



Main (α) relaxation and excess wing in $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass investigated by mechanical spectroscopy



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ABSTRACT

The dynamic mechanical relaxation behaviour of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass was investigated by mechanical spectroscopy as a function of temperature. The mechanical spectra show the evidence of an “excess wing” process at the lower temperatures. The α -relaxation spectra of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass was described with a Kohlrausch–Williams–Watts (KWW) function, with the exponent $\beta_{KWW} = 0.5 \pm 0.02$. The fragility parameter m of the $Zr_{50}Cu_{40}Al_{10}$ is $m = 57 \pm 5$. The values of m and β_{KWW} are found to agree with the correlation found for other glasses $m = 250(\pm 30) - 320\beta_{KWW}$ [R. Böhmer, K.L. Ngai, C.A. Angell et al. J. Chem. Phys. 99 (1993) 4201–4209]. Aging experiments give strong evidence that the observed “excess wing” is a submerged secondary process and not part of the α process.

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1. Introduction

Metallic glasses are a relatively new class of materials that show attractive properties for potential use as functional and engineering materials [1–3]. The dynamics is very important for the understanding of the physical properties of glass forming materials [4,5]. One conventional way of studying the dynamics of glasses and glass-forming liquids are relaxation measurements (i.e., dielectric and mechanical relaxation). The relaxation spectra are characterized at minimum by a main (or α) relaxation and a secondary (β or excess wing) relaxation at higher frequency [4,6–8]. The α relaxation is associated to the cooperative motion of atoms or molecules in the liquid. While the secondary relaxation is associated with the local non-cooperative motion of molecules or atoms [5,9]. The understanding of the nature of the α relaxation and β relaxation processes and their correlation is fundamental for the understanding of the glass transition, diffusion and mechanical properties in metallic glasses [10].

The relaxation time, $\tau_{\alpha}(=(2\pi\nu_{\text{peak}})^{-1})$, of α process for glass forming materials increases by several orders of magnitude over a small temperature range on decreasing the temperature from above the glass transition temperature T_g . The temperature

dependence of the α relaxation is often described with the Vogel–Fulcher–Tammann (VFT) equation [11]:

$$\tau_{\alpha} = \tau_{\infty}^{\alpha} \exp\left(\frac{B}{T-T_0}\right) \quad (1)$$

where τ_{∞}^{α} is the relaxation time in the limit of high temperatures and T_0 is the Vogel temperature and B a parameter. The temperature dependence of relaxation time τ_{β} is often hard to describe above the glass transition due to the smaller intensity of the β with respect to the α process. In the glassy state τ_{β} is found to obey an Arrhenius-type equation:

$$\tau_{\beta} = \tau_{\infty}^{\beta} \exp\left(\frac{U_{\beta}}{RT}\right) \quad (2)$$

where, τ_{∞}^{β} is the high temperature limit of τ_{β} , U_{β} is the activation energy, and R is the gas constant.

Metallic glasses often display, even below T_g , a not well-resolved β relaxation, or “excess wing” [6]. This is probably partly due to the more limited range of frequency that can be accessed in mechanical relaxation versus dielectric relaxation (since the latter cannot be used for studying metallic glasses). Dixon and co-workers [12] proposed that the “excess wing” is not a separate process but part of the α relaxation. However, several following investigations have shown that the “excess wing” is not a separate process but a submerged β relaxation process [13]. This seems to be somewhat still an object of controversy in metallic glasses and only few studies are focused on the excess

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wing in metallic glasses [14,15]. In here we present some new results on the effect of aging on the excess wing in a metallic glass.

Mechanical spectroscopy is a powerful tool to investigate the atomic mobility and mechanical relaxation for metallic glasses. One of the difficulties in studying the α and β processes in metallic glass forming liquids over a broad range of temperatures is their ability to crystallize very quickly. Thus, it is necessary to select a suitable alloy that can be supercooled. $Zr_{50}Cu_{40}Al_{10}$ metallic glass shows an excellent glass forming ability (GFA) and a large supercooled liquid region [16,17].

