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The nature of the glass transition in metallic glasses

J X Zhang[†], M H Chen[†], D M Lin[†], G G Siu[‡] and M J Stokes[‡]

[†] Department of Physics, Zhongshan University, Guangzhou 510275,
People's Republic of China

[‡] Department of Applied Science, City Polytechnic of Hong Kong, Hong Kong

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Abstract. Specimens of the metallic glasses a-Pd_{77.5}Ni₆Si_{16.5}, a-Pd_{85.5}Si_{14.5}, a-Pd_{77.5}Cu₆Si_{16.5}, a-Fe₄₀Ni₄₀P₁₂B₈ and a-Pd₈₀Si₂₀ are studied by using a mini-inverted torsion pendulum (the mass of the inertial part is about 6 g) to measure simultaneously the temperature variation of the internal friction (IF), the relative shear modulus $(f/f_0)^2$ and the relative change in electric resistance $\Delta R/R_0$ in vacuum. Two IF peaks, P_g and P_x , corresponding to the glass transition temperature T_g and the crystallisation temperature T_x are observed for all specimens except a-Pd₈₀Si₂₀. For a-Pd₈₀Si₂₀, only one IF peak is observed but this tends to split into two IF peaks when the scanning rate increases. Corresponding sudden changes are observed in the relative shear modulus and electric resistance at T_g and T_x . It is suggested that the glass transition in metallic glass occurring during heating is a quasi-reversible, quasi-first-order phase transformation and the measurements of IF, $(f/f_0)^2$ and ΔR and with the differential scanning calorimeter are repeatable if the highest temperature is about 30 K below T_x .

1. Introduction

Advances in the study of metallic glass, applying modern characterisation techniques that include internal friction (IF) measurements, make it possible to understand the nature of the glass transition. It has been observed that one or more IF peaks will appear near the glass transition temperature T_g and the crystallisation temperature T_x in a heating process (Soshiroda *et al* 1976, Mo *et al* 1981, Morito and Egami 1984, Li and He 1986, Chen and Morito 1985, He and Li 1987). The transformations indicated by these peaks are mostly irreversible, but an IF peak indicating a reversible and repeatable transformation near T_g in the metallic glass a-Pd_{77.5}Cu₆Si_{16.5} has recently been reported (He and Li 1987). However, the studies concentrate on IF alone, or at best IF together with the oscillation frequency. This limits the amount of information that can be extracted from the IF study of the glass transition. In this work, measurements of the temperature variation of the IF, the relative shear modulus $(f/f_0)^2$, and the relative resistance change $\Delta R/R_0$ were simultaneously carried out by temperature scanning *in situ* using a mini-inverted torsion pendulum. It is determined that the quasi-reversibility or quasi-repeatability of obtaining the IF peak P_g near the glass transition temperature T_g is a general property for the metallic glasses a-Pd_{77.5}Ni₆Si_{16.5}, a-Pd_{77.5}Cu₆Si_{16.5}, a-Pd_{85.5}Si_{14.5} and a-Fe₄₀Ni₄₀P₁₂B₈. DSC measurements confirm this quasi-reversibility and show that it is possible that a latent heat is associated with a phase change in the

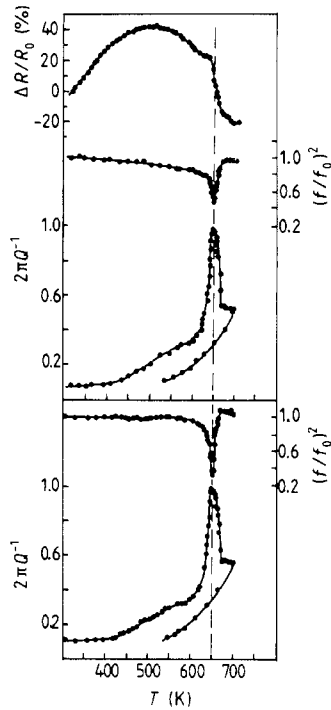


Figure 1. A comparison of measurements for the a-Pd₈₀Si₂₀ specimen with (upper panel) and without (lower panel) additional electrical connections ($\dot{T} = 4 \text{ K min}^{-1}$, $f_0 = 0.4 \text{ Hz}$).

temperature region around T_g . Hence, it is suggested that the glass transition of metallic glasses is a quasi-reversible quasi-first-order phase transformation.

