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Relaxation behaviors of bulk metallic glass forming $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ alloy

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Abstract

Low frequency internal friction and differential scanning calorimetry were applied to investigate calorimetric glass transition as well as relaxation characteristics of the supercooled liquid states in a bulk metallic glass-forming $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ alloy. A dramatic decrease in structural relaxation time of the supercooled liquid was exhibited by internal friction measurements. The dependence of temperature on the relaxation time fits well with the Vogel–Tammann–Fulcher form. Based on the free volume theory the calorimetric glass transition was explained as the relaxation of supercooled liquid inspired at the experimental timescale. The results exhibit that the calorimetrical glass transition is a mainly kinetic process in this glass.
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Glasses respond to external stresses differently than crystals do. In a crystal, a small external force induces an elastic response on an acoustic time scale. Glasses have internal rearrangements occurring on time scales ranging from the microscopic to the cosmic [1]. It is becoming clear that the glass transition should provide the key to the dynamic and history-dependent behavior throughout the glassy phase [2]. On the dynamical view, such the glass transition is a result of the dramatic increase in structural relaxation time as a liquid is cooled to low temperature [3]. For many glass-forming liquids, the relaxation time can be fit with a Vogel–Fulcher–Tammann form [2,4,5] $\tau = \tau_0 \exp[A/(T - T_0)]$, where T_0 is related to the glass transition. Relaxation in glasses [6–9], called secondary relaxation to distinguish it from the primary relaxation in supercooled liquid, is generally believed to be well described in terms of the Arrhenius–Kramers picture, with a relaxation time τ_V given by the Arrhenius relation $\tau_V = \tau_0 \exp(V/k_B T)$, V is the energy of the barrier between averaged two energy minima of the system. The reported Arrhenius behavior indicates that there may be no phase transition at all; the glass transition may be a kinetic effect [10].

The metallic glass formers have been expected to be ideal system for the studying the glass transition since they are comparable to a hard-sphere system [11,12]. In recent years, several bulk metallic glasses (BMGs) have been prepared by quenching techniques [13–16]. Compared with the conventional metallic glass, BMG offers the ideal materials to investigate the transition of glass within the wide window of temperature and time. Internal friction (IF) is well known to be very sensitive to the relaxation in condensed matter [17]. A few investigations of IF for conventional metallic glasses have been performed from room temperature up to crystallization temperature [18–21]. IF has been found to remains constant, then rises exponentially with temperature up to crystallization temperature. Crystallization makes the IF decrease rapidly. A wide distribution of activation energies for the glass relaxation has been suggested [20].

In this paper we have connected the glass transition with the relaxation of the supercooled liquid in a BMG-forming $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ alloy. The relaxation behaviors in the amorphous alloy were measured by multi-function internal friction apparatus. The characteristics of the glass transition T_g were observed by differential scanning calorimetry (DSC). The internal friction measurements exhibit the relaxation of supercooled liquid, which can fit the VFT

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equation. The calorimetric glass transition was explained as the relaxation of supercooled liquid inspired at the experimental timescale by the free volume theory.

$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10.0}Be_{27.5}$ BMG was prepared by sucking the melt into copper module with a cooling rate of approximately 100 K/s. Thermal properties (the end temperature and onset temperature of the glass transition) were studied by DSC performed in a Perkin–Elmer DSC-7 under flowing purified argon gas at different heating rates. The size of the specimen sheets used for the measurement of IF was about 60 mm length, 2 mm width, 1.2 mm thickness, and cut from one sample. The IF measurements were processed in a multi-function internal friction apparatus with a vacuum of about 1×10^{-3} Pa. The internal friction measurements were carried out under a protective argon atmosphere at 0.5×10^5 Pa. A compound torsion pendulum was used to achieve low frequencies (less than 10 Hz and larger than 10^{-3} Hz) under the forced oscillation mode. The sensitivity of the IF measurements is about 4×10^{-4}. In a forced-vibration experiment the experimental phase angle θ is calculated as $\tan \theta = a/b$ where a and b are the coefficients of expansion of the sample's torsion angle θ in Fourier series:

