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Fragility measurement of Pd-based metallic glass by dynamic mechanical analysis

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ABSTRACT

The measurement of fragility of glass-forming liquids involves either the determination of viscosity at different temperatures above the glass transition or the measurement of the dynamic glass–liquid transition by calorimetry or dilatometry at different heating rates. Significant data dispersion is observed when comparing fragility parameters obtained by different techniques. Dynamic mechanical analysis (DMA) is widely used for characterizing glass transition in polymer science while it is still seldom used in metallic glasses. In this work we determine the relaxation time (τ) vs temperature of a $Pd_{77.5}Si_{16.5}Cu_6$ glass by means of DMA measurements. The measured range of relaxation times cover the whole region from glass transition ($\tau > 100$ s) to times of the order of 10^{-2} s. The fragility parameter obtained for this alloy is found significantly higher than the values obtained from previous viscosity and calorimetric techniques. The application range, limitations and correctness of the technique are discussed.

1. Introduction

The viscosity of metallic glass-forming liquids at temperatures above and around the glass transition point is one of the main parameters determining their glass-forming ability (GFA). Viscosity $\eta(T)$ or, equivalently, the characteristic relaxation time $\tau(T)$ of the liquid increases several orders of magnitude when approaching glass transition. The fragility parameter of a liquid is defined as

$$m = \left.\frac{\mathrm{d}\log\,\eta}{\mathrm{d}(T_g/T)}\right|_{T=T_g} \quad (1)$$

where T_g is chosen as the temperature where $\eta(T_g) = 10^{12}$ Pa s [1]. An equivalent expression can be written substituting viscosity by relaxation time $\tau(T)$, in which case glass transition temperature is usually defined by $\tau(T_g) = 100$ s. The fragility m is then a measure of the viscosity rate of change when temperature decreases towards glass transition, just before the structural change of the liquid is arrested in the glassy state. Above the glass transition temperature, strong liquids with low fragility parameters have viscosities several orders of magnitude higher than fragile liquids with high m values.

Determining viscous behaviour near T_g is of interest for many technological and fundamental aspects of metallic glasses. The stability of the supercooled liquid is enhanced by a high viscosity in this temperature region, this inhibits crystal nucleation where it is thermodynamically most favoured and gives the possibility of quenching metallic glass parts with large sizes. At the atomic level, strong and fragile liquids are characterized by more or less rigid atomic arrangements. In metallic systems, where the inter atomic forces have low directionality, the rigidity of the liquid structure is promoted either by glue atoms, like B and Si, that form strong bonds with the surrounding metallic atoms, by the formation of close packed atomic arrangements with low energy and low volume per atom or by the presence of strong interatomic potentials with low anharmonicity. After the liquid structure is congealed at the glass transition, this rigidity of the atomic structure is responsible of various glass properties like deformation behaviour, fracture toughness and the elastic response.

Viscosity of metallic glasses near glass transition has been measured by parallel plate rheometry [2], creep tests [3] and bending experiments [4], and determination of relaxation times near T_g has been obtained from modulated calorimetry [5]. All these techniques require high stability of the supercooled liquid in order to measure the relaxation behaviour above T_g, and are then limited to compositions with high GFA. The evaluation of the fragility parameter of metallic systems is usually performed by calorimetric techniques [6]. The signature of glass transition in calorimetric experiments is observed at the same time scale than viscosity relaxation, then the heating rate dependent T_g can be used as an alternative way to determine the fragility of glasses. However, the lack of a well-defined equivalence between heating rate and relaxation time results in a systematic difference between the fragility values obtained by viscosity or relaxation time measurements and the ones obtained from the calorimetric response at different heating rates, the former being always higher than the latter.

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In this work we will determine the relaxation time temperature dependence of $Pd_{77.5}Si_{16.5}Cu_6$ metallic glass ribbons by means of Dynamic Mechanical Analysis (DMA). This technique will allow us to measure the relaxation times near and above the glass transition temperature, where fragility parameter is defined. The use of DMA gives unique insight into the relaxation spectrum [7] and the viscoelastic behaviour of metallic glasses [8,9].

2. Materials and methods

Metallic glass ribbons of $Pd_{77.5}Si_{16.5}Cu_6$ where obtained by melt spinning with ribbon thickness of 20–30 μm. The glassy nature of the samples was confirmed by X-ray diffraction and Differential Scanning Calorimetry (DSC). Mechanical spectroscopy was realized with a TAinstruments Q800 Dynamic Mechanical Analyzer. The experiments were realized in tension mode, ribbon pieces 10 mm long were fixed with a preload force of 0.15 N. The amplitude of the oscillation was fixed to 1 μm, these preload and amplitude values were found to be adequate in order to avoid the failure of the ribbons during the softening associated to glass transition. The experiments were realized at different heating rates going from 0.25 to 5 K/min and different frequency values ranging from 0.01 to 100 Hz. Temperature ramps were performed from room temperature up to 500 °C, thus obtaining the dynamic mechanical response of the material through glass transition and crystallization.