Our interpretation of the experimental results does not contradict the well-established theory that the glass transition, i.e. the *liquid* \leftrightarrow *glass* transition, is characterised as an apparent, diffuse, second-order transition (see, e.g., Zallen 1983), in contrast with the solidification transition at T_f (f for fusion) which occurs via crystallisation. Originally, the liquid \leftrightarrow glass transition was defined in a cooling process, in which it is recognised as an entropy crisis. The glass transition we are concerned with in this work is studied in the first instance in a heating process and then during thermal cycling below the crystallisation temperature, and it is a *glass* \leftrightarrow *viscoelastomer* transition at best, where the term ‘viscoelastomer’ refers to a substance in a state with very high viscosity and is used to remind us that the specimen is still solid after the transition. This glass transition refers to an abrupt change of the solid-state viscosity η , which indicates that the specimen has fairly large creep ($\Delta R/R_0$ increases drastically; see figure 5, later), upon heating or during thermal cycling, which is reversible below T_v (T_v is above the glass transition temperature T_g but below the crystallisation temperature T_x ; see § 3).

2. Experimental procedure

A mini-inverted torsion pendulum is used for the simultaneous measurements of the internal friction Q^{-1} , relative shear modulus $(f/f_0)^2$ and $\Delta R/R_0$, where f and f_0 are the oscillation frequencies at the measuring temperature and room temperature respectively, and where $\Delta R = R - R_0$, R and R_0 being the corresponding electric resistances. The mass of the pendulum parts including the upper grip, upper rod and inertia member

is less than 30 g, and the mass of the inertia member is only 6 g. The conventional DC four-terminal potential method is adopted for measuring the electric resistance simultaneously, and a silver wire of diameter ≈ 0.1 mm processed in the form of a coil is press-connected to the grips at the two ends of the specimen for voltage measurement. Comparison of measurements with and without these additional connections for the a-Pd₈₀Si₂₀ specimen (figure 1) shows that the influence on Q^{-1} and $(f/f_0)^2$ is negligible. Simultaneous measurements of the $\Delta R/R_0$ versus T curve make it possible to determine the glass and crystallisation temperatures T_g and T_x unambiguously.

Measurements were made on five metallic glass samples, a-Pd_{77.5}Ni₆Si_{16.5}, a-Pd_{85.5}Si_{14.5}, a-Pd_{77.5}Cu₆Si_{16.5}, a-Fe₄₀Ni₄₀P₁₂B₈ and a-Pd₈₀Si₂₀, each of which had approximate dimensions $0.04 \times 1.5 \times 25$ mm³ (thickness \times width \times length) and a mass of about 10 mg. The measurement frequency is in the range 0.2 to 1.1 Hz, and IF measurements were performed with continuous heating, with a rate within the range 2 to 6 K min⁻¹. The internal friction Q^{-1} is calculated from

$$2\pi Q^{-1} = \frac{1}{n} \sum_{m=1}^n \frac{A_m^2 - A_{m+1}^2}{A_m^2}$$

where A_m is the amplitude of the m th oscillation. A Perkin-Elmer DSC-2C was used for the DSC measurements.

3. Results

The temperature variation curves for the internal friction Q^{-1} , relative shear modulus $(f/f_0)^2$ and resistance $\Delta R/R_0$ are shown in figures 2(a), 2(b), 2(c) and 2(d) for the specimens a-Pd_{77.5}Ni₆Si_{16.5}, a-Pd_{85.5}Si_{14.5}, a-Pd_{77.5}Cu₆Si_{16.5} and a-Fe₄₀Ni₄₀P₁₂B₈, respectively (hereafter referred to as specimens (a), (b), (c), (d)). For each specimen, two IF peaks P_g and P_x are observed, at: (a) 646 and 683 K; (b) 634 and 684 K; (c) 635 and 688 K; (d) 651 and 684 K. The heating rate was 6 K min⁻¹. The first- and the second-peak temperatures are denoted as T_{pg} and T_{px} respectively.

Figure 2 presents some common features. In general, the peaks P_g and P_x of the IF correspond respectively to the abrupt drop and sudden rise of the relative shear modulus $(f/f_0)^2$. The minimum between P_g and P_x of the IF coincides with that of the relative shear modulus $(f/f_0)^2$; the corresponding temperature is denoted as T_v . The temperature dependence of the electric resistance $\Delta R/R_0$ has a gradual rise and descent when the temperature is below T_{pg} , followed by a local minimum corresponding to the IF peak P_g and the sudden drop of $(f/f_0)^2$. The minimum leads to a local maximum at T_v . This coincides with the minima for IF and $(f/f_0)^2$. An abrupt drop above T_v corresponds to the sudden rise of $(f/f_0)^2$ in the temperature range around the IF peak temperature T_{px} . The local minimum in $\Delta R/R_0$ at T_{pg} is shown to correspond to the glass transition (see the following paragraphs), so the temperature T_{pg} is simply the glass transition temperature T_g . The abrupt drop of $\Delta R/R_0$ is generally accepted as coinciding with crystallisation (Luborsky 1983, Güntherodt and Beck 1981, Zatuska *et al* 1985), so T_{px} is determined as the crystallisation temperature T_x . Hence, the IF peaks P_g and P_x are determined as the glass transition peak and the crystallisation peak, respectively.