2. Experimental

Model alloy with composition $Zr_{50}Cu_{40}Al_{10}$ (at.%) was prepared by tilt cast equipment in an arc furnace [16]. Thermal properties of the metallic glass were determined by a standard commercial instrument differential scanning calorimetry (DSC) (Perkin Elmer, DSC-7). Dynamic mechanical measurements were carried out in an inverted torsion mode using a mechanical spectrometer described by Etienne et al. [18]. Experiments were performed using a sinusoidal stress, either at a fixed frequency (ranging from 10^{-2} to 10 Hz) during continuous heating with a constant heating rate or at a given temperature with different frequencies. Experimental samples with the dimensions of 40 mm (length) \times 2 mm (width) \times 1 mm (thickness) were prepared using electric discharge machining. All the experiments were performed under a high vacuum atmosphere. The complex shear modulus ($G^* = G' + iG''$) was determined in the frequency domain by applying a periodic shear stress and measuring the corresponding strain. Strain amplitude was lower than 10^{-4} during the testing process.

3. Results and discussion

Fig. 1 shows the dynamic mechanical properties of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass as cast at a fixed driving frequency (0.3 Hz) with a constant heating rate (3 K/min). Similarly to what were observed in other metallic glasses [19–21], three different temperature regions are observed. Region (I) (300–550 K): In the glassy state well below the glass transition, G' is high and nearly constant and the viscoelastic component G'' is almost negligible, and the mechanical behaviour is nearly elastic. Region (II) (550–760 K): A maximum in G'' occurs at a temperature called T_{α} , such that relaxation time $\tau_{\alpha} = (2\pi\nu)^{-1}$ (in this case $\nu = 0.3$ Hz). In this range, G' decreases with increasing temperature. The temperature T_{α} thus separates the supercooled liquid region from the glassy region. Region (III) ($T > 760$ K): Both the storage modulus G' and loss modulus G'' increase drastically with the increasing temperature due to the crystallization.

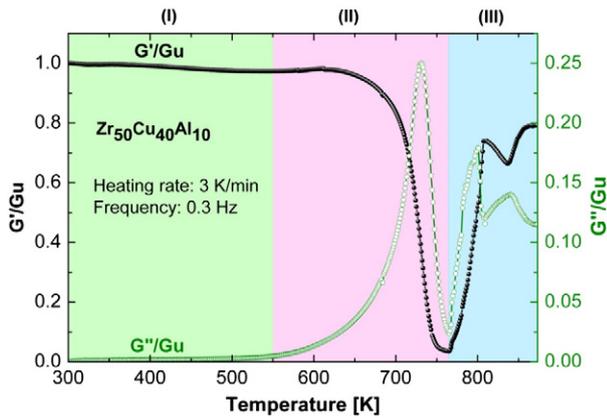


Fig. 1. The storage modulus G' and loss modulus G'' vs temperature in $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass. G_u is the unrelaxed modulus, assumed to be equal to G' at room temperature. Experiments are carried out during continuous heating (3 K/min) and with a constant driving frequency (0.3 Hz).

Fig. 2 shows the spectra of the storage modulus G' and the loss modulus G'' varying temperature from the supercooled region to the glassy state. The peak maximum of α relaxation in the loss modulus G'' and the onset of the storage modulus G' shift to lower frequency with increasing measurement frequency. No pronounced β relaxation is evident in the loss modulus G'' for temperatures below the glass transition in the case of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass. A master curve obtained in the framework of the time temperature superposition (TTS) at a reference temperature 675 K is presented in Fig. 3. The separation between the α and β process (or more precisely here the excess wing) as well as their shape as observed in a master curve is not correct since the two processes have very different temperature dependence of their shape and relaxation time, so that the TTS over the entire range cannot be valid. However, the master curves are very useful to evidence the differences in the spectra of the investigated glass formers.

The α relaxation peak in the isothermal spectra can be described with the stretched exponential or Kohlrausch–Williams–Watts (KWW) function [22]:

$$G''(\omega) = \Delta G_{\alpha} L_{i\omega} \left[-\frac{d\varphi_{\alpha}(t, \tau_{\alpha})}{dt} \right] \quad (3)$$

with $\varphi_{\alpha}(t, \tau_{\alpha}) = \exp \left[-(t/\tau_{\alpha})^{\beta_{KWW}} \right]$

where $L_{i\omega}$ indicates the Laplace transform and β_{KWW} is the Kohlrausch exponent which value is between 0 and 1. Low values of β_{KWW} reflect a large deviation from a pure exponential decay. ΔG ($= G_u - G_r$, G_u the unrelaxed modulus and G_r the relaxed modulus) is the relaxation

