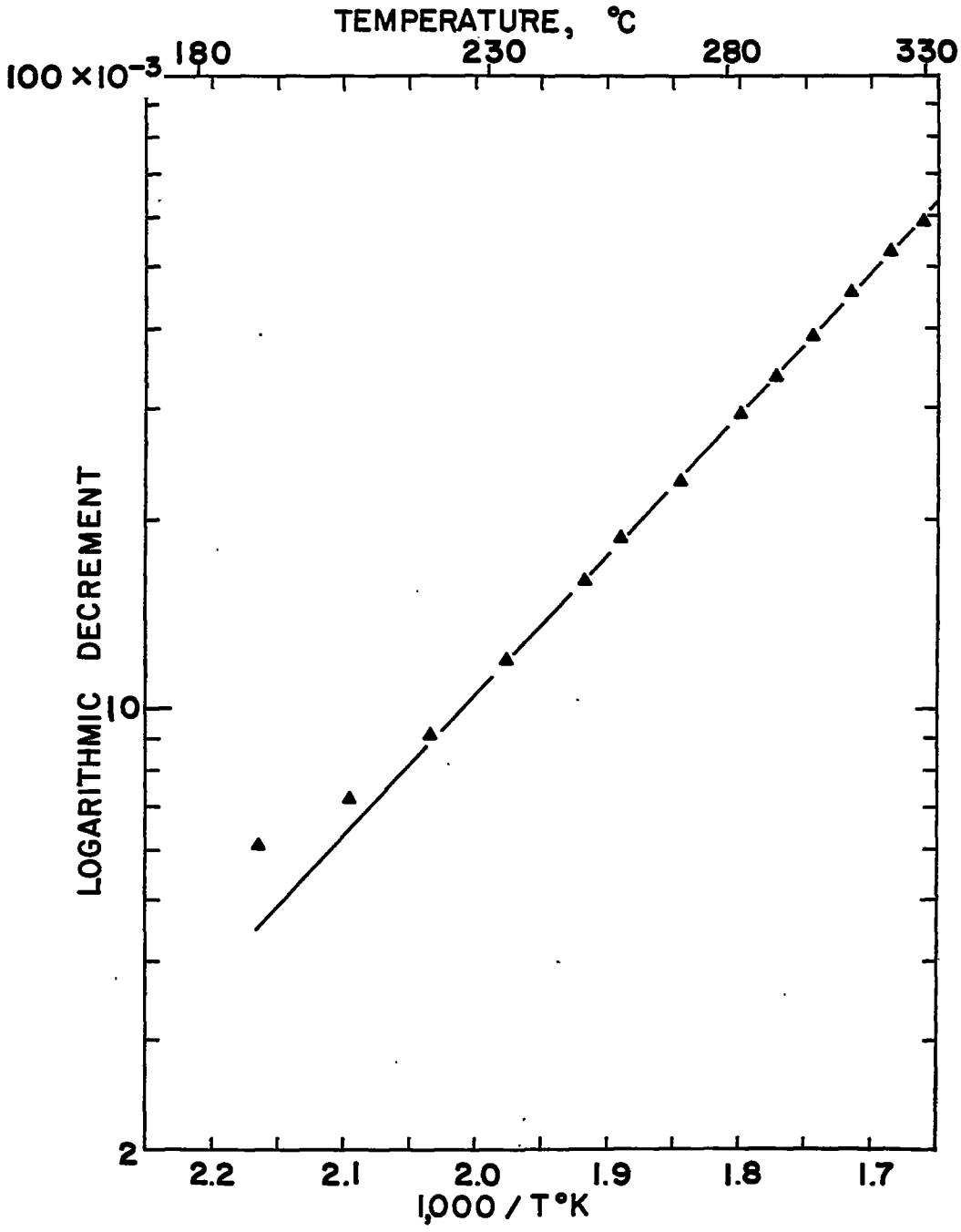

Figure 16.- A replot of figure 16 to demonstrate the linear relationship between log δ and $1/T$ above 220° C.

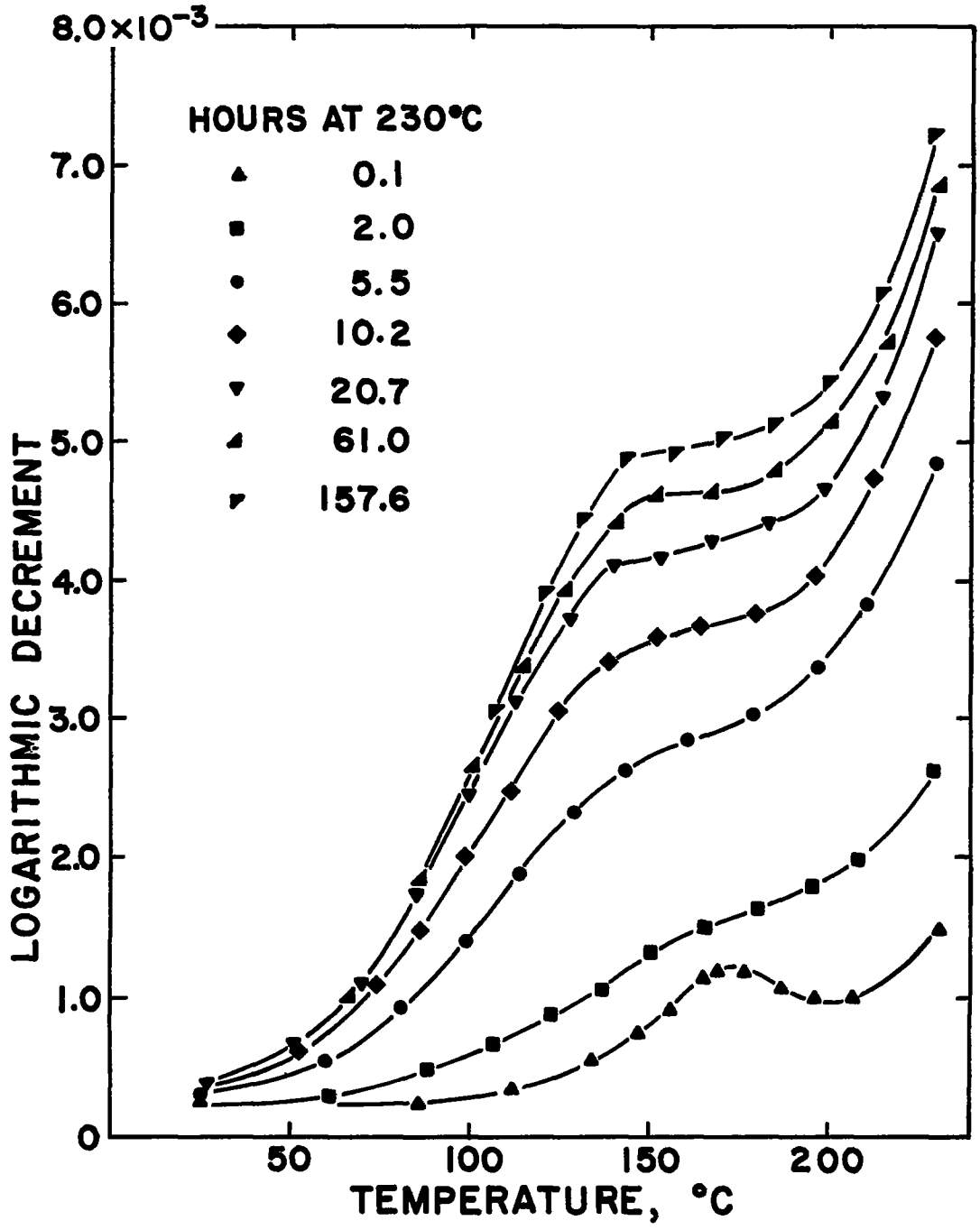

Figure 17.- Temperature dependence of internal friction of specimen 2 after aging at 230° C for the times indicated. Measurements were made in torsional vibration at 0.080 cps.