To study the reversibility of obtaining the glass transition peak P_g , simultaneous measurements during thermal cycling, in which the rates of temperature change on heating and cooling were equal and opposite, were made and the results for the specimens

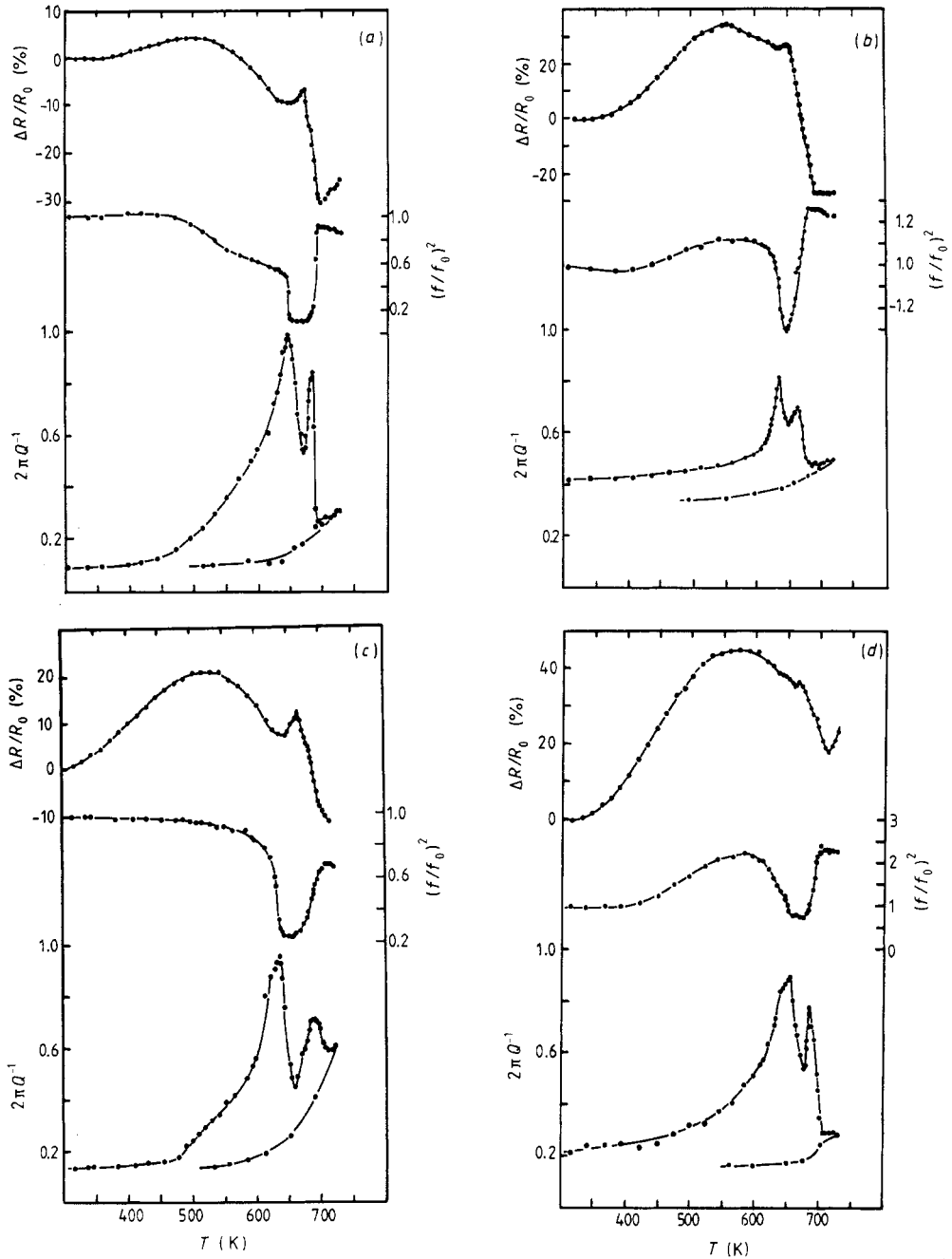


Figure 2. The temperature dependence of Q^{-1} , $(f/f_0)^2$ and $\Delta R/R_0$ for the following specimens: (a) a-Pd_{77.5}Ni₆Si_{16.5} ($f_0 = 0.4$ Hz); (b) a-Pd_{85.5}Si_{14.5} ($f_0 = 0.3$ Hz); (c) a-Pd_{77.5}Cu₆Si_{16.5} ($f_0 = 0.3$ Hz); (d) a-Fe₄₀Ni₄₀P₁₂B₈ ($f_0 = 0.2$ Hz) (all for $\dot{T} = 6$ K min⁻¹).

