Comment

On the nature of density changes upon structural relaxation and crystallization of metallic glasses

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A B S T R A C T

On the basis of the Interstitialcy theory, we suggest a quantitative explanation of density changes occurring upon structural relaxation and crystallization of metallic glasses.

1. Introduction

It is long well known that the density ρ of metallic glasses in the vast majority of cases increases upon annealing both due to structural relaxation taking place below the glass transition temperature T_g and crystallization occurring above T_g. While structural relaxation leads to an increase of ρ by about 0.1–0.5%, fully crystallized samples are by 0.3–3 % denser as compared with their initial state depending on chemical composition and production quenching rate [1–4]. Some Pd-, Mg- and Ce-based glasses, however, display anomalous behavior since their density *decreases* upon crystallization by up to 1% [5,6] or even more [7,8].

Density change reflects internal atomic rearrangements occurring in non-crystalline structure upon ageing and adequate understanding of their intrinsic nature constitutes a problem of major importance. The literature offers several approaches to this problem. Early interpretations ascribed density changes within the amorphous state to a variation of the topological short-range order [9] or decrease of the free volume (regions of reduced local packing density) frozen-in upon glass production [10]. However, any detailed understanding of density changes upon structural relaxation/crystallization within the framework of these notions was not achieved.

Wang and co-workers suggested a phenomenological "flow units" model, which implies the existence of "solid like" regions with closed-packed structure and "liquid like" defects "without stress resistance" [11]. Compared with the elastic matrix, these defects constitute groups of atoms exhibiting a lower packing density, a higher

energy dissipation rate and lower shear modulus. This concept was used for the interpretation of a number of different relaxation phenomena in metallic glasses [12–14]. In particular, it was applied to density changes observed upon structural relaxation [15] and crystallization [16]. A drawback of this model is that the defect concentration is derived not from a particular physical picture of relaxation but actually is determined by a flexible fitting function.

On the other hand, volume effects occurring upon structural relaxation and crystallization can be interpreted within the framework of the Interstitialcy theory suggested by Granato [17,18]. The theory assumes that melting of simple metallic crystals is related to the rapid multiplication of dumbbell interstitials (=interstitialcies), in line with recent experimental data [19,20]. These defects remain identifiable structural units in the liquid state [21] being now an integral part of the structure rather that its "defects" in the usual understanding of this term. Rapid melt quenching freezes some part of these defects (we omit quotation marks hereafter) in the solid glassy state and its structural relaxation is determined by thermoactivated change of interstitialcy-like defect concentration. Such an approach allows explanation of different phenomena related to structural relaxation of metallic glasses (for a review, see [22,23]). In particular, it gives an interpretation of the heat release due to structural relaxation-induced densification [25,26]. It was also suggested that the increase of the internal energy due to the non-crystallinity is basically related to the elastic energy of interstitialcy defects frozen-in upon glass production and the heat release upon crystallization can be considered as the dissipation of this energy [27,28]. This hypothesis was convincingly confirmed by

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recent experiments, which showed that all heat effects detected by differential scanning calorimetry including those taking place upon crystallization can be explained within the framework of the Interstitialcy theory [29,30].

The interpretation of volume changes using the Interstitialcy theory is based on the expected change of the volume ΔV upon creation of an interstitialcy defect, which can be represented as [24,25]

$$\frac{\Delta V}{\Omega} = -1 + \alpha_i, \tag{1}$$

where "-1" corresponds to the creation of an interstitialcy defect, α_i is the so-called relaxation volume, which reflects the relaxation of structure after defect creation and Ω is the volume per atom. Then, if a defect concentration c is created, the volume increases by ΔV and the relative volume change becomes

$$\frac{\Delta V}{V} = (\alpha_i - 1)\, c. \tag{2}$$

The relaxation volume α_i for close-packed metallic structures is estimated to be in the range 1.3 to 2 [24,25]. The concentration of frozen-in defects c can be determined from the main equation of the Interstitialcy theory, which relates it with the unrelaxed ($=$high-frequency) shear modulus G of glass [17,23],

$$G = \mu \quad \exp(-\alpha_g \beta c), \tag{3}$$

where μ is the shear modulus of the maternal crystal corresponding to $c = 0$, dimensionless α_g is the second invariant of interstitialcy defect strain field [28] and dimensionless shear susceptibility β is usually about 17 to 20 for metallic glasses [31]. Taking into account that $-\frac{\Delta V}{V} = \frac{\Delta \rho}{\rho}$ and combining Eq. (2) with Eq. (3), one arrives at the relative density change upon crystallization of glass,

$$\left(\frac{\Delta \rho}{\rho}\right)_{cryst} = \frac{(\alpha_i - 1)}{\alpha_g \beta}\, ln\frac{\mu}{G}, \tag{4}$$

where $\Delta \rho = \rho_{cryst} - \rho$ with ρ and ρ_{cryst} being the densities of glass and maternal crystal, respectively. Assuming $\alpha_g \approx 1$ [17], taking into account that the shear susceptibility β is known and α_i is a constant, it follows from Eq. (4) that the relative density change upon crystallization as a function of frozen-in defect concentration $c = \frac{1}{\alpha_g \beta} ln \frac{\mu}{G}$ should be a linear dependence with the slope equal to $(\alpha_i - 1)$. After a minor modification, Eq. (4) can be applied for structural relaxation in the glassy state. This route is employed in the present Letter. We analysed available experimental data on density and shear modulus changes and found that, indeed, Eq. (4) can be used for the understanding of volume change phenomena occurring upon structural relaxation and crystallization of metallic glasses.

