



Theoretical analysis of the interconnection between the shear elasticity and heat effects in metallic glasses



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ABSTRACT

Changes of the shear modulus and heat effects occurring upon structural relaxation and crystallization of metallic glasses are analysed within the framework of two approaches, the interstitialcy theory and elastic dipole model. The former approach assumes that elastic and heat effects are determined by dumbbell interstitial defects inherited from the melt. The analysis within this framework is based on the postulate that the internal energy change is proportional to the shear modulus and defect concentration change. The elastic dipole model takes into account that dumbbell interstitials are in fact elastic dipoles and the change of the internal energy is determined by their elastic strain fields, which are considered within the framework of non-linear theory of elasticity. In spite of fully different phenomenology, both approaches lead to very similar theoretical expressions for the elastic and heat effects. The interconnection between these approaches, their advantages and problems are discussed.

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1. Introduction

It is well known that ageing of metallic glasses is accompanied by exothermal and endothermal heat effects and simultaneously leads to the changes of their shear elasticity [1–3]. These phenomena are observed both below the crystallization onset temperature and above it, i.e. in the range of structural relaxation within the glassy state as well as upon crystallization. While irreversible structural relaxation below the glass transition temperature T_g leads to the heat release, reversible structural relaxation near and above T_g results in either heat absorption (upon heating) or heat release (upon cooling) and crystallization is always accompanied by the heat release. Independent of the temperature range, heat release always leads to an increase of the shear modulus while heat absorption always results in its decrease [4,5]. In the literature, heat effects and shear modulus changes taking place within the glassy state are discussed using different approaches [1–3]. Heat release induced by crystallization is considered in a general sense as a consequence of lower internal energy of the reference crystal (i.e. the one, which was used for the glass production) [6]. Shear modulus growth upon crystallization is interpreted as the disappearance of additional internal atomic displacements, which are characteristic of non-crystalline state [6,7]. In any case, specific atomic mechanisms responsible for heat

effects and shear modulus changes occurring upon annealing of glass remain a subject of long-term debates.

A unified approach to these phenomena is suggested within the framework of the interstitialcy theory proposed by Granato [8,9]. While this theory was initially tested on FCC copper, it is now generally accepted that dumbbell (split) interstitials (= interstitialcies) exist in all main crystalline structures and represent the basic state of interstitials in simple metals [10,11]. The topological features of these defects in complex (two- or multiautomic) materials are quite similar [9] and, therefore, the theory is expected to be valid for alloys as well. Granato argued that melting of metals takes place through rapid multiplication of interstitialcy defects, which leads to a drastic decrease of the shear modulus and loss of the shear stability [8,9,12]. A vanishing shear modulus is a signature of liquid [13]. Interstitialcy defects retain their individuality in the liquid state [14] and can be considered as structural heterogeneities. The “string” atoms, which were repeatedly noticed in computer simulations of supercooled liquids and glasses [15,16], resemble the signatures of interstitialcies in crystals [14,17]. In crystals, the “string” character of interstitialcies is quite evident, since external loading brings into string-like motion several tens of atoms around the defect nucleus [18].

Melt quenching freezes a part of these defects in solid glass. Structural relaxation and crystallization are then interpreted as a change of the concentration of interstitialcy defects leading to an increase/decrease of the shear modulus and related exothermal/endothermal heat effects depending on temperature and preliminary heat treatment [4,5]. This

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conceptual framework offers qualitative and quantitative explanations for quite a few effects associated with structural relaxation and crystallization of metallic glasses (for a review, see Ref. [5]). In particular, it becomes possible to relate the heat effects occurring upon structural relaxation and crystallization of metallic glass with the relaxation of the shear modulus.

A fully independent but nonetheless closely related to the Interstitialcy theory approach to these issues was recently suggested in Ref. [19]. It is based on the fact that dumbbell interstitials represent a particular case of “elastic dipoles” — atomic configurations with the local symmetry lower than that of the surrounding matrix [20]. These defects create local internal strains, which lead to an increase of the internal energy, interaction with the applied shear stress and related shear softening of glass. The hypothesis on the presence of such defects in glassy structure leads to relatively simple equations connecting the changes of the internal energy (which can be released as heat) and shear modulus with the concentration of elastic dipoles. Special investigations revealed a good agreement of the calculation with the experimental data for both structural relaxation and crystallization of metallic glasses [4,19].

The purpose of the present work consists in *i*) comparative analysis of the results on the relationship between elastic and thermal effects in metallic glasses obtained within the framework of the Interstitialcy theory [8,9] and elastic dipole model [4,19] and *ii*) derivation of generalized interrelations based on the peculiarities and advantages of both approaches. Our main conclusion is that in spite of fully different starting points, these approaches lead to very close mathematical expressions, which describe the changes of the shear elasticity and heat effects in metallic glasses. The heat effects are intrinsically connected with shear modulus relaxation through the concentration of interstitialcy defects (or, equivalently, elastic dipoles). Within this framework, crystallization leads simply to the disappearance of these defects determining the change of the shear modulus.

