



The impact of fragility on the calorimetric glass transition in bulk metallic glasses



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ARTICLE INFO

Article history:

Received 6 June 2014

Received in revised form

19 July 2014

Accepted 26 July 2014

Available online 15 August 2014

Keywords:

Metallic glasses

Thermodynamic properties

Viscosity

ABSTRACT

The glass transition of bulk metallic glasses with various fragilities as well as strong oxide glasses is studied using differential scanning calorimetry (DSC). It is found that the liquid fragility determined from equilibrium viscosity measurements is very well correlated with the scaled maximum slope of the DSC heat flow during the glass transition. We compare the correlation found in this work and those correlations with fragility from previous studies on other classes of glass-formers and find that the slope, which describes the curvature of the enthalpy on a reduced temperature scale, is a quantity better correlated with fragility, as it reflects the timescale of the non-equilibrium relaxation and the distribution of relaxation times in the glassy state. The present findings are supported by a recent theoretical report for calculated enthalpy curves with different fragilities from a model of selenium using the enthalpy landscape approach.

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1. Introduction

The laboratory glass transition observed on cooling is a kinetic freezing-in of the structural relaxation process as the system's internal time scale crosses the experimental time scale. As the glass transition temperature, T_g , is approached during cooling, the relaxation time, τ , (or viscosity, η) of the supercooled liquid changes with temperature following different patterns for different liquids. This is the basis of the “fragility” concept, proposed by Angell [1], to describe different scaling behaviors of the relaxation times of supercooled liquids with respect to temperature. For fragile liquids (e.g., o-terphenyl), the relaxation time varies in a strongly non-Arrhenius fashion; whereas strong liquids, such as GeO_2 and SiO_2 , exhibit an Arrhenius-like behavior of the relaxation time [2]. A kinetic fragility, or steepness index, m , is defined [1] as the slope of $\log_{10}\tau$ vs. T_g/T at the glass transition temperature T_g .

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

or defined with viscosity, η ,

$$m = \left. \frac{d \log_{10} \eta}{d(T_g/T)} \right|_{T=T_g}, \quad (2)$$

where the scaling parameter T_g is commonly chosen at the temperature where the structural relaxation time is around 100 s [3] or the equilibrium viscosity reaches 10^{12} Pa s [4], which are the values conventionally adopted in defining the fragility m [1,5].

Kinetically strong and fragile liquids are observed to have small and large values of m , respectively. The temperature dependence of η (or τ) can be described with the empirical Vogel-Fulcher-Tammann (VFT) equation [6,7],

$$\eta = \eta_0 \exp\left(\frac{D^* T_0}{T - T_0}\right), \quad (3)$$

where the pre-exponential factor η_0 is the theoretical infinite-temperature limit of the viscosity [8]. T_0 and D^* are fitting parameters. The VFT-fragility parameter D^* is an alternative description of the fragility of the liquid and can be related to m by the equation [5],

$$D^* = 590/(m - 17), \quad (4)$$

where the constant 17 is the minimum value of m for D^* determined from viscosity data as the viscosity changes by 17 orders of magnitude for all liquids from T_g ($\eta(T_g) \sim 10^{12}$ Pa s) to the infinitely

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high temperature limit ($\sim 4 \times 10^{-5}$ Pa s). The constant changes to 16 for the values of D^* determined from relaxation time data [5].

Although efforts have been devoted toward describing the fragility using various phenomenological models [9], its origin still remains elusive. The fragility of a liquid can be determined from kinetic data; e.g., equilibrium viscosity or relaxation time. It is, however, known to correlate with other physical properties of glass-formers [10–15], most notably, the thermodynamics of the supercooled liquid. The temperature dependence of the scaled excess entropy, for example, has been shown to have the similar temperature-scaling behavior as that of the relaxation time and can be used to define a thermodynamic fragility [16]. In bulk metallic glass-forming liquids, the changing rate of configurational entropy has been recently demonstrated to be related to their viscosity behavior and fragility [17]. The change in the specific heat capacity ΔC_p at T_g scaled by entropy of fusion S_m has been shown to correlate with the fragility of 54 non-polymer glassformers [18]. Also, the enthalpy hysteresis during cooling and heating throughout the glass transition has been reported to correlate with the fragility of molecular glass-formers [19]. However, in some metallic glass compositions the enthalpy hysteresis is difficult to establish due to the interference of crystallization that can occur shortly after the completion of the glass transition. In such cases this can lead to an increasing uncertainty in the correlation. There is a well known relation derived by Moynihan [4] that the fragility is correlated with the reduced glass transition width, $\Delta T_g/T_g$, as measured using DSC [4,20] however, the extent of deviation from this relation is not trivial [20]. A theoretical approach to fragility has been taken by Mauro et al. [21], who calculate the viscosity of liquid selenium using a model that combines the enthalpy landscape approach with non-equilibrium statistical mechanics [22]. In their simulation, they manipulate the fragility of selenium while keeping a constant T_g and show that a higher fragility leads to a sharper turn of the enthalpy-temperature curve at the same T_g during cooling.

In this work, we experimentally investigate how fragility relates to the DSC-scans during the glass transition in bulk metallic and oxide glass systems and examine relevant thermodynamic and kinetic quantities related to fragility. We show that the slope of scaled DSC-scans on heating reflects the timescale of the non-equilibrium relaxation shortly before regaining equilibrium as well as non-exponentiality and is well correlated with fragility.

