The dynamic shear response of the Zr base bulk metallic glass around the calorimetric glass transition temperature

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The dynamic shear response of a bulk $Zr_{55}Cu_{25}Ni_5Al_{10}Nb_5$ metallic glass has been investigated in the vicinity of calorimetric glass transition temperature, T_g. Similar to other glass formers, the Zr base bulk metallic glass exhibits typical features of the dynamic glass transition. The intermediate fragility index, m, indicates that the Zr base alloy belongs to the category of relatively strong glass formers in the general classification scheme. On the other hand, the time temperature equivalence principle is found to be applicable for constructing the master curve of dynamic shear modulus as well as shear viscosity over the temperature range studied. Theses master functions can be fitted with phenomenological models, such as generalized Maxwell model, or a Kohlrausch-Williams-Watts (KWW) relation, and therefore reflect a broad distribution of local structural relaxation time for dynamic glass transition in the Zr base bulk metallic glass.

1. Introduction

In recent years, the development of multi-component glass forming alloy system enables the fabrication of metallic glasses in bulk form at very low critical cooling rate, e.g. less than 10 K/s [1–5]. These bulk metallic glasses (BMGs) usually exhibit a distinct glass transition process, large supercooled liquid region and high thermal stability with respect to crystallization. Consequently, the successful synthesis of BMGs leads to interesting advances in the studies of not only basic science but also engineering application of this class of condensed materials. A number of measurements of mechanical spectroscopy have been performed by various authors to investigate the kinetic nature of glass transition of metallic glasses [6–15]. Perera *et al.* [8–10] have carried out the dynamic tensile measurements for PtNiP, PdNiP and ZrTiCuNiBe amorphous alloys with different glass forming ability (GFA). It is demonstrated that the relaxation dynamics of metallic glass around the calorimetric glass transition temperature, T_g, can be analyzed in terms of the concept of fragility [16, 17]. Moreover, they found that a significant increase in the glass forming ability of metallic alloys is accompanied by only a moderate decrease in the fragility parameter. In order for quantitative characterization of the viscoelastic behavior of metallic glasses during dynamic glass transition, various empirical relations have been used, for instance Kohlrausch-Williams-Watts (KWW) function, generalized Maxwell model etc. [8–10, 15].

In the present study, we present our experimental results on the dynamic shear response of a novel quinary ZrNiCuAlNb BMG with high thermal stability. From the isothermal viscoelastic data, the average activation energy for dynamic glass transition and therefore fragility parameter are deduced. Meanwhile, the master curves of dynamical shear moduli as well as shear viscosity obtained in terms of the time temperature equivalence principle are described with different empirical relations.

2. Experimental

An ingot of nominal composition of $Zr_{55}Cu_{25}Ni_5Al_{10}Nb_5$ was synthesized by arc-melting

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a mixture of pure metals in a titanium-gettered argon atmosphere. Then, cylindrical specimens of 5 mm in diameter and 80 mm in length were prepared by sucking the remelted alloy into the copper mould.

X-ray diffractometry (XRD) with Cu Kα radiation was applied to determine the fully amorphous nature of the as-cast cylindrical samples. The thermal stability of the $Zr_{55}Cu_{25}Ni_5Al_{10}Nb_5$ metallic glass was examined by differential scanning calorimeter (Perkin-Elmer DSC-7) at the heating rate of 10 K/min under an argon atmosphere. The DSC curves for this alloy exhibit a distinct glass transition, followed by a wide supercooled liquid region before crystallization at higher temperatures. It is revealed that the glass transition temperature (T_g), onset crystallization temperature (T_x) and supercooled liquid region, T_x-T_g, are 650, 629 and 79 K, respectively. These characteristic parameters indicate that the alloy has high thermal stability, which allows us to measure the mechanical spectroscopy far into supercooled liquid region through glass transition.

The dynamic shear modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$, where the real part G' and imaginary part G'' are defined as the storage and the loss modulus respectively, was measured by a mechanical spectrometer described by Etienne *et al.* [18]. This apparatus enables measurements as a function of either temperature in the range from 300 to 873 K or frequency in the range from 10^{-4} to 1 Hz, with a resolution in shear modulus G′ smaller than 10^{-3}. Rectangular specimens (30 * 3 *1 mm) are gripped to the oscillating system. All measurements are performed under a high vacuum condition.

