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Ideal elastic, anelastic and viscoelastic deformation of a metallic glass

A. I. TAUB
Research and Development Center, General Electric Company, P.O. Box 8, Schenectady, New York 12301, USA

F. SPAEPEN
Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

The elastic, viscoelastic and anelastic components of the homogeneous strain response of the metallic glass $Pd_{82}Si_{18}$ to an applied stress have been examined. The elastic response is fully reversible, instantaneous and linear. The measured elastic modulus, E, and temperature dependence, $d(\ln E)/dT$, are 84 ± 8 GPa and $(-3.2 \pm 0.6) \times 10^{-4}\,C^{-1}$, respectively. The viscoelastic flow is non-recoverable and, if the configuration remains constant, is characterized by a constant strain rate. This strain rate varies linearly with the stress, τ, in the low stress regime ($\tau < 300$ MPa), becoming non-linear for higher stresses. For isoconfigurational flow, the strain rate has an Arrhenius-type temperature dependence with an activation energy of -200 ± 15 kJ mol^{-1}, independent of stress and thermal history. The magnitude of the strain rate is strongly dependent on the degree of structural relaxation and therefore on thermal history. During isothermal annealing the viscoelastic strain rate varies inversely with time. The anelastic response is a transient that, at 500 K, contributes to the flow for approximately fifty hours after a stress increase and is fully recovered upon stress reduction. A spectrum of exponential decays is required to model this flow component. The anelastic strain, γ_A, varies linearly with the magnitude of the stress change, $\Delta\tau$, over the entire stress range tested: $\gamma_A/\Delta\tau = (8.0 \pm 0.8) \times 10^{-6}$ MPa^{-1}.

1. Introduction

When a material is subjected to an applied stress, its strain response is generally made up of several components, each differing by its dependence on time, by the degree to which it is recovered upon removal of the stress, and by the linearity of the response [1]. Glassy metallic alloy systems have been reported to exhibit at least four of these strain components:

(a) ideal elasticity (recoverable, instantaneous, linear stress–strain relation) [2, 3];

(b) anelasticity (recoverable, time-dependent, linear stress–strain relation) [4–8];

(c) viscoelasticity (permanent, time-dependent, linear stress–strain relation) [5, 6, 9, 10]; and

(d) instantaneous plasticity (permament, instantaneous, non-linear stress–strain rate relation) [11].

In this study, an amorphous Pd-based alloy was tested in the homogeneous flow regime. Testing in the homogeneous flow regime eliminates the strain contribution of the instantaneous plastic flow mechanism [12, 13]. For each of the three remaining strain components, the time dependence, recoverability and linearity are examined in detail. The effect of structural relaxation on each type of strain is also discussed.

2. Results

The tensile creep flow of amorphous $Pd_{82}Si_{18}$ wires was measured by the technique described previously [9]. Both as-quenched and pre-annealed specimens were tested. The pre-anneals served to stabilize the structure of the specimens, thus permitting isoconfigurational testing. For pre-annealed specimens that were to undergo stress

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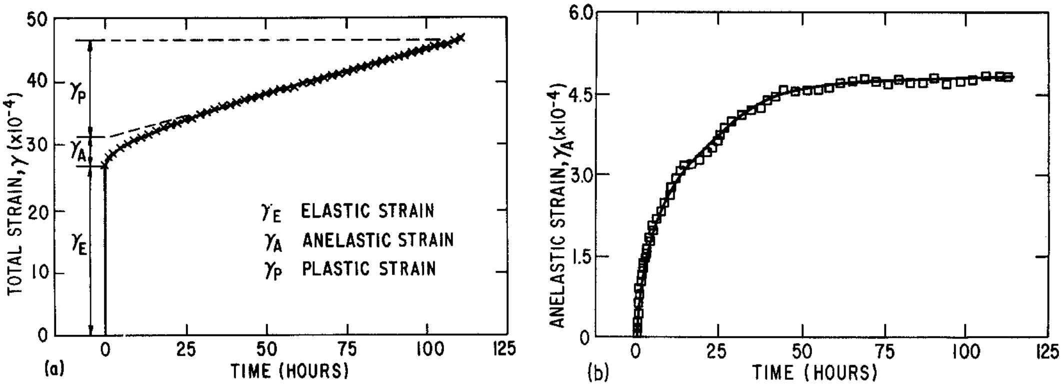

