Dynamics of the strong metallic glass $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$

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ABSTRACT

$Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass (BMG) presents higher corrosion resistance, lower glass transition temperature and lower density than most BMGs. Dynamic properties of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ BMG were investigated by mechanical spectroscopy. The structural (α) process in the isothermal spectra is well described by a Kohlrausch-Williams-Watts (KWW) function with $\beta_{KWW} = 0.505$. At high frequency, an extra contribution to the α process (i.e. an excess wing) is observed with a much smaller frequency dependence of the loss shear modulus $G''(f) \sim f^{-0.37}$, indicating the presence of a submerged secondary peak. The temperature behaviour of the α relaxation time, τ_α, is characterized by a very small steepness index (i.e. strong behaviour). We find that results for this BMG show a deviation of the correlation between fragility and β_{KWW} generally found in glass formers. Results in the literature for other BMGs suggest that this deviation may not be an exception for BMGs, since very similar values of β_{KWW} (~0.5) have been found for BMGs independently of their steepness index.

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1. Introduction

One of the more striking behaviors in the glass forming materials is the observed change of many orders of magnitude of their dynamical properties (i.e. viscosity, relaxation time, etc.) without any apparent change of their structure [1]. The presence of an increased local order on approaching the glass transition has been suggested by simulations, but any direct experimental evidence of this ordering has been elusive to date [2]. It is maybe even more striking that the dynamical behaviour is apparently identical in materials very different from a chemical point of view such as metallic glasses and polymers, encompassing all different type of chemical interaction (ionic, covalent, hydrogen bonded, coulombic, etc.). Although it is not completely clear whether all observation found for more classical glass formers are valid for BMGs, since the latter have been discovered more recently and are relatively less studied.

One of the main methods of investigation of the dynamics is by relaxation measurements (i.e. dielectric relaxation and mechanical relaxation) [3–7]. Relaxation spectra of glass forming materials are generally characterized by at least two types of relaxation: (i) the structural (also called α) relaxation, which is linked to the glass transition phenomenon and is observable near the glass transition, and (ii) the secondary relaxations (named β, γ, etc.), which are usually connected to the local atomic or molecular movements, and more evident in the glassy state [8].

In the past decade, bulk metallic glasses (BMGs) have inspired considerable interest due to their unique combination of structural and functional properties, such as higher strength, larger elasticity, lower elastic modulus and excellent corrosion resistance. Compared with other organic glass formers (i.e. polymers), metallic glasses have a long-range disordered atomic structure [3,9–11]. There are still many open issues to better understand BMGs like the origin of the plasticity and the connection between α and β relaxation [12,13]. Recently, a correlation between the β relaxation and intrinsic plasticity in metallic glasses has been found [14]. In parallel, it was found that the activation energies of the β relaxation and shear transformation zone (STZ) in the BMGs are of the same order of magnitude [12], and the origin of the β relaxation has been associated with diffusion of the smallest atoms in the metallic glasses [15].

Dynamical mechanical analysis is an effective strategy to study the atomic mobility in metallic glasses. Herein we investigate the dynamic mechanical properties of a $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ metallic glass having a relatively low glass transition temperature as a function of temperature or frequency.

2. Experimental section

$Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass was prepared as described in Ref. 16. Differential scanning calorimetry (DSC) experiment was performed using a standard commercial instrument (Perkin Elmer, DSC-

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7) under high purity dry nitrogen at a flow rate of 20 ml/min. The amorphous nature of the glassy sample has been verified by X-ray diffraction (XRD).

Dynamic mechanical measurements were carried out in an inverted torsion mode using a mechanical spectrometer, as described by Etienne et al. [17]. These shear dynamic mechanical measurements have been performed by a specific device, which was designed in INSA de Lyon (France). The experiments were performed under sinusoidal stress, either at a fixed frequency in the ranges from 10^{-4} to 1 Hz with a constant heating rate or at a given temperature with different frequencies. The experimental samples with the dimension of 30 mm (length) × 3 mm (width) × 1 mm (thickness) were prepared with a wire cutting machine. All the experiments are performed in a high vacuum atmosphere. The complex shear modulus $G^*(f) = G'(f) + iG''(f)$ is obtained by applying a periodic shear stress, and measuring the corresponding strain. The strain amplitude was lower than 10^{-4}. Isochronal experiments were performed with a constant driving frequency of 0.3 Hz and at a constant heating rate of 3 K/min. Isothermal experiments were performed in the frequency range between 10^{-2} and 2 Hz at various temperatures (range from 330 to 425 K by step of 5 K). In the current research, 24 frequencies could be obtained at a fixed temperature. The experimental annealing during the current work could be negligible due to one testing cycle time is very short.

