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Correlation between flow and relaxation dynamics in supercooled metallic liquid

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ABSTRACT

The enthalpy relaxation time and structural α-relaxation time of bulk metallic glass (BMG) $Zr_{41.2}Ti_{13.8}Cu_{10}Ni_{22.5}Be_{22.5}$ (Vit1) were measured using differential scanning calorimetry (DSC). The strain rate dependence of the flow behavior of Vit1 BMG from homogeneous flow to brittle fracture (strain rate between 10^{-4} and 10^{0} s^{-1}) was also carefully investigated via compression test at elevated temperatures above the glass transition temperature T_g. The correlation between flow and relaxation dynamics can be established based on the experimentally characterized enthalpy relaxation time and structural α-relaxation time. The specific role played by enthalpy relaxation and structural α-relaxation in the flow of supercooled metallic liquid are recognized as: enthalpy relaxation corresponds to the annihilation of the free volume and determines the presence of stress overshoot; structural α-relaxation corresponds to the diffusion of the free volume and determines the presence of brittle fracture. With the obtained results, we might draw the conclusion that glasses cannot flow, even at infinitely slow loading rate.

1. Introduction

Whether glass flows extremely slow or does not flow at all is an elusive question [1]. Unlike crystalline materials where dislocation theory of plasticity offers an atomic level explanation [2], the deformation mechanism of glassy materials remains a challenging problem in condensed matter physics [3]. Moreover, deformation of glassy materials depends strongly on temperature, especially near the glass transition temperature T_g [4–8]. In fact, the rapid slowdown of flow dynamics in the supercooled liquid accompanied by the breakdown of the Stokes–Einstein relation is the most salient feature associated with glass transition [1]. Therefore, the understanding of the flow mechanism of supercooled liquid near T_g is an issue of central importance for shedding light on the nature of glass transition.

Deformation under shear stress of amorphous systems is generally attributed to localized shear transformations of flow units (or shear transformation zone, STZ), which are atomic regions on the scale of tens or perhaps hundreds of atoms [8]. The operation of shear transformation is facilitated by the presence of nearby free volume [5]. Various theories on flow of metallic glasses have been developed in the past several decades, such as the free volume theory [4] and shear transformation theory and so on [9–11]. Recent works indicate the intimate relationship between local atom rearrangement of STZ and the β relaxation process, and also that the percolation of STZs might correspond to α relaxation [12], where α relaxation refers to a large scale irreversible atom rearrangement of the supercooled liquid and β relaxation is a locally reversible atom rearrangement of the supercooled liquid. It has been also demonstrated that the temperature dependence of the enthalpy relaxation time (τ_{en}) and structural α-relaxation time (τ_{st}) for $Zr_{58.5}Cu_{15.6}Al_{10.3}Ni_{12.8}Nb_{2.8}$ bulk metallic glass (BMG, Vit106a), follow an Arrhenius form and a Vogel–Fulcher–Tammann (VFT) form, respectively [13–15]. It was also proved that enthalpy relaxation did persist above T_g [16], though with a steeper temperature dependence. Based on the correlation between enthalpy change during relaxation and free volume reduction [17], the enthalpy relaxation time can be used to depict the annihilation rate of free volume [18] (i.e. small enthalpy relaxation time implies a rapid annihilation of the free volume, and *vice verse*). In the flow behavior of supercooled metallic liquid at temperature above T_g, the occurrence of the well-known stress overshoot during flow on the stress–strain curves is attributed to the mechanism that the annihilation rate of free volume is beaten by the creation rate [19] which is closely related to strain rate. Structural α-relaxation time is related to the long range rearrangement of atoms in the supercooled liquid [1]. An average structural α-relaxation time for glass transition can be measured by calculating the time required for the transition from glass to supercooled liquid during heating [20], reversely, which can be regarded as the characteristic time required to "freeze" supercooled liquid into glass during cooling. The phenomenon of localized shear fracture of the supercooled liquid at high strain rates can be regarded as a unique behavior due