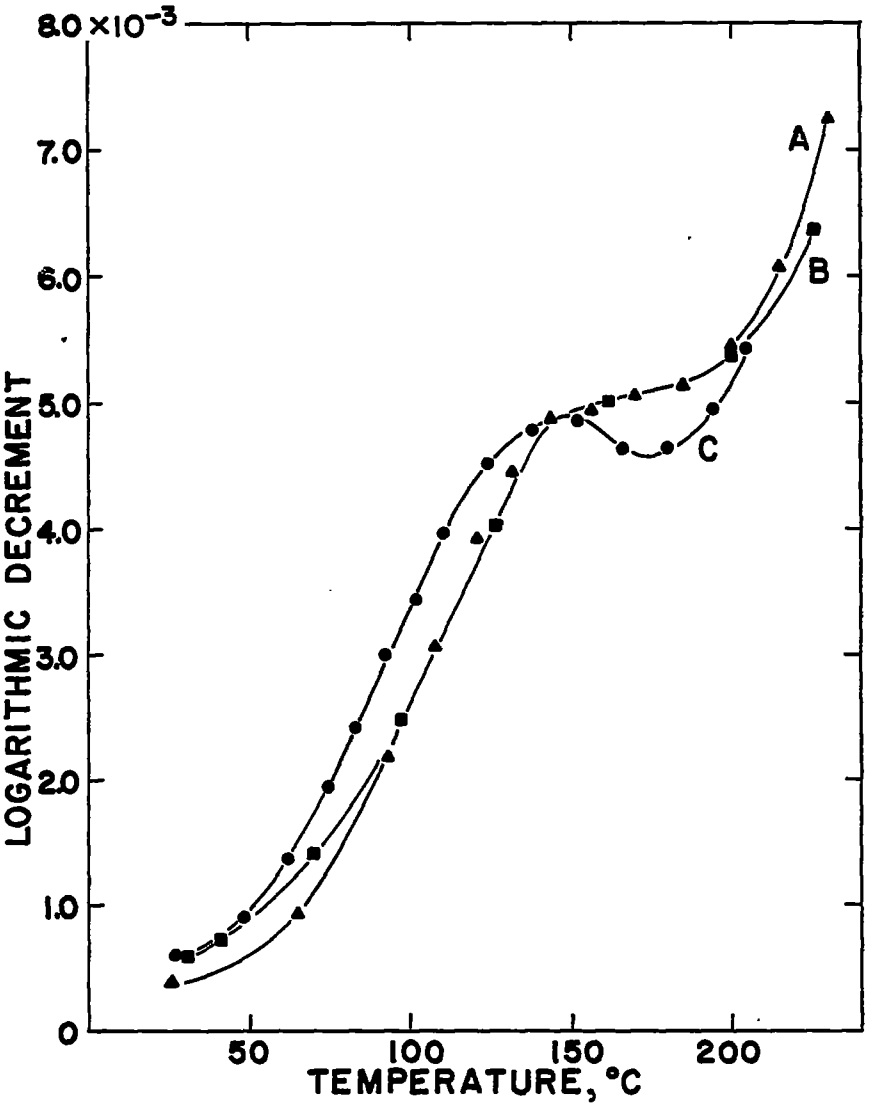

Figure 18.- A comparison of internal-friction behavior shown by three different specimens after sufficient aging to develop fully the second peak. All measurements were made in torsional vibration. Curve A shows results for specimen 2 aged for 157.6 hours at 230° C, frequency = 0.81 cps; curve B shows results for a polycrystalline specimen aged 110 hours at 200° C, frequency = 1.80 cps; curve C shows results for specimen 3 aged 144 hours at 203° C, frequency = 0.55 cps. The polycrystalline specimen was tested in air at atmospheric pressure, and points shown have been obtained by subtracting 0.00120 from experimental observations to allow for difference between room-temperature damping in air at atmospheric pressure and helium at 10 millimeters pressure.