$$a = \frac{2}{k} \sum_{i}^{k} \theta_i(t)\cos\left(\frac{2\pi i}{k}\right), \qquad b = \frac{2}{k} \sum_{i}^{k} \theta_i(t)\sin\left(\frac{2\pi i}{k}\right)$$

where k is the number of measured values of the sample's torsion angle θ. A set of the θ values defines the hysteretic loop. All measurements were automated using a personal computer. The details of the apparatus are given elsewhere [17].

Fig. 1 shows a typical temperature dependence of IF (Q^{-1}) and relative shear modulus (G_T/G_{300}) determined at 1 Hz from room temperature to 670 K at the heating rate of 0.5 K/min. G_{300} is the shear modulus determined by
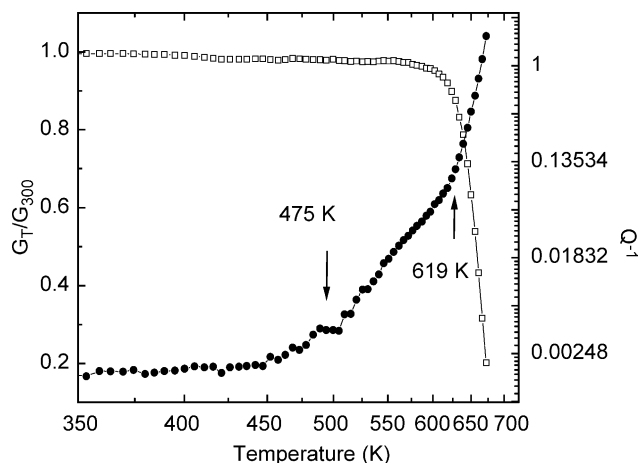

Fig. 1. The temperature dependence of Q^{-1} and G_T/G_{300} for the frequencies of 1 Hz at heating rate of 0.5 K/min. G_{300} referred as the shear modulus measured by IF apparatus at 300 K.

multi-function internal friction apparatus at 300 K. With DSC results the end temperature of the glass transition of the BMG is 619 K at the heating rate of 0.5 K/min. So the window of the temperature contains the glassy zone, the glass transition, and the supercooled liquid region of the BMG forming alloy. The relative shear modulus is found to decrease gradually and slowly with temperature increasing from room temperature up to 619 K. Above 619 K, the temperature dependence of G_T/G_{300} decreases rapidly, implying a obvious softening. The Softening exhibits the glassy state disappears and a typical characteristic of liquid appears. On the other hand, Q^{-1} increases gradually with the increasing temperature, but two kinks can be found in the curve of the Arrhenius plot of Q^{-1}. Above 475 K the temperature dependence of Q^{-1} increases significantly with temperature, leading to the first kink at about 475 K. The kink is well below the end temperature of the glass transition (619 K). So the rapid increase of Q^{-1} is due to the relaxation occurring in glassy state. Even though the nature of the complicated glassy relaxation cannot be clear here, the result exhibits the measurement of IF is sensitive to the relaxation in glass. The second kink occurs at the end temperature of the glass transition. No obvious peak is found near 619, indicating no particular relaxations, such as phase transition, correspond to calorimetrical glass transition [6,17]. The observation supports the view that the calorimetric glass transition is a mainly kinetic process [7]. The kink at 619 K is due to the different mechanisms of the relaxation between in glass and supercooled liquid.