(a) are shown in figure 3. As long as the temperature of the cycling does not exceed T_v , which corresponds to the minima of IF and $(f/f_0)^2$, the appearance of the glass transition peak can be repeated, but T_g shifts to a higher value. Excepting this minute shift, other

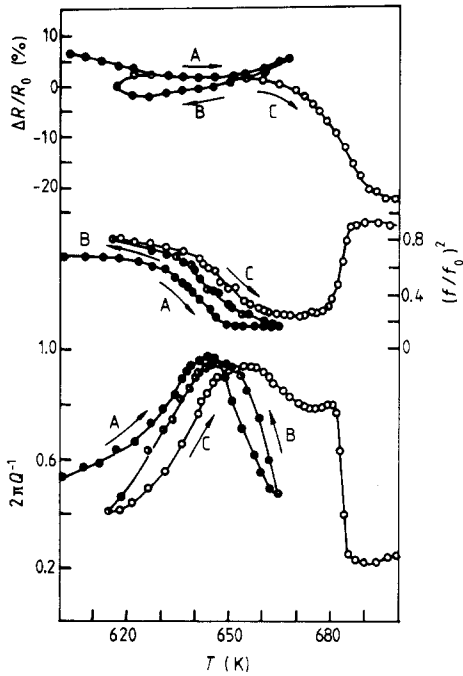


Figure 3. The quasi-repeatability and quasi-reversibility of the behaviour of the IF peak P_g during the thermal cycle for a-Pd_{77.5}Ni₆Si_{16.5} for $f_0 = 0.4$ Hz, $\dot{T} = 6$ K min⁻¹. (A, ascending; B, descending; C, ascending.)

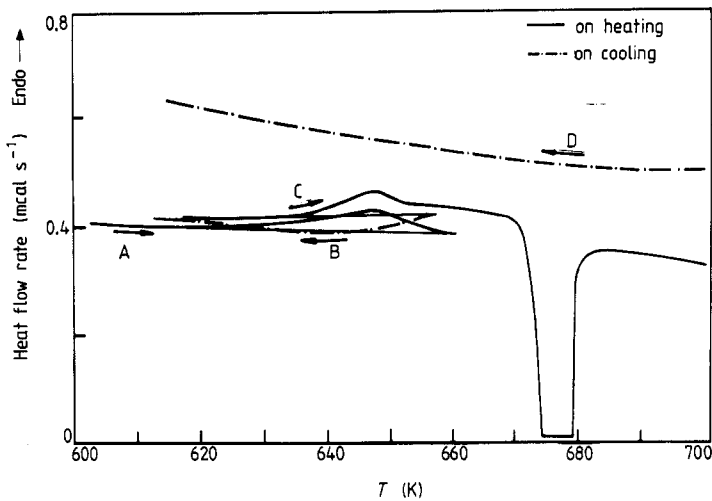


Figure 4. The effect of thermal cycling on the glass transition in DSC measurements for a-Pd_{77.5}Ni₆Si_{16.5} for $\dot{T} = 5$ K min⁻¹. (A, C, ascending; B, D, descending.)

general features are still preserved, e.g. the coincidence of the minima of IF and $(f/f_0)^2$ with the maximum of $\Delta R/R_0$ at T_v . Hence, obtaining the IF peak P_g is quasi-reversible or quasi-repeatable.

DSC measurements were performed to provide further and complementary information; see figure 4. The coincidence of the IF peak P_g , the abrupt drop of $(f/f_0)^2$ and the local minimum of $\Delta R/R_0$ is shown to be not accidental but to correspond to an

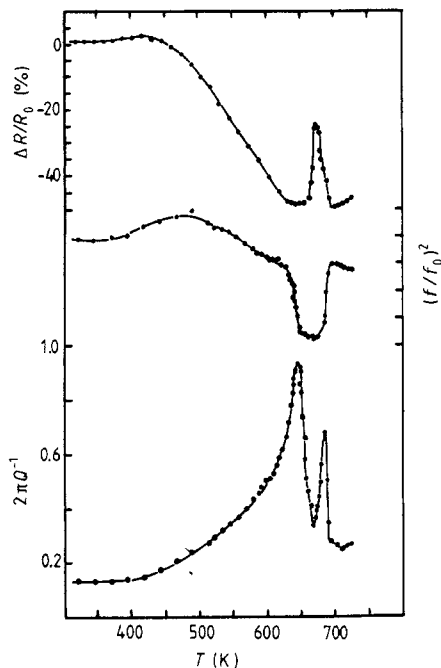


Figure 5. The effect of stress for a-Pd_{77.5}Ni₆Si_{16.5} with $\sigma = 0.12$ MPa, $\dot{T} = 6$ K min⁻¹ and $f_0 = 0.4$ Hz.

