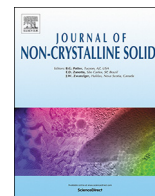




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Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Relationship between the heat effects and shear modulus changes occurring upon heating of a metallic glass into the supercooled liquid state

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ARTICLE INFO

Keywords:

Metallic glasses
Structural relaxation
Heat effects
Shear modulus

ABSTRACT

Precise measurements of shear modulus changes and heat effects occurring upon heating of bulk glassy $Pd_{40}Ni_{40}P_{20}$ from room temperature into the supercooled liquid region are performed. It is found the absorbed heat increases linearly with the shear modulus measured near room temperature, in excellent agreement with the prediction of the Interstitial theory.

1. Introduction

The non-crystallinity of glasses leads to spontaneous atomic rearrangements upon heat treatment. This phenomenon is generally referred to as structural relaxation (SR). In the case of metallic glasses (MGs), this phenomenon was documented long ago [1]. It was found that SR in certain cases leads to drastic changes of MGs' physical properties (e.g. viscosity [2], diffusivity [3]) within macroscopically non-crystalline state. Meanwhile, experimental manifestations of the SR remain a matter of extensive investigations hitherto [4,5,6]. The underlying reason is related to the fact that SR physical nature remains largely elusive and its understanding constitutes a challenging issue, which is important from both scientific and application viewpoints.

The most popular approach assumes that elementary SR atomic rearrangements take place in the regions of locally reduced density called "free volumes". This intuitively clear idea was suggested in the middle of the 80s of the past century [7,8] on the basis of earlier free volume model of plastic deformation of MGs [9] and has been used for the interpretation of experimental data so far [10] despite of the criticism in several directions [11,12]. Other approaches consider "defects" responsible for the SR as "shear transformation zones" [13], "soft zones" [14], "flow units" ("liquid-like regions") [15], "quasi-point defects" [16], elementary transitions between adjacent basins in the potential energy landscape [17], etc.

Amongst all other approaches to structural relaxation of MGs, one can separate the Interstitial theory (IT) [18,19], which assumes a generic relation of relaxation phenomena in MGs with the maternal

crystalline state. The IT argues that melting of metallic crystals is related to the rapid multiplications of interstitial defects in the most stable dumbbell form, in line with recent experimental observations [20]. These "defects" remain identifiable structural units in both liquid state [21] and glass produced by melt quenching [22] although they lose their geometrical image as two atoms trying to occupy the same potential well. Structural relaxation is then interpreted as a change of the concentration of these "defects" (we omit quotation marks hereafter). The IT-based approach gives a consistent understanding of quite a few SR-related phenomena in MGs, as reviewed in Ref. [23]. In particular, it was found that the IT gives impressively exact description of the heat release/absorption kinetics both for structural relaxation and crystallization [24]. It was also suggested that the excess internal energy of glass with respect to the maternal crystal is mainly controlled by the elastic energy of the interstitial defect system, which dissipates as heat upon SR below the glass transition temperature T_g and as well as upon crystallization [25]. Since changes of elastic energy are controlled by the instantaneous shear modulus, one should expect a relationship between heat release/absorption and changes of the shear modulus. Indeed, this relationship was confirmed in our previous works [26–29] for different experimental situations. In the present work, we employ the IT-based approach sketched above to analyse another type of experiments – measurements of the heat effects and shear modulus changes occurring upon heating of glass into the supercooled liquid region. Like in the previous cases mentioned above, we found the IT provides a good quantitative description of the experiment.

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<https://doi.org/10.1016/j.jnoncrysol.2018.06.044>

Received 28 May 2018; Received in revised form 28 June 2018; Accepted 30 June 2018

0022-3093/ © 2018 Published by Elsevier B.V.

2. Experimental details

We performed experiments on prototypical non-crystalline $Pd_{40}Ni_{40}P_{20}$ (at.%), which was studied earlier in many works (e.g. Ref. [30]) and can be considered as a model glass. The initial molten alloy was treated in B_2O_3 flux and then quenched by the melt suction method. The non-crystallinity of samples was verified by X-rays. Calorimetric measurements were performed using a Hitachi DSC 7020 instrument operating in flowing high purity (99.999%) N_2 atmosphere. The instrument was calibrated by using melting temperatures and enthalpies of pure (99.99%) In, Sn, Pb and Al. Measurements were performed in aluminum pans on 40–60 mg samples. Measurements of the shear modulus were carried out by the electromagnetic acoustic transformation (EMAT) method [31]. The advantage of this method consists in the absence of acoustical contact between the sample and exciting/receiving coils. The transverse resonant vibration frequency f (450–550 kHz) of sample ($5 \times 5 \times 2$ mm³) was determined as the frequency corresponding to the maximum of the shear vibration amplitude upon frequency scanning. Measurements of the vibration frequency were automatically performed every 10–20 s depending on temperature. The error of these measurements gradually increased from about 5 ppm far below T_g up to ≈ 100 ppm in the supercooled liquid state. The shear modulus was calculated as $G = G_{rt} f^2 / f_0^2$, where $G_{rt} = 38.6$ GPa is the initial room-temperature shear modulus of the glass under investigation [32] and f_0 is the initial room-temperature transverse vibration frequency. This way of G -calculation ignores possible density change occurring upon SR, which can be estimated to be at most 0.5% and, therefore, the maximal possible error in the calculation of G is about the same. The heating rate in calorimetric and shear modulus measurements was accepted to be 3 K/min as a compromise between a rate low enough for precise measurements of the shear modulus and a rate high enough to derive heat flow data at a good precision.