3. Results and discussion

Fig. 1(a) shows representative DSC curves of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass obtained at heating rate 20 K/min. In Fig. 1 the step in the heat capacity corresponding to glass transition temperature $T_g = 395$ K,
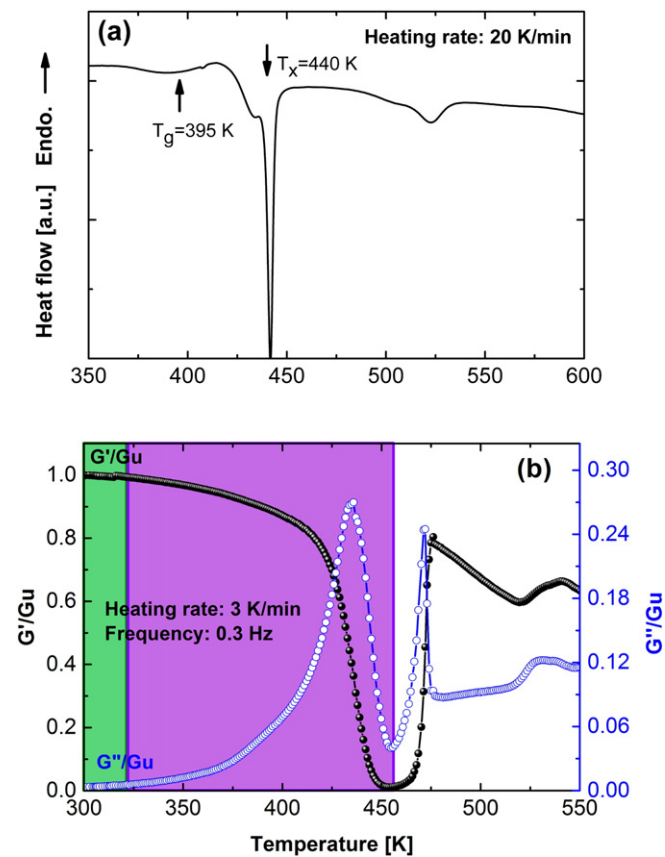
and an intense peak due to the crystallization on heating at 440 K. Fig. 1(b) presents the storage (G') and loss (G'') dynamic shear modulus in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ BMG as a function of temperature at a constant frequency (0.3 Hz) during continuous heating between room temperature to 573 K. G_u is the unrelaxed modulus. Similarly to other BMGs [3,9, 18–20], three distinct temperature regions can be observed in Fig. 1(b): (i) At lower temperature: the BMG is in a vitreous state, the behaviour in this temperature range is mainly elastic with a large storage modulus. G' is nearly independent of temperature, and G'' is very small. (ii) At intermediate temperature: a drastic decrease of the storage modulus is observed and viscous flow is induced when a mechanical stress is applied in the supercooled liquid region (SLR). This is associated to a drastic decrease in the viscosity, which is strain rate dependent and a transition from solid-like to liquid-like behaviour. In this range mechanical relaxation occurs, characterized by a maximum in the viscoelastic component (loss). It should be noted that the peak temperature depends on the measurement frequency and in this case it corresponds to the temperature at which $\tau = 0.5$ s thus higher than glass temperature from DSC measurements where $\tau \sim 100$ s. (iii) At higher temperature both G' and G'' exhibit a drastic increase, when crystallization occurs. For the results below the temperature range of interest is the intermediate range (ii).