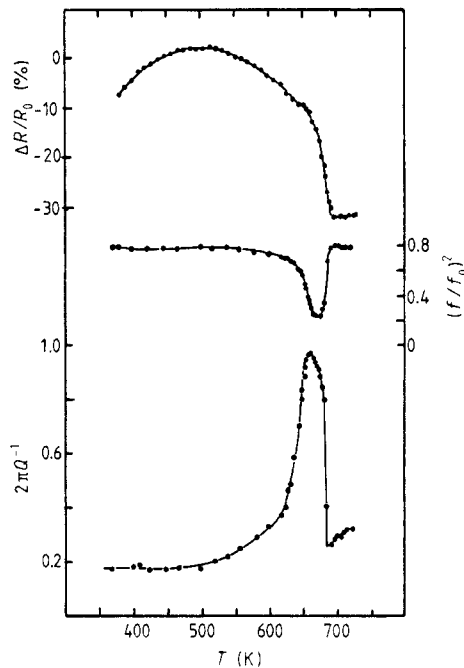


Figure 6. The effect of annealing at 660 K for 10 min: the temperature dependence of Q^{-1} , $(f/f_0)^2$ and $\Delta R/R_0$ for the a-Pd_{77.5}Ni₆Si_{16.5} specimen.

endothermic peak in the stage with temperature increasing. This suggests that the glass transition does occur. DSC measurements also confirm the quasi-reversibility of obtaining the IF peak P_g . In thermal cycling, an endothermic peak that coincides with the IF peak P_g in the stage with temperature increasing corresponds to an exothermic peak in the descending temperature stage. The endothermic peak is obtained again in the following ascending temperature stage but shifts to a higher temperature. A large endothermic peak, which coincides with the IF peak P_x , appears in the final stage with temperature ascending. This indicates crystallisation. For specimens (b), (c) and (d), similar thermal cycling effects are observed. The endothermic peak that is obtained upon heating and the exothermic peak obtained upon cooling occur over a temperature interval of about 40 K. They become more easily perceivable on comparing them against the baselines drawn for the heating trace (A) and cooling trace (B), i.e. by extrapolating the flat portion at low temperature over the peak region. The baseline does not shift to higher values but remains at the same value for each trace after the peak region. However, in thermal cycling, the baselines shift to higher values on going from A to B, then to C.

The effects of stressing and pre-annealing are shown in figures 5 and 6 respectively for specimen (a). A stress of 0.12 MPa in the specimen causes a distinct maximum of $\Delta R/R_0$ at T_v (due to creep), and a slight shift of the temperatures T_g and T_x to lower values (figure 5). After pre-annealing, the increase in T_g and the decrease in T_x cause the peaks P_g and P_x to merge into one. The combined peak has a low-temperature side corresponding to T_g and a high-temperature side corresponding to T_x (figure 6). Around T_v , the $(f/f_0)^2$ curve has a sharp minimum and the $\Delta R/R_0$ curve is flattened. This is similar to the result for the a-Pd₈₀Si₂₀ specimen shown in figure 1(a).

Table 1. The dependence on the heating rate (\dot{T}) of peak temperature T_g in DSC and IF curves.

	DSC				IF		
\dot{T} (K min ⁻¹)	1.25	5.0	40	80	2.0	6.0	
T_g (K)	640	647	657	659	643	640, 646, 649†	

† With different frequency of internal friction measurements.

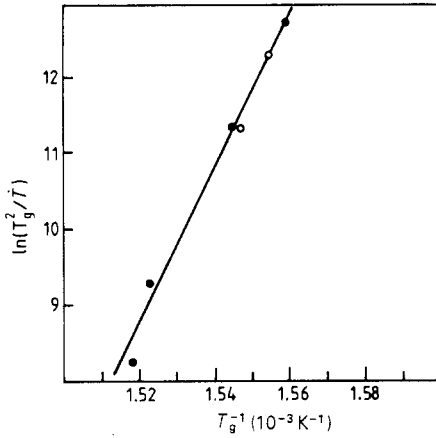


Figure 7. $\ln \dot{T}/T_g^2$ versus T_g^{-1} for a-Pd_{77.5}Ni₆Si_{16.5} (●, DSC data; ○, IF data).

