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Densification-induced heat release upon structural relaxation of Zr-based bulk metallic glasses

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ABSTRACT

The investigation of the heat release related to the densification occurring upon structural relaxation of Zr-based metallic glasses has been performed. A linear relationship between the heat release and relative volume change has been determined. The data analysis provides further evidence for the mechanism of structural relaxation based on the relaxation of interstitialcy-like structural "defects" inherited from the melt.

1. Introduction

The density of metallic glasses (MGs) is usually by about 0.3–2% [1–3] smaller than that of their initial (maternal) crystalline alloys. It is therefore considered that MGs have certain amount of frozen-in excess volume – so called "free volume" usually denoted as Δv_f. Structural relaxation of MGs taking place upon ageing below the glass transition temperature T_g normally leads to the densification of structure [1–3]. This is understood as a decrease of Δv_f that changes many MGs' physical properties [4–6]. The free volume concept is currently very popular in describing relaxation phenomena in MGs [5,7,8] although it is criticized in several directions [8–11]. The free volume does not have any rigorous definition [6,10] and usually experimentally assessed from macroscopic measurements as $\Delta v_f = -\Delta V/V_0$, where V_0 and ΔV are the initial volume of glass and its change upon structural relaxation, respectively.

The densification upon structural relaxation below T_g is accompanied by the release of heat [1]. Van den Beukel and Sietsma suggested that this effect is conditioned by the free volume annealing [4]. They postulated the simplest linear relationship between the molar heat ΔH_μ released upon densification and the free volume Δv_f:

$$\Delta H_\mu = \beta \Delta v_f. \tag{1}$$

The proportionality coefficient β here represents a phenomenological parameter, which has no theoretical interpretation. Nonetheless, the linear dependence (1) was experimentally confirmed for Zr- [12–14], Au- [15] and Cu-based [16] bulk MGs.

On the other hand, computer simulation [17] gives the evidence that enthalpy changes during structural relaxation of metallic glasses cannot be solely determined by the free volume change. It was noticed that the enthalpy release upon structural relaxation is much larger than that expected from the total volume shrinkage of sample and many researchers have inaccurately attributed the calorimetry signals entirely to the free volume changes [6].

A fully different interpretation of the experimentally observed relationship (1) was recently suggested in Ref. [18]. It was argued that the densification and enthalpy release observed upon structural relaxation can be alternatively explained by the annealing of interstitialcy-like kinetic units ("defects") frozen-in upon glass production. This idea is based on the Interstitialcy theory [19,20], which assumes that melting of simple metals occurs through the rapid generation of interstitials in the dumbbell form (=interstitialcies) that was recently confirmed by careful experiments on aluminum single crystals [21]. These "defects" retain their individuality in the liquid state [22] and melt quenching

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freezes a part of them in the solid glass. The relaxation phenomena in glass are then interpreted as a change of the "defect" concentration. This approach provides consistent successful interpretation of various relaxation phenomena in metallic glasses (for a review, see Ref. [23] and papers cited therein). The heat release upon structural relaxation (as well as upon crystallization) within the framework of this approach is conditioned by the release of the elastic strain energy related to interstitialcy-like "defects" [18,24–26]. The analysis given in Ref. [18] shows that the experimentally observed linear relationship (1) should be preferably explained in terms of the relaxation in the system of interstitialcy-like "defects". According to this work, the derivative of molar enthalpy ΔH_μ released upon relaxation over the relative volume change $\Delta \upsilon_f$ is given as

$$\beta_{IT} = \frac{d\Delta H_\mu}{d\Delta \upsilon_f} = \frac{\left(1+\ \ln\dfrac{G}{\mu}\right) G V_\mu}{(\alpha_i - 1)}, \tag{2}$$

where α_i is the relaxation volume, which characterises the volume relaxation after creating an interstitialcy-like "defect", V_μ is the molar volume ($V_\mu = m_\mu/\rho$), G and μ are the shear moduli of glass and maternal crystal, respectively [18]. In line with the relationship (1), Eq. (2) implies that the molar heat ΔH_μ released upon structural relaxation linearly increases with a decrease of the relative volume $\Delta V/V_0$ of glass. The analysis [18] showed that Eq. (2) correctly explains detailed experimental data taken on Au-based bulk metallic glass [15].

In this work, we present an experimental investigation of the isothermal volume relaxation and related heat release for three Zr-based bulk metallic glasses. Using calorimetric and dilatometric data, we determined the experimental values of the coefficient β in Eq. (1) as well as its theoretical values given by Eq. (2). A good correspondence between the experimental and theoretical data is observed providing thus the evidence that the dilatation-induced heat release can be related to interstitialcy-like "defects" frozen-in upon glass production.

2. Methods

Bulk metallic glasses under investigation ($Zr_{47}Cu_{45}Al_7Fe_1$, $Zr_{46}Cu_{45}Al_7Ti_2$ and $Zr_{56}Co_{28}Al_{16}$ (at.%)) were prepared by melt suction into a copper mold. The samples were checked by X-ray diffraction to be fully amorphous.

The heat flow was measured by differential scanning calorimetry (DSC) using a TA DSC Q2000 instrument in flowing nitrogen atmosphere. The DSC signal was analysed in terms of the molar heat flow $\Delta W = W - W_0$, where W and W_0 are the current heat flow and initial heat flow at room temperature, respectively. The relative error of W-determination was estimated to be $\approx 0.05\%$. The glass transition temperatures determined at 3 K/min according to the onset of heat absorption were found to be 686 K, 672 K and 723 K for $Zr_{47}Cu_{45}Al_7Fe_1$, $Zr_{46}Cu_{45}Al_7Ti_2$ and $Zr_{56}Co_{28}Al_{16}$ glasses, respectively.