Usually, near the glass transition temperature the non-exponential relaxation of a supercooled liquid can be exhibited by the frequency dependence of the susceptibilities [22]. Internal friction is connected with the elastic modulus as follows: $Q^{-1} = G''/G'$, where G' and G'' are storage and loss modulus. The complex shear modulus G with the frequency ω can be written as $G' + iG''$. So G' and G'' at a given frequency can be determined from the measurements of IF. Fig. 2 shows the temperature dependence of G' and G'' determined by the measurements of IF at a heating rate of 4 K/min at frequencies of 0.05, 0.2, 1 Hz. During heating G' is found to decrease rapidly within a temperature scope, which is depended on the frequency loaded, and increases with increasing frequency With further increasing temperature the storage modulus tends to zero, exhibiting a typical liquid state. At the same time, the curve of G'' exhibits a typical asymmetrical peak with smaller slop on the left side is exhibited for each frequency, which is common to all equilibrium susceptibility measurements for supercoooled liquid [23], and corresponds to the primary relaxation (α process). The inverse of the frequency at peak in curve of G'' can be preferred as the averaged relaxation time of the supercooled liquid at the peak temperature [23]. Therefore, the increase peak temperature with the increasing frequency indicates the averaged relaxation time decreases with increasing temperature.
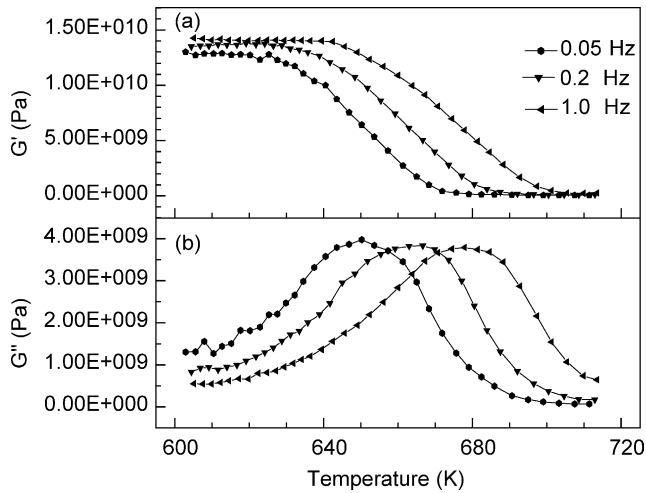
Fig. 2. The temperature dependence of G' and G'' at frequencies of 0.05, 0.2, and 1 Hz at heating rate of 0.5 K/min.

In Fig. 3, the logarithm of the peak frequency versus the reciprocal the peak temperature measured at mutli-frequencies at the heating rate of 4 K/min is shown. As previously described macrostructural relaxation is usually depicted by the Vogel–Tammann–Fulcher equation

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

where τ is the relaxation time, T_0 and B are the temperature-independent constants. Substituting the relaxation time with the inverse peak frequency, we fit the data in Fig. 3. T_0, B fitted well (seen in Fig. 3) are 352 K $(9.44 \pm 1.64) \times 10^3$ K. The values of T_0 and B are the same as that determined by viscosity measurement [24]. This confirms that the increasing viscosity with the decreasing temperature corresponds to the α relaxation of supercooled liquid.
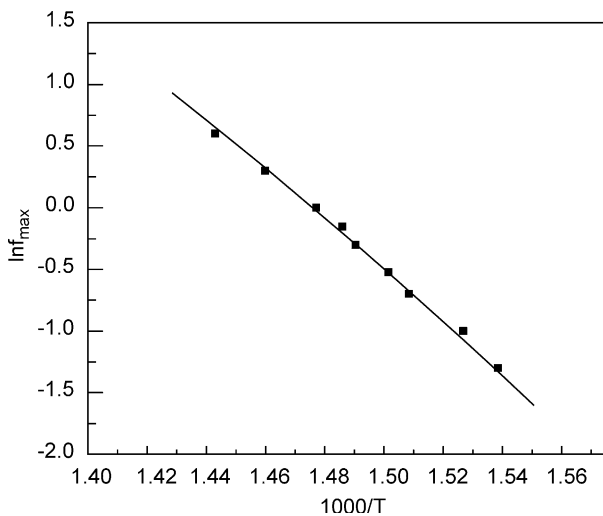

