



On the origin of heat effects and shear modulus changes upon structural relaxation and crystallization of metallic glasses



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ABSTRACT

It is well known that structural relaxation below the glass transition and crystallization of metallic glasses are accompanied by the heat release and increase of the shear modulus. In the present work, these effects are studied in detail for sixteen Zr-, Pd- and La-based metallic glasses and analyzed within the framework of the Interstitialcy theory. The obtained results imply that the increase of the shear modulus and heat effects occurring upon structural relaxation and crystallization are conditioned by the same mechanism – a change of the elastic energy related to the system of interstitialcy defects frozen-in upon glass production. In particular, the heat of crystallization constitutes a direct manifestation of the dissipation of the elastic energy related to this defect system, which disappears upon crystallization.

1. Introduction

The non-equilibrium nature of metallic glasses (MGs) results in the two pronounced phenomena occurring upon annealing – structural relaxation and crystallization. The basic experimental features of these phenomena were determined long ago [1]. Structural relaxation takes place upon ageing below the glass transition temperature T_g and affects the structural parameters of the non-crystalline state leading to certain variations of different MGs' physical properties – internal energy [2], density, elastic constants and internal friction [3], shear viscosity [4], electrical resistivity [5], magnetic properties [6], etc. Heat treatment below T_g in the supercooled liquid state or at higher temperatures results in the formation of multi-phase [1] or single-phase [7] crystalline structures. Compared to structural relaxation, crystallization results in much more severe changes of the physical properties [1].

There are quite a few different approaches on the physical nature of processes responsible for structural relaxation. Most often, structural relaxation of MGs is considered to be a result of a change of the concentration of certain structural “defects” like free volumes [8,9], shear transformation zones [10], soft zones [11], flow units (liquid-like regions) [12], quasi-point defects [13], quasi-nearest atoms [14], elementary transitions between adjacent basins in the potential energy landscape [15], etc. All these approaches do not assume any relationship of the “defects” with crystallization processes. An exception is presented by Gulzar et al. [16] who found a phenomenological relationship of flow units concentration with crystallization kinetics.

The only approach known to us, which traces a genetic relationship between the properties of glass, its structural relaxation/crystallization and properties of the maternal crystal, is given by the Interstitialcy theory (IT) [17,18]. The IT argues that melting of metallic crystals is related to the rapid generation of interstitial defects in the dumbbell (split) form called interstitialcies, in line with recent experimental data on pure aluminum and indium [19,20]. These defects remain identifiable structural units in the liquid state [21] and freeze in the solid glass produced by melt quenching. Computer modelling shows that while these “defects” in the melt or glass do not have any clear geometrical pattern (like two atoms trying to reside the same lattice site in simple crystals) they nonetheless display all properties characteristic of dumbbell interstitials in crystalline metals – strong sensitivity to the external shear stress, distinctive local shear strain fields and characteristic low- and high frequency modes in the vibration spectra of atoms constituting the “defects” [22,23]. Structural relaxation of glass is then considered as a change of the concentration (or energy state) of these interstitialcy-type “defects”, which inherit the properties of dumbbell interstitials in the maternal crystal. It was found that this general concept provides a quantitative description for quite a few phenomena related to structural relaxation of MGs, as reviewed in Ref. [24].

However, further investigation showed that the IT-based approach can be applied not only to structural relaxation but to crystallization as well [25–28]. It is argued that crystallization of MGs is related to the dissipation of the elastic energy determined by the system of

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interstitialcy-type “defects” (interstitialcy defects thereafter) frozen-in from the melt upon glass production as suggested in Refs. [25,26]. These defects disappear upon crystallization and their elastic energy is released as the heat of crystallization. The convincing confirmation of this hypothesis was given in recent works, which showed that i) the kinetics of heat absorption/release both upon structural relaxation and crystallization of a metallic glass can be rather precisely described within the framework of the IT [27] and ii) the elastic energy of the interstitialcy defect system calculated within the framework of the IT coincides within the error with the heat of crystallization [28].