3. Results

DSC scans of $Pd_{77.5}Si_{16.5}Cu_6$ ribbons show the characteristic thermal behaviour of this material [3,10]. At 20 K/min, the onset of glass transition is found at $T_{g,\,onset} = 630$ K, the inflection point of the glass transition signature at $T_{g,\,inf} = 638$ K and the onset of crystallization at $T_x = 679$ K. In order to compare the calorimetric and the dynamic mechanical responses, DSC scans with heating rate of 5 K/min were also performed, showing the onset of glass transition at $T_{g,\,onset} = 625$ K and the onset of crystallization at $T_x = 664$ K.

Fig. 1 shows the Young modulus E as a function of temperature calculated from DMA measurements at 1 K/min. The relation between strain and stress when applying oscillating deformations with frequency f results in a complex Young modulus $E(\omega, T) = E'(\omega, T) + iE''(\omega, T)$ dependent on $f = \omega/2\pi$ and composed by the storage (E') and loss (E'') moduli. At low temperatures the glass has a pure elastic response, strain and stress are in phase and only E' has significant values. At higher temperatures, when the applied frequency approaches the main relaxation time of the material, the sample becomes viscoelastic and there is a lag between strain and stress. The dynamic glass transition at each frequency is observed when the storage modulus decreases from the low temperature value, whereas at the same time the loss modulus increases reaching its maximum at the temperature were the main relaxation time of the material coincides with the characteristic time of the applied perturbation $\tau = 1/\omega$.

Fig. 2 shows the storage modulus as a function of frequency at 15 different temperatures from 601 to 643 K. At the lower temperatures the storage modulus does not present significant changes from the low temperature value or, equivalently, the infinite frequency value. At higher temperatures, the storage modulus corresponding to the lower frequencies decrease due to the onset of the dynamic glass transition while the high frequency response is still mainly elastic.

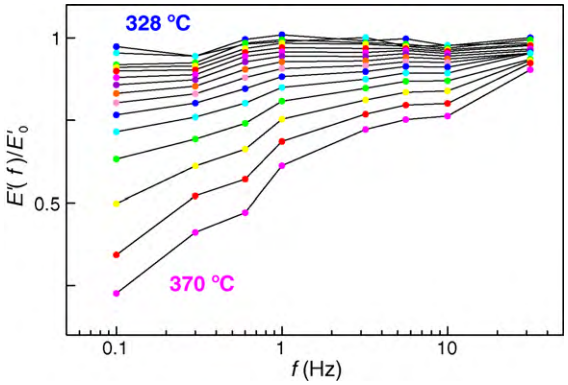

Fig. 2. Storage modulus E' in function of frequency at 15 different temperatures between 328 °C and 370 °C. The values obtained at each temperature are linked by a solid line.

4. Discussion

The distinct relaxation peak of the loss modulus observed in $Pd_{77.5}Si_{16.5}Cu_6$ ribbons allows us to obtain the temperature dependence of the α-relaxation time $\tau(T)$ of the material. In Fig. 3, with red symbols, the relaxation times $\tau = 1/\omega$ are depicted as a function of the temperature corresponding to the loss modulus maximum. As observed in Fig. 3, the peak temperatures measured correspond to relaxation times going from 1.6×10^{-2} to 1.6 s obtained from DMA tests with frequencies going from 10 to 0.1 Hz. The access to smaller relaxation times or, equivalently, higher temperatures is limited by crystallization of the material while the access to large relaxation times and low temperatures is limited by the relation between heating rate and DMA frequency, these bounds will be discussed later.

