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Enthalpy recovery and free volume relaxation in a $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ bulk metallic glass

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ABSTRACT

We report on the free volume of the $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ bulk metallic glass in terms of its enthalpy recovery and volumetric relaxation below the glass transition temperature, T_g. Glassy samples are isothermally annealed below T_g using differential scanning calorimetry and the resulting enthalpy recovery, ΔH_r, is measured upon re-heating into the supercooled liquid region. Volumetric changes below T_g are measured isothermally using Thermo-Mechanical Analysis. The total changes in the relative free volume, $\Delta v_f/v_m$, between the initially glassy state and the equilibrium liquid are calculated from the volumetric relaxation. The measured values of ΔH_r and $\Delta v_f/v_m$ correlate well within the framework of free volume theory and a linear relationship is found between the two.

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1. Introduction

The formation of a glass during undercooling from the liquid is associated with the “freezing in” of a certain amount of excess free volume as the liquid falls out of equilibrium at the glass transition temperature, T_g. According to the Cohen and Turnbull model of an ideal hard sphere system [1], the free volume, v_f, is assumed to vary linearly with temperature as

$$v_f = v_m \alpha_f (T - T_0) \quad (1)$$

where α_f is the difference between the volumetric thermal expansion coefficients of the liquid and the glass, $\alpha_f = \alpha_{liq} - \alpha_{glass}$ [2,3]. By substituting this expression for the free volume into the Doolittle equation for viscous flow [4], where $\eta = \eta_0 \exp(b v_m / v_f)$, the empirical Vogel–Fulcher–Tammann (VFT) equation is obtained:

$$\eta = \eta_0 \exp\left(\frac{D^* T_0}{T - T_0}\right) \quad (2)$$

with the relation $\alpha_f = b/(D^* T_0)$.

The parameter D^* is the kinetic fragility of the material; the most fragile glass-formers have a fragility of around 2, whereas the strongest are on the order of 100. The VFT temperature, T_0, is the temperature at which the barriers with respect to flow would approach infinity [5]. The pre-exponential factor, η_0, is kept fixed at a value of 4×10^{-5} Pa s, according to the relation $\eta_0 = h/v_m$, where h is Planck’s constant and v_m is the atomic volume [6].

In the present study we investigate the free volume of the $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ (Vitreloy $1b^{TM}$) BMG alloy at temperatures below T_g using independent measurements of enthalpy recovery and length relaxation. The isothermal relaxation in length is used directly to determine the amount of free volume relaxation occurring in the glassy sample. We compare the amount of structural relaxation occurring in the enthalpy and the volume, and relate these within the framework of a free volume model based on equilibrium viscosity data taken in the vicinity of T_g.

2. Experimental methods

Fully amorphous rods of $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ were supplied by Liquidmetal©Technologies. Calorimetric experiments were carried out with a power-compensated Perkin-Elmer Diamond differential scanning calorimeter (DSC) in high-purity aluminum pans under a constant flow of high-purity argon gas. Temperature and heat flow calibration of the DSC was carried out for each heating rate according to the standard phase transformations of indium, zinc and K_2SO_4 (β-α). The dilatometric measurements were carried out in a Netzsch Thermo-Mechanical Analyzer (TMA 402). To investigate the enthalpy and free volume changes on a long time scale, the specimens were first equilibrated in the supercooled liquid region at a temperature of 700 K and immediately cooled down to room temperature with a rate of 0.416 K/s; this assured the same enthalpic state for each of the amorphous samples. Enthalpy relaxation was carried out in the DSC by first heating the sample – with masses ranging from 80 to 100 mg – to the desired temperature, before the onset of the calorimetric glass transition, with a rate of 0.416 K/s, and then holding it isothermally for the necessary amount of time to ensure complete relaxation into the equilibrium liquid. The isothermal annealing times were taken from Ref. [7]. These annealing times were chosen to be long enough to completely relax the sample while avoiding the crystallization events measured isothermally in Ref. [8]. After