Figure 1 Strain response to equivalent shear stress increase from 105 to 156 MPa. Sample pre-annealed at testing temperature of 500 K for 343 h. Symbols × and □ are actual data. Solid lines are least-square fit curves using the five exponential decay formulation described in the text. (a) Total equivalent shear strain ($\gamma = \sqrt{3}\,\epsilon$, where ϵ is the uniaxial tensile strain). (b) Equivalent anelastic shear strain, γ_A, obtained by subtracting the ideal elastic and viscoelastic strains.

reductions during the creep test, load cycling was conducted during the anneal in order to eliminate any structural relaxation that might be associated with load removal during the test [14].

Fig. 1a shows a typical strain against time plot obtained for a pre-annealed specimen after a stress increase. The pre-anneal in this case was 325 h at 500 K. The instantaneous alongation, γ_E, is characterized by ideal elasticity. The steady-state strain, γ_P, established after approximately 50 h, is viscoelastic. The anelastic strain contribution, γ_A, is the transient flow that occurs before the steady-state condition is established.

2.1. Ideal elasticity

The elastic response of specimens pre-annealed at 500 K for 325 h was measured at 293, 424 and 500 K. In all cases, the response was instantaneous, completely reversible and linear.

The tensile elastic modulus (i.e., Young's modulus), at 293 K, was determined to be 84 ± 8 GPa. This is in good agreement with the value of 88 GPa obtained by Davis [11] for $Pd_{80}Si_{20}$.

Using the values of the moduli determined at all three temperatures, and assuming a linear temperature dependence, we found that $d(\ln E)/dT = (-3.2 \pm 0.6) \times 10^{-4}\ C^{-1}$. This is to be compared with the dynamic measurement value of $-2.9 \times 10^{-4}\ C^{-1}$ obtained by Berry and Pritchet [15].

Structural changes in the amorphous state have been shown to affect the elastic stiffness of metallic glasses [2]. Increases in modulus approaching 10%, relative to the as-cast condition, have been reported for many systems annealed near the glass transition temperature [3]. In our tests, the pre-anneal for 325 h at 500 K was sufficient to stabilize the structure and no changes in modulus were observed during the loading and unloading tests.

2.2. Anelasticity

Fig. 1b shows the anelastic component of the total strain of Fig. 1a, obtained by subtracting the ideal elastic and viscoelastic contributions to the strain. The time-dependent, transient nature of the flow is evident. Additional anelastic flow is not resolvable after approximately two days.

Complete recoverability is a requirement for true anelastic behaviour. In Fig. 2, the results of a test of this condition are examined by observing the response to a stress cycle from 35 to 71 to 35 MPa. The entire response is plotted in Fig. 2a. The elastic response is seen to be completely and instanteously recovered on stress reduction ($\gamma_E = -\gamma_{E'}$, where $\gamma_{E'}$ is the elastic recovery). In Fig. 2b, only the anelastic contribution is shown. Complete recoverability of this strain response is verified ($\gamma_A = -\gamma_{A'}$, where $\gamma_{A'}$ is the anelastic recovery).

