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Enthalpy relaxation of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ bulk metallic glass forming alloy

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Abstract

A new experimental method was developed to study the isothermal enthalpy relaxation kinetics below the glass transition region of bulk metallic glass forming alloys using differential scanning calorimetry. The method was applied to the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ alloy and the results reveal that the enthalpy relaxes in an Arrhenius-like fashion. The activation energy obtained from the Arrhenius fit is comparable to the activation energy required for the diffusion of the medium size atoms. This suggests that solid-state diffusion is the governing mechanism for the enthalpy relaxation process. The stretching exponents for the relaxation are close to unity, which indicates that this alloy is a rather strong glass former. This is confirmed by Vogel–Filcher–Tammany (VFT) fits of the heating rate dependence of the glass transition.

Keywords: Amorphous materials; Calorimetry; Zr–Cu–Ni–Al–Nb

1. Introduction

The recently processed Vitreloy 106a with composition $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ is the best beryllium free Zr-based bulk metallic glass former known today. It is possible to produce centimeter scale amorphous ingots of this alloy with critical cooling rates of less than 10 K/s (as low as 1.75 K/s) [1]. This paper focuses on the kinetics of the V106a alloy in the vicinity of the glass transition temperature, T_g (668 K at 0.33 K/s). Since this alloy has a thermally very stable supercooled liquid around T_g with no interference of phase separation or nanocrystallization, it is possible to measure the enthalpy relaxation. The relaxation of the frozen-in enthalpy towards the equilibrium state can measured as a function of time at a constant temperature [2]. This represents an advancement compared to the well-known enthalpy recovery experiments, in which the enthalpy reduction during an isothermal relaxation below the calorimetric glass transition is recovered as an “overshooting” at the glass transition during a subsequence DSC run [3,4]. This new method not only yields the total enthalpy change but also the functional form of the enthalpy change during relaxation as well as the characteristic relaxation time.

2. Experimental methods

Master alloys of this composition were prepared by arc melting the elements with purities ranging from 99.9 to 99.999%. The master alloys were re-melted and water quenched into a steel tube, producing a single ingot of 4 mm thickness. The calorimetric measurements were performed using a Perkin-Elmer Pyris differential scanning calorimeter (DSC) purged with 99.999% purity argon. The DSC specimens, of weight 90–170 mg, were first subjected to a pre-annealing treatment, in which they were heated at a rate of 0.33 K/s until completion of the glass transition and cooled to room temperature at 1 K/s to give all samples the same thermal history and initial enthalpic state. Isothermal anneals where performed on the pre-annealed samples at temperatures selected within the calorimetric glass transition region and within the glassy region, as low as 30 K below T_g. The heating rate to reach the isothermal temperature was 1 K/s. The time for the isothermals was selected to allow complete relaxation of the frozen-in enthalpy towards the equilibrium state. After the isothermal anneals the specimens were first cooled to room temperature with a rate of 1 K/s and, subsequently, a enthalpy recovery experiment with constant heating rates of 0.1 K/s was performed until completion of crystallization. This allowed also measuring a subsequent baseline for the isothermal anneals.

3. Results and discussion

Fig. 1 illustrates schematically the DSC enthalpy relaxation signal (B) from the glassy state into the relaxed state (C) along

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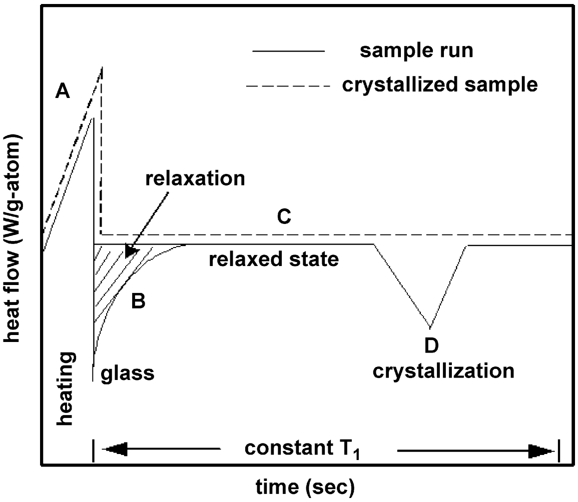