The dynamic mechanical properties in amorphous materials are sensitive to the temperature as well as the driving frequency [3]. To characterize the relaxation behaviour of the dynamic mechanical properties in the metallic glass, experiments were carried isothermally, in a range from 330 to 430 K, varying stress frequency.
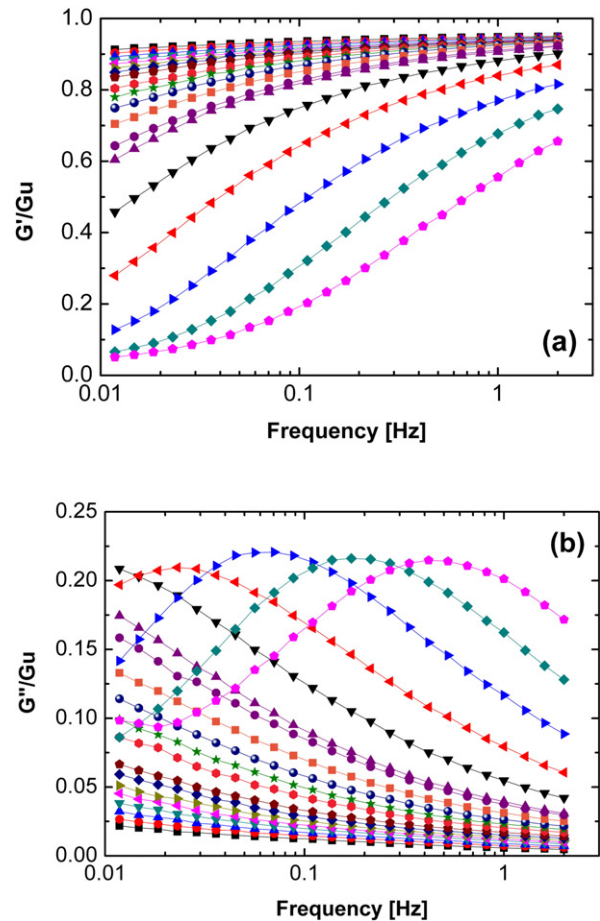

Fig. 1. (a) DSC curve in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass (heating rate: 20 K/min). (b) The storage modulus G' and loss modulus G'' as the function of temperature for $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass. G_u is the unrelaxed modulus, assumed to be equal to G' at room temperature. Experiments were carried out during continuous heating (3 K/min) and with a constant driving frequency (0.3 Hz).

Fig. 2. DMA curves in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ metallic glass as a function of frequency at different temperatures (330 to 425 K by step of 5 K from down to up): (a) The normalized storage modulus G'/G_u and (b) the normalized loss modulus G''/G_u, respectively.

Fig. 2 shows the storage G′ and the loss modulus G″ in the $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass at various temperatures as a function of the drive frequency. At higher temperatures, the peak maximum of α relaxation is evident in the loss modulus G″ and it shifts to lower frequency with decreasing temperature. It should be noted that there is no distinct β relaxation in the loss modulus G″ spectra even for temperatures below the glass transition temperature for $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass.

Applying the time-temperature superposition (TTS) principle, master curves can be obtained using a simple horizontal shift. When this principle is applied, it is necessary to take into account its limited validity. The TTS is strictly valid only if the shape (relaxation breadth) of the relaxation is independent of temperature, thus limited if the shape of the relaxation is temperature dependent or if there is a not negligible contribution of the secondary relaxation. In our case the master curve has a shape very close to that of the isothermal spectra, indicative of a small dependence of the relaxation breadth on temperature in the investigated range and a negligible contribution from the β process (Fig. 3).

The α peak in the loss modulus spectra (Fig. 2) can be well described with a Kohlrausch-Williams-Watts (KWW) relaxation function [21]:

$$G''(\omega) = \Delta G_{\alpha} L_{i\omega}\left[-\frac{d\varphi_{\alpha}(t,\tau_{\alpha})}{dt}\right]$$
$$with \quad \varphi_{\alpha}(t,\tau_{\alpha}) = \exp\left[-(t/\tau_{\alpha})^{\beta_{KWW}}\right] \tag{1}$$