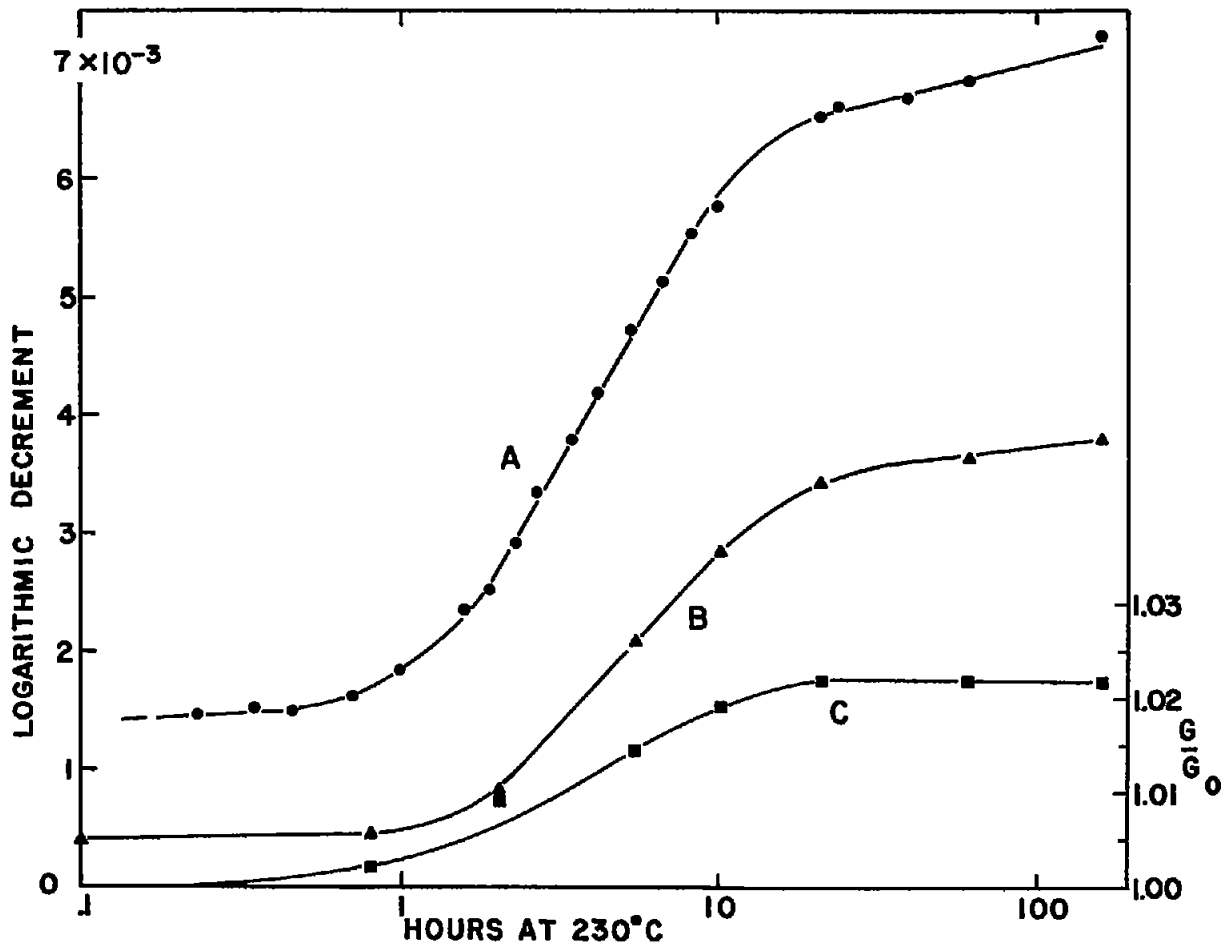

Figure 19.- Changes in isothermal internal friction and shear modulus of specimen 2 with aging time at 230° C. Measurements were made in torsional vibration at 0.8 cps. Change in shear modulus G is expressed by ratio G/G_o where G_o is modulus at start of aging. Curve A indicates internal friction at 230° C; curve B indicates internal friction at 120° C; curve C indicates relative change in shear modulus G/G_o.

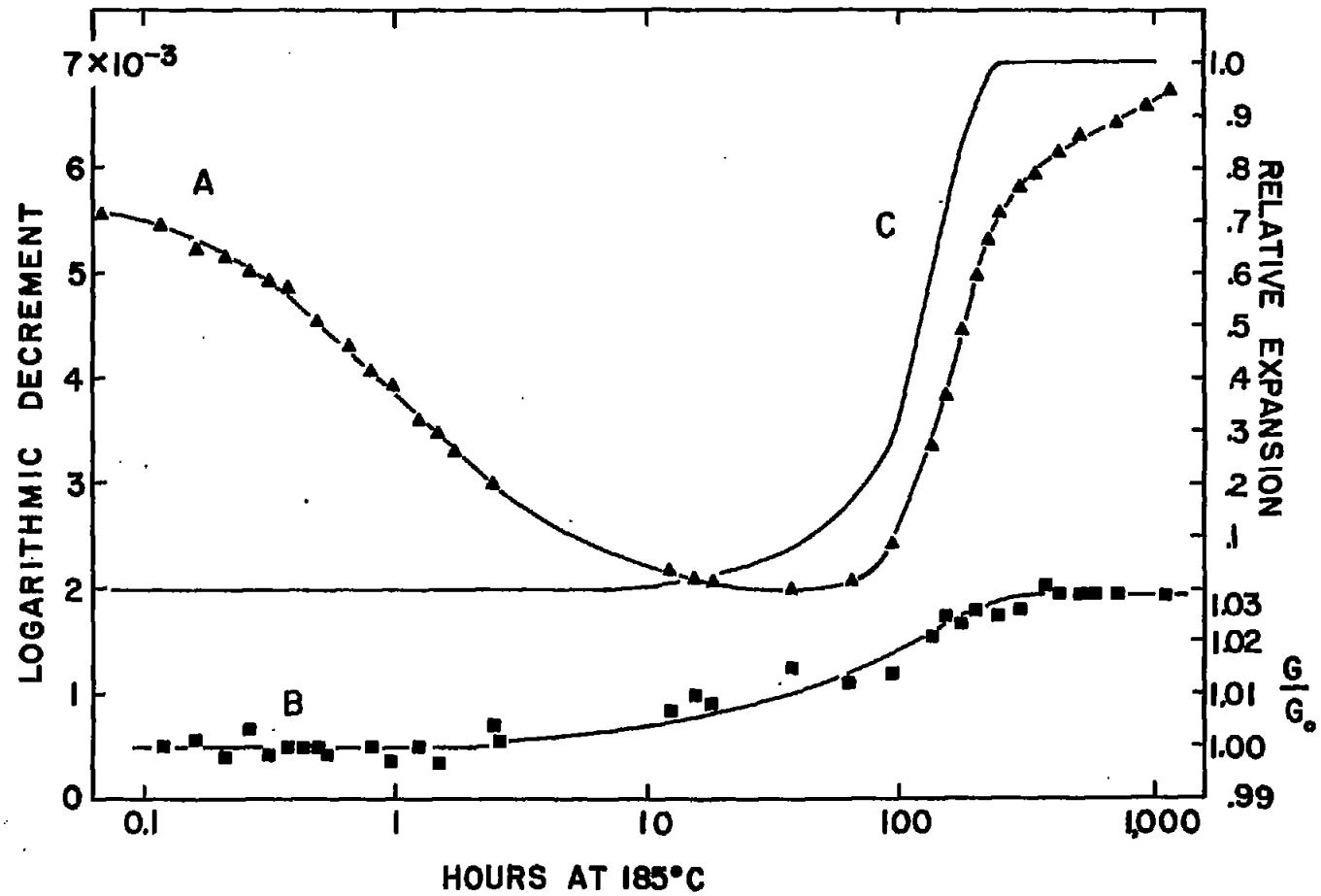

Figure 20.- Changes in polycrystalline specimens of Al alloy containing 4 percent Cu on aging at 185° C. Curves A and B are for torsional vibration at 1.4 cps. Curve A indicates isothermal internal friction at 185° C. Points shown are experimental observations after subtraction of room-temperature decrement prior to aging; curve B indicates relative change in shear modulus G/G_0; curve C indicates relative expansion at 185° C, taken from the results of Lankes and Wassermann (ref. 45).

