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Correlation between the fragility of supercooled liquids and thermal expansion in the glassy state for Gd-based glass-forming alloys

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Abstract
Dilatometric measurements were performed to obtain the average thermal expansion coefficients of a series of Gd-based bulk metallic glasses. The fragilities of these alloys were determined based on differential scanning calorimetry measurements. It was found that there is a linear correlation between the fragility parameter of supercooled liquids and the average thermal expansion coefficient in Gd-based bulk metallic glass-forming alloys.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since it was proposed by Angell [1], the concept of fragility has been widely used to classify the strong–fragile characteristics of glass-forming liquids. This concept is based on an analysis of plots of logarithmic viscosity ($\log(\eta)$) as a function of inverse(scaled) temperature (T_g/T). Liquids exhibiting linear Arrhenius behaviour are described as 'strong' and those which depart from linearity (with Vogel–Tamman–Fulcher (VFT) behaviour) as 'fragile'. When the data are plotted as $\log(\eta)$ against T_g/T (herein referred to as an Angell plot) the slope at the glass transition defines the fragility index $m = [\mathrm{d}[\log(\eta)]/\mathrm{d}[T_g/T]]_{T=T_g}$ [2]. For a strong liquid, a lower limit of fragility of $m_{\min} \approx 16$ has been established, while more fragile systems tend to have $m > 100$ [3]. Actually, the temperature dependence of viscosity near T_g can be denoted by the value of $\Delta H_\eta/T_g$ (where ΔH_η is the activation energy for viscous flow) [4]. Previous studies confirmed that for most glass-forming liquids the activation energy for the glass transition (ΔH_g) has a similar value to the activation energy for viscous flow (ΔH_η) within the glass transition region. ΔH_g is therefore substituted for ΔH_η to determine the

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strong–fragile character of glass-forming liquids. ΔH_g can be determined by the dependence of T_g on the heating rate, which can be derived from differential scanning calorimetry (DSC) measurements. By this approach, the strong–fragile character of glass-forming liquids can be easily established without viscosity measurements.

Recently, some correlations between the fragility of a supercooled liquid and some physical properties, such as the vibrational properties and Poisson's ratio, have been demonstrated for a number of simple nonmetallic glass formers [5, 6]. Novikov *et al* found that the fragility parameter m of a glass-forming liquid is an increasing linear function of the ratio of instantaneous bulk to shear moduli, K_∞/G_∞, or its Poisson ratio of the glass. Scopigno *et al* reported that the fragility of a supercooled liquid correlates with the temperature dependence of its nonergodicity factor α, as determined by the vibrational dynamics at very low temperatures ($T \to 0$), and the higher the fragility, the higher the value of α [7]. It was also found that the so-called boson peak, i.e. excess vibrations in the THz frequency range, has a larger amplitude in strong glass formers than in fragile ones [8]. Also, the intensity of the fast relaxation relative to that of the boson peak at T_g is an increasing function of fragility [9–11]. These correlations can assist in understanding the long-standing issues of glass formation and the nature of glass. Therefore, it is necessary to carry out more extensive investigation on the fragility embedded in the properties of the glassy state.

In this work, we report the fragilities of supercooled liquids in $Gd_{55}Al_{25}Co_{20}$, $Gd_{55}Al_{25}Co_{10}Cu_{10}$, $Gd_{55}Al_{25}Ni_{10}Co_{10}$ and $Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$ glass-forming alloys. Dilatometric measurements are performed for the above bulk metallic glasses (BMGs) and the thermal expansion coefficients are obtained. Then, the correlation between the average thermal expansion parameter and the fragility of supercooled liquid in the Gd-based alloys is investigated.

2. Experimental procedure

The $Gd_{55}Al_{25}Co_{20}$, $Gd_{55}Al_{25}Co_{10}Cu_{10}$, $Gd_{55}Al_{25}Ni_{10}Co_{10}$ and $Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$ alloys were prepared by arc melting pure Al, Cu, Co, Ni and Gd in a Ti-gettered argon atmosphere. The purity of Gd was about 99.5 wt%, and the other elements had a purity of at least 99.9 wt%. The alloy ingots were remelted and suck-cast into a Cu mould to obtain cylindrical rods with a diameter of 2 mm and a length of 60 mm. The structure of the transverse cross sections of as-cast alloys was ascertained using x-ray diffraction (XRD, Cu Kα radiation). A differential scanning calorimeter (Netzsch DSC 404C) was used to study the thermodynamic properties at different heating rates. The dilatation measurements were conducted with a conventional dilatometer (Netzsch DIL 402C). The initial length of the sample was 20 mm and the compression load during measurement was 25 N.