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to strain rate induced "freeze" of the liquid [21]. Although the relaxation process usually takes an exponential form [13], under mean field assumption as adopted in the flow theories [4,5], the relaxation times can be considered as a linear average measure of the characteristic time of the structure evolution when the flow is turned on. On the other hand, based on dimensional analysis [22], the reciprocal of strain rate $(1/\dot{\varepsilon})$ is also of time dimension. The flow of supercooled liquid is conducted by flow units. Based on mean field theory, if we assume an average activation process of flow units during flow and the strain carried by each flow unit is 1, the reciprocal of strain rate $(1/\dot{\varepsilon})$ could be considered as the average time interval between the consecutively activation of flow unit. From this aspect of view, we might take it as the characteristic time of the flow [23] of supercooled metallic liquid, i.e. the strain rate induced time. Moreover, recalling the fictive stress model [24], two relaxation times, i.e. an initial relaxation time and a transient relaxation time, are also required to empirically characterize the flow behavior of metallic glass. Bearing all these clues in mind, one cannot help to thinking about that: would there be some underlying correlations between the relaxation time and the characteristic time of flow when stress overshoot or fracture starts to occur?

To answer the above question, in the present study, we attempted to measure the enthalpy relaxation time and structural α-relaxation time of a BMG (here, Vit1 with composition of $Zr_{41.2}Ti_{13.8}Cu_{10}Ni_{22.5}Be_{22.5}$ was used, as most of the thermodynamic data of this alloy can be found in literature [25]) by thermal analysis [13]. The flow behaviors of the BMG in a wide range of strain rate from 10^{-4} to 10^{0} s^{-1} were carefully investigated at elevated temperatures above T_g to detect the onset strain rates for the occurrence of the stress overshoot and that of the brittle fracture. As a result, the correlation between flow and relaxation dynamics was established from the angle of the quantitative and qualitative consistence between the relaxation time and the characteristic time of flow. Based on the free volume model [19] and incorporation of relaxation dynamics, the roles played by enthalpy relaxation and structural α-relaxation in the flow of supercooled metallic liquid can be clarified as: enthalpy relaxation corresponds to the annihilation of the free volume and determines the presence of stress overshoot; while structural α-relaxation corresponds to the diffusion of the free volume and determines the presence of brittle fracture.

2. Experimental procedure

$Zr_{41.2}Ti_{13.8}Cu_{10}Ni_{22.5}Be_{22.5}$ (at.%) BMG (Vit1) was selected for differential scanning calorimetry (DSC) analyses and compression test due to its outstanding glass forming ability and thermal stability in the supercooled liquid region. Rods of 3 mm in diameter of the alloy were prepared by copper-mould suction casting [26]. The amorphous structures of the specimens, both as-cast and thermally compressed samples, were verified by X-ray diffraction (XRD) (Philips 'XPert PRO diffractometer, Cu Kα radiation) and DSC under a heating rate of 20 K/min. The prepared alloy revealed that the temperatures at the onset of the glass transition, at the end of glass transition, and at the onset of the crystallization are 626, 663, and 709 K, respectively. The enthalpy relaxation time and structural α-relaxation time were measured by DSC and the experimental principle and details can be found in [13]. The isothermal annealing temperatures for enthalpy relaxation were selected as 588 K, 598 K, 608 K, 613 K, 618 K and 623 K. The time for the isothermals was selected to allow complete relaxation of the frozen-in enthalpy towards the equilibrium state, ranging from 2 h to 5 min, as proposed in [13]. The heating rates adopted to get the structural α-relaxation time were 3 K/min, 6 K/min, 15 K/min, 30 K/min, 60 K/min and 120 K/min. Cylindrical specimens of aspect ratio 1:1 [27] for compression test were carefully prepared to ensure the two ends being parallel. The high temperature compressive stress–strain curves were obtained with a Zwick/Roell mechanical testing system. The selected temperatures of the compression experiments are 633 K, 648 K, 663 K ($T_{g\text{-}end}$), 669 K, 676 K, and 682 K in the supercooled liquid region. The fluctuation of the temperature in the furnace during compression was below ±2 K. At each test temperature, the sample was quickly placed in the preheated furnace and held for 10–3 min to attain thermal equilibrium before compression. The compression tests with strain rate ranging between 10^{-4} and 10^{0} s^{-1} were conducted. The adopted strain rate of each stress–strain curve was carefully selected to attain an "as accurate as possible" value of the strain rate at which stress overshoot or fracture starts to occur. Graphite powders were smeared onto the ends of the sample for lubrication.