Fig. 3. The logarithm of the frequency versus $1/T$ at the peaks in the curves of G'' determined by the internal friction measurements. The solid line fitted with the equation $f^{-1} = f_0^{-1} \exp[B/(T - T_0)]$.
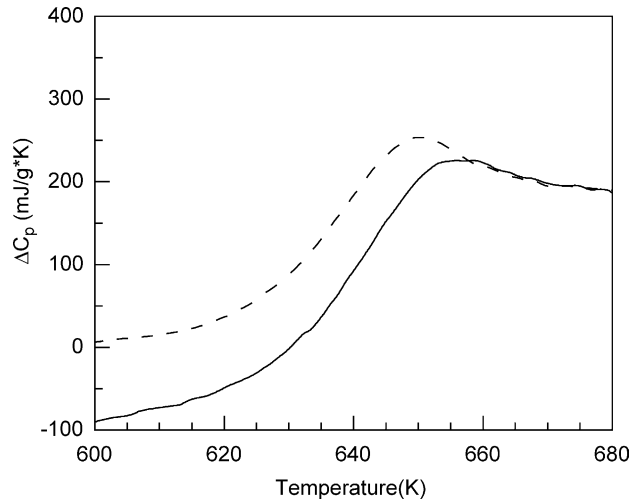

Fig. 4. The DSC curves for the as-cast and annealed samples at the heating rate of 40 K/min. The solid line is obtained from the as-cast sample; the dashed line is obtained from the sample cooled from 683 K at the cooling rate of 2 K/min.

On the point of dynamics the glass transition is relative to the relaxation of supercooled liquid. Usually, the glass transition is observed by DSC during heating. The glass transition is companied with an obvious endothermic process. Fig. 4 shows the DSC curves of two samples at a heating rate of 0.667 K/s. One is as-cast sample formed by cooper model sucking, whose cooling rate is about 100 K/s. The other is the BMG sample after the pre-treatment in Perkin–Elmer DSC7. The process involved the heating up to 683 K (above the end temperature of glass transition 651 K) at heating rate of 0.667 K/s and the cooling down to room temperature at a cooling rate of 2 K/s. The solid line is the curve of the as-cast sample. The dashed line is the curve of the annealed sample. An obvious difference between the two curves is found at the glass transition. The glass transition process in the annealed sample shifts to a lower temperature. At the same time the height of the glass transition peak increases. The main difference of the two samples is the different formation condition, in which the cooling rate of the as-cast sample formation (about 100 K/s) is much larger than that of annealed sample (2 K/s).

In order to quantify the nature of the glass transition a defect concentration c_D was introduced [25,26]. According to the free-volume theory the defect concentration is related to the reduced free volume x by $c_D = \exp(-1/x)$ [25,26]. At a constant pressure x in a supercooled liquid is a function of temperature, can be called equilibrium free volume x_{eq}. With Turnbull's view x_{eq} corresponds to VFT, can be written as $x_{eq} = (T - T_0)/B$, where T_0 and B are the Vogel–Fulcher–Tammann constants [25]. Glass is a non-ergodic state, in which x is larger than x_{eq}. As Speapen's view the rate of disappearance of defect concentration is proportional to the product of the concentration of relaxation defects [26]. Therefore, the change in defect concentration due to
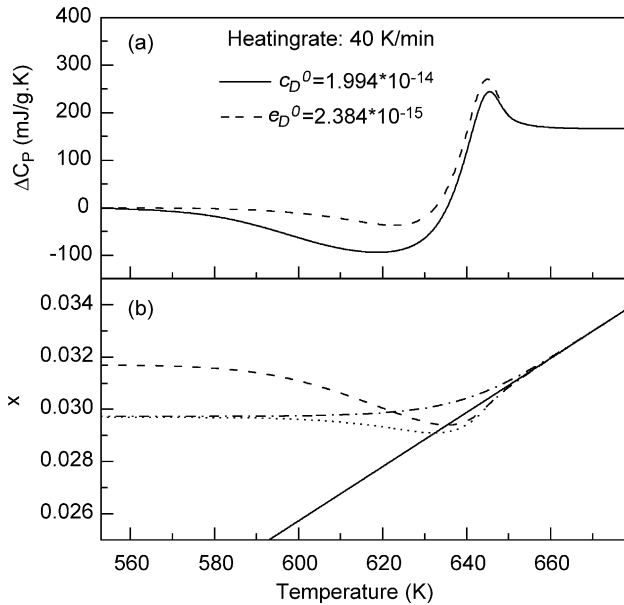
Fig. 5. (a) The simulated DSC with free volume theory for the as-cast and annealed sample. (b) The temperature dependence of free volume x corresponding to the DSC curves in Fig. 4.