3. Results and discussion

Figure 1 shows the XRD patterns of the transverse cross sections of the cast rods of $Gd_{55}Al_{25}Co_{20}$, $Gd_{55}Al_{25}Co_{10}Cu_{10}$, $Gd_{55}Al_{25}Ni_{10}Co_{10}$ and $Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$ alloy rods of 2 mm in diameter. The broad diffraction peaks indicate the full vitrification of the samples. The DSC curves of the four BMGs at a heating rate of 20 K min^{-1} are shown in figure 2.

Several approaches are used to quantize the 'fragility strength' [10, 12] of supercooled liquids, among which the fragility parameter, m, is often applied. Except for the method defining the fragility parameter mentioned above, the following equation is also used to

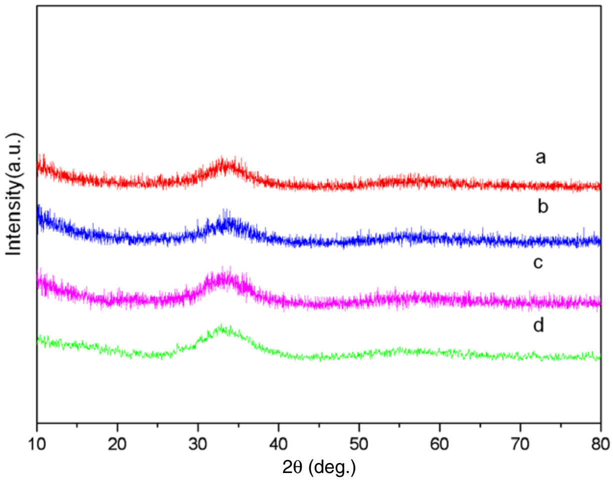

Figure 1. XRD patterns of (a) $Gd_{55}Al_{25}Co_{20}$, (b) $Gd_{55}Al_{25}Ni_{10}Co_{10}$, (c) $Gd_{55}Al_{25}Cu_{10}Co_{10}$ and (d) $Gd_{55}Al_{25}Cu_{10}Co_{5}Ni_{5}$ cylindrical rods with a diameter of 2 mm.

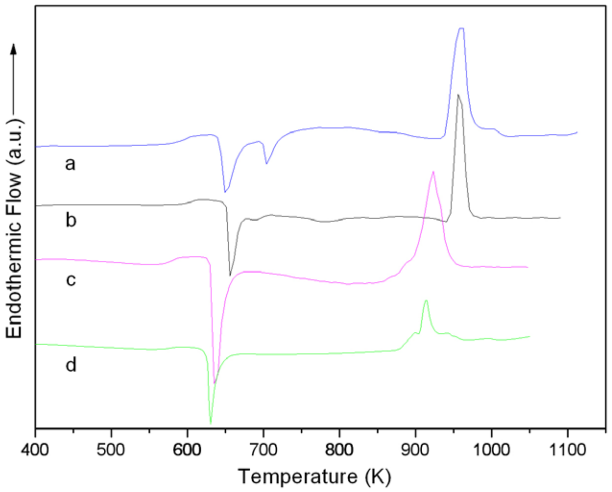

Figure 2. DSC traces of (a) $Gd_{55}Al_{25}Ni_{10}Co_{10}$, (b) $Gd_{55}Al_{25}Co_{20}$, (c) $Gd_{55}Al_{25}Cu_{10}Co_{10}$ and (d) $Gd_{55}Al_{25}Cu_{10}Co_{5}Ni_{5}$ bulk metallic glasses at a heating rate of 20 K min^{-1}.

calculate the fragility parameter [13]:

$$m = \frac{\Delta H_g}{RT_{g,20}} \tag{1}$$

where R is the gas constant and ΔH_g is the activation enthalpy for the glass transition. $T_{g,20}$ is used here to ensure a uniform comparison, and is the glass transition temperature at a DSC scanning rate of 20 K min^{-1}. The value of ΔH_g can be calculated [14–16] by the Kissinger equation:

$$\frac{AQ}{T_g^2} = \exp\left(-\frac{\Delta H_g}{RT_g}\right) \tag{2}$$

where A is a constant, Q is the heating rate during the DSC scan, T_g is the glass transition temperature and R is the gas constant. According to equation (2), the activation energy for the glass transition of an amorphous phase, ΔH_g, can be obtained. For each measurement to determine the value of ΔH_g, the sample was first heated at a heating rate of 20 K min^{-1} to a temperature lower than its glass transition temperature and held for 5 min to erase the effect of its previous thermal history. After the isothermal hold, the sample was cooled at 10 K min^{-1}