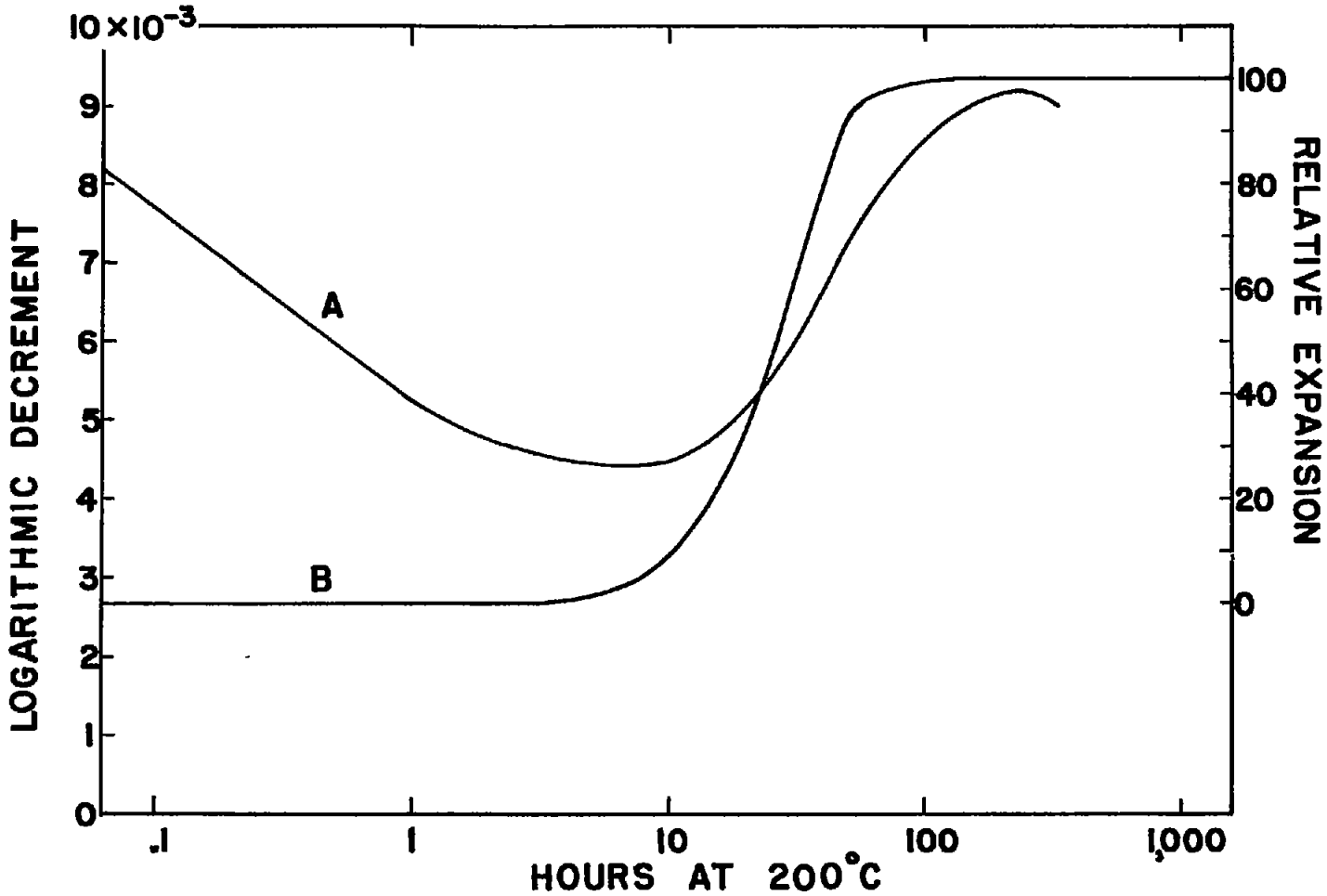

Figure 21.- Changes in polycrystalline specimens of Al alloy containing 4 percent of Cu on aging at 200° C. Curve A indicates internal friction at 200° C from the results given by Kê (ref. 31); frequency of measurement was not given but is estimated to be 1 ± 0.5 cps; room-temperature decrement (also unknown) is estimated to be 0.0015 ± 0.0005; curve B indicates the relative expansion at 200° C, taken from the results of Lankes and Wassermann (ref. 45).

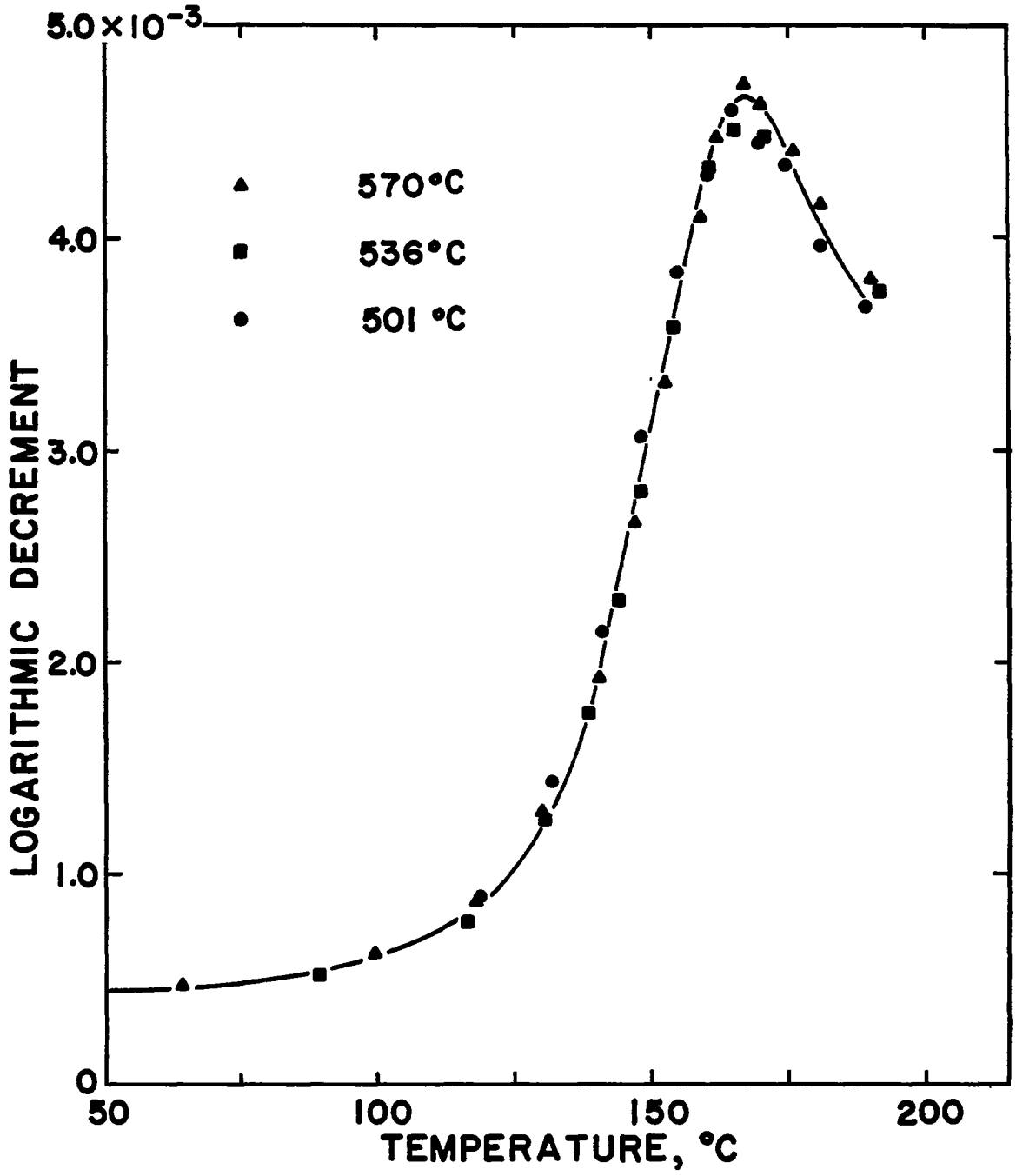

Figure 22.- Initial peak of polycrystalline Al alloy containing 4 percent Cu on first cooling from 190° C after quenching from solution-treatment temperatures indicated. Measurements were made in torsional vibration at 0.396 cps.