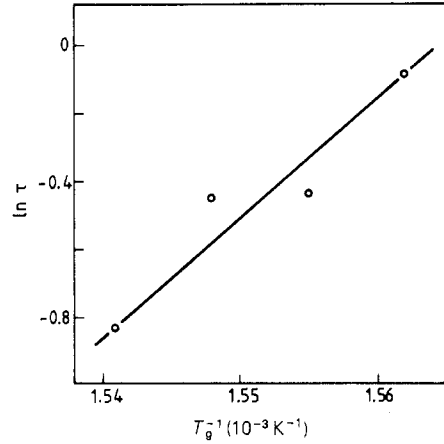


Figure 8. $\ln f^{-1}$ versus T_g for a-Pd_{77.5}Ni₆Si_{16.5} ($\tau = f^{-1}$).

Table 2. The frequency dependence of the peak temperature T_g in IF curves.

f (Hz)	0.18	0.40	1.1
T_g (K)	640	646	649

Table 1 shows the effect of the rate T of temperature increase on the glass transition temperature T_g from DSC measurements. Figure 7 shows the Kissinger graph of $\ln(\dot{T}/T_g^2) = -\Delta E_g/kT_g + \text{constant}$ (Kissinger 1957), where E_g is the enthalpy and k is the Boltzmann constant. Both are for specimen (a). The activation enthalpy ΔE_g associated with the viscoelastic component of the glass transition is thus determined as 8.1 eV for a-Pd_{77.5}Ni₆Si_{16.5} and 10.7 eV for a-Pd_{85.5}Si_{14.5}.

Table 2 shows the effect of the oscillation frequency f for a constant rate of temperature increase (6 K min⁻¹) obtained from IF measurements. Figure 8 shows the Arrhenius graph. Both are for specimen (a). The slope of the $\ln f^{-1}$ versus T_g^{-1} curve gives the activation energy ΔE_g associated with the anelastic component of the glass transition IF peak P_g (7.2 eV for a-Pd_{77.5}Ni₆Si_{16.5}), which is comparable with the previous value based on DSC measurements.

Figure 9 shows the effect of scanning rate for the specimen a-Pd₈₀Si₂₀ at a rate of temperature increase of 6 K min⁻¹. Unlike in figure 1(a), where the rate is 4 K min⁻¹, a plateau of $\Delta R/R_0$ at T_g is observed. T_x shifts slightly to a higher value and the IF peak tends to split into two. The splitting of the IF peak is confirmed by DSC measurements and is shown in figure 10 for a-Pd₈₀Si₂₀. At a rate of 5 K min⁻¹, only a large exothermic

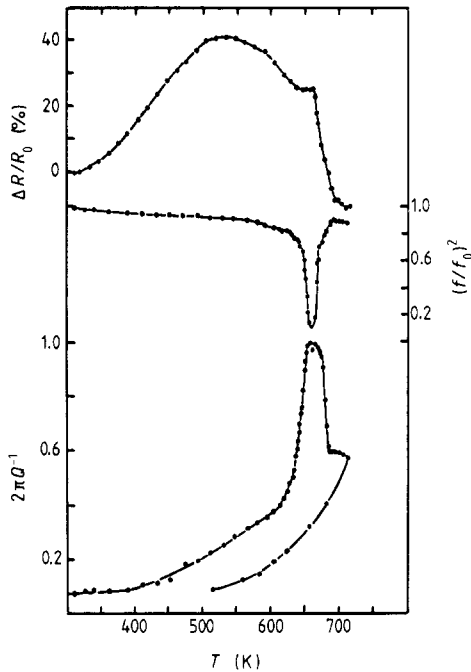


Figure 9. The effect of the scanning rate on IF for a-Pd₈₀Si₂₀ for $\dot{T} = 6 \text{ K min}^{-1}$, $f_0 = 0.4 \text{ Hz}$.

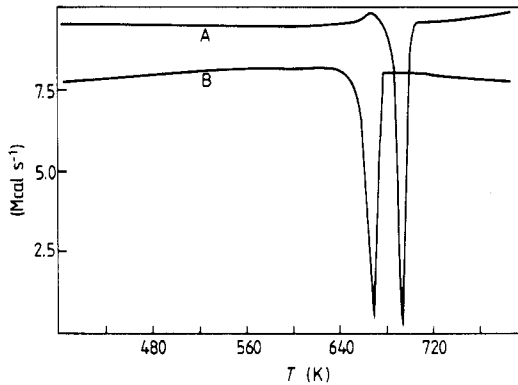


Figure 10. The effect of the scanning rate on DSC measurements for a-Pd₈₀Si₂₀. $\dot{T} = \text{(A) } 80; \text{(B) } 5 \text{ K min}^{-1}$.

peak corresponding to crystallisation can be seen. A distinct endothermic peak situated at 667.7 K does appear when the rate of increase of temperature is 80 K min^{-1} (however, low-frequency IF measurements at such a high rate are problematic).