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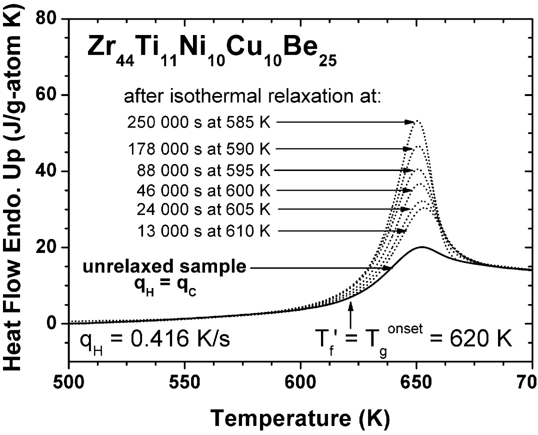

Fig. 1. Enthalpy recovery curves (dotted lines) after isothermal relaxation into the equilibrium liquid at the specified temperatures. The solid line represents the curve of an unrelaxed sample, i.e. heated with the same rate, q_H, as that of an immediately preceding cooling, q_C, from the supercooled liquid region.

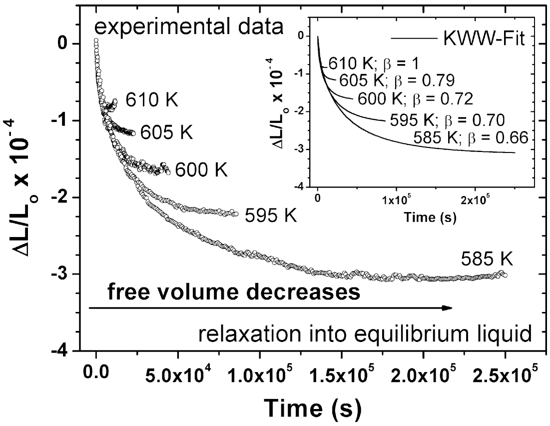

Fig. 2. Experimental relative changes in length, $\Delta L/L_o$, of amorphous samples of $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ during relaxation into the equilibrium liquid for the annealing temperatures are shown (open circles). The fits of the experimental data to the stretched exponential (KWW) function are also shown (inset). The stretching exponent parameter, β, reaches unity in the proximity of the glass transition.

completion of annealing the samples were first cooled to room temperature with a rate of 0.416 K/s and then subsequently heated with the same rate throughout the glass transition, where the enthalpy recovery was measured, and past the crystallization event to a temperature of 853 K. Volumetric measurements of the relaxation below T_g were carried out in the TMA (dilatometer mode) using a vertical, fused silica loading probe. The glassy samples were heated with a rate of 0.416 K/s to the desired temperatures and then held isothermally where the length relaxation was directly measured. The load on the sample's surface was supplied by a spring-loaded linear variable differential transformer and was calculated to be 0.20 ± 0.04 mN.

Additionally, beams with rectangular cross-sections between 0.2 and 1.0 mm^2 and lengths of approximately 13 mm were cut from the samples and a three-point beam-bending method was used to measure the viscosity in the vicinity of the glass transition. A beam, supported at each end by sharp edges, is subjected in the center to a constant force provided by a fused silica loading probe with a wedge-shaped head, and the corresponding deflection of the beam is measured isothermally. Using this technique viscosities ranging from 10^7 to 10^{14} Pa s can be determined [9].

The absolute specific heat capacity of this alloy in the glassy, supercooled liquid and crystalline state was determined using the DSC step-method outlined in Ref. [10]. Additionally, a NETZSCH STA 449 C differential thermal analyzer (DTA) was used to detect the melting point and heat of fusion of the sample enclosed in a graphite crucible with high-purity argon as the purging gas.

3. Results and discussion

In Fig. 1 the enthalpy recovery curves of the annealed samples (dotted lines) are shown after heating with the rate $q_H = 0.416$ K/s throughout the glass transition. The recovery curves are shown alongside a scan of the unrelaxed sample (solid line), i.e. a sample that was heated with the same rate, q_H, as that of an immediately preceding cooling, q_C, from the supercooled liquid region. It was established previously that if the convention $q_H = q_C$ is held, the measured onset temperature of the glass transition on heating, $T_g{}^{\text{onset}}$, approximates the limiting fictive temperature [11]. The amount of enthalpy recovered, ΔH_r, after heating throughout the glass transition was calculated as the area between the respective recovery curve and that of the unrelaxed sample from 500 K to 700 K. At 700 K all samples are equilibrated in the metastable, supercooled liquid region.