where $L_{i\omega}$ indicates the Laplace transform and β_{KWW} (≤1) is the Kohlrausch exponent. Smaller is β_{KWW} larger is the 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 strength. The β_{KWW} obtained from the fit to a KWW function to the isothermal spectra is $\beta_{KWW} = 0.505$ (the solid line shown in Fig. 3) and in the investigated range is found to be independent of temperature. In the high frequency tail of the master curve (Fig. 3) is present a small deviation of the data from the KWW behaviour to a slower frequency dependence (i.e. an excess wing), $G''(f) \sim f^{-0.37}$. To make this deviation more evident the same data are reported in a log-log scale in the insert of Fig. 3. This extra contribution can be indicative of the presence of a submerged secondary peak. It has been shown for several organic materials by aging and high pressure experiments that the excess wing in glassy materials is an unresolved β relaxation [22,23]. Similarly, recent aging experiments have shown that the excess wing in some metallic glasses is not part of the α process [18], since their separation between the two processes increases with aging.
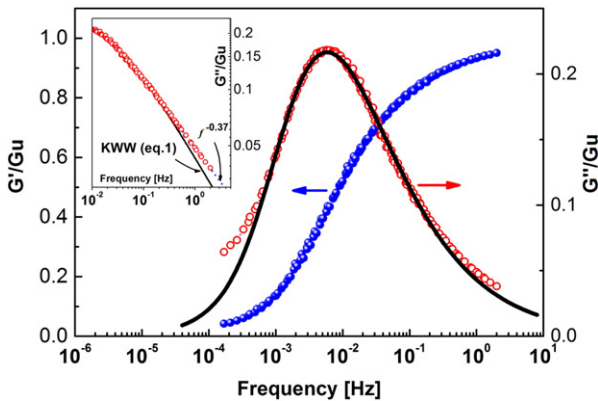
The master curve (Fig. 3) was obtained with respect to the reference temperature T_r ($= 400$ K). To obtain this master curve, the loss spectra is shifted by the frequency shift factor a_T [23]

$$\ln a_T = \ln\tau - \ln\tau_r \tag{2}$$

where τ and τ_r are the relaxation time at temperature T and T_r, respectively. Assuming an activated (i.e. Arrhenius) behaviour of the relaxation time τ, it follows [24,25]

$$\ln a_T = \frac{U}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right) \tag{3}$$

where R is gas constant, depending on the temperature range U is the apparent activation energy for α and β process.

Fig. 4 presents the shift factor a_T as a function of isothermal temperature for the $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass (as-cast state), it is evident a decrease of the temperature dependence of a_T at lower temperature. Generally the apparent activation energy of the α process is found to increase with decreasing temperature, while the behaviour in Fig. 4 would correspond to a decrease of the activation energy. This apparent decrease is due to the fact that (i) the shift factor at lower temperature (i.e. below T_g) is dominated by the temperature dependence of the β process, which has a smaller activation energy than the α process and (ii) the non-equilibrium nature of the glassy state. As a first approximation the data in Fig. 4 can therefore be used to estimate the apparent activation energy of the α process in the supercooled state and that of the β process in the glassy state.

Metallic glasses have a relatively simple structure (without side groups able to relax independently) thus the α relaxation is due to the cooperative motion of atoms while the β process is a so called Johari-Goldstein relaxation linked to the local atomic movement [26,27]. Using Eq. (3) we determined the apparent activation energy for α relaxation U_{α} and Johari-Goldstein relaxation U_{β}. The values of activation energy for U_{α} and U_{β} for the as-cast sample are $U_{\alpha} = 2.71 \pm 0.02$ eV and $U_{\beta} = 0.817 \pm 0.016$ eV, respectively. Thus the activation energy of α relaxation of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass is about 3 times of the Johari-Goldstein relaxation, similarly to what is observed for La-based metallic glasses [27]. Seen as evidence of the relaxation between the U_{α} and U_{β} in other typical metallic glasses, the ratio of U_{β}/U_{α} varies from 3 to 8 [27–29].

The temperature dependence of the α relaxation time τ_{α} in glass forming materials is well described by the Vogel-Fulcher-Tamman (VFT) equation [8,23]:

$$\tau_{\alpha} = \tau_{\infty}^{\alpha}\exp\left(\frac{B}{T-T_0}\right) \tag{4}$$

Fig. 3. Master curve of the normalized storage modulus G′/G_u and the normalized loss modulus G″/G_u in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ metallic glass, respectively. The reference temperature is 400 K (the temperature ranges from 400 to 425 K). In the insert is the high frequency flank of the loss modulus showing the deviation from the KWW functions (Eq. (1)) to a power law with larger exponent.
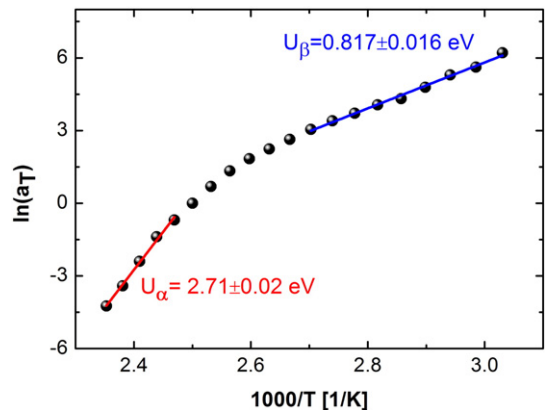

Fig. 4. Temperature dependence of the shift factor a_T used to establish the master curve in $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ bulk metallic glass (the temperature ranges from 330 to 425 K).

where τ_∞^α is the relaxation time in the limit of high temperatures and T_0 is the Vogel temperature.

