



Interrelationship between heat release and shear modulus change due to structural relaxation of bulk metallic glasses



Yu.P. Mitrofanov ^a, D.P. Wang ^b, W.H. Wang ^b, V.A. Khonik ^{a,*}

^a Department of General Physics, State Pedagogical University, Lenin St. 86, Voronezh 394043, Russia

^b Institute of Physics, Chinese Academy of Sciences, Beijing 100190, PR China

ARTICLE INFO

Article history:

Received 5 January 2016

Received in revised form

23 March 2016

Accepted 25 March 2016

Available online 30 March 2016

Keywords:

Metallic glasses

Relaxation

Shear modulus

Interstitial defect

ABSTRACT

Within the framework of the Interstitialcy theory it is shown that the amount of heat released during structural relaxation of metallic glasses must be proportional to the room-temperature change of the shear modulus. This prediction is verified by using experimental data taken on seven bulk metallic glasses. It is found that the kinetics of exothermal heat flow upon structural relaxation is determined by shear modulus relaxation. The released heat per one kinetic relaxation unit (“defect”) for all glasses practically coincides with the “defect” formation enthalpy calculated using the Interstitialcy theory providing further support for the description of structural relaxation on the basis of this approach.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Structural relaxation (SR) of metallic glasses (MGs) below the glass transition temperature T_g leads to a decrease of the enthalpy, which is detected by differential scanning calorimetry (DSC) as exothermal heat flow. In spite of decades-long investigations, the nature of this effect remains a matter of debates. A popular interpretation of this phenomenon is based on the free volume model, which assumes that the enthalpy decrease originates from the annihilation of the excess free volume frozen-in upon glass production. This approach postulates a linear relationship between the changes of the enthalpy and volume induced by SR [1]. Such a relationship was experimentally documented on Zr- [2–4], Cu- [5] and Au-based [6] bulk MGs. However, any quantitative theoretical interpretation of this dependence is still lacking. Computer simulations [7] show that the enthalpy relaxation cannot be solely ascribed to the volume change. It was also argued [8,9] that the elastic energy related to the volume change is much smaller than the experimental heat release and, therefore, the dilatation must play a minor role in the observed enthalpy change. Nonetheless, the free volume-based notions are quite popular in describing relaxation phenomena in MGs [10–12]. From the phenomenological

viewpoint, the kinetics of volume and enthalpy relaxation are often described by stretched exponential Kohlrausch-Williams-Watts function [13,14].

On the other hand, there are both experimental and theoretical indications that all heat effects in bulk MGs – heat release below T_g , heat absorption above T_g and crystallization-induced heat release – are determined by the macroscopic shear elasticity [8,9,15–19]. These works strongly support the relaxation of interstitialcy-type kinetic units (“defects”) as the underlying mechanism responsible for the enthalpy change in agreement with the Interstitialcy theory [20–22]. Meanwhile, the instantaneous shear modulus G (i.e. G measured during the time much smaller as compared with the characteristic time of SR) is the key physical quantity controlling the enthalpy relaxation. It was found within the framework of this approach that the heat flow W (i.e. the heat per unit time and unit mass) occurring upon warming-up of glass is controlled by the shear moduli of glass and parent crystal and can be expressed as [15].

$$W(T) = \frac{\dot{T}}{\rho\beta} \left[\frac{G_{rt}}{\mu_{rt}} \frac{d\mu(T)}{dT} - \frac{dG(T)}{dT} \right], \quad (1)$$

where \dot{T} is the heating rate, β is the dimensionless shear susceptibility, ρ is the density of glass, G , G_{rt} and μ , μ_{rt} are the shear moduli of glass and parent crystal at a temperature T and room temperature, respectively. It was determined that Eq. (1) gives a good

* Corresponding author.

E-mail address: khonik@vspu.ac.ru (V.A. Khonik).

description of the kinetics of heat release and heat absorption both below and in the glass transition region (Refs. [15–19]). It was later shown that a more general and more precise form of the heat flow kinetics can be obtained if the room temperature shear moduli in Eq. (1) are replaced by the shear moduli at current temperature T . The heat flow then becomes [23]

$$W(T) = \frac{\dot{T}}{\rho\beta} \left[\frac{G(T)}{\mu(T)} \frac{d\mu(T)}{dT} - \frac{dG(T)}{dT} \right]. \quad (2)$$

In this paper, Eq. (2) is used for the interpretation of heat release during SR for a number of BMGs. A simple relationship between heat release Q_{sr} and shear modulus change ΔG due to SR is found, which can be naturally described in terms of the Interstitialcy theory. It is also determined that the released heat per one kinetic relaxation unit (“defect”) for all glasses under investigation practically coincides with the “defect” formation enthalpy calculated within the framework of the Interstitialcy theory.