The temperature dependence of the specific heat capacities for the equilibrium liquid and crystalline states far above the Debye temperature is found through non-linear fitting of the experimental data to the two equations according to Kubaschewski [12]:

$$C_p^l = 3R + aT + bT^{-2} \tag{3}$$

$$C_p^x = 3R + cT + dT^2 \tag{4}$$

where R is the gas constant and C_p^l and C_p^x are the specific heat capacities of the liquid and crystalline states, respectively. The fitting constants were determined to be $a = 0.00653$, $b = 7.09 \times 10^6$, $c = -0.00799$ and $d = 1.94 \times 10^{-5}$ in their respective units. The difference in enthalpy between the liquid and crystalline states can be expressed by integrating Eqs. (3) and (4) and offsetting with the experimentally determined heat of fusion, $\Delta H_f = 9.3$ kJ/g-atom.

$$\Delta H^{1-x}(T) = \Delta H_f + \int_{T_f}^{T} \Delta C_p^{1-x}(T')dT' \tag{5}$$

where T_f is taken as the temperature at which the Gibbs free energy of the liquid and crystal states are equal (951 K).

The structural relaxation of each sample below the glass transition temperature is quantified here, in part, by the enthalpy recovery measured upon reheating after isothermally annealing into the equilibrium liquid. We are able to determine the initial enthalpic state of the glassy sample at a certain temperature by measuring the enthalpy of recovery, ΔH_r, for that temperature from the specific heat curves in Fig. 1 and adding it to the value of the enthalpy difference between the supercooled liquid and crystal, ΔH^{l-x}, from Eq. (5). The structural relaxation is also quantified here by the direct measurement of the change in length of an amorphous sample during annealing. Fig. 2 shows the relative change in length, $\Delta L/L_o$, of the amorphous samples as they are relaxed from the glassy state into the equilibrium liquid region during isothermal annealing at the temperatures indicated. Relaxation processes in amorphous materials are usually found to be best described with a Kohlrausch–Williams–Watts (KWW), stretched exponential function [13–16]. The change in length, ΔL, during isothermal relaxation below the glass transition was found here to obey a KWW function of the form:

$$\Delta L(t) = \Delta L_{eq}(1 - e^{-(t/\tau)^{\beta}}) \tag{6}$$

where ΔL_{eq} is the total change in length after the sample has relaxed into the equilibrium state, t the time, τ a characteristic relaxation time and β is the stretching exponent parameter ($0 < \beta \le 1$). The inset in Fig. 2 shows the fitted curves of the experimental data. It can be seen here that the values of β increase monotonously with increasing annealing temperature and assume unity close to the glass transition. If no temperature changes occur during the relaxation, the measured reduction in volume is attributed solely to the reduction of the excess free volume. Furthermore, assuming that structural relaxation occurs isotropically, the relative change in free volume of the amorphous sample, $\Delta v_f/v_m$, can be approximated by its relative change in length, $\Delta L/L_o$

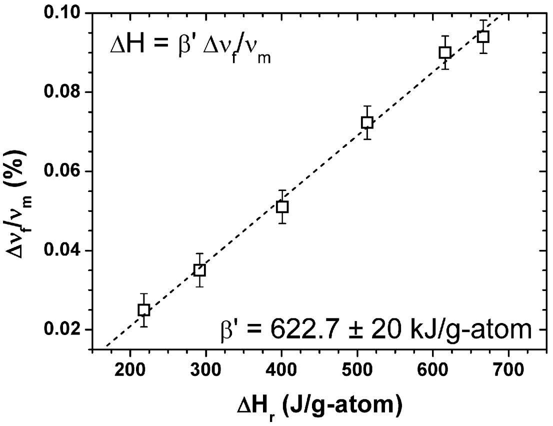

Fig. 3. The experimentally determined values $\Delta v_f/v_m$ vs. ΔH_r are shown here for each annealing temperature (open squares) along with a linear fit to the data (dashed line). The proportionality constant β' was found to be 622.7 ± 20 kJ/g-atom.