Fig. 5(a) shows the relaxation time τ_α ($=(2\pi f_{peak})^{-1}$) from the best fit of the isothermal spectra (Fig. 2) of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ to Eq. (1) together with two values at lower temperature estimated from the shift factor (when the peak maximum is outside the frequency range and the fit using Eq. (1) is not meaningful). Over the observed dynamic range the temperature behaviour of τ_α is very well described by a simple activated behaviour (thus a fit with a VFT equation give results with very large parameters' errors).

A parameter often used to describe the dynamics of amorphous materials is the steepness index, m, or "fragility" [30,31]:

$$m = \frac{\partial \log(\tau_\alpha)}{\partial\left(\frac{T_g}{T}\right)}\Bigg|_{T=T_g} \qquad (5)$$

Glass forming materials are classified into "strong" and "fragile" glass formers depending on whether m is large or small. The dynamic fragility parameter m is generally correlated with the degree of deviations from Arrhenius behaviour, with larger values of m indicating larger deviations from the Arrhenius behaviour. So far BMGs have been found to show an intermediate value of the fragility parameter.

Often the parameter m is determined from the VFT best fit parameters, in this case the error in the determination of m using this method would be too large to be meaningful. However, we can determine m from its definition (Eq. (5)) taking advantage of the almost Arrhenius
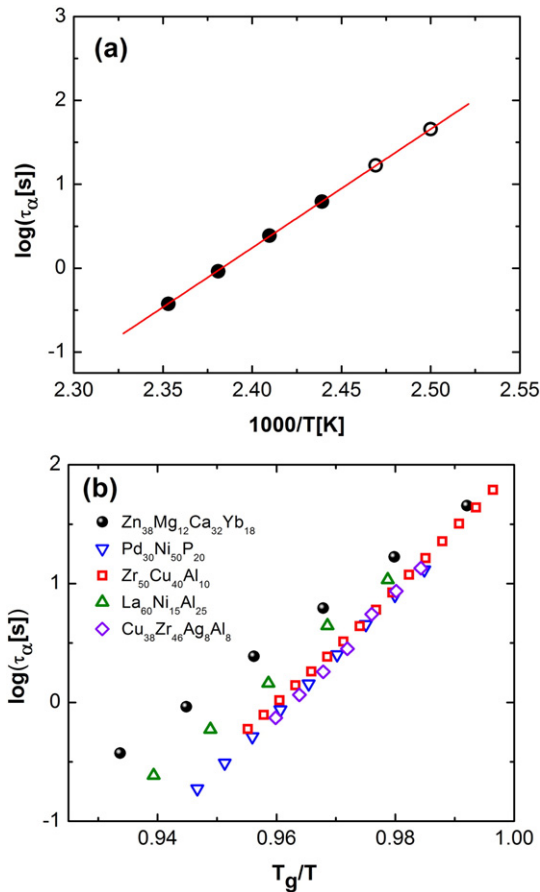

dependence of τ_α and the data are measured at sufficiently low frequency, requiring only a small extrapolation to $\tau_\alpha = 100$ s. From the apparent activation energy of τ_α we find $m = 36 \pm 1$. This value is considerably lower than that found for other metallic glass formers from mechanical measurements as evident comparing the temperature behaviour of τ_α with other BMG (Fig. 5(b)), and much smaller than the fragility for polymers and most organic molecules [32,33]. Considering determination of m from mechanical measurements alone, to our knowledge $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ has the smallest value reported so far for BMGs. Previous m determination using DSC measurements of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ found $m = 46$ [34] which is larger than what we found but still smaller than most [9], and also reported the lowest value of m for a Ce-based BMGs with $m = 21$ [35], for this last there are no mechanical relaxation data available determine m. A possible reason for difference in the value of m determined from DSC respect to that determined by mechanical relaxation may be due to the "unconventional" way used to determine m in BMGs from DSC. Conventionally, m is determined by DSC measurement from the rate dependence of T_g obtained by cooling at different rate, starting from a well-defined equilibrium state [36], however due to the propensity of BMGs to crystallize this is not possible. Thus m is determined from the T_g dependence on heating rate from the glassy state, and thus this value of m can be affected by the non-equilibrium nature of the glassy state (i.e. different level of physical aging). Notwithstanding this difference it is evident that $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ is one of the strongest BMGs known so far, and the strongest for which mechanical relaxation data are available.