The linearity condition for true anelastic flow requires that the total anelastic strain, after the complete decay of the transient, be directly proportional to the magnitude of the stress change. To check this requirement, a creep sample was subjected to sequential stress increases at 500 K, and the anelastic strain determined in the manner illustrated in Fig. 1. Table I lists the observed anelastic strain values for the stress increments and a linear relation is verified such that $\gamma_A/\Delta\tau =$

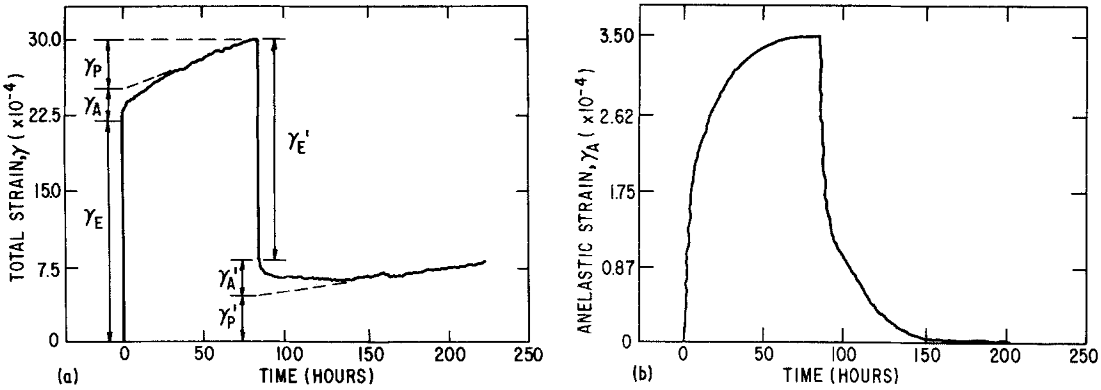

Figure 2 Strain response to stress cycle from 35 to 71 to 35 MPa. Sample pre-annealed at testing temperature of 500 K for 575 h. (a) Total strain γ; (b) anelastic strain γ_A.

$(8.0 \pm 0.8) \times 10^{-6}$ MPa^{-1}, where τ is the equivalent shear stress $\tau = \sigma/\sqrt{3}$ and σ is the uniaxial tensile stress.

A corrollary of the linearity postulate is the superposition (additivity) of the responses [1]. In another load cycle experiment, this principle was checked. The stress was raised in two steps from 35 to 71 MPa and from 71 to 106 MPa. The associated anelastic strains were $(3.5 \pm 0.2) \times 10^{-4}$ and $(3.8 \pm 0.3) \times 10^{-4}$. The stress was then reduced in one step to 35 MPa, with a corresponding anelastic recovery of $(7.0 \pm 0.3) \times 10^{-4}$. The superposition of the responses was thus verified.

Although several investigators have examined the effect of structural changes on the anelastic relaxation spectrum of metallic glasses [2, 4], no systematic investigation of the effect of structural change on the anelastic creep response of these glasses has been reported. We observed no change in the anelastic response of the pre-annealed specimens during the testing, indicating that the 325 h pre-anneal at the testing temperature sufficiently stabilized the structure. It is possible that the anelastic creep response changes during the early stages of annealing, but in this work no observations have been made in this regime.

2.3. Viscoelasticity

The viscoelastic flow exhibited by well-annealed samples (i.e., no structural relaxation occurring during the test) is characterized by a constant strain rate. Referring to Fig. 1, the viscoelastic component is shown to contribute throughout the test, although constant strain-rate steady-state flow is not fully established until after the decay of the anelastic transient.

Viscoelastic flow must, by definition, produce a permanent strain. The test shown in Fig. 2a can be used to check this requirement. The total viscous flow, γ_P, up to 84 h when the stress was reduced, is $(5.0 \pm 0.3) \times 10^{-4}$. The observed permanent set $\gamma_{P'}$, is $(5.7 \pm 0.5) \times 10^{-4}$, verifying non-recoverability of the flow.

The linearity of the viscoelastic stress–strain rate relation has been discussed elsewhere [16]. The transition from linear to non-linear behaviour was shown to be an inherent property of metallic glasses. For $Pd_{82}Si_{18}$ specimens pre-annealed and

TABLE I Total anelastic strain for various stress increases*

Equivalent shear stress range, $\tau = \sigma/\sqrt{3}$ (MPa)	Total anelastic equivalent shear strain, $\gamma_A = \sqrt{3}\epsilon_A$ ($\times 10^{-4}$)	$\gamma_A/\delta\tau$ ($\times 10^{-6}$ MPa^{-1})
54–105	4.0 ± 0.3	7.8 ± 0.6
105–156	4.7 ± 0.3	9.0 ± 0.6
156–207	4.2 ± 0.3	8.1 ± 0.6
207–259	4.2 ± 0.3	8.1 ± 0.6
259–310	3.6 ± 0.7	7.2 ± 1.2
310–363	3.8 ± 0.3	7.2 ± 0.6
363–383	1.7 ± 0.3	8.4 ± 1.8

*Specimens pre-annealed at testing temperature of 500 K for 343 h.