2. Interstitialcy theory

The principal hypothesis of the Interstitialcy theory is that the change of the internal energy U per unit mass due to a change of the interstitialcy defect concentration c in a crystal can be accepted as [8,9]

$$\rho \partial U \approx \alpha G \partial c \quad (1)$$

where ρ is the density, α is a phenomenological dimensionless constant and G is the shear modulus. Eq. (1) implies that the change of the internal energy is dominated by the shear deformation. Using the definition of the shear modulus as the second derivative of the elastic energy with respect to the shear strain [21], Granato writes down the change of the shear modulus with the defect concentration in the form [8]

$$\frac{\partial G}{\partial c} = \alpha \frac{\partial^2 G}{\partial \varepsilon^2}, \quad (2)$$

where ε is the shear strain. The requirement that the shear modulus in crystal must be an even periodic function of the shear displacement in the simplest case leads to the relation $\frac{1}{4} \frac{\partial^2 G}{\partial \varepsilon^2} = -\beta G$, where β is dimensionless “shear susceptibility”. Since the second derivative of the shear modulus with respect to the shear strain represents the 4th-order shear modulus, the shear susceptibility is then equal to the ratio of this modulus to the shear modulus (i.e. to the 2nd-order shear modulus) taken with the opposite sign. A qualitative estimate of the shear susceptibility given by Granato is $4\pi^2$ [8]. Eq. (2) leads to the dependence of the shear modulus on the interstitialcy defect concentration [8,9],

$$G = \mu \exp(-\alpha\beta c), \quad (3)$$

where μ is the shear modulus of defect-free reference crystal. Using a numerical fit for copper, Granato estimated that $\alpha \approx 1$ [8]. It is seen that with β mentioned above, the dependence (3) gives a very strong decrease of the shear modulus with interstitialcy defect concentration. Eq. (3) actually constitutes the main equation of the Interstitialcy theory.

In general, the above consideration applies to the crystalline state. However, assuming that interstitialcy defects in glass are indeed inherited from the melt as sketched above, Eq. (3) can be applied to the glassy state. Then, the defect concentration can be precisely monitored by measurements of the shear modulus. It is also worthy of notice that Eq. (1) does not include any volume effects (dilatation) related to the defect structure.¹ This agrees with later works [4,19], which showed that the volume effects are indeed insignificant for the consideration of elastic and heat effects in metallic glasses.

The application of Eq. (3) for an analysis of structural relaxation of glass gives a number of successful interpretations of structural relaxation-induced phenomena in metallic glasses (see Ref. [5] for a review and related citations). Structural relaxation within the framework of this approach results in a change of the interstitialcy defect concentration, which through Eq. (3) alters the shear modulus while the latter defines the activation free energy for the relaxation in the defect structure. The defect concentration c then becomes dependent on temperature and thermal prehistory. The corresponding example is shown in Fig. 1, which gives defect concentration dependence in bulk glassy $Pd_{40}Ni_{40}P_{20}$ in the initial state (run 1) and after heating into the supercooled liquid region (run 2) [22]. In the initial state, c is about 2.3% (similar concentrations are typical of other metallic glasses [5]) and slowly decreases with temperature manifesting irreversible structural relaxation. At about T_g , c rapidly increases leading to a decrease of the shear elasticity and drop of the shear viscosity. Because of significant irreversible structural relaxation occurring after heating into the supercooled liquid region and cooling back to room temperature, the 2nd heating run starts at notably smaller c . It is interesting to note that due to large underlying relaxation time, the main part of irreversible structural relaxation takes place not upon heating, as one would expect, but upon cooling, as pointed out in Ref. [23]. Such a behavior is characteristic of metallic glasses [5]. It is also worthy of notice that quenching of glass to room temperature after certain heat treatment below and near T_g leads to the quenching of current defect concentration. It is then becomes possible using $c(T)$ dependence (Fig. 1) and Eq. (3) to predict the effect of high temperature annealing on room-temperature shear modulus of metallic glass [24].

Structural relaxation results in a change of the internal energy, which is manifested as heat effect. The latter can be calculated as follows. Combining Eqs. (1) and (3), one obtains the change of the internal energy,

$$\rho \Delta U = \frac{\mu}{\beta} [1 - \exp(-\alpha\beta c)] = \frac{\mu}{\beta} (1 - G/\mu). \quad (4)$$

It is seen that the increase of the internal energy is determined by the interstitialcy concentration, which is reflected by the shear modulus. In turn, a decrease of the defect concentration in glass leads to the release of the enthalpy H (per unit mass) defining the heat flow $W = \frac{dH}{dt} = \dot{T} \frac{dH}{dT}$, where t , T and \dot{T} are time, temperature and heating rate, respectively. Accepting the vanishing role of volume effects and taking into account Eq. (1), the heat flow at constant pressure becomes $W \approx \dot{T} \frac{dU}{dT} = \dot{T} \frac{\alpha G}{\rho} \frac{dc}{dT}$. Expressing the defect concentration from Eq. (3)

¹ Actually, Granato [8,9] considered the second term in Eq. (1), which reflects the changes of the elastic energy due to the dilatation upon interstitialcy concentration change. However, numerical fit for copper showed that this term can be neglected.

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