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Universal relationship between crystallization-induced changes of the shear modulus and heat release in metallic glasses

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ABSTRACT

It is widely known that crystallization of metallic glasses is accompanied by a strong heat release. Current literature considers this phenomenon in a general sense as a result of structural ordering and related decrease of the excess enthalpy. The only specific interpretation for the crystallization-induced heat release was recently suggested on the basis of the Interstitialcy theory and elastic dipole model. This work presents measurements of the heat release and changes of the shear modulus taking place upon crystallization of a series of Zr- and Pd-based metallic glasses. The analysis of the performed experiment provides further clear support for the interpretation of the heat release as a result of the disappearance of interstitialcy-like "defects" (elastic dipoles) frozen-in from the melt upon glass production and related dissipation of their elastic energy. Analytically, the heat release is controlled by the change of the shear modulus upon crystallization constituting thus a universal relationship between these quantities.

1. Introduction

It is a matter of general experiences that heat treatment of metallic glasses (MGs), as well as of all other glasses, leads to different kinds of heat effects. The first two of them are determined by structural relaxation within the glassy state, which defines *i*) heat release below the glass transition temperature T_g and *ii*) heat absorption above T_g in the supercooled liquid state. The third heat effect is conditioned by the crystallization of glass leading to a strong heat release [1,2]. The absolute magnitude of third effect is much bigger than that of the first two.

Meanwhile, the physical nature of all three heat effects remains so far unclear and constitutes a matter of extensive debates. A popular concept for the origin of aforementioned heat effects *i*) and *ii*) was proposed by van den Beukel and Sietsma [3] who considered that the heat effects in the glassy state are determined by the amount of the "free volume", which lead to either heat release or heat absorption depending on the relaxation kinetics. The concept, on the one hand, was supported by subsequent investigations [4–7] but, on the other hand, was criticized in several directions [8–13].

Another interpretation of the heat effects in MGs was recently suggested in Ref. [14]. It was considered that the heat release/absorption below and near T_g upon structural relaxation can be explained by annealing/creation of structural units ("defects") similar to dumbbell (split) interstitials (called interstitialcies) in simple metals. This idea is based on the Interstitialcy theory [15,16], which argues that melting of simple metals occurs through the rapid generation of interstitialcies. These defects are found in all basic monoatoimic crystalline structures [17–20] and their important role in melting was repeatedly noted in the literature [21–23]. Recent experiments [24] on aluminum single crystals provide strong support for this mechanism of melting, in close agreement with the predictions of the Interstitialcy theory. These "defects" retain their individuality in the liquid state and can be identified as "strings" [25] noticed many times in computer simulations of liquids and glasses [26,27]. It is said that strings resemble the signatures of interstitialcies in crystals [25,27,28]. Moreover, the string description of interstitialcies was accepted in the original version of the Interstitialcy theory [15]. The notion that the liquid state has a few percent of interstitialcy "defects" leads to a successful interpretation of certain properties of equilibrium and

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supercooled liquids [29,30].

Melt quenching freezes a part of these "defects" in solid glass. It can be then assumed that they preserve the same basic properties characteristic of the maternal crystalline state. Indeed, molecular dynamic simulation of non-crystalline copper shows that the structure contains nano-sized regions with particular internal strain fields and low frequency vibration modes fully analogous to those created by interstitialcies in crystalline Cu, although these regions cannot be identified as certain topological elements [31,32]. A number of relaxation phenomena in MGs were successfully described assuming that heat treatment leads to a change of the concentration of interstitialcy-like "defects" frozen-in from the melt (for a review, see Ref. [33]). In particular, any change of the "defect" concentration results in the release/absorption of the "defect" formation enthalpy leading to the heat effects mentioned above that can be described analytically [33–35]. It was suggested and verified that this approach explains the amount of the heat released upon crystallization of MGs [36,37] and, moreover, provides an impressively exact description of the crystallization heat release kinetics [38]. This implies that the nature of the heat effects occurring upon structural relaxation and crystallization of MGs is determined by the elastic energy related to interstitialcy "defects", which dissipates as heat upon structural relaxation (below T_g) and crystallization. In the glass transition region, the amount of interstitialcy "defects" increases that results in the heat absorption.

On the other hand, split interstitials represent a particular case of "elastic dipoles" – local atomic configurations with the point symmetry, which is lower than that of the surrounding material. The elastic dipoles interact with the applies stress and define certain amount of the frozen-in elastic energy. Any change of their concentration or energy (for example, due to a change of mutual orientation) then leads to the heat release or heat absorption. This conceptual framework was recently developed in Ref. [39] on the basis of the macroscopic theory of non-linear elasticity. It was found that it gives very similar analytical expressions for the heat effects as compared with the Interstitialcy theory, despite fully different starting points [37,39].

In this work, we measured the crystallization heat for several Zr- and Pd-based MGs and compared it with the change of the internal energy calculated using the Interstitialcy theory and elastic dipole model. A good correspondence between these quantities is found. The obtained results provide further strong support for the understanding of crystallization-induced heat release as the dissipation of the elastic energy related to the interstitialcy "defects"/elastic dipoles frozen-in from the melt upon glass production. Since both Interstitialcy theory and elastic dipole model imply that the crystallization heat release is controlled by the shear moduli of glass and maternal crystal, as verified for all MGs under investigation, one can distinguish certain universal relationship between these quantities.