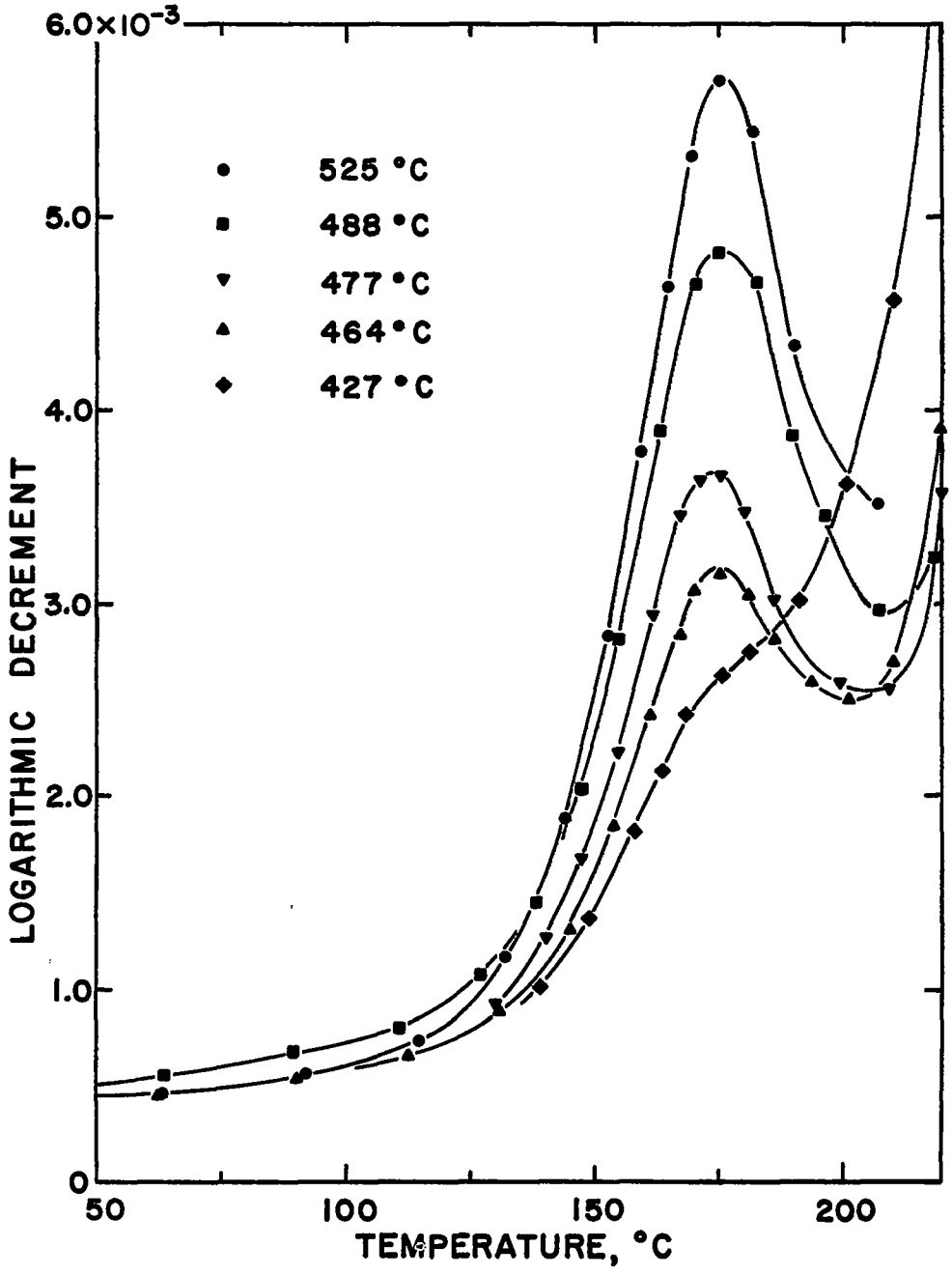

Figure 23.- Initial peaks on first cooling shown by a polycrystalline specimen of Al alloy containing 4 percent of Cu after quenching from 525° C and from four temperatures below the phase boundary following an anneal to establish equilibrium. Measurements were made in torsion at 0.90 cps.

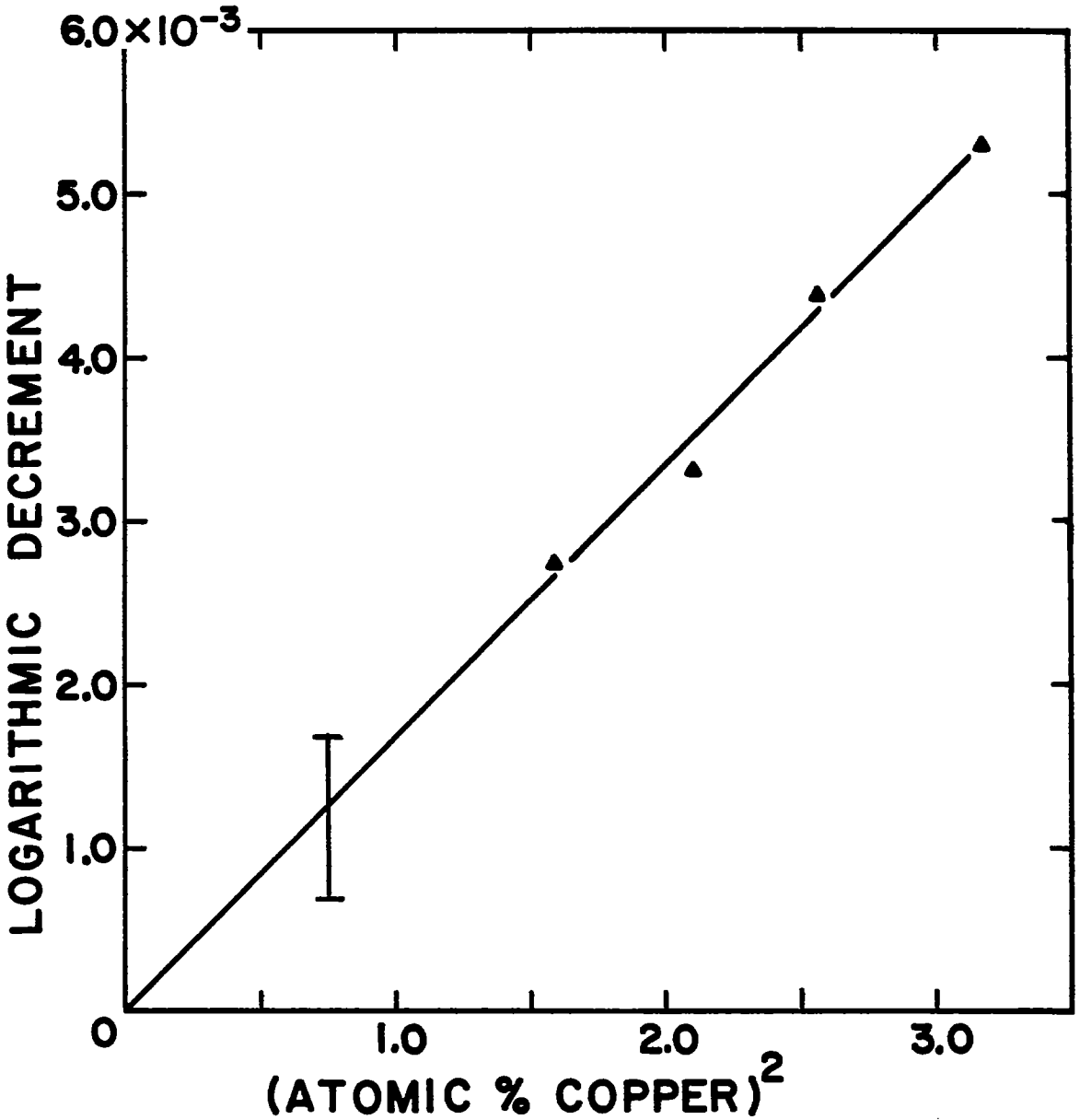

Figure 24.- Initial peak heights of figure 23 plotted against the square of atomic percentage of copper remaining in solution.