2. Heat release due to structural relaxation and related activation energy spectrum

Relaxation of the enthalpy of the initial glass is characterized by the heat flow W . After annealing of the initial glass above room temperature, the relaxed (preannealed) glass is described by the heat flow W_{rel} . The difference $\Delta W_{sr} = W - W_{rel}$ gives SR-induced heat release per mole,

$$Q_{sr} = \frac{m_\mu}{\dot{T}} \int_{T_0}^T \Delta W_{sr}(T) dT, \quad (3)$$

where m_μ is the molar mass and the low temperature integration limit T_0 corresponds to the beginning of the exothermal heat flow. On the other hand, Eq. (2) can be rewritten as

$$W(T) = \frac{\dot{T}G(T)}{\rho\beta} \frac{d}{dT} \ln \frac{\mu(T)}{G(T)}. \quad (4)$$

Using relationships (2) and (4), the exothermal heat flow $\Delta W_{sr}(T)$ can be calculated as

$$\Delta W_{sr}(T) = -\frac{\dot{T}\Delta G(T)}{\rho\beta} \frac{d}{dT} \ln \frac{\mu(T)}{\Delta G(T)}, \quad (5)$$

where $\Delta G(T) = G_{rel}(T) - G(T)$ with G and G_{rel} being the shear moduli of the initial and relaxed glass, respectively. With Eq. (5), the heat release Q_{sr} becomes

$$\begin{aligned} Q_{sr} &= \frac{m_\mu}{\rho\beta} \int_{T_0}^T \mu(T) d \left[\frac{\Delta G(T)}{\mu(T)} \right] = \\ &= \frac{m_\mu}{\rho\beta} \int_{T_0}^T \Delta G(T) \left[\frac{1}{\Delta G(T)} \frac{d\Delta G(T)}{dT} - \frac{1}{\mu(T)} \frac{d\mu(T)}{dT} \right] dT. \end{aligned} \quad (6)$$

The analysis of experimental data shows that the inequality $\frac{1}{\mu} \frac{d\mu}{dT} \ll \frac{1}{\Delta G} \frac{d\Delta G}{dT}$ is always fulfilled for all glasses under investigation, i.e. the temperature coefficient of the shear modulus of the parent crystal is negligible as compared with the temperature coefficient of the shear modulus change ΔG , which characterizes SR. Thus, Eq. (6) can be simplified as

$$Q_{sr} \approx \frac{m_\mu}{\rho\beta} \int_{T_0}^T d\Delta G(T) = \frac{m_\mu}{\rho\beta} [\Delta G(T) - \Delta G_0], \quad (7)$$

where $\Delta G_0 = G_{rel}(T_0) - G(T_0)$.

The difference between the shear moduli of as-cast and relaxed bulk MGs is absent above T_g (see, for example, Refs. [16,18]), and, therefore, $\Delta G(T) \rightarrow 0$ upon $T \rightarrow T_g$. Thus, if a glassy sample is heated from room temperature $T_0 = T_{rt}$ up to T_g then the heat Q_{sr} released during SR can be calculated as

$$Q_{sr} = -\frac{\Delta G_{rt} V_\mu}{\beta}, \quad (8)$$

where $V_\mu = m_\mu/\rho$ is the molar volume and $\Delta G_{rt} = \Delta G_0$ is the difference between shear moduli of initial and relaxed glass at room temperature. Equation (8) shows that the linear relationship between the released heat and shear modulus change multiplied by the molar volume must be observed.

Structural relaxation of MGs is widely accepted to occur with a distribution of underlying activation energies [22,24]. Using Eq. (1), we have suggested a procedure of deriving the activation energy spectrum (AES) of structural relaxation [25]. Taking into account the refined heat flow law (2), this procedure has to be revisited as follows.

The concentration Δc_{sr} of “defects” annealed out during SR is $\Delta c_{sr} = c_{rel} - c$, where c and c_{rel} is the concentration of “defects” in the initial and relaxed glass, respectively. Then, the AES becomes $n_0 = \frac{d\Delta c_{sr}}{dE_0}$ with $E_0 = AT$ being the characteristic activation energy at $\dot{T} = const$, where the parameter A weakly depends on the heating rate and attempt frequency [26]. Then, the SR-induced heat flow ΔW_{sr} can be rewritten as

$$\Delta W_{sr}(E_0) = \frac{\dot{T}A\mu(E_0)}{\rho\beta} \frac{d}{dE_0} \frac{\Delta G(E_0)}{\mu(E_0)}. \quad (9)$$

The quantity ΔG can be calculated using the basic equation of the Interstitialcy theory [20,21], $G(T) = \mu(T) \exp[-\alpha\beta c(T)]$ (where the dimensionless $\alpha \approx 1$), as

$$\Delta G \approx -G_{rel}\beta\Delta c_{sr}. \quad (10)$$

With this equation, formula (9) can be rewritten:

$$\Delta W_{sr} = \frac{\dot{T}AG_{rel}}{\rho} \left[\frac{d\Delta c_{sr}}{dE_0} + \Delta c_{sr} \frac{d(\ln G_{rel}/\mu)}{dE_0} \right]. \quad (11)$$

We have analysed all experimental data derived for the present investigation and found that in all cases $\frac{d\Delta c_{sr}}{dE_0} \gg \Delta c_{sr} \frac{d(\ln G_{rel}/\mu)}{dE_0}$ and, thus, the second term in Eq. (11) can be exempted from further analysis. Therefore, the exothermal heat flow ΔW_{sr} can be simply determined from the AES:

$$\Delta W_{sr}(E_0) = \frac{\dot{T}AG_{rel}(E_0)}{\rho} n_0(E_0). \quad (12)$$

Eq. (12) gives a simple way for the calculation of the AES from the experimental DSC data as

$$n_0(E_0) = \frac{\rho}{\dot{T}AG_{rel}(E_0)} \Delta W_{sr}(E_0). \quad (13)$$

This equation is similar but not identical to the expression for the AES derived earlier in Ref. [25] on the basis of the simplified heat flow law (1). In this work, Eq. (13) is used to derive activation energy spectra of seven bulk MGs using DSC data.

Download English Version:

<https://daneshyari.com/en/article/1605882>

Download Persian Version:

<https://daneshyari.com/article/1605882>

[Daneshyari.com](https://daneshyari.com)