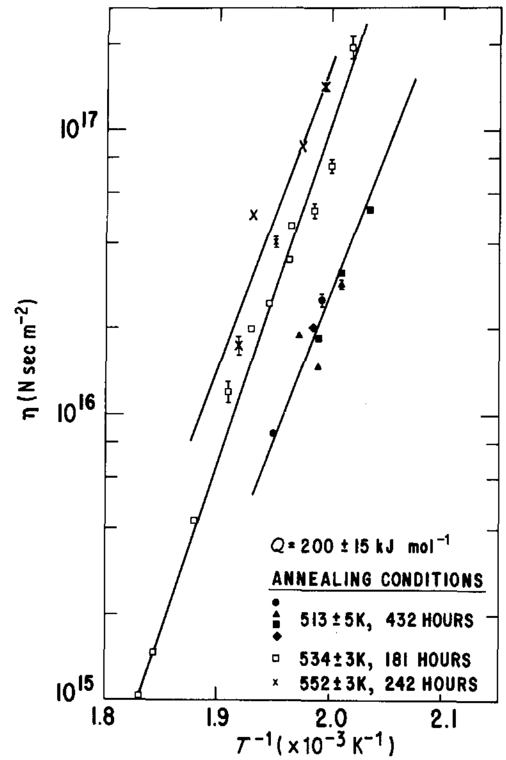

Figure 3 Isoconfigurational viscosities, η, obtained after the indicated annealing treatments.

tested under the same conditions as those discussed in this study, the limiting condition for linear flow was established at an equivalent shear stress $\tau = 300$ MPa.

The temperature dependence of the isoconfigurational viscoelastic strain rate has been measured. The results are reported in terms of the viscosity, $\eta = \tau/\dot{\gamma}_p$ (see Fig. 3). To stabilize the structure, the specimens were pre-annealed under an argon atmosphere with no applied stress. The annealing temperatures and times are indicated. These pre-anneals enabled us to test the specimens in the temperature range 490 to 525 K, without observing additional structural relaxation. The absence of structural change was verified in each case by returning to the initial testing temperature at the end of the temperature cycle and observing no significant change from the initial value of the viscosity. The activation energy, Q, found for the isoconfigurational viscosity of these specimens is 200 ± 15 kJ mol^{-1}, in agreement with other measurements for specimens pre-annealed at lower temperatures [9, 17]. Tests at different stresses also showed no change in the activation energy.

Although the activation energy for isoconfigurational flow is stress and thermal history independent, the magnitude of the viscoelastic strain rate is highly dependent on the degree of structural relaxation and therefore on thermal history. Previous investigations [9, 17] have shown that the viscosity can be changed by many orders of magnitude, even when annealing at temperatures as low as $T_g - 200$ (T_g is the glass transition temperature). Fig. 4 shows viscosity against time histories for specimens tested under different stresses, at 500 K, from the cast state (Curves A to C). The linear increase of viscosity with time has previously been observed [17, 18]. Note that for the stress range tested ($39 < \tau < 155$ MPa), the viscosity annealing kinetics are stress independent. Furthermore, there is evidence that subsequent annealing kinetics are not affected by previous thermal history. Curve D is for a specimen that was sequentially pre-annealed at 424 K for 225 h, 444 K for 175 h, 466 K for 152 h, and 487 K for 240 h. The specimen was then creep tested at 502 K. During the test, the viscosity was found to increase linearly with time from an initial value of 5×10^{15} N sec m^{-2}. In Fig. 4, the viscosity against time plot for this test is shown with the origin shifted to coincide with the other curves. The subsequent annealing kinetics are seen to be the same as those for the as-cast specimens, implying that the kinetics of structural relaxation are independent of the thermal history.