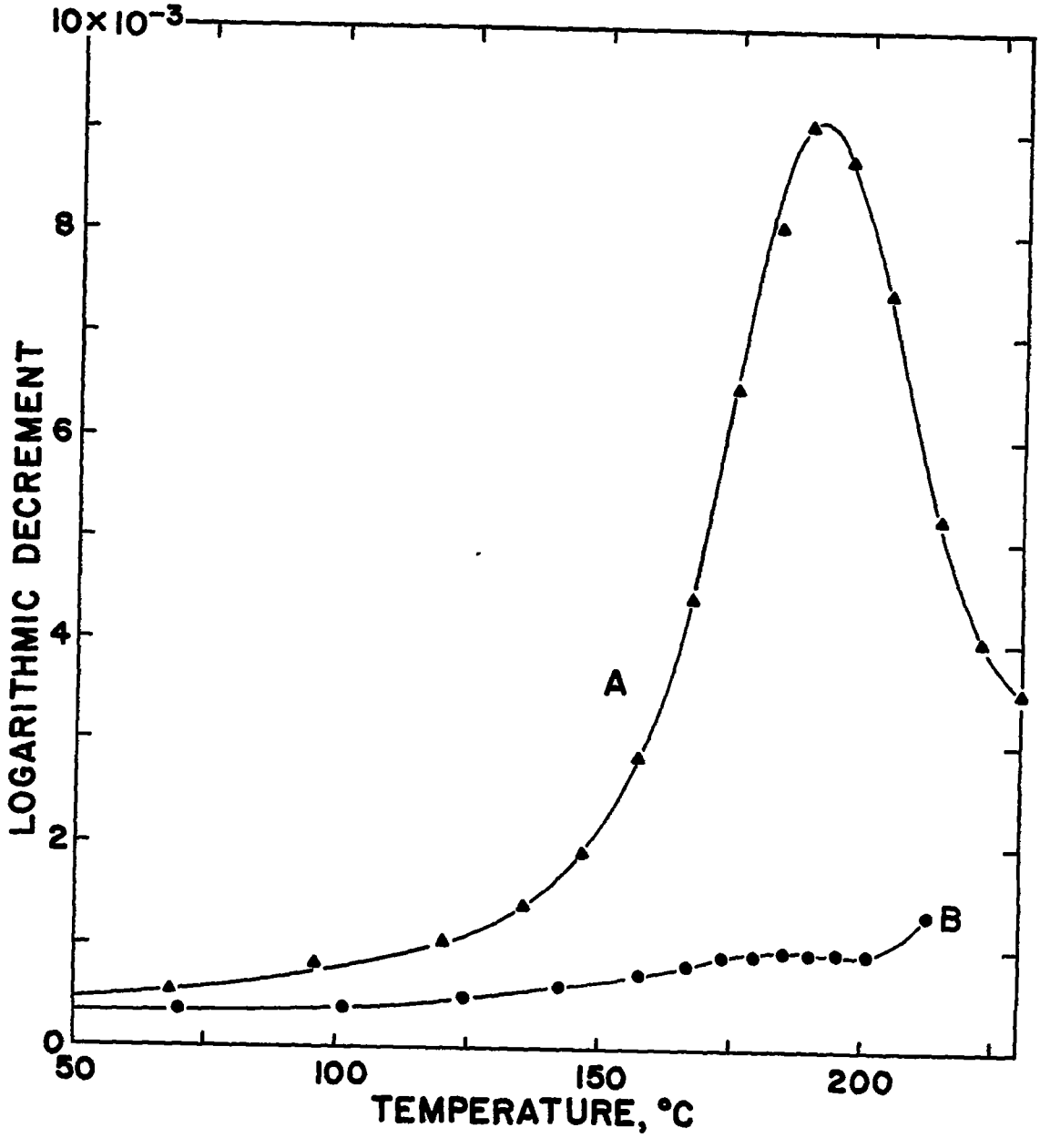

Figure 25.- Initial peak on first cooling for single crystals of Al alloy containing 4 percent Cu oriented with <100> nearly parallel to the specimen axis. Curve A shows results for specimens 4 and 5 tested together in flexure at 2.8 cps; curve B shows results for specimen 5 tested in torsion at 1.4 cps. All points shown in curve A have been reduced by 0.0014 to correct for higher background in flexure apparatus.