One of the basic parameters of the IT is the shear susceptibility $\beta = -\frac{1}{4G} \frac{\partial^2 G}{\partial \varepsilon^2}$ (G is the shear modulus and ε the applied shear strain [17]), which is directly related to the anharmonicity of the interatomic potential. This quantity also determines the shear softening of glass with respect to the maternal crystal and kinetics of heat release/absorption occurring due to a change of the defect concentration [25,28]. The shear susceptibility, therefore, constitutes a universal integral parameter of MGs [29]. The methods for the determination of this quantity suggested so far are related to the glassy state [29]. In the present work we measured the heat effects and shear modulus changes occurring upon heating for a number of MGs and, on this basis, independently derived the shear susceptibilities for structural relaxation and crystallization. It was found that these quantities coincide within the experimental uncertainties. Therefore, on the one hand, the shear susceptibility constitutes a physical parameter linking structural relaxation and crystallization of metallic glasses. On the other hand, this fact confirms the aforementioned hypothesis that both structural relaxation and crystallization of MGs are related to the same mechanism – thermoactivated change of the concentration (or energy state) of interstitialcy defects frozen-in upon glass production.

2. Experimental

Sixteen metallic glasses listed in Table 1 produced by melt suction (Zr- and La-based) and melt jet quenching (Pd-based) were chosen for the investigation. All glasses in the initial state as well as after structural relaxation obtained by heating into the supercooled liquid region (i.e. above the calorimetric glass transition temperature T_g) were checked by X-ray diffraction to be fully amorphous. Heating above the calorimetric crystallization onset temperature T_x by 70 to 100 K results in the fully crystalline state with no signs of the first diffuse X-ray halo characteristic of the initial glassy structure.

Differential scanning calorimetry (DSC) was performed using a

Hitachi DSC 7020 in flowing N_2 (99.999% pure) atmosphere. The instrument was calibrated using the melting points and enthalpies of 99.99% pure In, Sn, Pb and Al. The error in the calculation of heat effects did not exceed 3.5%. The baseline of the calorimeter for every measurement run was corrected by subtracting the heat flow of the fully crystallized sample obtained at the same heating rate of 3 K/min. Temperature dependences of the shear modulus were determined by the electromagnetic acoustic transformation (EMAT) method (see e.g. Ref. [27]) using $5 \times 5 \times 2 \text{ mm}^3$ samples vibrating at transverse resonant frequencies $f = 500\text{--}600 \text{ kHz}$ according to the relationship $G = G_0^{RT} \times f^2/f_0^2$, where f_0 and G_0^{RT} are the initial room-temperature vibration frequency and shear modulus, respectively. Changes of the density occurring upon structural relaxation and crystallization are ignored in this calculation. Since the relative error in the determination of the frequencies f and f_0 increased from about 10 ppm near the room temperature to ≈ 100 ppm near T_g , the total error in the determination of G/G_0^{RT} did not exceed possible density changes (0.5–2%). Shear modulus measurements were performed in vacuum $\approx 0.013 \text{ Pa}$ at a heating rate of 3 K/min.

3. Calculation of the shear susceptibility

The shear susceptibility of glass can be determined from the increase of the shear modulus and related heat release occurring upon structural relaxation using the method described in Ref. [30], i.e.

$$\beta_{rel} = \frac{\Delta G_{rel}}{\rho Q_{rel}}, \quad (1)$$

where $\Delta G_{rel} = G_{rel}^{RT} - G_0^{RT}$ is the room-temperature increase of the shear modulus due to structural relaxation (G_{rel}^{RT} is the room-temperature shear modulus after relaxation), Q_{rel} is the corresponding heat release and ρ is the density.

The change of the internal energy per unit mass ΔU due to crystallization of glass within the framework of the IT is given as $\rho \Delta U = \frac{1}{\beta_{cr}}(\mu - G)$, where G and μ are the shear moduli just before and after crystallization, respectively [28]. The shear susceptibility β_{cr} in this equation cannot be *a-priori* considered equal to the shear susceptibility β_{rel} in Eq. (1). Accepting the aforementioned hypothesis that the elastic strain energy of the interstitialcy defect system is released as the crystallization heat Q_{cr} , the last equation can be rewritten as

$$\beta_{cr} = \frac{\mu - G}{\rho Q_{cr}}, \quad (2)$$

Table 1

Parameters of MGs under investigation: density ρ , heat of crystallization Q_{cr} , shear modulus just before crystallization G , shear modulus after crystallization at the same temperature μ , heat of structural relaxation Q_{rel} , shear modulus G_0^{RT} , shear modulus G_{rel}^{RT} , shear susceptibility upon structural relaxation β_{rel} , shear susceptibility upon crystallization β_{cr} , shear susceptibility data taken from the literature β_{rel}^{lit} .