The β_{KWW} of glass forming materials is generally correlated with the fragility parameters m, more fragile materials (larger m) have in general smaller β_{KWW} [33]. In particular Böhmer et al. show that this correlation can be well described for organic as well inorganic materials as $m = 250(\pm30) - 320\beta_{KWW}$ [33]. We have previously found that this correlation was within the experimental error satisfied for several BMGs [37], however, for $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ BMG from the β_{KWW} determined from the best fit of the isothermal spectra the correlation would predict $m = 90 \pm 30$, which is much larger than the measured value ($m = 36$ herein and $m = 46$ from DSC [34]). Thus in this case there is a clear deviation from the correlation of Böhmer et al. [33].

To investigate further whether $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ is the only BMGs exception we took into consideration the temperature behaviour of τ_α for other BMGs previously measured: $Zr_{50}Cu_{40}Al_{10}$ ($\beta_{KWW} = 0.5$, $m = 57$) [18], $La_{60}Ni_{15}Al_{25}$ ($\beta_{KWW} = 0.56$, $m = 51$) [19] and $Zr_{55}Cu_{30}Ni_5Al_{10}$ (this is not in the figure) ($\beta_{KWW} = 0.498$, $m = 48$) [20], $Cu_{38}Zr_{46}Ag_8Al_8$ ($\beta_{KWW} = 0.51$, $m = 59$) [20], $Pd_{30}Ni_{50}P_{20}$ ($\beta_{KWW} = 0.6$, $m = 57$) [37], are reported in Fig. 5(b). For the BMGs in Fig. 5(b) it is evident a significant range of fragilities ($36 \le m \le 59$) which, according to the correlation between β_{KWW} and m, should correspond to a range of β_{KWW} ($0.60 \pm 0.09 \le \beta_{KWW} \le 0.67 \pm 0.09$). However comparing the β_{KWW} found from the best fit of isothermal spectra

Fig. 5. (a) The relaxation time τ_α of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ versus inverse temperature. In the investigated range the apparent activation energy of τ_α has very small temperature dependence, as showed by the Arrhenius fit to the data (solid line). (b) Fragility plot. The $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ has the lower fragility than most BMGs. $Pd_{30}Ni_{50}P_{20}$ data are from Ref. [37], $Cu_{38}Zr_{46}Ag_8Al_8$ data are from Ref. [20], $Zr_{50}Cu_{40}Al_{10}$ data are from Ref. [18] and $La_{60}Ni_{15}Al_{25}$ data are from Ref. [29], respectively.
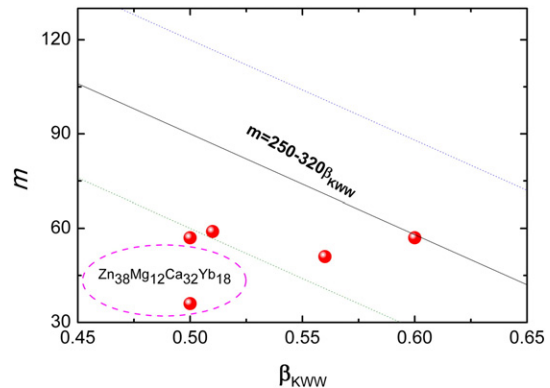
Fig. 6. Steepness index versus β_{KWW} for the BMGs in Fig. 5(b). The solid line is the correlation from Böhmer et al., the dotted lines show the uncertainty of the correlation.

(Fig. 6) are found to be all smaller than what is expected from the correlation between m and β_{KWW}, with $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ showing the more significant deviation. This result suggests that the correlation between β_{KWW} and m may have a more limited validity in BMGs than in other glass formers.

The stretching parameter β_{KWW} describes breadth of the relaxation function and the fragility parameter m the deviation from the Arrhenius behaviour. Both parameters being ascribed to the cooperative nature of the relaxation, with smaller β_{KWW} and larger m associated to a more cooperative relaxation. The correlation found from Böhmer and coworkers is one of the main correlations supporting this point of view [33]. However, this correlation has been found to not agree with the changes of the fragility and β_{KWW} at high pressure. In fact, while the fragility for non-associated liquids decreases with pressure [38] while β_{KWW} remains constant [39]. Thus there are some limits to this point of view and these new results on BMGs may be important to better understand them.