3. Results

Fig. 1 shows the DSC curves of $Zr_{41.2}Ti_{13.8}Cu_{10}Ni_{22.5}Be_{22.5}$ bulk metallic glass (BMG) under different heating rates. It can be seen that with increasing heating rate the characteristic temperature $T_{g\text{-}onset}$ and $T_{g\text{-}end}$ shift to higher temperature. Using equation $\tau_{st} = (T_{g\text{-}end} - T_{g\text{-}onset})/q$, where q is heating rate, an average structural α-relaxation time for glass transition can be obtained based on each DSC curve. Fig. 2 shows the isothermal enthalpy (ΔH_0) relaxation curves of $Zr_{41.2}Ti_{13.8}Cu_{10}Ni_{22.5}Be_{22.5}$ BMG as a function of time at different annealing temperature. As proposed by Busch et al. [18], the enthalpy relaxation process can be characterized by the equation: $H(t) = H_g - \Delta H(t) = H_g - \Delta H_0 \phi(t)$, where $\phi(t) = 1 - \exp[-(t/\tau_{en})^{\beta}]$, H_g is the enthalpy of the BMG before enthalpy relaxation; ΔH_0 is the relaxation enthalpy during isothermal annealing; β is the stretching exponent; τ_{en} is the enthalpy relaxation time. Based on this expression, we can obtain the enthalpy relaxation time at each temperature. At temperature below 613 K, the stretching exponent β is approximately unit, suggesting a single relaxation mechanism of Vit1 BMG. However, it is found that compressed relaxation dynamics (with stretching exponent β = 1.51 remarkably over 1 at temperature above 613 K) was observed approaching $T_{g,}$ indicating complex atomic motions in the relaxation dynamics of the Vit1 BMG near T_g [28]. For comparison, both the structural α-relaxation time (red circle) and enthalpy relaxation time (black square) were plotted in Fig. 3. The similar crossover of the two relaxation times was also reported in previous work [13].

Fig. 4(a) shows the true stress–true strain curves of $Zr_{41.2}Ti_{13.8}Cu_{10}Ni_{22.5}Be_{22.5}$ bulk metallic glass (BMG) under strain rate $\dot{\varepsilon}$ ranging from 5×10^{-4} to 3×10^{-2} s^{-1} at 633 K. At strain rates below 2×10^{-3} s^{-1}, stress–strain curves show monotonous increase in the flow stress σ in the initial stage of deformation followed by a steady state flow with a stress plateau. At strain rate above 5×10^{-3} s^{-1}, a stress overshoot occurs before the flow stress reaches a steady value. Further increase of strain rate to 2×10^{-2} s^{-1} leads to stronger stress overshoot. At even higher strain rate $\dot{\varepsilon} = 3 \times 10^{-2}$s^{-1}, the BMG sample comes to failure via localized shearing, just like what happened for BMG at room temperature. These results demonstrate that the deformation

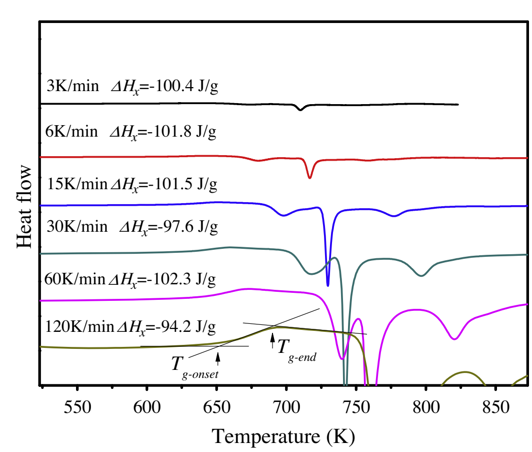

Fig. 1. The DSC curves of Vit1 ($Zr_{41.2}Ti_{13.8}Cu_{10}Ni_{22.5}Be_{22.5}$) BMG at different heating rates (3 K/min, 6 K/min, 15 K/min, 30 K/min, 60 K/min and 120 K/min, from top to bottom). Based on the heating rate dependent $T_{g\text{-}onset}$ and $T_{g\text{-}end}$, an average structural α-relaxation time for glass transition can be obtained based on each DSC curve.