Fig. 1. Schematic of the enthalpy relaxation signal from the glassy state into the supercooled liquid state along with the isothermal crystallization. The range marked by (A) in the signal indicates the heating of the sample with constant heating rate up to the temperature T_1. The exothermic heat release due to relaxation is marked by (B) followed by the supercooled liquid region (C). The crystallization event is marked by (D) in the diagram. The dashed line represents the baseline of the crystalline sample.

with a hypothetical isothermal crystallization (D). This relaxation proceeds via an exothermic heat release (shaded area). The change with time of the relaxation, $\Delta H(t)$, is calculated by integrating the heat flux over the period of time that takes the glassy state to reach the equilibrium state or relaxed state. If $\dot{Q}$ is the heat flux in W/g-atom, the ΔH after a certain time t into the relaxation is, in J/g-atom, given by

$$\Delta H(t) = \int \dot{Q} = \int_{t_{\text{glass}}}^{t} \frac{\mathrm{d}Q}{\mathrm{d}t}\mathrm{d}t. \tag{1}$$

The frozen-in enthalpy is completely relaxed when t is equal to the time to reach the equilibrium state, t_{relaxed}, and at that time the $\Delta H(t_{\text{relaxed}})$ is the total enthalpy change during relaxation, ΔH_{total}. The enthalpy of the relaxing material as a function of time, $H(t)$, is calculated by subtracting $\Delta H(t)$ from the enthalpy of the glass before relaxation, H_g (see Eq. (2)). The relaxation processes in the glass transition region are usually not found to follow an exponential law but obey a stretched exponential function [5–7]. The enthalpy relaxation can therefore be fitted with the stretched exponential function, $\phi(t)$ which is often used to characterize response functions:

$$H(t) = H_g - \Delta H(t) = H_g - \Delta H_{\text{total}}\phi(t); \tag{2}$$

where

$$\phi(t) = 1 - e^{-(t/\tau)^{\beta}} \tag{3}$$

The average relaxation time, τ and the stretching exponent, β were obtained by fitting the normalized enthalpy relaxation signal, $\Delta H(t)/\Delta H_{\text{total}}$, with the stretched exponential function, $\phi(t)$.

Four examples of isothermal enthalpy relaxation curves at different temperatures are shown in Fig. 2. In this plot, the exothermic enthalpy change increases with decreasing temperature. At the same time, a longer time for relaxation and a smaller value of β are observed. The first is attributed to the slowdown of the relaxation kinetics with decreasing isothermal temperature. The stretching exponent β represents the width of the distribution of the relaxation time. Where a small value of β corresponds to broader distribution of relaxation time (or to a less exponential response), a value close to 1 indicates a single exponential relaxation response, which suggests the dominance of a single relaxation mechanism. The stretching exponent of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ alloy increases linearly with temperature and approaches unity close to the calorimetric glass transition (see inset of Fig. 2). This indicates that the alloy is a strong supercooled liquid. It is well known in fact, that in strong liquids the stretching exponent approaches unity, whereas in fragile liquids β can become as low as 0.5 [8].

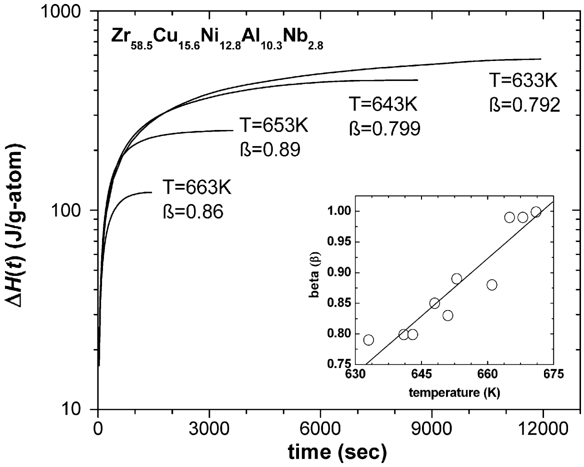

Fig. 2. Isothermal enthalpy relaxation curves as a function of time for different temperatures. The stretched exponential function was used to fit the DSC data. β is the stretching exponent and reaches unity in the proximity of the glass transition (see inset plot).