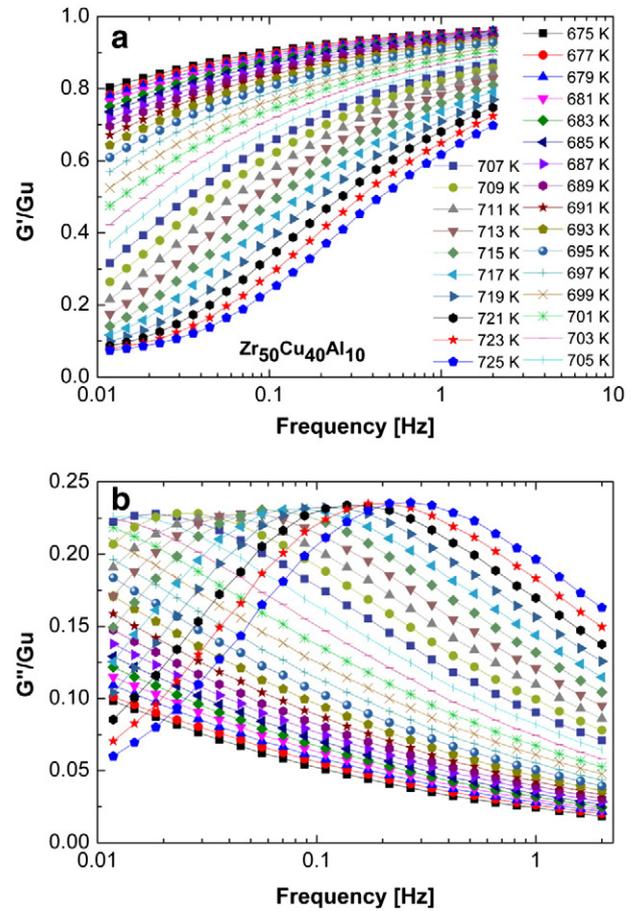


Fig. 2. DMA curves in $Zr_{50}Cu_{40}Al_{10}$ as a function of frequency at different temperatures (675–677–679–681...725 K): (a) The normalized storage modulus G'/G_u and (b) the normalized loss modulus G''/G_u , respectively. G_u is the unrelaxed modulus, assumed to be equal to G' at room temperature.

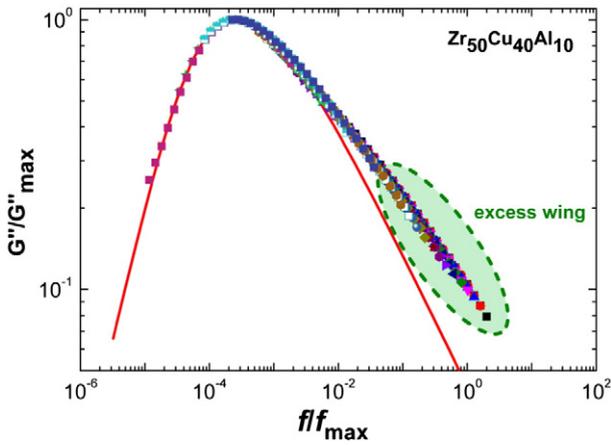


Fig. 3. Master curve: showing the dependence of the normalized loss modulus vs the normalized frequency in $Zr_{50}Cu_{40}Al_{10}$ metallic glass. Here, f_{max} corresponds to the frequency for which G''_{max} is detected at 675 K. The solid line is a KWW function with Kohlrausch exponent $\beta_{KWW} = 0.5 \pm 0.02$.

strength. The solid line shown in Fig. 3 corresponds to a KWW function with $\beta_{KWW} = 0.5$; this value of β_{KWW} was found from the fit to the isothermal spectra. The deviation of the data at high frequency (i.e. an excess wing) to a much slower frequency dependence, $G''(\omega) \sim \omega^{-0.36}$, is indicative of the presence of a submerged secondary peak. In principle it could be objected that the excess wing is part of the α process or that it could be due to a decrease of the β_{KWW} of the α -process.