For certain properties, such as the Curie temperature [19, 20], a "cross-over effect" is observed during structural relaxation, indicating a thermal history memory. On the other hand, the viscosity does not appear to exhibit this property.

3. Discussion

Anelastic flow in many crystalline alloys can be characterized as a single process, of time constant, $\hat{\tau}$, and saturation value, γ_A^0, with the general form of an exponential decay:

$$\gamma_A = \gamma_A^0(1 - e^{-t/\hat{\tau}}). \quad (1)$$

An attempt was made to fit the flow observed in these tests with this relation combined with a viscoelastic term

$$\gamma(t) = \gamma_A^0(1 - e^{-t/\hat{\tau}}) + \dot{\gamma}_p t. \quad (2)$$

A typical least-squares fit, using γ_A^0, $\hat{\tau}$ and $\dot{\gamma}_p$ as free parameters, is shown in Fig. 5. Only the anelastic strain is shown, the viscoelastic strain, $\dot{\gamma}_p t$, having been subtracted from the total strain. As a result of this subtraction, the anelastic data

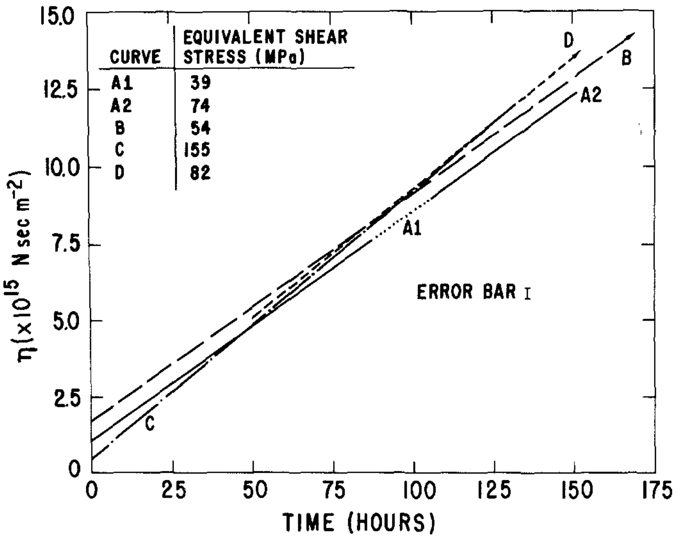

Figure 4 Viscosity as a function of annealing time for specimens tested at the indicated stresses. Curves A to C were taken from samples creep tested from the as-cast state. The stress on the sample of Curve A was increased after 80 h of testing. Curve D was taken from a sample pre-annealed, as described in the text. The origin for Curve D was shifted to $t = 50$ h.

reach a peak value at approximately 70 h, and then drop. This is physically unrealistic, and is only an artifact of the fit value for the viscoelastic strain rate, $\dot{\gamma}_p$, being higher than the actual value. In addition, the data start higher than the fitted curve and then cross it twice before reaching the peak value. Similar systematic deviations were observed in every case examined in this manner. This incompatibility of the data with a single-process exponential decay is an indication of the existence of an anelastic site spectrum. The existence of such a spectrum in the more common glassy systems is well established [21]. Recent work on metallic glasses has shown that anelastic flow in these materials is also governed by a spectrum [8, 15]. The anelastic flow can then be expressed as

$$\gamma_A = \sum_j \gamma_A^j (1 - e^{-t/\hat{\tau}_j}), \qquad (3)$$

where the sum is replaced by an integral for the case of a continuous spectrum. Fitting experimental data by an exact method to such a relation is difficult and one must resort to an approximation technique [22]. The finite spectrum approach was chosen, employing a least-squares fit to the prefactor of five exponential decays, with predetermined time constants spaced by a factor of three ($\hat{\tau}_j = 0.2$, 0.6, 1.8, 5.0 and 17 h). The smallest time constant is limited by the data acquisition rate, one point every 0.1 h. The decay with the largest time constant, 17 h, reaches 95% of its final value after 50 h. From the recovery tests, it is known that additional anelastic flow is undetectable after this time. Therefore, this spectrum spans the necessary time constants. Performing a least-squares fit to the data with Equation 3, combined with a viscoelastic term