2. Experimental

Glassy $Zr_{56}Co_{28}Al_{16}$, $Zr_{55}Co_{25}Al_{20}$, $Zr_{46}Cu_{45}Al_7Ti_2$, $Zr_{65}Al_{10}Ni_{10}Cu_{15}$, $Pd_{40}Cu_{30}Ni_{10}P_{20}$, $Pd_{41.25}Cu_{41.25}P_{17.5}$ and $Pd_{40}Ni_{40}P_{20}$ (at.%) produced by melt suction (Zr-based MGs) and melt jet quenching (Pd-based MGs) were chosen for the investigation. All glasses were checked by X-ray diffraction to be fully amorphous. Differential scanning calorimetry was performed using a Hitachi Exstar DSC 7020 instrument in flowing Ar atmosphere. Room-temperature shear moduli G_{rt} for the MGs under investigation in the initial state were taken from the references [14,40–44]. Temperature dependences of the shear modulus were determined by the electromagnetic acoustic transformation (EMAT) method (e.g. Ref. [45]) using $5 \times 5 \times 2$ mm^3 samples vibrating at resonant frequencies $f = 500–600$ kHz according to the relationship $G = G_{rt} \times f^2/f_0^2$ (i.e. neglecting the density changes of about 1%), where f_0 is the initial room-temperature transverse vibration frequency. The relative error in the determination of G/G_{rt} increased from about 10 ppm near the room temperature to ≈100 ppm near T_g. Shear modulus measurements were performed in vacuum ≈0.013 Pa.

3. Results

Differential scanning calorimetry scans for $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ glass taken as an example at a rate of 30 K/min are shown in Fig. 1, where *run 1* corresponds to the initial state. All three heat effects are observed: *i*) heat release below T_g (see the inset), *ii*) heat absorption above $T_g \approx 652$ K in the supercooled liquid region and *iii*) large crystallization heat release peak, which begins at ≈735 K and is centered at $T \approx 764$ K. *Run 2* represents featureless heat flow after the full crystallization obtained by heating up to 870 K. To exclude the effect of the instrument baseline, the difference between the heat flow observed in *run 1* and *run 2* was calculated, $\Delta W = W_{run1} - W_{run2}$, as shown in Fig. 1. DSC scans for other MGs under investigation show similar patterns and are not given here.

The crystallization heat was calculated as $Q_{cr} = \int_{T_1}^{T_2} \Delta W \, dT/\dot{T}$, where $\dot{T}$ is the heating rate, the temperatures T_1 and T_2 are taken just below and just above the crystallization peak, as exemplified by the arrows in Fig 1. The quantities Q_{cr} thus determined for all MGs under investigation are listed in Table 1.

Crystallization-induced change of the internal energy within the framework of both Interstitialcy theory and elastic dipole model is determined by the shear moduli of glass G and corresponding crystal μ. The precision of shear modulus measurements with the EMAT technique used in the present investigation increases with a decrease of the heating rate. For these measurements, we accepted the rate of 5 K/min (for PdCuNiP and PdNiP glasses) or 3 K/min (for all other MGs) as a compromise between the quality of the data and reasonable measurement time. On the other hand, we found that this rate is unacceptably low for DSC measurements because of the significant oxidation of small Zr-based samples (tens of milligrams) during long measurement runs and related rather strong change of the crystallization heat release. Thus, DSC measurements of Zr-based MGs were performed at high heating rates of 20 or 30 K/

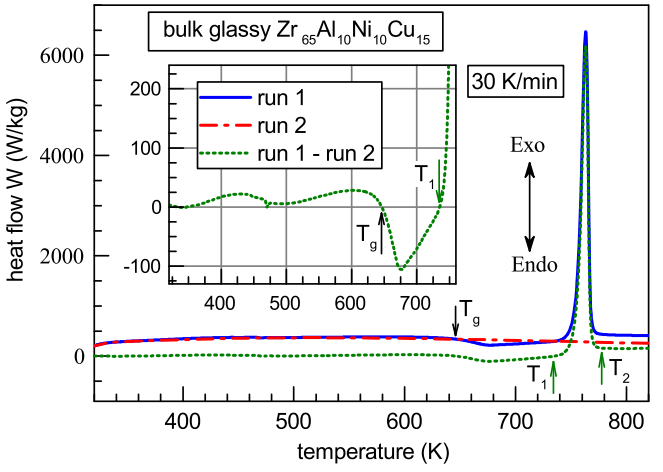

Fig. 1. DSC traces of glassy $Zr_{65}Al_{10}Ni_{10}Cu_{15}$ in the initial state (*run 1*), after full crystallization (*run 2*) and the difference between these runs. The inset gives shows this difference on an enlarged scale demonstrating the heat release below T_g. The vertical arrows just below and just above the crystallization peak indicate temperature positions of the integration limits, which were used to calculate the crystallization heat release. The glass transition temperature is also indicated.