Fig. 4 shows the temperature dependence of the structural relaxation time τ_{α} ($1/(2\pi f_{max})$) in $Zr_{50}Cu_{40}Al_{10}$ determined from the best fit of the loss modulus spectra in Fig. 2 with Eq. (3) showing a not activated behaviour that can be described with the VFT equation (Eq. (1)). The best fit of the VFT equation to the data of $Zr_{50}Cu_{40}Al_{10}$ is obtained for $\log(\tau_{\alpha}^{\infty}) = -14.6 \pm 1.6$, $B = 8041 \pm 1423$ K and $T_0 = 482 \pm 20$ K, respectively. The values of B and τ_{∞} fall within the range of the values found for other metallic glasses [23–25].

A parameter often used to describe the dynamics or supercooled liquids is the fragility [5,26,27]. Glass forming materials are classified into “strong” and “fragile” glass formers depending on whether m is small or large, respectively. The dynamic fragility parameter m shows the degree of deviations from Arrhenius behaviour, with larger values of m indicating larger deviations from the Arrhenius behaviour. Thus

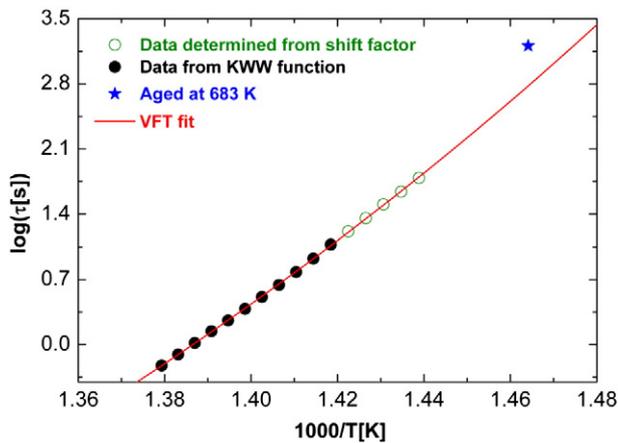


Fig. 4. The structural (α) relaxation time of $Zr_{50}Cu_{40}Al_{10}$ metallic glass as a function of inverse temperature determined from the best fit of loss modulus G'' spectra (solid symbols) and the relaxation time determined from the shift factor (open symbol(s)) for those spectra (Fig. 2(b)). The solid lines present VFT (Eq. (1)) fits to the experimental data. The star symbol for $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass is determined by the aging experiment (the aging temperature is 683 K).

metallic glass forming liquids have been found to show an intermediate value of the fragility parameter.

The fragility parameter m is connected to B and T_0 as [23]

$$m = \frac{BT_g}{\ln 10 (T_g - T_0)^2} \quad (4)$$

from which using the best fit parameters to the VFT equation for $Zr_{50}Cu_{40}Al_{10}$ we find the fragility parameter $m = 57 \pm 5$. As showed by Böhmer et al. for different glassy materials the fragility parameter m is often correlated with the Kohlrausch exponent β_{KWW} according to $m = 250(\pm 30) - 320\beta_{KWW}$ [28]. For the determined value of $\beta_{KWW} = 0.5$ the value expected from this correlation is $m = 90 \pm 30$ that is in agreement (within the experimental error) with the value for $Zr_{50}Cu_{40}Al_{10}$ metallic glass. A validation of this correlation was recently shown also for other bulk metallic glasses [24]. The β_{KWW} determined from the fit to the isothermal spectra could be potentially larger than reported if the contribution of the excess wing could be subtracted, but the frequency range is too small for doing such operation. A larger value for β_{KWW} , would give a smaller m thus in better agreement with the value of m determined from the temperature dependence of τ_{α} .

Physical aging measurement was performed at the aging temperature $T_a = 683$ K in $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass with a driving frequency of 0.3 Hz (Fig. 5). For the aging measurement, the as cast sample was heated to the aging temperature T_a with a constant heating rate of 3 K/min, then the samples were held at this temperature. As shown in Fig. 5, the physical aging induces an increase of the storage modulus G' ($\sim 5\%$) and a decrease of the loss modulus G'' . Thus the physical aging in metallic glass decreases the viscous component and the glass becomes more elastic (and generally more brittle). Similar aging behaviour has been observed in other metallic glasses [29–31].