3. Results and discussion

3.1. Dynamic shear moduli

Fig. 1 shows the frequency dependence of storage modulus G′ and loss modulus G″ for $Zr_{55}Cu_{25}Ni_5Al_{10}Nb_5$ BMG at different temperatures around glass transition. The moduli have been normalized with the unrelaxed modulus Gu. As shown in Fig. 1, the loss modulus exhibits a peak related to the main relaxation at high temperatures, where the laboratory time scale (inversely proportional to the applied frequency) approaches the relaxation time for atomic arrangement in the metallic glass. Note that the position of loss peak corresponding to the strong decrease of the storage modulus is shifted towards higher frequency as the test temperature is raised. Meanwhile, the more pronounced relaxation behavior characteristic of a discernible maximum occurs. This is due to the shortening of characteristic relaxation time, $\tau_{\max}$, with increasing temperature for the Zr base alloy. Typically, the value of $\tau_{\max}$ is deduced from the relation: $\omega_{\max}\tau_{\max} = 1$, where $\omega_{\max}$ is angular frequency of the maximum. And the well-known Vogel Fulcher equation [17]: $\tau = \tau_0\exp[-A/(T - T_0)$, where τ_0, A and T_0 are fitting parameters, may describe the temperature dependence of the characteristic relaxation time. Nevertheless, within the limited temperature range, for instance, from 678 to 693 K for the Zr base alloy, the variation of $\tau_{\max}$, with temperature is well fitted using an Arrhenious equation, as shown in Fig. 2. Therefore, the apparent activation energy for main relaxation is estimated to be 5.6 eV.

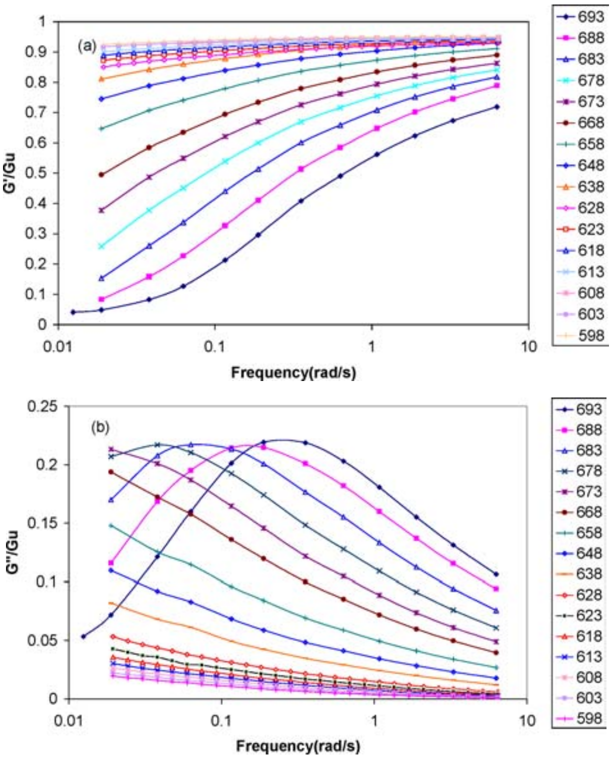

Figure 1 (a) The variation of storage modulus, G'/Gu, with frequency for bulk $Zr_{55}Cu_{25}Ni_5Al_{10}Nb_5$ metallic glass at different temperatures.(b) The variation of loss modulus, G''/Gu with frequency for bulk $Zr_{55}Cu_{25}Ni_5Al_{10}Nb_5$ metallic glass at different temperatures.

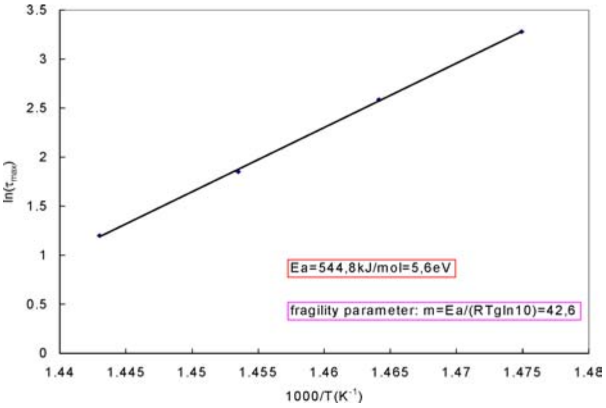

Figure 2 An Arrhenious plot of the temperature dependence of the characteristic relaxation time estimated from the modulus curve in Fig. 1b.