From the set of $\tau(T)$ data obtained, the fragility parameter can be calculated fitting a VFT function

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \quad (2)$$

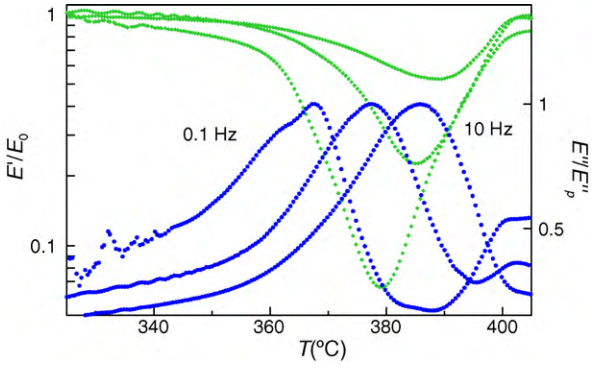

Fig. 1. Temperature change of the storage modulus E' (rhombic symbols) and the loss modulus E'' (circles) obtained for frequencies of 0.1, 1 and 10 Hz with a heating rate of 1 K/min. E' is normalized by the low temperature value E'_0 and E'' is normalized by the peak maximum value E''_p.

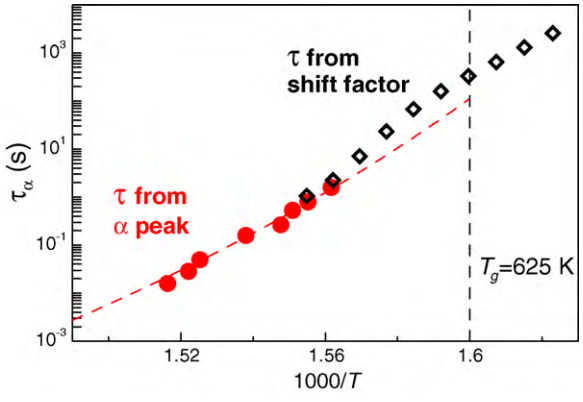

Fig. 3. Relaxation time vs 1000/T obtained from determination of loss modulus maximum position (circles) and from the calculation of the shift factor a_T (rhombic symbols). Dashed line: VFT function fitted to the data obtained from the loss modulus peaks.

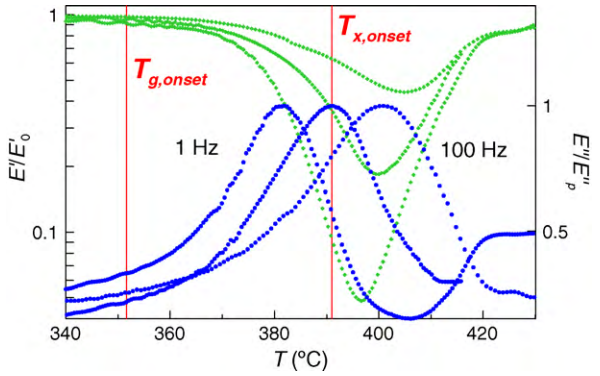

Fig. 4. Temperature change of the storage modulus E' (rhombic symbols) and the loss modulus E'' (circles) obtained for frequencies of 1, 10 and 100 Hz with a heating rate of 5 K/min. The glass transition and crystallization temperatures obtained from DSC at the same heating rate are denoted by solid vertical lines.

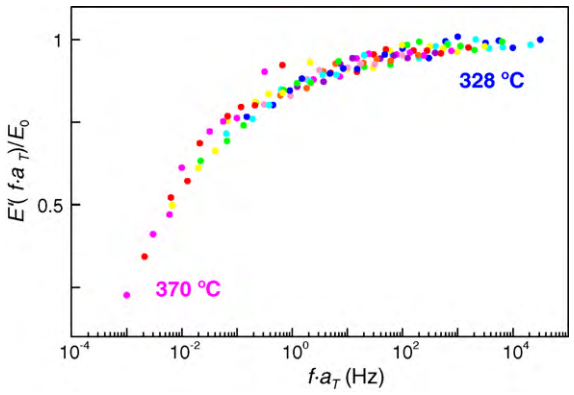

Fig. 6. Master curve of the storage modulus E' obtained applying a temperature dependent shift factor a_T to the frequency domain of the data previously shown in Fig. 2.

with three fitting parameters B, T_0 and τ_0, and then computing m using Eq. (1). However, the range of data is not large enough to obtain a unique set of B, T_0 and τ_0 values with enough confidence. Setting the value of $\log(\tau_0) = -14.5$ [11] and letting free only B and T_0, the fitted VFT function gives a value of $m = 82$ and a $T_g = 625$ K, this T_g corresponding to the temperature at which the fitted function reaches a value of 100 s. Viscosity measurements realized by means of creep experiments [3] obtained values of $m = 75$ and a $T_g = 622$ K corresponding to the temperature at which $\eta(T_g) = 10^{12}$ Pa s.