$$\gamma(t) = \sum_j \gamma_A^j (1 - e^{-t/\hat{\tau}_j}) + \dot{\gamma}_p t, \qquad (4)$$

and using γ_A^j and $\dot{\gamma}_p$ as free parameters, an excellent fit to the data was produced (see the solid lines in Fig. 1). Note that the fit value for the viscoelastic strain rate, $\dot{\gamma}_p$, is reasonable, since it does not produce an artificial peak in the anelastic strain. This method provides an analytic expression from which the total anelastic flow can be computed. However, fitting the data with a finite sum

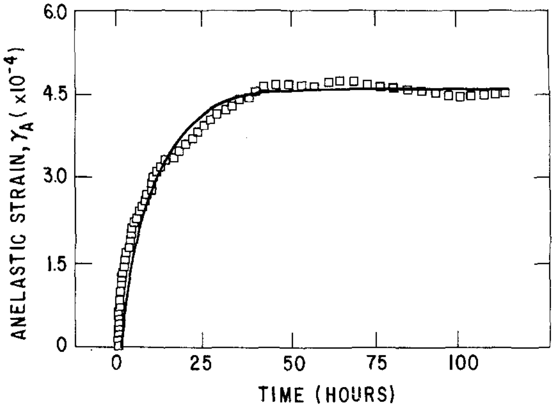

Figure 5 The equivalent anelastic shear strain, γ_A, computed from the data of Fig. 1a, using a single-exponential decay formulation. The symbols are the actual data points, from which the fitted viscoelastic strain has been subtracted. The solid line is the least-squares fit.

of exponentials whose time constants are arbitrarily predetermined, yields a non-unique solution and therefore no physical significance could be attributed to the weights of the resulting spectrum [1, 22].

4. Conclusions

The homogeneous strain response of amorphous $Pd_{82}Si_{18}$ to an applied stress consists of three components: elastic, anelastic and viscoelastic strains.

The elastic response is fully reversible, instantaneous and linear. The tensile elastic modulus, at 293 K, was determined to be 84 ± 8 GPa. The temperature dependence is $d(\ln E)/dT = (-3.2 \pm 0.6) \times 10^{-4}\ C^{-1}$.

The anelastic response is a transient that follows stress increases and is fully recovered upon stress reduction. For a $Pd_{82}Si_{18}$ specimen pre-annealed and tested at 500 K, the anelastic transient contributes measurably to the flow for approximately 50 h. The transient cannot be described by a single-process expoential decay. However, a sum of exponential decays, spanning a spectrum of time constants from 0.2 to 17 h, provides an excellent fit to the data.

The total anelastic strain, after the complete decay of the anelastic transient, varies linearly with the magnitude of the stress change over the entire stress range tested: $\gamma_A/\Delta\tau = 8.0 \pm 0.8 \times 10^{-6}\ MPa^{-1}$. The superposition principle was shown to apply to anelastic flow.

The isostructural viscoelastic flow is non-recoverable and is characterized by a constant strain rate. The activation energy for isoconfigurational flow was found to be $200 \pm 15\ kJ\ mol^{-1}$, independent of the annealing temperature used to stabilize the structure. When structural relaxation occurs, the viscoelastic strain rate changes by many orders of magnitude. The strain rate has been observed to vary inversely with time. The rate of decrease was found to be both stress independent and thermal history independent.

The viscoelastic strain rate–stress relation is linear only in the low-stress regime, a transition to non-linear behaviour occurring at approximately 300 MPa. The anelastic strain, on the other hand, remains linear over the entire stress range tested (0 to 383 MPa).

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