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Sub-T_g relaxation times of the α process in metallic glasses

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ABSTRACT

The current view of structural relaxation in metallic glasses assumes the presence of primary and secondary processes with different activation energies. While the faster, secondary process can be well characterized in the out-of-equilibrium state below the glass transition temperature T_g, the experimental direct determination of the primary process in this temperature region is more difficult due to the long relaxation times. In this work, we merge new and literature data to analyze the temperature behavior of the primary relaxation time below T_g as observed by mechanical spectroscopy and stress relaxation of metallic glasses of different fragility. We compare these results with the microscopic structural relaxation times previously measured with X-ray photon correlation spectroscopy. The coincidence between the macroscopic and microscopic relaxation times allows us to discuss the underlying mechanisms responsible of primary relaxation over different length scales, as well as to propose an overall picture of the primary relaxation behavior in the glassy regime near T_g.

1. Introduction

A detailed knowledge of the relaxation behavior of metallic glasses is crucial for gaining understanding of some key properties of these materials, such as glass-forming-ability, shape formability, mechanical response and thermal stability. The current understanding of relaxation dynamics of metallic glasses is based on the presence of a secondary or β relaxation, also termed Johari-Goldstein (JG) or 'slow' β relaxation in order to avoid confusion with the fast β processes also found in liquid dynamics [1]. This JG or β relaxation is thought to be the precursor of the primary or α relaxation [2,3]. From a macroscopic point of view, the α process is associated with the transition from an elastic (solid) to a viscous (liquid) response under the application of an external force. When the force is applied during an extended period of time shorter than the α relaxation time, τ_α, the system behaves as an elastic medium, for longer times it relaxes as a viscous fluid. The β relaxation is currently viewed as a reversible or anelastic-like process, preceding irreversible or liquid-like local movements, whose volume fraction increases with increasing temperature, finally leading to a global viscous response near the glass transition temperature T_g [4].

Above T_g, glass-forming systems are in internal equilibrium. In this regime, the relaxation dynamics, along with all other intrinsic properties, is not dependent on the previous temperature and pressure conditions and is usually probed by mechanical spectroscopy or viscosity measurements [5–7]. The fragility parameter m [8] is used to characterize the temperature dependence of the α relaxation time $\tau_\alpha(T)$ in this region. The apparent local activation energy of the liquid near T_g is related to fragility via $E_\alpha^{liq} = mRT_g \ln 10$, where R is the gas constant.

Below T_g, glasses are arrested in out-of-equilibrium configurations. In this regime, physical aging and rejuvenation may be induced by the ambient conditions or by thermal and mechanical treatments [9–12]. Through physical aging and rejuvenation, the glass changes from one so-called isoconfigurational state to another; in a first order approach, the particular glass configuration can be described by a fictive temperature T_f [13]. We will define here the range of temperatures below, but not far from, T_g as the sub-T_g region. In this temperature range the β process shows short relaxation times, of the order of seconds or less and can be probed experimentally by conventional mechanical spectroscopy or calorimetric techniques [14,15]. In metallic glasses, the activation energy of the secondary process generally follows an overall $E_\beta \approx 26RT_g$ empirical correlation [3]. The activation of shear transformation zones (STZs) also shows similar energy barriers as reviewed in ref. [16]. On the other hand, the α process involves long times and the presence of in situ physical aging complicates the determination of $\tau_\alpha(T)$ of an

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isoconfigurational glass. The order of magnitude of the aging time τ_{aging} is similar to τ_α and it is therefore difficult to avoid a simultaneous change of the glassy configuration during the required long experimental probes [17].

In this work, we compile and analyze some previous results of measurements of τ_α both above T_g in the equilibrated liquid and in the sub-T_g region. Together with some new stress relaxation results, they give us a panorama picture of the primary relaxation of isoconfigurational metallic glasses in the sub-T_g region. Finally, we discuss the implications of the presented results on the current microscopic and Potential Energy Landscape (PEL) views of α and β processes [4,18].