It is known that the concept of fragility has been proposed to characterize one common feature of dynamic glass transition, the departure from the Arrhenious temperature dependence of relaxation times. Accordingly, glass forming materials are classified into three broad groups: strong, intermediate and fragile, in terms of the fragility parameter, defined as [19]

$$m = \left.\frac{d\log_{10}\tau(T)}{dT_g/T}\right|_{T=T_g} \qquad (1)$$

where T is the temperature, T_g is the glass transition temperature and $\tau(T)$ is the characteristic relaxation time.

The strong glass forming systems, which exhibit only small changes of local atomic configuration, have an Arrhenious like or thermally activated behavior. The value of m for these materials is small and has an estimated lower limit of $\sim$16. In contrast, the fragile ones with a thermally sensitive local atomic configuration display a distinct non-Arrhenious behavior. Corresponding values for fragility index are found to be up to $m = 191$. In the whole, the larger the degree of deviation from the Arrhenious law, the greater the value of m. For example, the self-reinforcing tetrahedral network oxide glass formers, such as SiO_2 or GeO have $m \approx 20$ and therefore belong to the category of strong liquid, while fragile liquids, such as ionic glass formers without directional bonds have large values of $m > 100$ [17].

When the temperature dependence of $\tau_{\max}$ follows an Arrhenious law for relatively narrow temperature region around T_g, the fragility parameter can also be calculated from the equation [20]:

$$m = \frac{E_a}{RT_g \ln 10} \tag{2}$$

where R is the gas constant. As a result, the fragility parameter for the Zr base alloy studied in the present work is determined to be 42.6. This value is comparable to that of other BMGs with fragility strength in the range of $30 < m < 70$ [10]. It is further confirmed that the fragility of the multi-component bulk glass-forming alloy is intermediate, lying between the strong and fragile extremes.

Fig. 3 shows that a master curve for $G'(\omega)$ or $G''(\omega)$ can be constructed by shifting the remaining isothermal spectra along the frequency axis to superpose onto a selected curve. The reference temperature is chosen to be 658 K. This suggests that the time-temperature equivalence principle is valid in the temperature region studied. The shifted data extend over approximately seven orders of magnitude. During the main relaxation, the loss modulus presents a maximum corresponding to a significant drop of storage modulus in the broadened frequency range. As demonstrated in the previous work [8, 10, 15], the master relaxation functions of metallic glasses could be described reasonably well using either generalized Maxwell equation:

$$G'(\omega)/Gu = \frac{(\omega^2\tau^2)^{\beta'}}{1 + (\omega^2\tau^2)^{\beta'}} \quad 0 < \beta' \leq 1 \tag{3}$$

where the parameter β'=1 corresponds to a single Maxwell element, whereas a value of β'<1 suggests a distribution of relaxation times, or the empirical Kohlrausch-Williams-Watts (KWW) function:

$$\Phi(t) = A\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{4}$$

where Φ(t) is a relaxation function, A is an adjustable parameter, τ is a characteristic relaxation time and β is a stretching parameter, which quantitatively characterizes the non-Debye (non-exponential) character of the relaxation function, another canonical property of the dynamic glass transition in conventional glass forming systems.