From these experimental results, we reach the following conclusions.

(i) Providing the glass transition temperature T_g is characteristically lower than the crystallisation temperature T_x (e.g. by 30 K according to figures 2–4), then (a) endothermic and exothermic peaks obtained quasi-reversibly appear near T_g in DSC measurements for increasing and decreasing temperature scanning respectively; and (b) a definite IF peak P_g obtained quasi-repeatably appears near T_g .

(ii) The height and the peak temperature of the IF peak P_g at the glass transition temperature T_g depend on both the measuring frequency and the rate of temperature

increase. This implies that the peak P_g is associated with both anelasticity and viscoelasticity. It also implies that the glass transition is associated with both reversible and irreversible diffusion processes.

(iii) The creep strain increases with temperature for $T < T_v$ but decreases with increasing temperature for $T > T_v$. This indicates that the solid-state viscosity η decreases sharply with temperature increase in the region of the glass transition, but η increases with temperature when crystallisation starts.

For clarifying these results, a clear picture of the structure of the glassy specimens in the temperature region around T_g is essential. The model of degeneration of short-range order (SRO), which is similar to that proposed by He and Li (1987) and Egami (1978a, b), is adopted for the discussion in the following section.

4. Discussion

DSC measures the heat flow to or from the sample as a function of the temperature of the sample. The DSC curve has the same shape as the C_p - T curve (giving the temperature dependence of the specific heat at constant pressure), since $C_p = \dot{H}/\dot{T}M$ where \dot{H} is the heat flow, T the heating or cooling rate (fixed) and M the specimen mass. The endothermic peak occurring in DSC measurements during heating may have different interpretations. This behaviour may reflect variation in the specific heat only and thus be interpreted as indicating a second-order transition, i.e. the solid transformation in this work is not distinct from the liquid-glass transition. However, in a DSC trace, the characteristic behaviour of C_p for a second-order transition will have a step change in baseline as a result of the discontinuous change in the specific heat (e.g. see those for As_2S_3 obtained by Blachnick and Hoppe (1979) and for $Au_{0.8}Si_{0.1}Ge_{0.1}$ by Chen and Turnbull (1968), see figures 1.8 and 1.9 in Zallen (1983)). The curves A and B, in contrast, have the same baseline below and above T_g (this is blurred by shifting for curve C). This makes us prefer the alternative interpretation that the endothermic peak occurring during heating and the creep behaviour shown in figure 5 indicate the existence of a latent heat and an abrupt change of viscosity η for the glass \leftrightarrow viscoelastomer transition on heating through T_g . This viewpoint is consistent with the kinetical discussion of the IF peak at T_g . However, more evidence is expected to be obtained in further study.

With the existence of a latent heat for heating through T_g , the glass transition, i.e. the glass \leftrightarrow viscoelastomer transition, could be taken as a quasi-reversible, quasi-first-order phase transformation.

Interpretation in terms of a latent heat rather than a change in specific heat for the endothermic peak obtained during heating would require the structure change in the temperature range of the transition to dominate over the unlocked diffusion motion of atoms or atom clusters. Using the model of degeneration of SRO, metallic glass near the temperature T_g can be described as an assembly of SRO clusters moving cooperatively. The clusters are separated from each other by disordered films constructed from large atoms, which deviate from the stoichiometry ratio (e.g. Pd atoms in a - $Pd_{85.5}Si_{14.5}$). On heating ($T < T_v$), the change of solid structure includes the reduction of the cluster size, the degree of SRO and thus the solid-state viscosity, and the increase of the number of clusters. It follows partial chemical bond breaking on heating when $T < T_v$, i.e. an endothermic peak will appear. If the transition is quasi-reversible for $T < T_v$, an exothermic peak will be observed on cooling. However, cluster motion, although it is of

secondary importance in the temperature range around T_g , may have an effect on the shift of the baseline from A to B etc.

At T_g , an IF peak corresponds to the DSC peak because a maximum of $\sigma \Delta l$ —where Δl is a relative shear displacement between clusters or within clusters under the oscillation stress in IF measurements and σ is the shear stress across clusters or the disordered film boundaries between clusters—results from a critical average size of clusters and an appropriate solid-state viscosity η between cluster boundaries. The product $\sigma \Delta l$ is proportional to both the energy dissipation ΔW in an oscillation period and the internal friction Q^{-1} (Ke 1954). In contrast, Δl is negligible due to the high value of the viscosity η for $T \ll T_g$ and σ is too small for $T_g < T < T_v$ to produce a large value of $\sigma \Delta l$.