2. Experimental

Metallic glass ribbons with chemical compositions (at.%) of $Mg_{65}Cu_{25}Y_{10}$, $Zr_{46}Cu_{46}Al_8$, $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Pd_{43}Ni_{10}Cu_{27}P_{20}$ were produced by melt spinning. All the samples were characterized by X-ray Diffraction (XRD) with a Bruker D8 Advance apparatus and by Differential Scanning Calorimetric analysis (DSC) with NETZSCH 404 F3 and Perkin Elmer DSC-7 instruments. Dynamic Mechanical Analysis (DMA) and static relaxation tests were performed in a TA Q800 apparatus. The DMA measurements were performed at different frequencies, from 0.01 to 100 Hz, and constant heating rates of 0.5–2 K min^{-1}. Static stress-relaxation tests were performed on $Zr_{46}Cu_{46}Al_8$ and $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ applying an 'instantaneous' deformation, typically 10 μm on a 10 mm piece of ribbon, and monitoring the time evolution of the stress under isothermal conditions. The stress evolution, $\sigma(t)$, was followed at each temperature step during 30 min in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and 60 min in $Zr_{46}Cu_{46}Al_8$. From DMA and static stress relaxation curves, the relaxation times and the shape parameters of the relaxation functions were obtained by non-linear fitting of the models discussed below. The fittings were performed minimizing the least-squares error weighting each data point by the experimental error. The associated standard errors of the parameter estimates are depicted in Figs. 1, 3 and 4. Elongation viscosity measurements were performed on $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ ribbons applying a constant force and a constant heating rate of 2 K min^{-1}. X-ray Photon Correlation Spectroscopy (XPCS) was performed on $Mg_{65}Cu_{25}Y_{10}$ and $Pd_{43}Ni_{10}Cu_{27}P_{20}$; the experimental details are described in the corresponding refs [19,20].

Although following different thermal protocols, all the results presented here correspond to ribbons that were previously annealed above the glass transition temperature, thereby dramatically reducing the effect of in situ physical aging during the probes. Therefore, we will consider that the effect of aging is small and that the results give us insight into the temperature dependence of the α-relaxation times of isoconfigurational glassy states. All the experimental results, except the stress relaxation tests of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, were already reported in previous works [19–25]. These works were devoted to the study of physical aging, and the results of the aged samples were presented together with those corresponding to as-quenched states and partially aged samples. The discussion of the change of relaxation dynamics during the aging process can be found there. Here we will compare the different systems and focus on the isoconfigurational relaxation dynamics which is not discussed in the previous works.

3. Results

The range of frequencies in conventional DMA experiments permits the full characterization of the α-peak above T_g, but it only determines the high-frequency side of the peak in the out-of-equilibrium region below T_g. However, in systems where the β-process is not present, or exhibits low intensity, the assumption of a constant peak shape and the application of the time-temperature-superposition (TTS) principle permits the estimation of $\tau_\alpha(T)$. In $Mg_{65}Cu_{25}Y_{10}$ and $Zr_{46}Cu_{46}Al_8$ glasses the DMA signal was interpreted in this way and the fitting of an empirical Cole-Cole (CC) function gave an estimation of $\tau_\alpha(T)$ below T_g as