The physical aging behaviour is clearly non-exponential, and the characteristic aging time τ_{aging} can be determined from the analysis of the evolution of the loss modulus G'' [32,33] described by:

$$G''(t_{aging}) = A \left[\exp\left(-\frac{t_{aging}}{\tau_{aging}}\right)^{\beta_{aging}} \right] + G''(t_{aging} \rightarrow \infty) \quad (5)$$

where $A (= G''(t_{aging} = 0) - G''(t_{aging} \rightarrow \infty))$ is the change in G'' during the aging process. β_{aging} is the stretch exponent. From the best fit (solid line in Fig. 5), we obtain $\beta_{aging} = 0.47 \pm 0.01$, which is in agreement from the best fit of the master plot of the loss modulus. In agreement with Lunkenheimer et al. [32], we found that the value of β_{aging} is smaller than that determined isothermally.

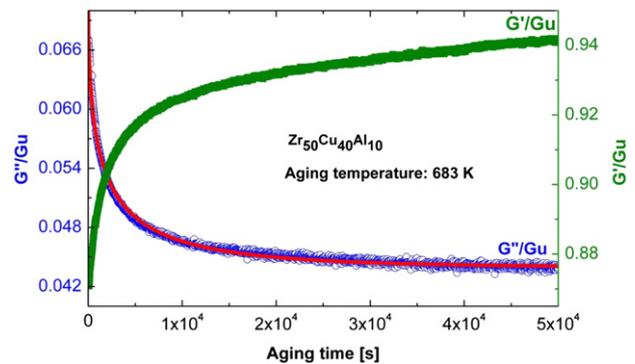


Fig. 5. Evolution of the storage modulus G' and loss modulus G'' of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass with the annealing time. Aging temperature is $T_a = 683$ K and the driving frequency is 0.3 Hz. The fit has R^2 value of 0.992. The solid line is fitted by Eq. (5). The best fitting parameters are as follows: $A = 0.02821$, $\tau_{aging} = 1618 \pm 23$ s, $\beta_{aging} = 0.47 \pm 0.01$ and $G''(t_{aging} \rightarrow \infty) = 0.04387$.

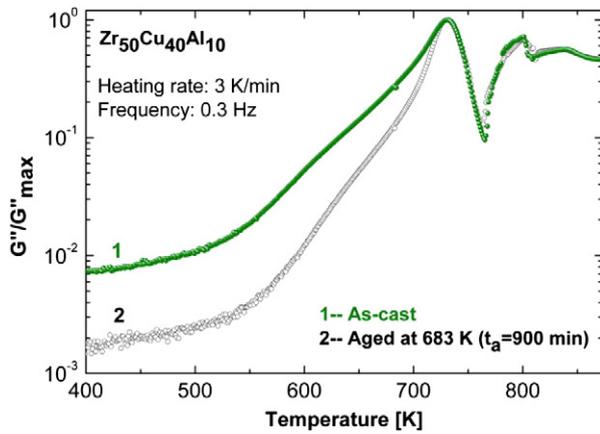


Fig. 6. Evolution of the loss modulus G'' with the temperature of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass: (1) As-cast state and (2) after aged at 683 K (aging time is 900 min).

A comparison of the loss at constant frequency before and after the physical aging is shown in Fig. 6. The physical aging strongly affects the loss modulus at lower temperatures (well below T_{α}), while the part of the losses related to the α -process remains almost unchanged. This result clearly shows that the high frequency wing in Fig. 3 is indeed a separate process which is affected by aging and agree with previous investigations, suggesting that physical aging leads to a decrease of the local atomic mobility below the glass transition temperature [34,35].

4. Conclusion

The α relaxation and excess wing in $Zr_{50}Cu_{40}Al_{10}$ metallic glass former were studied by mechanical spectroscopy. The loss modulus of $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass is well described by the KWW relaxation function with $\beta_{KWW} = 0.5 \pm 0.02$. The fragility parameter m of the $Zr_{50}Cu_{40}Al_{10}$ was found to be $m = 57 \pm 5$. Interestingly, the values of β_{KWW} and m are in agreement with the correlation between m and β_{KWW} found by Böhmer et al. [28]. However, this procedure of determination of β_{KWW} from the master curve may be smaller than the value estimated from relaxation times. Aging experiments on this bulk metallic glass show a strong decrease of the mechanical losses at lower temperature while the loss related to the α process is practically unaffected. This aging experiment thus confirms that the observed excess wing is not part of the α process but a separate secondary process (i.e. a submerged β process) and that this β -process is more sensible to aging than the α process.

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