The abrupt change of the solid-state viscosity η cannot occur over the whole specimen at once—this is similar to the situation where interface motion is needed in a first-order phase transformation—and it is thus a spread of the transition. Therefore it takes place gradually and is manifested as a spread-out endothermic peak occurring during heating in DSC measurements, but the IF measurements reflect the effect of the sum of the product $\sigma \Delta l$ and the peak is quite distinct. The quasi-first-order phase transformation is a convenient indicator for distinguishing the glass–viscoelastomer transition from the liquid–glass transition.

Furthermore, it is desirable to investigate the relaxation behaviour of the metallic glass near the glass–viscoelastomer transition. In general, the IF peak temperature of an anelastic relaxation process increases with stress frequency during a phase transition but it is independent of the rate of temperature change. In contrast, an IF peak may shift with the heating rate—e.g. in an allotropic transformation—i.e. when heating rate increases, the IF peak shifts to higher temperature, and vice versa, but the peak is unchanged when the stress frequency changes in a phase transition (Nowick and Berry 1972). However, the metallic glass behaves differently. Its IF peak temperature depends on both the stress frequency and the rate of temperature change. This shows that the IF peaks in the glass transformation are associated with both anelastic and viscoelastic relaxations. Two activation energies following Arrhenius and Kissinger equations (Lin *et al* 1985) are obtained: $H_1 = 7.2$ eV, based on the $\ln f^{-1} - T_g^{-1}$ curve, and $H_2 = 8.2$ eV, based on the $\ln \dot{T}/T_g^2 - T_g^{-1}$ curve for specimen (a). The activation enthalpy of the anelastic relaxation H_1 is less than H_2 , that of the viscoelastic relaxation, and the anelastic process is thus more probable than the viscoelastic one since the potential barrier H_1 is lower. Hence, the anelastic process in clusters is dominant, and the viscoelastic process at boundaries is secondary. From the model of degeneration of the SRO, a qualitative description can be obtained wherein the metallic glass near the glass–viscoelastomer transition responds to an applied oscillation stress with an anelastic shear due to stress-induced reversible diffusion in SRO clusters and an irreversible viscoelastic strain (or shear) at the cluster boundaries. The metallic glass near the glass–viscoelastomer transition can thus be treated as an anelastic–viscoelastic solid and be described using a mechanical model that is a combination of the Voigt model and the Maxwell model using four parameters (figure 11). This explains the quasi-reversible and quasi-repeatable behaviour of the IF peaks. When the temperature rises to above T_v , the boundaries start to crystallise irreversibly and the clusters start to undergo a polymorphic or eutectic transformation; then the crystallisation process occurs explicitly (Duhaj *et al* 1976).

If the temperature T_x is too close to T_g , as in a-Pd₈₀Si₂₀ (or even if $T_x < T_g$), or crystallisation nuclei exist as the result of pre-annealing, only one IF peak can be observed to appear upon heating as the two processes superimpose.

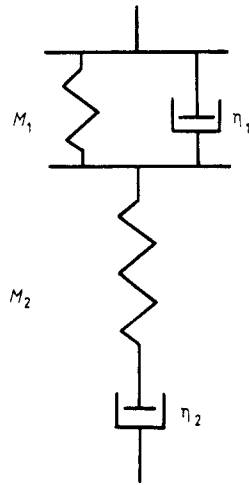


Figure 11. The four-parameter model (Ferry 1980, Aklonis and Macknight 1983). M_1 and M_2 are Hook springs and η_1 and η_2 are dashpots. The damping behaviour of this system is described by

$$Q^{-1} \approx \Delta_1 \omega \tau_1 / [1 + (\omega \tau_1)^2] + \Delta_2 / \omega \tau_2$$

where $\tau_1 = \eta_1/M_1$ and $\tau_2 = \eta_2/M_2$ are relaxation times, Δ_1 and Δ_2 are relaxation strengths for the Voigt model (1) and the Maxwell model (2) respectively. The first term represents an anelastic process in clusters and the second a viscoelastic process at boundaries.

5. Summary

Simultaneous measurements of the internal friction, the relative shear modulus and the relative electric resistance change are carried out as metallic glass samples are heated. The IF measurements show resolution between the glass transition and the crystallisation for heating rates as low as 6 K min^{-1} . The results are compared with those of DSC measurements and it is suggested that the glass–viscoelastomer phase transformation (a solid-state transition) is a quasi-first-order, quasi-reversible phase transformation. In the theoretical framework of the model of degeneration of the sRO, a probable qualitative interpretation is given to provide an explanation for the relaxation behaviour of metallic glass near the phase transition in a process with increasing temperature.

Acknowledgments

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