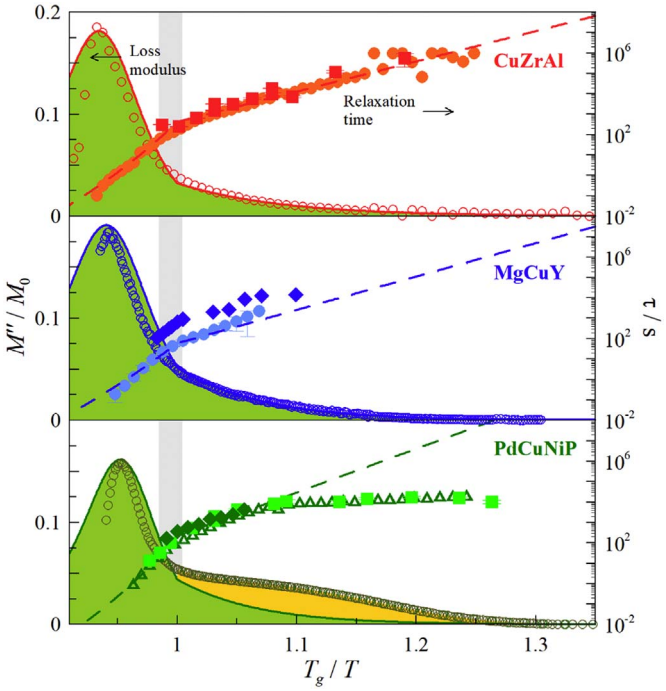

Fig. 1. Normalized loss modulus $M''(\omega,T)$ at $\omega/2\pi$ = 1 Hz; DMA measurements (open circles) and theoretical calculation considering an HN model and $\tau_\alpha(T)$ with VFT + Arrhenius behavior given by the parameters in Table 1 (continuous line). Relaxation times as a function of temperature; Static stress relaxation tests (squares), DMA measurements applying TTS principle (full circles), XPCS experiments (diamonds) and elongation viscosity (open triangles). Dashed lines correspond to $\tau_\alpha(T)$ with VFT + Arrhenius behavior given by the parameters in Table 1.

detailed in refs. [21,24]. As only the high-frequency side of the relaxation function is observed below T_g, using a more realistic asymmetric Havriliak-Negami (HN) function [26] does not significantly affect the estimation of $\tau_\alpha(T)$ while adding an extra fitting parameter along with the corresponding uncertainty.

Contrary to the cases of $Mg_{65}Cu_{25}Y_{10}$ and $Zr_{46}Cu_{46}Al_8$, mechanical spectroscopy of Pd-based glasses showed a prominent shoulder, manifesting the presence of a secondary relaxation. In this case, the average relaxation times $\tau_\alpha(T)$ and $\tau_\beta(T)$ as a function of temperature were estimated by considering two relaxation events combined with viscosity measurements as detailed in ref. [25]. Fig. 1 shows the normalized loss modulus $M''(\omega,T)$ measured in DMA isochronal tests at $\omega/2\pi$ = 1Hz (open circles) and the $\tau_\alpha(T)$ obtained from DMA tests at different frequencies (full circles).

Isothermal static stress relaxation tests give direct access to the macroscopic response in the time domain. As discussed in ref. [4], the stress relaxation can be fitted by a stretched exponential decay, $\sigma(t) = \sigma_0 \exp(-(t/\tau_\alpha)^{\beta_{KWW}})$, thus obtaining the average relaxation time τ_α and the stretching exponent β_{KWW}. Fig. 2 shows the stress evolution of $Zr_{46}Cu_{46}Al_8$ and $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ at different temperatures and the corresponding fitted stretched exponential functions. The $\tau_\alpha(T)$ values obtained from the fittings are displayed in Fig. 1 as square symbols. In the case of $Mg_{65}Cu_{25}Y_{10}$ and $Pd_{43}Ni_{10}Cu_{27}P_{20}$, XPCS measurements gave direct access to the microscopic relaxation dynamics in the time domain by monitoring the decay of the autocorrelation function of the atomic positions under isothermal conditions as detailed in refs [19,20]. The values of $\tau_\alpha(T)$ obtained by this method are reproduced from those references as diamonds in Fig. 1.

Fig. 1 also shows a theoretical estimation of $\tau_\alpha(T)$ (dashed lines) and loss modulus $M''(\omega,T)$ (solid lines). This estimation of $\tau_\alpha(T)$ was calculated considering that at T_g the temperature dependence of the relaxation dynamics evolves from Vogel-Fulcher-Tamman (VFT), $\tau_\alpha(T) = \tau_0 \exp(B/(T-T_0))$ in the equilibrium liquid, to Arrhenius behavior,