2. Results

Let us first apply Eq. (4) to structural relaxation below T_g. Denote G_0 to be the initial room-temperature shear modulus of a sample measured after the first (very short) annealing at a temperature T_a and subsequent quenching to room temperature (T_{rt}). Let G is the room-temperature shear modulus of the same sample after further annealing (relaxation) at the same temperature T_a and quenching back to T_{rt}. Then, writing down Eq. (4) for the states characterized by the moduli G_0 and G and calculating the difference, one easily arrives at

$$\left(\frac{\Delta \rho}{\rho_0}\right)_{rel} \approx (\alpha_i - 1)\Delta c = \frac{(\alpha_i - 1)}{\alpha_g \beta}\, ln\frac{G}{G_0}, \tag{5}$$

where $\Delta \rho = \rho - \rho_0$, the densities ρ and ρ_0 correspond to the shear moduli G and G_0, respectively, and $\Delta c = \frac{1}{\alpha_g \beta} ln\frac{G}{G_0}$ is the change of the defect concentration due to annealing at the temperature T_a, which can be monitored by shear modulus measurements.

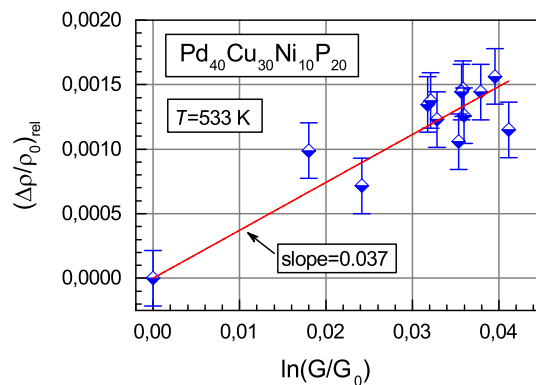Eq. (5) can be verified experimentally. To the best of our

Fig. 1. Dependence of the relative density change on the quantity $ln(G/G_0)$ (G_0 is the initial room-temperature shear modulus, G is the room-temperature shear modulus after certain annealing) upon structural relaxation of bulk glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ at $T = 533$ K. The data are calculated using density and shear modulus measurements by Harms et al. [32]. The error in $\Delta \rho / \rho_0$ corresponds to the error of original measurements [32] while the error along the abscissa does not exceed the symbols' size. The least square linear data fit drawn through the origin is shown.

knowledge, there is the only experiment described in the literature, which is suitable for this verification. This experiment was performed by Harms et al. [32] on bulk glassy $Pd_{40}Cu_{30}Ni_{10}P_{20}$. They subjected a sample to long-term annealing (up to 10,000 min) at $T = 533$ K (40 K below T_g and 140 K below the crystallization onset temperature). In the course of the annealing, the sample was periodically quenched to room temperature and precision density and shear modulus measurements by the resonant ultrasonic spectroscopy were performed. After each quenching and measurements, the sample was put back into the furnace, which was kept at the above temperature. In this way, the authors derived the dependences of the shear modulus and density as a function of the annealing time at $T = 533$ K.

The data on the shear modulus vs density obtained by Harms et al. [32] were digitized and converted to the form compatible with Eq. (5), i.e. as $(\Delta \rho / \rho_0)_{rel}$ depending on $ln\frac{G}{G_0}$. The obtained result is given in Fig. 1, which shows that this dependence can be quite well fitted by a linear function drawn through the origin (to ensure $\Delta \rho / \rho_0 = 0$ at $\Delta c = 0$), in accordance with Eq. (5). The slope of this dependence determined by the least-square fitting is found to be 0.037 ± 0.002 (0.97 adjusted r-square value).

The density changes given by Eq. (4) upon crystallization can be verified on metallic glasses of different chemical compositions. In order to check the linear functional form implied by this equation, it is reasonable to use the data taken for a glassy system based on the same metal since only in this case one can expect about the same value of the relaxation volume α_i. Amongst all metallic non-crystalline systems, zirconium-based glasses are most numerous and, therefore, most suitable for the analysis. Besides that, it is preferable to use the density and shear moduli data given by the same literature source because otherwise there occurs an uncontrolled scatter related to different production techniques (melt quenching rates), annealing treatments, amount of pores in samples, possible glass structure inhomogeneities, etc. However, we failed to find out a sufficient amount of experimental data on density and shear moduli changes upon crystallization in a single literature source. Therefore, the data taken on eight Zr-based metallic glasses from the papers by Wang et al. [4,33] (shear modulus measurements by the pulse echo overlap method) as well as our own experimental data taken on two other Zr-based glasses (shear modulus measurements by the electromagnetic acoustic transformation method) were accepted the for analysis.

The relative density change upon crystallization $(\Delta \rho / \rho)_{cryst}$ as a function of $ln\frac{\mu}{G}$ (G and μ are the room-temperature shear moduli of as-prepared glass and after full crystallization, respectively) for ten Zr-based glasses is shown in Fig. 2. The data points are notably scattered