3. Theoretical background

The excess internal energy (per unit mass) of glass with respect to the maternal crystal (which the glass was produced from) within the framework of the IT is determined by the shear moduli of glass and maternal crystal, i.e. [25]

$$\Delta U = \frac{1}{\beta\rho}(\mu - G), \quad (1)$$

where G is the instantaneous shear modulus of glass, μ is the instantaneous shear modulus of the maternal crystal, the dimensionless shear susceptibility β constitutes an integral parameter relating the shear softening (reduced shear modulus of glass), heat effects, anharmonicity of interatomic interaction with the defect structure of glass and ρ is the density. If glass is heated from room temperature T_{rt} to a temperature $T_{sql} > T_g$ in the supercooled liquid region, the corresponding internal energy difference with the help of Eq. (1) can be written down as $\Delta(\Delta U) = \frac{1}{\beta\rho}(G_{T_{rt}} - G_{T_{sql}} - \mu_{T_{rt}} + \mu_{T_{sql}})$, where the room temperature shear modulus $G_{T_{rt}}$ is dependent on thermal prehistory (i.e. on the degree of SR) while the moduli in the crystalline state $\mu_{T_{rt}}$ and $\mu_{T_{sql}}$ depend only on temperatures T_{rt} and T_{sql} , respectively. Since the shear moduli curves of glass merge above T_g (as exemplified below in Fig. 1), the shear modulus $G_{T_{sql}}$ in the supercooled liquid state also depends only on temperature T_{sql} . This is determined by the fact that glass loses the memory of thermal prehistory in the supercooled liquid state and its properties are determined only by temperature, as evidenced, for instance, by the recovery (rejuvenation) of the properties of differently preannealed samples upon multiple quenching from temperatures above T_g [33]. On the other hand, heating from T_{rt} to T_{sql} results in certain integral heat effect Q , which generally includes both heat release and heat absorption. The former component originates from a

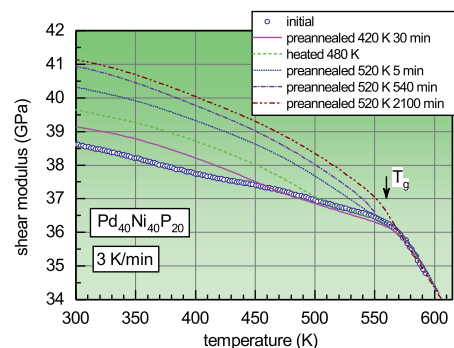


Fig. 1. Temperature dependence of the shear modulus of bulk glassy $Pd_{40}Ni_{40}P_{20}$ in the initial state and after indicated heat treatments. Calorimetric glass transition temperature is shown by the arrow.

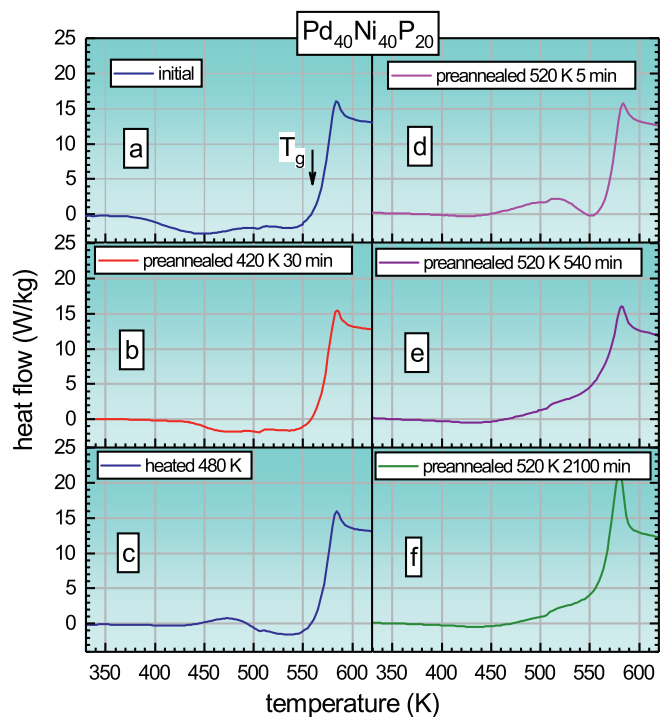


Fig. 2. DSC traces for the samples after the same annealing treatments as those applied for shear modulus measurements shown in Fig. 1.

decrease of the defect concentration leading to a release of their formation enthalpy and corresponding exothermal heat flow (see Fig. 2a below). Exothermal heat flow upon continued temperature increase is changed into heat absorption in the supercooled liquid region (see Fig. 2 below), which is related to an increase of the defect concentration, as discussed earlier [26,29].

Since the contribution of volume changes into the internal energy upon SR is small and can be neglected [34], one can accept that the change of the internal energy $\Delta(\Delta U)$ constitutes the total heat Q occurring due to heating $T_{rt} \rightarrow T_{sql}$, i.e.

$$Q \approx \frac{1}{\beta\rho}(G_{T_{rt}} - G_{T_{sql}} - \mu_{T_{rt}} + \mu_{T_{sql}}). \quad (2)$$

Since, as mentioned above, the moduli $G_{T_{sql}}$, $\mu_{T_{rt}}$ and $\mu_{T_{sql}}$ are independent of thermal prehistory, Eq. (2) shows that the heat Q should be a linear function of the room-temperature shear modulus $G_{T_{rt}}$ with the slope $dQ/dG_{T_{rt}} = \frac{1}{\beta\rho}$ and the intercept equal to $(-G_{T_{sql}} - \mu_{T_{rt}} + \mu_{T_{sql}})/\beta\rho$. It is this prediction given by Eq. (2), which is checked in this work.

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