N	Glass (at.%)	ρ	Q_{cr}	G	μ	Q_{rel}	G_0^{RT}	G_{rel}^{RT}	β_{rel}	β_{cr}	β_{rel}^{lit}
		$\left[\frac{\text{kg}}{\text{m}^3} \right]$	$\left[\frac{\text{J}}{\text{g}} \right]$	[GPa]	[GPa]	$\left[\frac{\text{J}}{\text{g}} \right]$	[GPa]	[GPa]			
1	Zr ₆₅ Al ₁₀ Ni ₁₀ Cu ₁₅	6271 [34]	89.2	26.97 [28]	37.82	13.0	30.30 [34]	31.88	19.3	19.4	22.3 [29]
2	Zr _{52.5} Ti ₅ Cu _{17.9} Ni _{14.6} Al ₁₀	6730 [34]	68.3	30.19	37.54	16.6 [33]	32.30 [34]	34.05 [33]	15.6	16.0	16.0 [33]
3	Zr ₅₆ Co ₂₈ Al ₁₆	6500 [35]	86.2	30.98 [28]	40.83	13.0 [30]	33.89 [34]	35.36 [30]	17.4	17.6	16.5 [29]
4	Zr ₅₅ Co ₂₅ Al ₂₀	6220 [35]	89.0	32.88	42.44	15.76	36.13 [44]	37.81	17.1	17.3	16.0 [28]
5	Zr ₄₆ Cu ₄₅ Al ₇ Ti ₂	7020 [34]	59.6	29.79 [28]	37.93	12.3	33.61 [34]	35.26 [30]	19.2	19.5	21.1 [29]
6	Zr ₄₆ Cu ₄₆ Al ₈	7021 [36]	70.0	30.00	40.37	10.7 [30]	34.30 [36]	35.85 [30]	20.5	21.1	18.7 [29]
7	Zr ₄₆ (Cu _{4/5} Ag _{1/5}) ₄₆ Al ₈	7177 [37]	62.8	30.30	38.57	12.2	33.80 [36]	35.37	18.0	18.3	–
8	Zr ₄₈ Cu ₄₈ Al ₄	7220 [34]	56.8	28.90	36.77	7.8	32.40 [34]	33.47	19.0	19.2	–
9	Zr _{47.5} Cu _{47.5} Al ₅	7130 [34]	67.0	28.60	37.13	13.6	32.40 [34]	34.08	17.3	17.9	–
10	Zr ₄₇ Cu ₄₅ Al ₇ Fe ₁	7000 [34]	75.2	29.94	40.14	11.2	33.75 [34]	35.26	19.2	19.4	–
11	Pd _{41.25} Cu _{41.25} P _{17.5}	9400 [39]	62.0	27.03 [28]	39.67 [28]	5.7 [41]	32.70 [34]	33.76 [30]	19.7	21.7	20.7 [29]
12	Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	9280 [38]	83.7	25.48 [28]	40.83 [28]	8.7 [30]	33.60 [34]	35.00	17.3	19.7	19.3 [29]
13	Pd _{43.2} Cu ₂₈ Ni _{8.8} P ₂₀	9380 [40]	58.7	29.09	36.38	11.8	34.50 [42]	35.86	12.7	13.2	–
14	Pd ₄₀ Ni ₄₀ P ₂₀	9405 [32]	100.6	32.30	51.98	13.0	38.60 [34]	41.10	20.5	20.8	21.0 [30]
15	La ₅₅ Al ₂₅ Co ₂₀	5802 [34]	45.6	14.36	19.45	7.2	15.42 [34]	16.39	23.3	19.2	20.9 [29]
16	La ₅₅ Ni ₁₀ Al ₃₅	5498	75.4	14.00	20.58	7.5	15.29 [43]	15.94	15.7	15.9	–

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