2. Materials and methods

Amorphous $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ (Vit.106a) was prepared by arc-melting elements with purities ranging from 99.9 to 99.999 at. % under a high-purity argon Ti-gettered atmosphere. The master alloys were then remelted in a Bühler arc melter and suction cast into water-cooled copper molds to form plates. Amorphous $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ (Au₄₉-BMG) was prepared by inductively heating the pure elements in an Al_2O_3 crucible inside of a high-purity argon-flushed atmosphere and tilt-casting into a water-cooled copper mold [23]. The $Pd_{43}Ni_{10}Cu_{27}P_{20}$ (Pd₄₃-BMG) alloy was prepared by arc-melting the mixture of the high-purity metallic elements. The alloy was subsequently melted and alloyed with P in evacuated quartz tubes with an induction furnace and quenched in water to obtain amorphous samples. Boron oxide was added into the quartz tube as a flux to retard crystallization. Amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit.1), $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ (Vit.1b) and $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit.4) were supplied by Liquidmetal[®] Technologies. Amorphous B_2O_3 and GeO_2 were made by heating crystalline samples from Alfa Aesar[®] well above their respective melting points and cooling with a cooling rate of approx. 50 K min^{-1} in dry air in a DTA (NETZSCH STA 449C) furnace. The samples were cut into disks with a mass ~ 20 – 60 mg . The

calorimetric measurements were performed in a power-compensated Perkin–Elmer Diamond DSC in aluminum or gold pans under a constant flow of high-purity argon. The DSC temperature was calibrated for each heating rate and each pan-type using the melting transition of indium and zinc standards. The DSC heat flow calibration was performed for each rate using the enthalpy of fusion of indium and zinc standards to account for the sensitivity changes upon increasing temperatures [24].

Amorphous samples are up-scanned in the DSC at 60 K min^{-1} throughout the glass transition after a pretreatment of cooling at the same scanning rate of 60 K min^{-1} from the supercooled liquid. The glass transition temperature T_g was defined as the onset of the endothermic DSC event. The heating rate is kept the same as the preceding cooling rate ($q_h = q_c$) in order to avoid the uncertain influence of the thermal history [25]. For each up-scan of the amorphous alloy samples, a scan of the crystallized sample is also performed to serve as the baseline. For amorphous B_2O_3 and GeO_2 , the crystalline baselines are estimated by linear extrapolations from the values of the glassy states due to the difficulty to crystallize these samples in the DSC.

The relatively high heating/cooling rate (60 K min^{-1}) is selected here so as to avoid possible crystallization during the pretreatment of some BMG compositions due to their limited thermal stability in the supercooled liquid region.

3. Results and discussion

3.1. Fragility and T_g -scaled slope of DSC scans

After normalization to the sample mass (m), gram-atomic mass (μ) and applied heating rate (q_h), the (crystalline) baseline subtracted DSC up-scan output signal (excess heat flow) is proportional to the apparent excess specific heat capacity, $\dot{Q}^{l,g-x} \cdot \mu / (m \cdot q_h) = \kappa \Delta C_p^{l,g-x}$, where $l,g-x$ denotes the difference between the liquid/glassy (l,g) and crystalline (x) states and the calibration coefficient $\kappa \approx 1$ given that the heat flow of the DSC is calibrated [24]. As such the excess heat flow can be treated as $\Delta C_p^{l,g-x}$ (see a comparison in the Inset of Fig. 1). In Fig. 1, the excess heat flow is plotted against the absolute temperatures scaled by the measured values of the respective onset of T_g . The maximum values of the slopes on the T_g -scaled heat flows during glass transitions are then determined as the characteristic slopes for the glass transitions. Table 1 summarizes the maximum slopes $d(\Delta C_p^{l,g-x})/d(T/T_g)|_{\max}$.

In Fig. 2, the metastable equilibrium viscosity data of these BMG-formers measured using three-point beam bending are displayed in a T_g -scaled Arrhenius plot (also called fragility-plot). The equilibrium state below T_g was achieved by long time isothermally annealing the amorphous sample until the system is relaxed and the viscosity approaches the equilibrium plateau. Then the Kohlrausch-Williams-Watts (KWW) relaxation function was used to fit the viscosity data to obtain the equilibrium viscosity [26]. The solid lines represent the VFT fit, yielding the VFT fragility parameter, D^* . All multicomponent Zr-based bulk metallic glass-formers show similar strong behavior ($D^* \sim 20$ – 26), while the Au₄₉-BMG ($D^* = 16.9$) and Pd₄₃-BMG ($D^* = 12$) are somewhat more fragile.

Fig. 3 shows the relation between the maximum value of the slope of the T_g -scaled DSC heat flow during the glass transition and the inverse VFT-fragility parameter, $1/D^*$. The slope for the very fragile four-component Pd₄₃-BMG is greater than the less fragile five-component Au₄₉-BMG, both of which have greater slopes than the relatively stronger Zr-based BMGs. Moreover, we include the calorimetric measurements for the network oxide glass-formers B_2O_3 and GeO_2 . The results extend the correlation towards the further strong extreme of the strong-fragile pattern; i.e., to larger

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