Isothermal volume relaxation due to structural relaxation was analysed by measuring samples' length change ΔL using a TA TMA Q400 instrument in flowing nitrogen atmosphere. The relative volume change was then calculated as $\Delta V/V_0 = 3\Delta L/L_0$, where L_0 is the length at the beginning of the isothermal annealing and ΔL is its change upon relaxation. The relative error of the volume determination was estimated to be $\approx 0.0005\%$. Dilatometric measurements were performed at temperatures $T_a = 523$ K, 623 K and/or 673 K depending on MGs' chemical composition. For all glasses, these temperatures are quite far below T_g.

Shear moduli of glass (G) and corresponding maternal crystal (μ) were measured by the electromagnetic acoustic transformation method (EMAT, see e.g. Ref. [23] for details). Neglecting the density changes (<1%) at any annealing temperature, the shear modulus of glass was determined as $G = G_0(1+g)$, where G_0 is the shear modulus at room temperature and $g = f^2/f_0^2 - 1$ is the relative shear modulus change with f_0 and f being the transverse resonant vibrating frequency (500–600 kHz) at room and annealing temperatures, respectively. The relative precision of transverse resonant frequency measurements was about 0.0005%. For room-temperature shear moduli of initial glasses we accepted $G_0 = 33.61 \pm 0.09$ GPa for $Zr_{47}Cu_{45}Al_7Fe_1$ and $Zr_{46}Cu_{45}Al_7Ti_2$ [27] and $G_0 = 33.89 \pm 0.05$ GPa for $Zr_{56}Co_{28}Al_{16}$ [27]. The shear moduli of corresponding crystals were calculated as $\mu = G_0(1+g_\mu)$, where $g_\mu = f_\mu^2/f_0^2 - 1$ with f_μ being the resonant frequency of the maternal crystal. For the crystalline state of MGs listed above, we found the room-temperature shear moduli of crystals (μ_0) to be 43.76 ± 0.18 GPa, 48.01 ± 0.18 GPa and 47.13 ± 0.12 GPa, respectively.

3. Results

Fig. 1 gives typical kinetic curves for the molar heat flow ΔW and relative volume change $\Delta V/V_0$ upon structural relaxation during 9 ks at the annealing temperature $T_a = 623$ K. One can see that both ΔW and $\Delta V/V_0$ quickly decrease with time. The inset in Fig. 1 shows that $\Delta V/V_0$ linearly decreases with the logarithm of time after a transient of about 1 ks. We present the data only for bulk $Zr_{47}Cu_{45}Al_7Fe_1$ glass, because the results for other temperatures and other glasses are quite similar.

To calculate the heat released during structural relaxation (i.e. ΔH_μ), one must integrate the $\Delta W(t)$-curve over the whole annealing time range. To do this, the absolute heat flow at the beginning of the isothermal annealing must be known. This quantity is hard to be correctly determined because of a transient in the DSC signal during switching from linear heating to an isotherm. Therefore, it is not possible to use Eq. (1) directly for the determination of β. However, we found an easy way to solve this problem and calculate β from isothermal experiments as follows.

The logarithmic time change of $\Delta V/V_0$ shown in the inset in Fig. 1 can be approximated as

$$\Delta V(t)/V_0 = \upsilon_0 + k_v \ln t, \tag{3}$$

where $k_\upsilon = \partial(\Delta V/V_0)/\partial \ln t$ and υ_0 can be accepted equal to $\Delta V/V_0$ at $t = 1$ s. Such "*lnt*-kinetics" is typical for the relaxation of different physical properties of metallic glasses during structural relaxation well below T_g [28,29]. Then, one can accept similar kinetics for the molar enthalpy, i.e.

$$H_\mu(t) = H_0 + k_H \ln t, \tag{4}$$

where $k_H = \partial \Delta H_\mu/\partial \ln t$ and $H_0 = H_\mu(t=1)$.

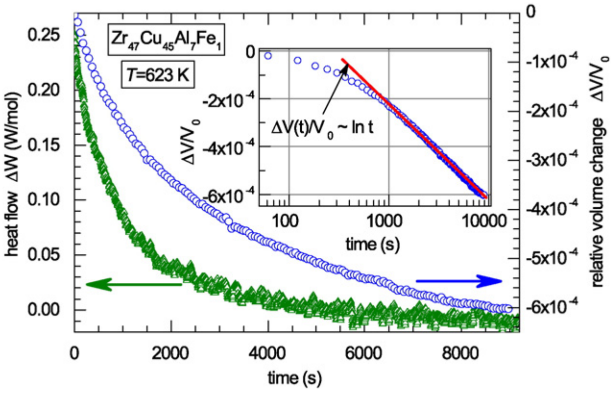

Fig. 1. Heat flow ΔW and relative volume change $\Delta V/V_0$ of bulk glassy $Zr_{47}Cu_{45}Al_7Fe_1$ during isothermal annealing at $T = 623$ K. The inset gives the relative volume change on the logarithmic time scale, which shows that $\Delta V/V_0$ logarithmically decreases with time. The errors of ΔW- and $\Delta V/V_0$-measurements are determined by the data scatter.