As mentioned above, the measurement of smaller relaxation times at high temperatures is limited by the crystallization of the material. Fig. 4 show the DMA results obtained at 5 K/min, the crystallization onset temperature obtained from DSC is indicated as a reference in the figure. Considering the position of the loss modulus peak, it can be observed that the dynamic glass transition at the higher frequencies is clearly overlapped with the crystallization process. This overlapping affects the shape of the loss modulus signal, cutting the high frequency wing and moving the peak artificially to lower temperatures. The measurement of larger relaxation times corresponding to low temperatures approaching glass transition is also restricted, this limit comes from the comparison between heating rate and applied frequency. If the period of the strain oscillations is similar to the inverse of the heating rate, the properties of the material change faster than the time required for measuring the dynamic mechanical response with adequate temperature resolution.

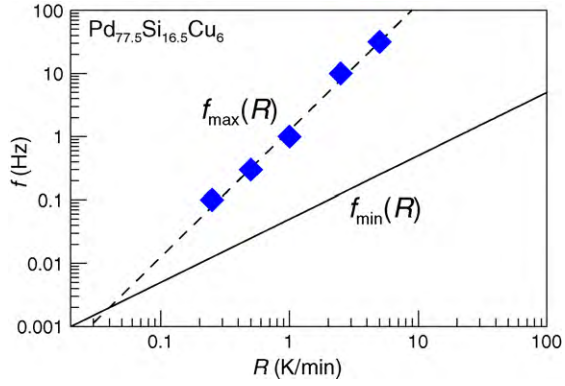

Fig. 5. Low and high frequency bounds for measuring the α-relaxation peak of $Pd_{77.5}Si_{16.5}Cu_6$ glass by dynamo-mechanical measurements as a function of the applied heating rate R. The overlapping between the frequency dependent response and the glass crystallization at each heating rate is denoted by rhombic symbols.

These frequency vs heating rate bounds are depicted in Fig. 5, the high frequency limit is calculated considering the frequencies of DMA tests that show overlapping between the loss modulus peak and the onset of crystallization. The low frequency bound is taken as $f = 3R$, implying that at least three oscillations per Kelvin are required for measuring the dynamic response with enough temperature resolution. The crossing of the two bounds in Fig. 5 implies that, for $Pd_{77.5}Si_{16.5}Cu_6$, it is not possible to measure α-relaxation peaks non-cut off by crystallization for frequencies not much lower than 0.01 Hz, this corresponding to relaxation times larger than about 16 s. Indeed, for the measurements we realized with the lowest heating rates we did not obtain dynamic response with clear loss modulus peaks for frequencies below 0.03 Hz, this corresponding to relaxation times of about 5 s.

Access to larger relaxation times and lower temperatures can be obtained from time temperature superposition (TTS) analysis [12]. The frequency response of a viscoelastic material scales with relaxation time, this implies that both the storage and loss modulus obtained for different frequencies at different temperatures become superimposed in a single master curve when properly shifted in the frequency domain. Fig. 6 shows the same storage modulus data previously shown in Fig. 2 but now as a function of frequency multiplied by the shift factor a_T computed for each temperature. The shift factor can be written as

$$a_T = \frac{\tau(T)}{\tau_{\text{ref}}} \tag{3}$$

where $\tau(T)$ and τ_{ref} are the relaxation times at temperature T and at a reference temperature. Therefore, the calculated shift factors give us access to the relaxation times corresponding to temperatures going from $T = 601$ to $T = 643$ K. In order to transform the calculated a_T values to relaxation times $\tau(T)$, the value of τ_{ref} can be set using as reference the relaxation times obtained from the direct measurement of the loss modulus peak at temperatures near 640 K.

The relaxation times obtained from TTS analysis of the storage modulus curves are depicted in Fig. 3 with rhombic symbols. Now, the whole range of relaxation times going from 1.6×10^{-2} to 10^3 s is covered and the fragility parameter can be calculated directly from the slope of the data at the glass transition point. In this work the fragility obtained using the whole set of measured relaxation times gives a value of $m = 96$, higher by far than previous measurements on $Pd_{77.5}Si_{16.5}Cu_6$ glass [3,13].

5. Conclusions

Measurements of relaxation times at temperatures above and near the glass transition have been performed on $Pd_{77.5}Si_{16.5}Cu_6$

metallic glass ribbons by dynamic mechanical analysis. The range of measured relaxation times spans from below the glass transition temperature at 625 K up to the onset of crystallization at about 660 K. This range has been obtained combining relaxation time temperatures directly measured from the loss modulus peak and relaxation times calculated from TTS analysis of the storage modulus curve. The fragility parameter calculated from the relaxation time data is found higher than previous reported values for $Pd_{77.5}Si_{16.5}Cu_6$.

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