We have attempted to fit the master curve of $G'(\omega)/Gu$ for the $Zr_{55}Cu_{25}Ni_5Al_{10}Nb_5$ BMG using above equations. Actually, it is found that the master curve of the elastic modulus over the testing frequency range can be well described with the KWW function, as illustrated in Fig. 3. Note that a smaller stretching parameter β is required at low frequencies than at higher frequencies, in order to fit the master curve for the storage modulus with the KWW relation. A superposition of two such equations, which offer a much better fit to the master curve, is given by:

$$\begin{aligned} G'/Gu(\omega) = {} & 6.53 \times 10^{10}\exp\left[-0.30\left(\frac{1}{\omega\tau}\right)^{0.60}\right] \\ & +1.55 \times 10^{10}\exp\left[-1.87\left(\frac{1}{\omega\tau}\right)^{0.16}\right] \\ & +G_0/Gu \end{aligned} \tag{5}$$

where G_0, the discrete contribution to the spectrum for viscoelastic solid as $\omega \to 0$, was chosen to be 3.0×10^9 Pa from the trend of the decay of the experimental data. τ is the characteristic relaxation time. The first term in this equation fits the shape of the initial part of the relaxation, while the second term fits the tail. Similar

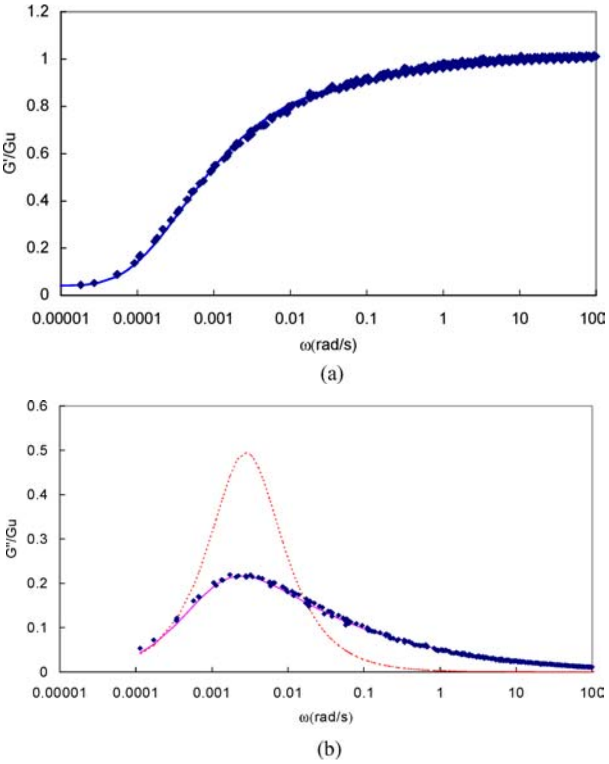

Figure 3 (a) The master curve for $G'/Gu(\omega)$ with the reference temperature of 658 K. The symbols show the measured values. The solid line is calculated from KWW relation Equation 5. (b) The master curve for $G''/Gu(\omega)$ with the reference temperature of 658 K. The symbols show the measured values. The solid line is calculated from Modified Maxwell Equation 6 with a stretching parameter $\beta' = 0.64$ and the dashed curve with β'=1 a single Maxwell element.

results have been reported for the Pt-Ni-P amorphous alloy [8].

As for the master curve of $G''(\omega)/Gu$, a modified Maxwell equation has been used as follows:

$$\boldsymbol{G}''(\omega)/Gu = \frac{\omega\tau}{1+(\omega^2\tau^2)^{\beta'}} \qquad 0 < \beta' \le 1 \qquad (6)$$

where β'=0.64. In order for comparison, the fit to $G'(\omega)/Gu$ using Maxwell model with a single relaxation time, is also revealed by the dashed line. Obviously, the simple relation with $\beta = 1$ is not able to fit the experimental data points. As Lee *et al.* suggested [15], there is no compelling reason why the storage and loss moduli should be governed by the same atomic relaxation mechanism for the frequency range considered, where the dynamic glass transition occurs.