In Fig. 3, the enthalpy relaxation times, τ are plotted (Δ) as a function of inverse temperature and compared with the relax-

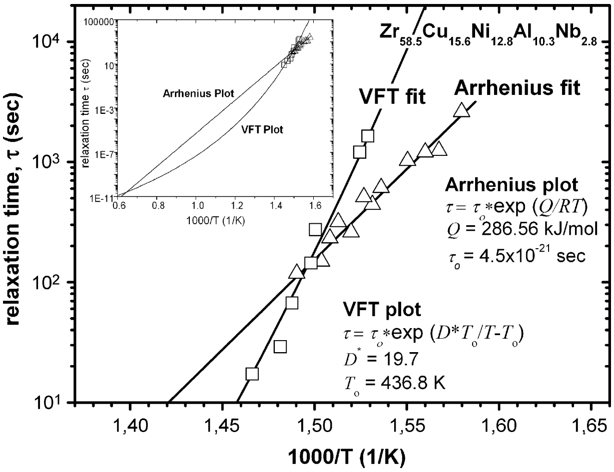

Fig. 3. Comparison of the enthalpy relaxation data (Δ) to the T_g shift data (□; from Ref. [9]) as a function of inverse temperature (Arrhenius fit vs. the VFT fit). The inset picture shows the extrapolation of both curves to a very low relaxation time, τ.

ation times (□) that have been determined in a separate study [9] by measuring the shift of the glass transition T_g with increasing heating rate. These relaxation data (□) were found to follow a Vogel–Fulcher–Tammann (VFT) relation, indicating that they are a measure for the structural α—relaxation time. The VFT equation is given by

$$\tau = \tau_0 \exp\left(\frac{D^* T_0}{T - T_0}\right), \tag{4}$$

in which D^* is the fragility parameter and T_0 is the VFT-temperature at which barriers with respect to flow would go to infinity. The high D^* value and the low T_0 value (19.7 and 436.8 K, respectively) resulting from the VFT-fit, indicate that this alloy is a rather strong liquid as also revealed by the stretching exponents that are close to unity (Fig. 2).

By fitting the enthalpy relaxation data (Δ) it is found, in the other hand, that they are best described by an Arrhenius equation rather than the VFT equation. This Arrhenius equation in terms of the relaxation time, τ is given by

$$\tau = \tau'_0 \exp\left(\frac{Q}{RT}\right), \tag{5}$$

where τ'_0 is the pre-exponential factor, R the gas constant, Q the activation energy and T is the absolute temperature. The fitted curve yields a τ'_0 of 4.5×10^{-21} s and a Q of 286.56 kJ/mol or 2.97 eV. In the plot of Fig. 3, it can be observed that the temperature dependence of the enthalpy relaxation is much weaker than the temperature dependence of the structural α—relaxation time, which is represented by the VFT fit to the heating rate dependence of the calorimetric glass transition. At low temperatures, the kinetics of enthalpy relaxation proceeds much faster than the α-relaxation. It is interesting to compare these findings with the mobility of the different atomic species in multicomponent glasses. In the case of the Zr–Ti–Cu–Ni–Be alloys, the atomic mobilities of the different species have been studied extensively. Masuhr et al. [10] analyzed the characteristic diffusion times for the different species around the glass transition. These times show Arrhenius behavior for the small and medium size atoms. The activation energies for diffusion of the small size atoms such as Ni are about 2 eV, whereas the medium size atoms have activation energies of about 3 eV, which is in good agreement with the activation energy of 2.97 eV that we find for the enthalpy relaxation of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ alloy after fitting the data (Δ) of Fig. 3 with Eq. (5). In Ref. [10], the time scale for the motion of the Zr atoms that can be regarded as constituting the backbone of the amorphous structure follows a VFT law, just like we find it for the α-relaxation. This suggest that local rearrangements of the medium size atoms, which are Al and Nb in our case, as well as the small atoms Cu and Ni are sufficient to cause relaxation into a low enthalpic state without involving the complete rearrangement of the backbone of the structure, which consists of the large atoms. In the case of $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$, it has been shown by isotope effect measurements [11] that these rearrangements involve collective hopping mechanisms for the small and medium size atom such as Cu or Co.