There are also some models in the literature predicting that, independently of the fragility, at the glass transition the exponent β_{KWW} should be 0.5 (see e.g. Ref. [39] and [40] and their references). Some experimental evidence for this behaviour in organic glass formers has been recently published [40] with deviation from $\beta_{KWW} = 0.5$ value attributed to other effects, like the presence of a secondary process (which however can only explain values of β_{KWW} smaller than 0.5). In Fig. 7 are reported the master curves for a series of BMGs [41]. Interestingly, for most BMGs $\beta_{KWW} \sim 0.5$ at the glass transition independently of the fragility, with the case presented herein an extreme case because of the very small fragility of $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ (Fig. 3). It remains to be better established if this nearly constant β_{KWW} for BMGs may be due to their less complex amorphous phase making them closer to the approximation underlying these models.

4. Conclusions

The dynamic mechanical properties of the $Zn_{38}Mg_{12}Ca_{32}Yb_{18}$ BMG were investigated using mechanical spectroscopy. The results indicated
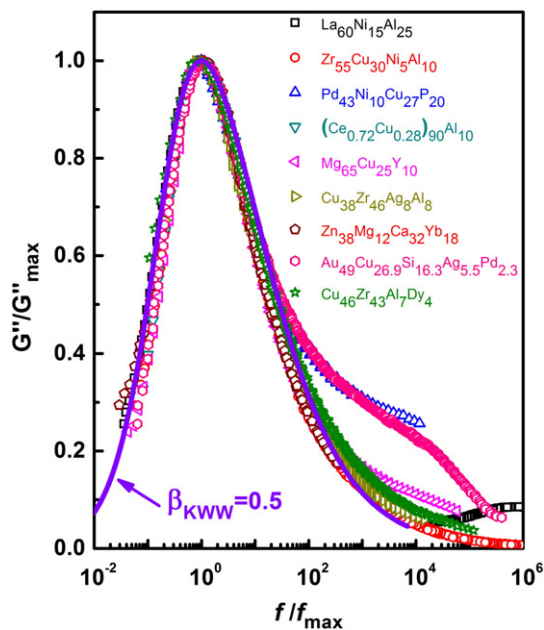
that the α process in the isothermal spectra can be described by KWW stretched exponential relaxation function with $\beta_{KWW} = 0.505$. From the temperature dependence of τ_{α} we determined a fragility $m = 36$, which is, to our knowledge, the smallest values found from mechanical measurements in the literature for BMGs. This value of m is much smaller than what is expected from previous correlations found between β_{KWW} and m in glass forming materials. Taking in consideration a larger sample of BMGs we found that the correlation between β_{KWW} and m appear not to be generally valid. This suggests that the assumed general relationship between these two parameters may be not valid for BMGs. The more important question is whether such deviation indicates that one of these two parameters does not reflect the underlying cooperative dynamics for BMGs or that for BMGs this correlation should have very different parameters than for other glass formers. On the other hand we observe that for many BMGs, $\beta_{KWW} \sim 0.5$. This result may support the applicability to BMGs of those models of the glass transition Refs. [42] and [43] that predict $\beta_{KWW} = 0.5$ independently of the fragility of the system. Mechanical measurements of BMGs on a broader range of fragility are however necessary to establish better the correlation or lack of between m and β_{KWW} as well as the range of values of β_{KWW}.

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Fig. 7. Master curves of the normalized loss modulus G''/Gu for nine representative BMGs [the data of the $La_{60}Ni_{15}Al_{25}$, $Zr_{55}Cu_{30}Ni_5Al_{10}$, $Pd_{43}Ni_{10}Cu_{27}P_{20}$, $(Ce_{0.72}Cu_{0.28})_{90}Al_{10}$, $Mg_{65}Cu_{25}Y_{10}$ and $Cu_{38}Zr_{46}Ag_8Al_8$ data adapted with permission from Qiao J.C. and Pelletier JM (Ref. [41]), Copyright 2014 by Elsevier.] together with a KWW function with $\beta_{KWW} = 0.5$. It suggests that for BMGs the relaxation function of the α process have $\beta_{KWW} \sim 0.5$.

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