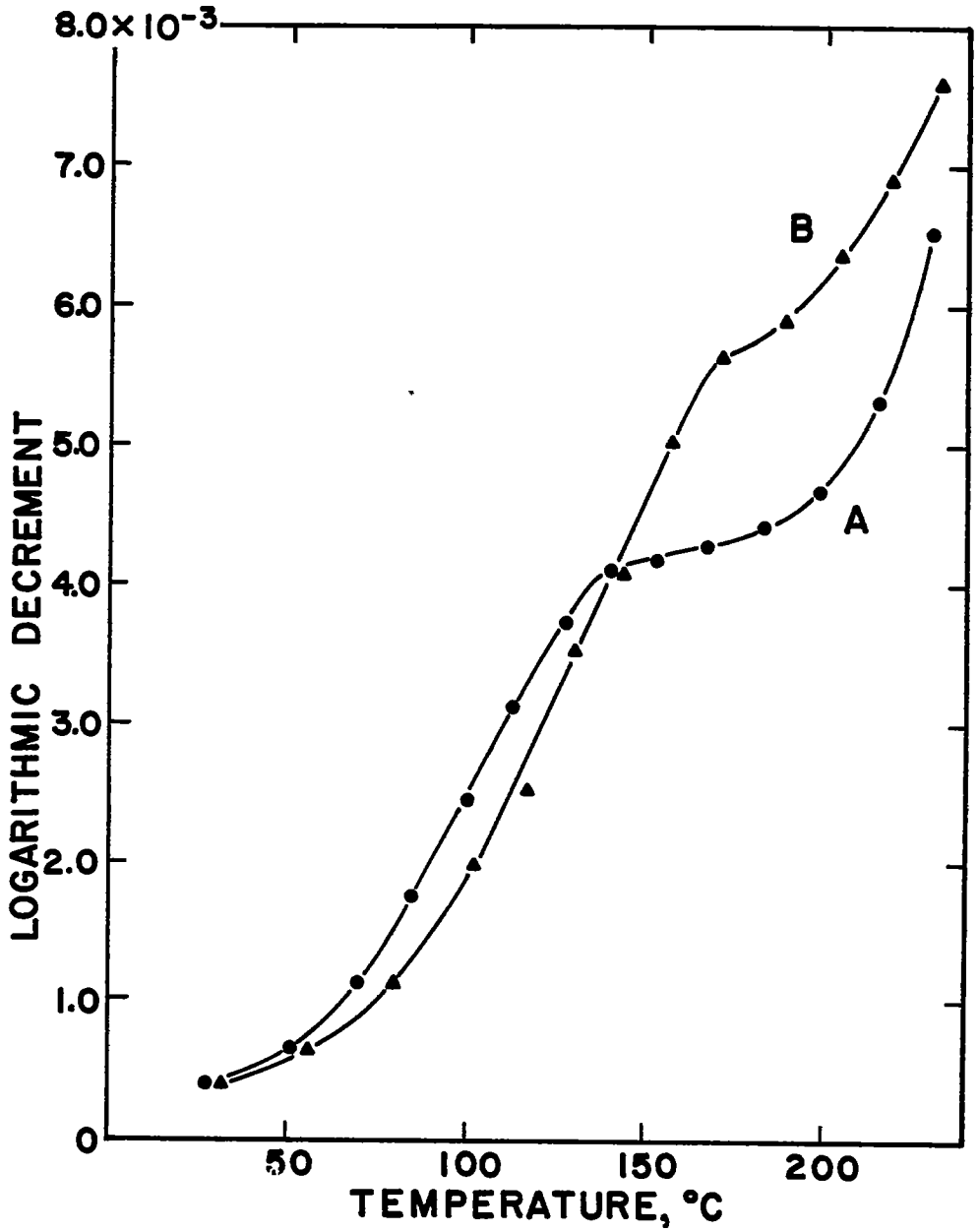

Figure 26.- Internal-friction behavior of nearly <100> oriented single crystals of Al alloy containing 4 percent Cu after sufficient aging at 230° C to develop fully the second peak. Curve A shows results for specimen 2 tested in torsional vibration at 0.81 cps after 20.7 hours aging at 230° C; curve B shows results for specimens 4 and 5 tested together in flexural vibration at 3.0 cps after 22.5 hours aging at 230° C.

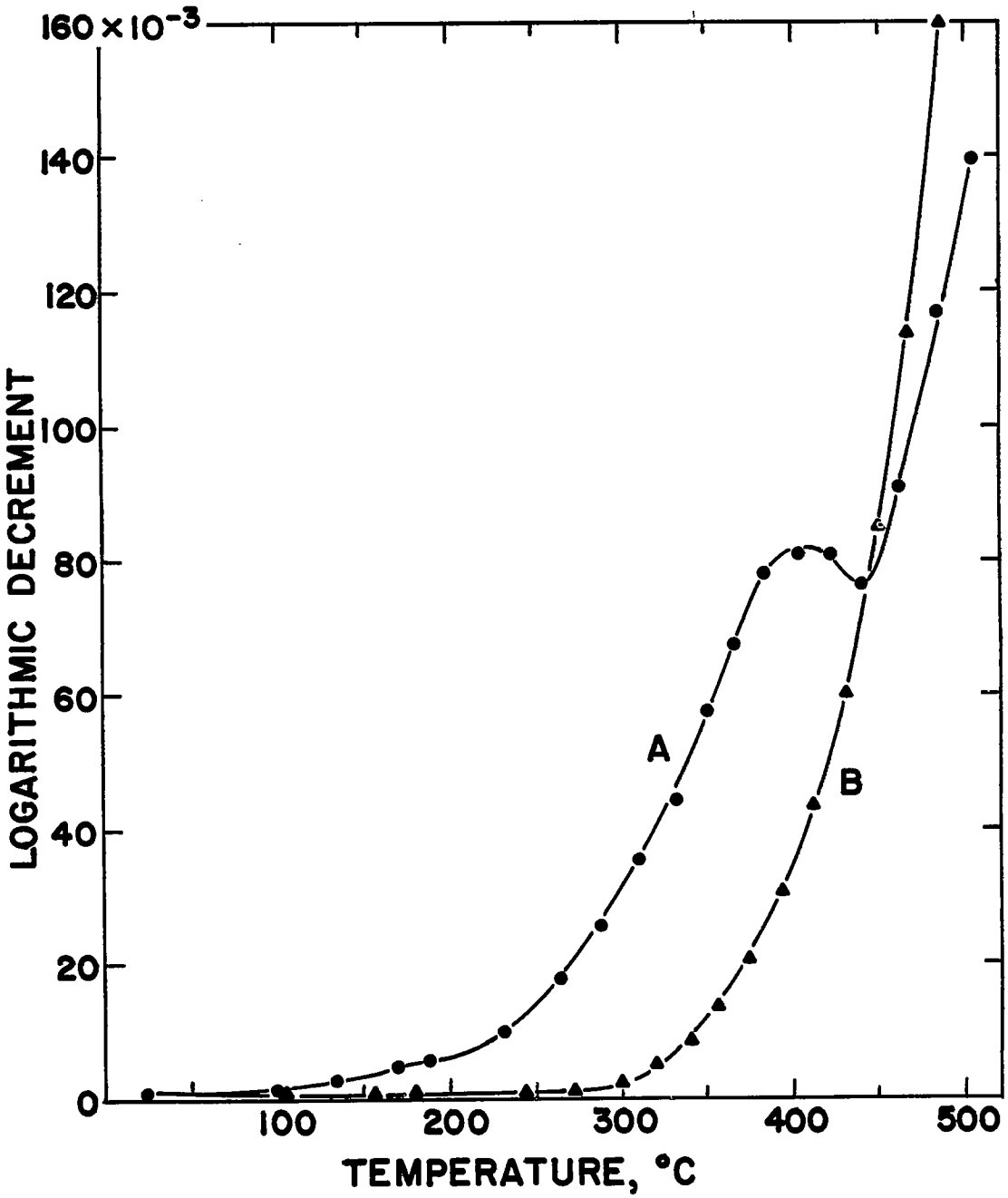

Figure 27.- Internal-friction behavior of single-crystal specimen 5 at high temperatures, after aging for 35.5 hours at 300° C. Measurements were made in torsional vibration at 1.4 cps. Curve A shows results when specimen is heated to 505° C; curve B shows results when specimen is cooled from 505° C after a stay of 1.5 hours.