3.2. 3.2. Dynamic shear viscosity

From the loss modulus, the dynamic shear viscosity, η' can be calculated from the equation $\eta\prime(\omega) = G\prime\prime(\omega)/\omega$. Fig. 4 shows the master curve for $\eta'(\omega)$ with the reference temperature of 658 K. It is illustrated that η' tends to reach a constant value of η'_0 at sufficiently low frequencies, indicating Newtonian viscous flow. Usually, the low frequency viscosity is Arrhenius temperature dependent. As the driving frequency is increased above a critical value, the dynamic shear viscosity becomes dependent on the frequency due to the transition from Newtonian to non-Newtonian flow. In the non-Newtonian region, dynamic viscosity is inversely proportional to frequency. In fact, it has been found that the shear rate dependence of viscosity for the glass forming system follows a power law, i.e. $\eta \propto \bar{\gamma}^{-n}$ with $n < 1$ and commonly $n \approx 0.8$ for amorphous polymers, whereas, $n = 1$ for the metallic glassy alloys, e.g. ternary Pt-Ni-P [8] and quarternary Pd-Ni-Cu-P alloy [21]. Furthermore, our experimental data for the quinary Zr-Ni-Cu-Al-Nb alloy at sufficiently high frequencies, where $\eta\prime(\omega) \propto \omega^{-1}$, are consistent with the behavior of other metallic glasses studied previously (see Fig. 4). Accordingly, it is reasonable to assume that the glass forming metallic alloy with $n = 1$ may form a special limiting case[8], taking into account the fact that the metallic glasses have a relatively simple microstructure, well comparable to a hard sphere system, while additional inter-molecular interactions, such as vibrational or rotational molecular modes, do exist in chain-like glass forming systems, e.g. organic polymers.

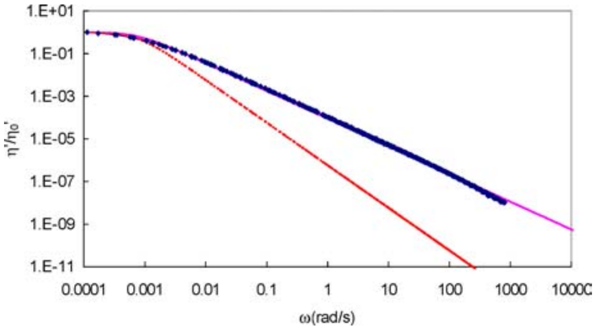

Figure 4 The master curve of dynamic shear viscosity $\eta\prime(\omega)/\eta\prime_0$ when the reference temperature is chosen to be 658 K. The solid line is the fit given by Equation 7 with $\beta' = 0.65$, while the dashed curve is the Maxwell relation with $\beta' = 1$.

According to Perera *et al.*[10], the independence of Newtonian viscosity on the rate of cyclic deformations is attributed to the relaxation of any internal stress at the sufficiently low frequencies, where the characteristic structural relaxation time is shorter than the timescale of the forced deformation. In the case of non-Newtonian flow, the characteristic structural relaxation time is, however, longer than the experimental timescale, leading to a build up of internal stresses under rapid oscillatory deformations. Once a critical stress level is reached, the flow facilitated by the preferential reordering along the direction of the imposed strain causes the drop of dynamic shear viscosity, which is accompanied by the release of the accumulated stress with the breakdown of the initial structure.

The quantitative characterization of the master curve of $\eta'(\omega)$ has been performed using the generalized Maxwell equation

$$\frac{\eta'(\omega)}{\eta'_0} = \frac{1}{1+(\omega^2\tau^2)^{\beta'}} \qquad 0 < \beta' \le 1 \qquad (7)$$

where β'=0.65 (see Fig. 4).

In order for comparison, the viscosity variation of a single Maxwell element ($\beta = 1$) with the same reduced time constant τ is also shown by the broken curve. As can be seen, the viscosity of the supercooled metallic alloy decays much more slowly in the non-Newtonian regime. The stretching parameter of$\beta' = 0.65$ for the viscosity data again reflects the underlying distribution of local relaxation kinetics rather than a single relaxation time.

4. Conclusion

The isothermal measurements of mechanical spectroscopy have been carried out to investigate the dynamic shear response of a $Zr_{55}Cu_{25}Ni_5Al_{10}Nb_5$ BMG around glass transition. Like in the other glass forming systems, the Zr base BMG exhibits typical features of the dynamic glass transition. From the temperature dependence of main relaxation time, the activation energy for the dynamic glass transition is deduced to be as large as 5.6 eV. The intermediate fragility index of m $\approx$ 42 indicates that the Zr base alloy is relatively strong liquid. It is found that the isothermal spectrum of dynamical shear modulus as well as shear viscosity can be simplified by a master curve in terms of time temperature equivalence principle over the temperature investigated. The fits of the master curves using KWW relation or modified Maxwell model suggest that the dynamic glass transition involve in a distribution of local structural relaxation time.

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