[17–19]:

$$\frac{\Delta v_f}{v_m} = 3\frac{\Delta L}{L_o} \tag{7}$$

Using Eq. (7) these changes in length can be seen as being representative of a total volumetric change due to the decrease in the excess free volume. The fits of experimental data to Eq. (6) (inset Fig. 2) reveal a strong temperature dependence in both τ and β. At lower annealing temperatures the time for relaxation increases, while the value of β decreases. As the annealing temperature approaches the glass transition, the values of β approach unity, indicating the presence of a purely exponential relaxation. The non-exponential behavior of the measured length relaxation is clearly observed at lower annealing temperatures, where the values of β range from 0.66 to 0.79. This suggests a broader distribution of relaxation times at lower temperatures than at those close to the glass transition. Similar non-exponential behavior was reported recently by Haruyama et al. for the quaternary $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG in volume relaxation experiments [20] and by Gallino et al. [10] and Zhang and Hahn [21] in enthalpy relaxation experiments on the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ and $Zr_{45}Cu_{39.3}Al_{7.0}Ag_{8.7}$ BMGs, respectively.

The reduction in the total enthalpy of the glass during annealing can be understood as the result of the reduction in the excess free volume that was present during formation of the glass during cooling from the supercooled liquid. Van den Beukel and Sietsma [22] assume a linear relationship of the form $\Delta H = \beta'(\Delta v_f/v_m)$ where ΔH is the change in enthalpy due to the change in relative free volume, $\Delta v_f/v_m$. v_m is taken here as the atomic volume at the liquidus temperature, $1.67 \times 10^{-29}\ \mathrm{m}^3$, and was determined previously for another BMG alloy with the very similar composition $Zr_{41.2}Ti_{13.8}Ni_{12.5}Cu_{10}Be_{22.5}$ (Vitreloy 1^{TM}) [23]. The constant β' therefore has the same units of enthalpy, i.e. kJ/g-atom. A linear relationship is found between the amount of enthalpy recovered, ΔH_r, and free volume relaxed, $\Delta v_f/v_m$, for each annealing temperature and is shown in Fig. 3. The value of β' is determined here to be 622.7 ± 20 kJ/g-atom. This result is in good agreement with similar studies performed on the quaternary $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG using direct density measurements to quantify the free volume change [20,24]. Slipenyuk and Eckert [24] report a value of $\beta' = 552 \pm 15$ kJ/g-atom and Haruyama et al. [20] report a value of 718.2 kJ/g-atom. It has been suggested that β' represents the formation energy of an amount of free volume with the magnitude of one atomic volume [22,24], which has been determined in these studies to be 2–3 times greater than the formation energy of a vacancy in a pure Zr crystal lattice [25].

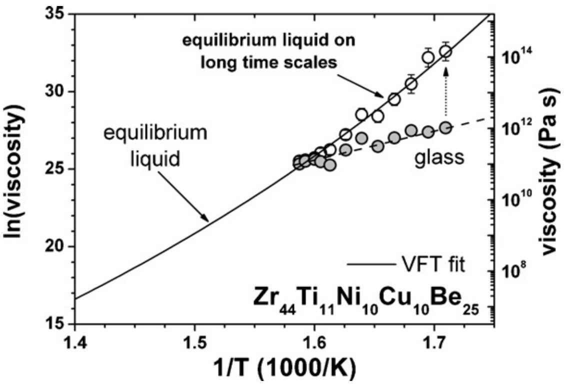

Fig. 4. Equilibrium viscosities (open circles) and viscosities of the glass immediately prior to relaxation (shaded circles) as a function of inverse temperature for the $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ alloy. The fit to the experimental data using Eq. (2) is given by the solid line. The dotted arrow schematically shows the isothermal path of relaxation into the equilibrium liquid from the glassy state (dashed line).