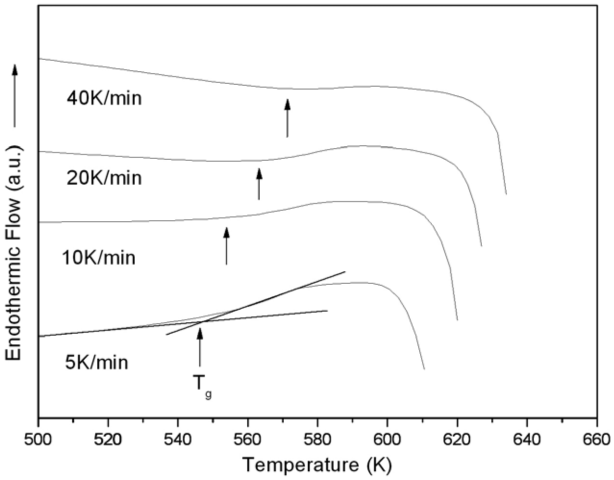

Figure 3. DSC traces of the $Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$ BMG at different heating rates.

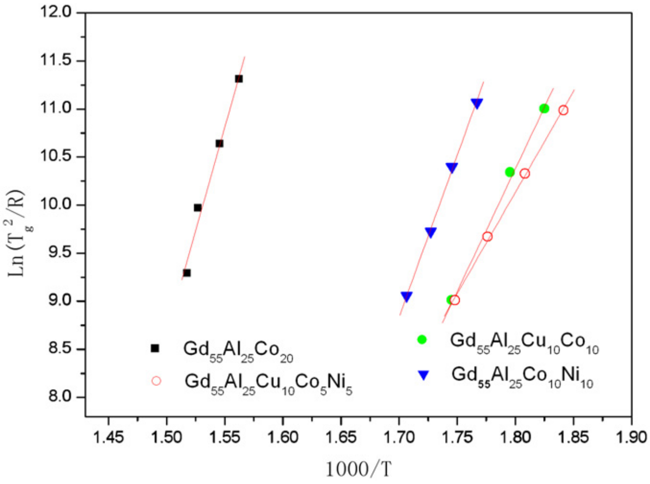

Figure 4. Kissinger plots for the four BMGs.

to room temperature, and then reheated through the crystallization region at a heating rate of 5, 10, 20 and 40 K min^{-1}.

DSC curves of $Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$ BMG at different heating rates are shown in figure 3 as an example. The glass transition temperature shifts to higher temperatures with increasing heating rate. The Kissinger plots for the $Gd_{55}Al_{25}Ni_{10}Co_{10}$, $Gd_{55}Al_{25}Co_{20}$, $Gd_{55}Al_{25}Cu_{10}Co_{10}$ and $Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$ BMGs are shown in figure 4.

From the best fit, the fragility parameters for the Gd-based alloys are obtained, as shown in table 1. The fragility ranks from strong to fragile as follows: $Gd_{55}Al_{25}Cu_{10}Co_5Ni_5 < Gd_{55}Al_{25}Cu_{10}Co_{10} < Gd_{55}Al_{25}Ni_{10}Co_{10} < Gd_{55}Al_{25}Co_{20}$. The small values of m are considered to be the empirical rules for designing the BMG formers, whose metastable-equilibrium supercooled liquids are stable. According to Angell's classification, these BMGs are glasses of intermediate strength.

Figure 5 shows the dilatometer (DIL) traces for $Gd_{55}Al_{25}Co_{20}$, $Gd_{55}Al_{25}Co_{10}Cu_{10}$, $Gd_{55}Al_{25}Ni_{10}Co_{10}$ and $Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$ BMGs at a heating rate of 5 K min^{-1}. For all BMGs, the dilatation curves are basically linear below T_g except in the vicinity of room temperature. This is attributed to the normal thermal expansion of materials.