structural relaxation during annealing process is governed by the differential equation

$$\frac{dc_D}{dt} = -k_r c_D (c_D - c_D^{eq}). \tag{1}$$

In this equation $c_D^{eq}(c_D^{eq} = \exp(-1/x_{eq}))$ is the defect concentration in metastable equilibrium, t denoted time and k_r is a temperature-dependent rate factor for structural relaxation. k_r has the form:

$$k_r = k_0 \exp\left(-\frac{E_f}{k_B T}\right),$$

where E_f is the relaxation activation energy and k_0 is a constant. Eq. (1) is much suitable for describing the relaxation in the metallic glasses [27]. B and T_0 for the BMG are used the values in above VFT equation. The calculated DSC signal is obtained by assuming the observed heat flow, given here as $\Delta C_P = \beta \, dx/dT$ [11]. In Ref. [28] numerical values are given for the other parameters involved.

The simulated DSC traces are shown in Fig. 5a. The solid and dashed lines are the traces for the as-cast sample and the annealed sample, respectively. The resultant calculations confirm that the difference between the curves in Fig. 4 is due to the difference between the excess free volumes in the two samples. The c_D^0 in the as-cast sample (7.31×10^{-12}) is three orders of magnitude larger than that in the annealed sample (2.67×10^{-15}). Correspondingly, the excess free volume in the as-cast sample is higher than that in the annealed sample. Fig. 5b shows the temperature dependence of the free volume x in the processes described above. During heating the higher excess free volume is found to anneal out and move to the equilibrium line at

the temperature higher than 480 K for the as-cast sample (see the dashed line in Fig. 5b). The free volume is produced in order to reach equilibrium only at a high temperature. The production of the free volume is an endothermic process, which corresponds to the glass transition process. At higher temperature the production of free volume is fast enough to keep up with the increase x_{eq}, which makes the specific capacity constant. When the sample is cooled down from 683 K for the cooling rate of 2 K/s (see the dash dot line in Fig. 5b), the decreasing x follows the equilibrium x_{eq} line firstly. Then, the x deviates from the equilibrium x_{eq} line at about 650 K, which corresponds to the glass transition temperature at the cooling rate of 2 K/s. The deviation means the supercooled liquid falling out of equilibrium. The value of x decreases until 585 K. This implies that the state of the specimen is frozen at 585 K at the cooling rate of 2 K/s. The reheating process is similar as the heating process of the as cast sample (see short dot line in Fig. 3). But the annihilation process of the excess free volume shift to higher temperature (~ 590 K). The above results indicate that the DSC curves are relative to the change of the free volume with the temperature. The calorimetric glass transition is the process companying with the free volume approaching/deviating the equilibrium free volume during heating/cooling. Therefore, the glass transition observed in DSC curves is a phenomenon, in which α is truncated/inspired by cooling/heating.

In conclusion, internal friction is used to determine the primary relaxation of supercooled liquid for Vit4 alloy. The primary relaxation can be depicted well by VFT equation:

$$f_{max} = f_0 \exp\left(\frac{-9440}{T - 352}\right).$$

With the free volume theory the glass transition is regarded as the relaxation process.

Acknowledgements

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