The equilibrium viscosities of $Zr_{41.2}Ti_{13.8}Ni_{12.5}Cu_{10}Be_{22.5}$ were determined in the vicinity of the glass transition using the three-point beam-bending method described in Section 2. The equilibrium viscosity data (open circles) are shown in Fig. 4 along with the viscosities of the glassy alloy immediately before relaxation (shaded circles). A non-linear fit of the VFT-equation (Eq. (2)) was performed to the equilibrium data (solid line), giving the fragility parameter, $D^* = 25.4$, and the VFT-temperature, $T_0 = 366.6$ K. The relative free volume of the equilibrium liquid, v_f/v_m, as a function of temperature was calculated using Eq. (1). The thermal expansion coefficient of the free volume, α_f, was determined to be $3.10 \times 10^{-5}\ \mathrm{K}^{-1}$, where α_{glass} was measured here as $2.22 \times 10^{-5}\ \mathrm{K}^{-1}$ using a dilatometric method and the value of α_{liq} was taken to be the same as that for Vitreloy 1^{TM} from Ref. [23].

In Fig. 5 we compare the enthalpy and relative free volume by adjusting the scale of the vertical axes until the curves for ΔH^{l-x} and v_f/v_m agree with each other within the glass transition region. The experimental enthalpy recovery data, ΔH_r, are shown here, as well as the relative free volume changes, $\Delta v_f/v_m$, determined from the volumetric relaxation experiments. By matching the curves of the enthalpy and relative free volume, both for the equilibrium liquid, we find good agreement between the two experimental data sets. More specifically, we notice that the difference in enthalpy between the glass and equilibrium liquid is, at any given annealing temperature, proportionally equal to the difference in relative free

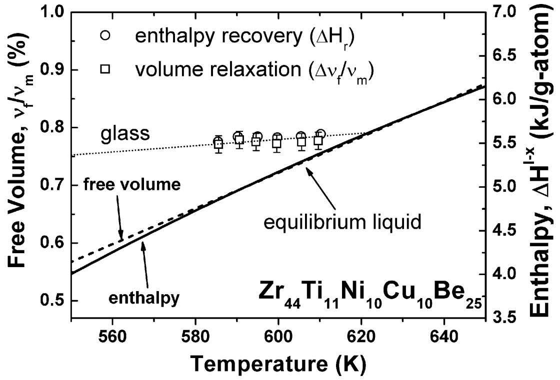

Fig. 5. Enthalpy recoveries, ΔH_r (open circles) and the changes in the relative free volume, $\Delta v_f/v_m$ (open squares) calculated from the changes in length during relaxation into the equilibrium liquid. The relative free volume curve (dashed line) of the equilibrium liquid is calculated with Eq. (1). The calculated enthalpy difference between the liquid and crystalline states using Eq. (7) is shown here as well (solid line).

volume. From the results shown in Fig. 5 we see a very consistent picture of enthalpy and free volume relaxation as analyzed with the techniques reported here.

4. Conclusion

The relative changes in free volume, $\Delta v_f/v_m$, of the $Zr_{44}Ti_{11}Ni_{10}Cu_{10}Be_{25}$ BMG alloy were determined here at temperatures below T_g using methods of enthalpy recovery measured in the DSC and length relaxation measured in the dilatometer. It was found that the kinetics of length relaxation can be well described with a stretched exponential function with β values approaching unity as the glass transition is approached. This is in good accordance with similar investigations into the enthalpy and volume relaxation in other Zr-based BMG systems. The isothermal change in length of the amorphous samples during relaxation into the metastable equilibrium liquid was used directly to determine the relative change in free volume. A linear relationship between ΔH_r and $\Delta v_f/v_m$ was found and the proportionality constant determined to be 622.7 ± 20 kJ/g-atom, which has been interpreted as the energy required for the formation of an amount of free volume with the magnitude of one atomic volume. Using equilibrium viscosity data taken near T_g, the functional form of the relative free volume of the equilibrium liquid according to Cohen and Turnbull was calculated. Furthermore, when the enthalpy and relative free volume curves in the equilibrium liquid are compared with each other, we find that the experimentally determined values of ΔH_r and $\Delta v_f/v_m$ show very good agreement, which supports the linear relationship established in this work.

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