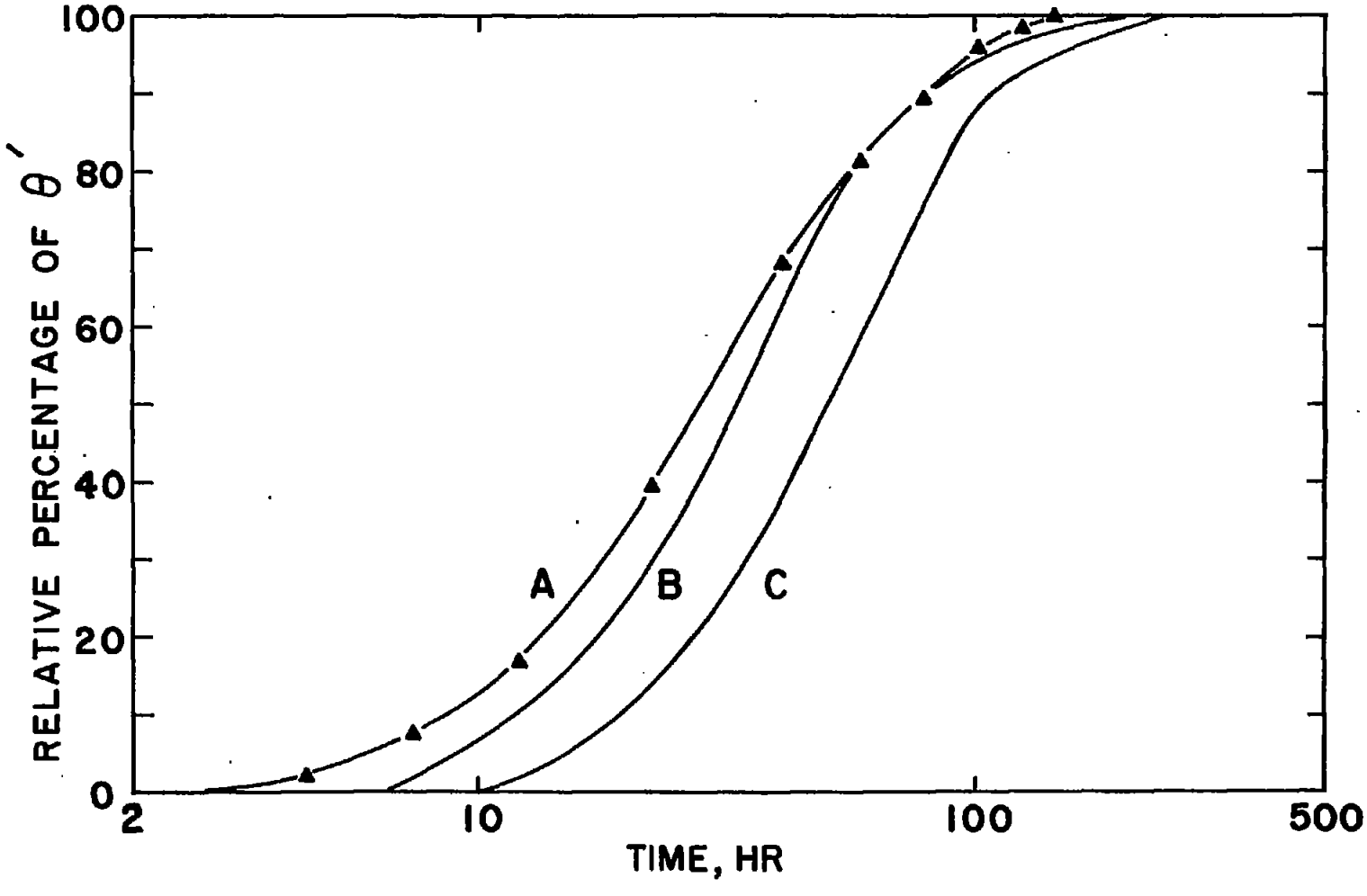

Figure 28.- Percentage of θ' phase as a function of aging time. Curve A shows results from internal-friction measurements, for an aging temperature of 203° C; curve B shows results from the dilatometric measurements of Lankes and Wassermann (ref. 45), for an aging temperature of 200° C; curve C shows results from the quantitative X-ray measurements of Guinier (ref. 44), for an aging temperature of 200° C.

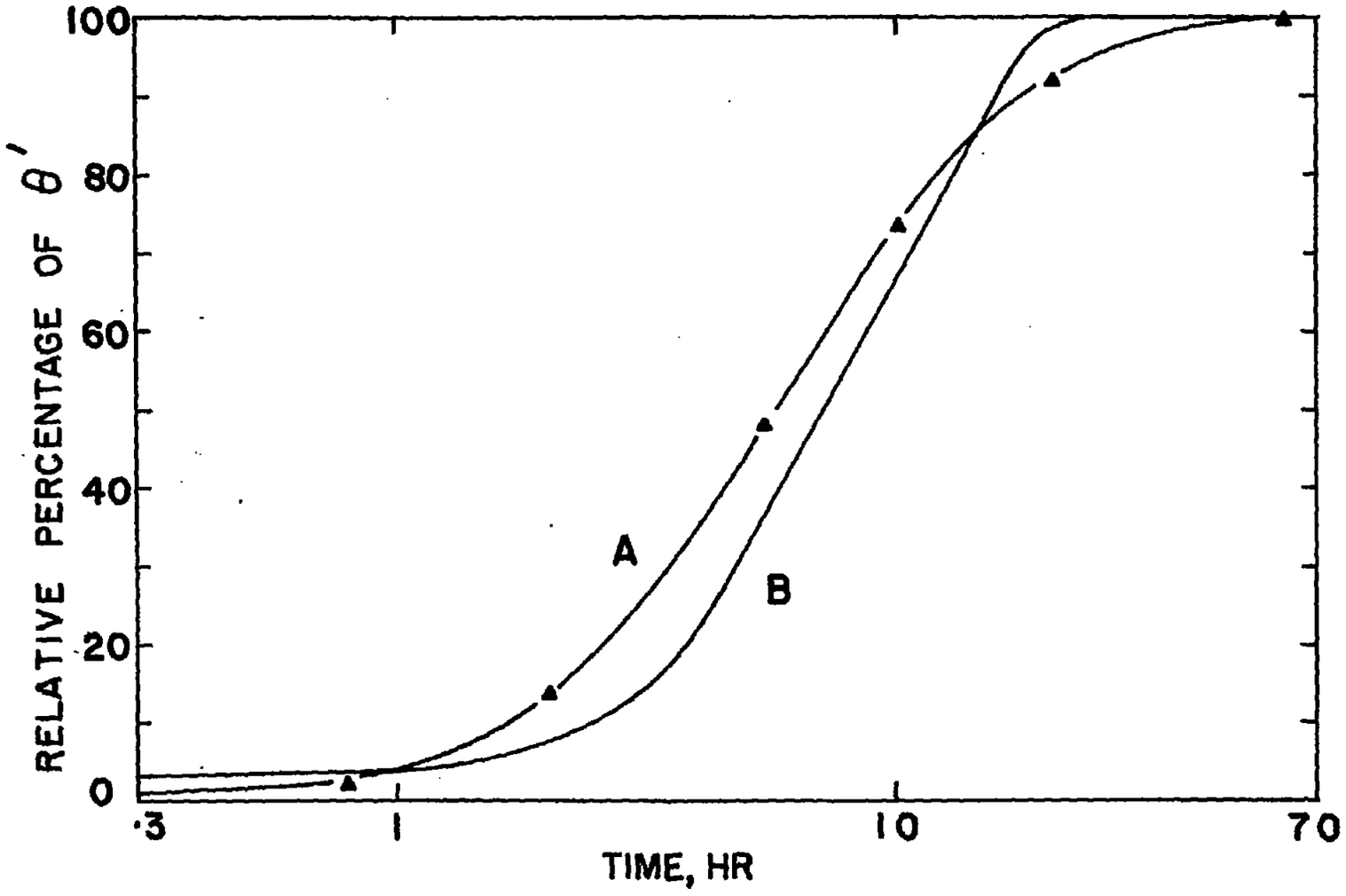

Figure 29.- Percentage of θ' phase as a function of aging time at 230° C. Curve A shows results from internal-friction measurements; curve B shows results from the dilatometric measurements of Lankes and Wassermann (ref. 45).