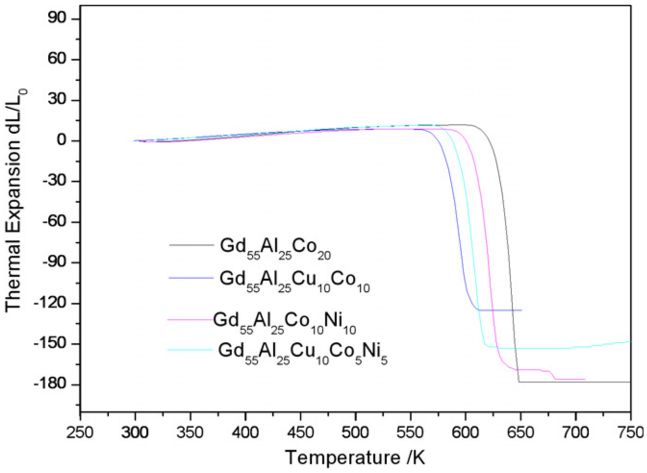

Figure 5. The thermal expansion curves of the four BMGs.

Table 1. The glass transition temperature at a heating rate of 20 K min^{-1}, the activation energy for the glass transition and the fragility parameter for the Gd-based BMGs.

Alloys	ΔH_g (kJ mol^{-1})	T_g (K)	m
$Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$	175	563	37.4
$Gd_{55}Al_{25}Co_{10}Cu_{10}$	210.6	563	45.4
$Gd_{55}Al_{25}Ni_{10}Co_{10}$	279.2	579	58.1
$Gd_{55}Al_{25}Co_{20}$	362.4	589	74.0

Table 2. The average thermal expansion coefficients α_{aver} and the fragility of supercooled liquids for four BMGs.

Alloys	α_{aver} (10^{-6})	m
$Gd_{55}Al_{25}Cu_{10}Co_5Ni_5$	4.83	37.4
$Gd_{55}Al_{25}Co_{10}Cu_{10}$	5.36	45.4
$Gd_{55}Al_{25}Ni_{10}Co_{10}$	5.86	58.1
$Gd_{55}Al_{25}Co_{20}$	6.55	74.0

Table 2 lists the average thermal expansion coefficients α_{aver} obtained by DIL experiments at a heating rate of 5 K min^{-1}. From the table, it is seen that in Gd-based BMGs the average thermal coefficient of expansion is an increasing linear function of the fragility parameters m, which is clearly observed in figure 6.

The average thermal coefficient of expansion α_{aver} is closely associated with the binding energy and stability of solids [17]. An alloy with a lower a_{aver} is more stable in the solid state. The fragility parameter m is associated with the stability of liquid at the glass transition temperature. Therefore, the relationship between a_{aver} and m correlates with the properties of the glass state with those of the supercooled liquid. This correlation further verifies the viewpoint, stressed by Scopigno *et al* [7], that the fragility of a liquid may be embedded in the properties of the glassy state. However, little work has so far been done and more investigations need to be carried out to determine whether the correlation between α_{aver} and m applies to other amorphous alloy systems.

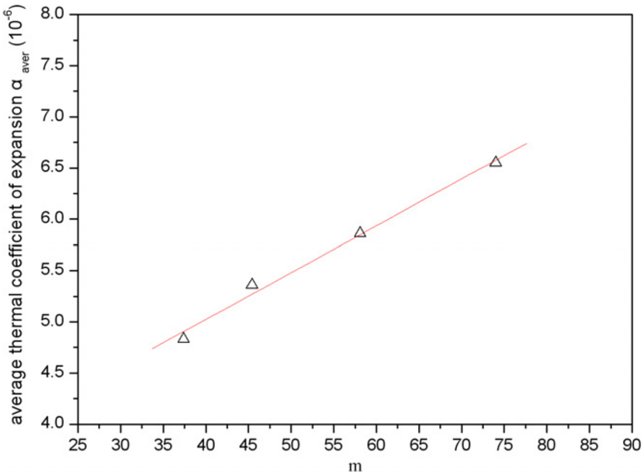

Figure 6. The correlation between the fragility of supercooled liquids and the average thermal coefficient of expansion in Gd-based BMGs.

4. Conclusion

The average thermal expansion coefficients were obtained based on dilatometric measurements in a series of Gd-based BMGs. A linear correlation was found between the fragility parameters m and the average thermal coefficient of expansion a_{aver} in these alloys. It seems that the fragility of supercooled liquids is indeed embedded in the properties of the glassy state.

Acknowledgments

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