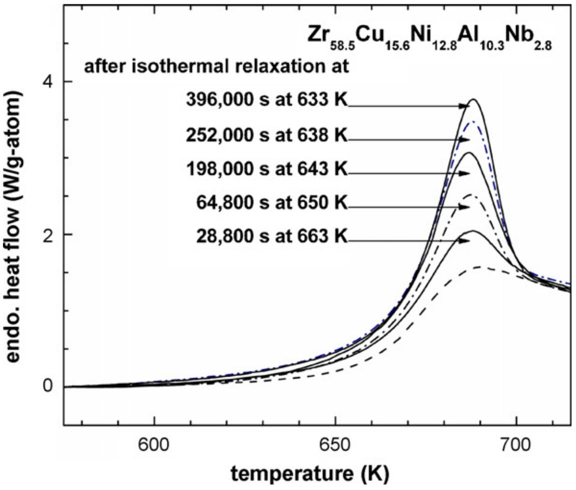

Fig. 4. Enthalpy recovery measurements after isothermal relaxation from the amorphous into the supercooled liquid state at different temperatures. In addition the measurement for an unrelaxed sample is shown (bottom dashed curve).

Five of the DSC enthalpy recovery experiments performed after the isothermal anneals are shown in Fig. 4. The annealed samples show a large endothermic heat recovery in the calorimetric glass transition region, whereas an unrelaxed reference (dashed line) does not exhibit this effect. The amount of enthalpy that was recovered during reheating the samples is that which was released during the isothermal annealing. A measure of this recovered enthalpy is the area between the curve of the relaxed sample and the unrelaxed material. In Fig. 5, the measured recovered heat changes (▲) are plotted into an enthalpy diagram as a function of temperature starting from the enthalpy of the supercooled liquid (solid curve) in positive ΔH direction. This enthalpy of the supercooled liquid was determined independently in reference to the crystallized samples in a separate study [9]. Fig. 5 also reports the total change in the enthalpy during relaxation, ΔH_{total} (○), calculated for each isothermal

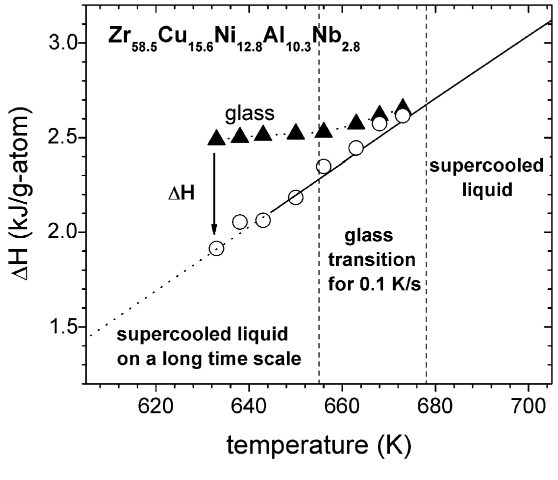

Fig. 5. Enthalpy diagram as a function of temperature for the supercooled liquid with respect to a crystalline mixture (continuous line; from Ref. [9]). The enthalpy change from the frozen-in amorphous state (▲) (measured from enthalpy recovery experiments) into the supercooled liquid state (○) (measured from relaxation experiments) are added to the diagram. The isentropic temperature T_K is assessed at 548 K in reference [9].

anneal experiment. This represents the reduction in enthalpy during relaxation as defined in Eq. (1) and it is plotted here starting from the amorphous alloy (▲) in negative ΔH direction. The lower the temperature the larger is the enthalpy release. It is interesting to note that the enthalpy release during relaxation does reach the extrapolated enthalpy of the supercooled liquid (solid line). The pathway of the relaxation is marked schematically by an arrow in the enthalpy diagram shown in Fig. 5. The reduction of the enthalpy during relaxation can be understood as the result of local rearrangements of the medium size atoms causing the reduction of the free volume that has been frozen-in throughout the glass transition. This equilibration towards the supercooled liquid state is associated with decrease in free volume and a further increase in short range order and thus a reduction in the entropy of the alloy.

4. Summary

The enthalpy relaxation of the $Zr_{58.5}Cu_{15.6}Ni_{12.8}Al_{10.3}Nb_{2.8}$ bulk metallic glass forming alloy was studied isothermally within the glass transition by means of calorimetric experiments. A novel experimental method was developed to study the enthalpy relaxation. The relaxation time is best fitted with the Arrhenius relation rather than the VFT equation. The activation energy of the enthalpy relaxation is comparable to the activation energy for the diffusion of the small and midsize atoms. The enthalpy relaxation, which is faster than the complete structural relaxation, therefore seems to be governed by the short-range diffusion of the midsize atoms.

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