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Abstract

Mechanical and thermal properties of materials are intricately linked. Particularly, this fully applies to metallic glasses. In this work, we study shear modulus behavior and heat effects occurring upon warming up of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ high entropy bulk metallic glass up to the full crystallization. Applying the Interstitialcy theory, we show that shear modulus relaxation data can be used to quantitatively predict exo- and endothermal effects related to structural relaxation, glass transition and crystallization of this glass. This fact suggests that the underlying physical mechanism responsible for this link can be conditioned by the relaxation of the system of structural defects, which by their properties are similar to dumbbell interstitials in metals.

Keywords	High entropy metallic glass; Shear modulus; Heat effects; Relaxation; Interstitialcy theory; Mechanical properties

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Dear editor and the referees,

I would like to submit the manuscript entitled, ***"*Link between shear modulus and enthalpy changes of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ high entropy bulk metallic glass*"*** to be published in ***Intermetallics.***

Mechanical and thermal properties of materials are intricately linked. Particularly, this fully applies to metallic glasses. In this work, we study shear modulus behavior and heat effects occurring upon warming up of high entropy $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ bulk metallic glass up to the full crystallization. Applying the Interstitialcy theory, we show that shear modulus relaxation data can be used to quantitatively predict exo- and endothermal effects related to structural relaxation, glass transition and crystallization of this glass. This fact suggests that the underlying physical mechanism responsible for this link can be conditioned by the relaxation of the system of structural defects, which by their properties are similar to dumbbell interstitials in metals.

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Best wishes & sincerely yours,

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Research highlights

- We studied shear modulus behavior and heat effects of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ high entropy bulk metallic glass.
- All thermal effects are related to the alteration of shear modulus of metallic glass.
- The anharmonicity of interatomic potential plays a critical role in the thermal flow and shear softening.

Link between shear modulus and enthalpy changes of $\mathbf{Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}}$ high entropy bulk metallic glass

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Abstract

Mechanical and thermal properties of materials are intricately linked. Particularly, this fully applies to metallic glasses. In this work, we study shear modulus behavior and heat effects occurring upon warming up of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ high entropy bulk metallic glass up to the full crystallization. Applying the Interstitialcy theory, we show that shear modulus relaxation data can be used to quantitatively predict exo- and endothermal effects related to structural relaxation, glass transition and crystallization of this glass. This fact suggests that the underlying physical mechanism responsible for this link can be conditioned by the relaxation of the system of structural defects, which by their properties are similar to dumbbell interstitials in metals.

Keywords: High entropy metallic glass; Shear modulus; Heat effects; Relaxation; Interstitialcy theory

1. Introduction

It is a basic feature of metallic glasses that exothermal and endothermal heat flow occurring upon heating is reflected in their shear elasticity [1-3]. Successive processes observed upon heating correspond to i) heat release due to irreversible structural relaxation below the glass transition temperature T_g, ii) heat absorption caused by reversible structural relaxation near and above T_g and iii) heat release owing to crystallization of the metallic glass [4-6]. Exothermal heat effects result in an increase of the shear modulus while endothermal heat effects lead to shear modulus decrease [7, 8]. The changes of the shear modulus and thermal flow in metallic glass are discussed by in different ways in the literature [1, 3, 9].

However, despite decades-long investigations, many important issues associated with the shear modulus and heat flow of metallic glasses remain unresolved, especially in high entropy bulk metallic glasses (HEBMG). These issues are largely connected with a correlation between the macroscopic shear modulus and the energy landscape of metallic glasses. The high entropy state of metallic glasses generally assumes the existence of certain additional heat effects, which have not been reported in the literature so far.

The Interstitialcy theory proposed by Granato [10, 11] provides a promising approach for a solution of this problem. This theory proposes that the melting of metal crystals is related to the rapid increase of interstitial defects in the most stable dumbbell form (=interstitialcy), which results in a sharp decrease in the shear modulus and a subsequent loss of shear stability [10-12]. A small or vanishing shear modulus constitutes a signature of the liquid state [13]. In this state, interstitial defects maintain their individuality [14], a fact that can be considered as a part of structural heterogeneity, and their significant role in melting has been repeatedly mentioned in the literature [15-18]. However, these defects in the liquid and solidified glassy states do not show a clear characteristic image like in crystals (two atoms trying to occupy the same potential well) but nonetheless retain very similar properties (strong shear susceptibility, specific strain fields, high formation entropy as well as low- and high-frequency features in their vibration spectra [19]. In recent years, quite strong evidence has been shown that enthalpy changes of metallic glasses below the crystallization onset temperature and above it are related to the changes of the shear modulus of metallic glasses [20-23]. The underlying physical origin can be understood as a relaxation of the system of dumbbell interstitial-type defects, which can be also considered as elastic dipoles.

In this paper, the connection between the heat flow (rate of enthalpy changes) and shear modulus is tested on a $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG. The temperature dependence of the heat flow and shear modulus of the glass is determined experimentally. The heat flow is then computed using the shear modulus relaxation data within the framework of the Interstitialcy theory and compared to the calorimetric data, showing a good agreement. Thus, a new approach to understand the nature of heat effects and of interstitial-type defects through measuring shear modulus in high entropy metallic glasses is provided.

2. Theoretical background

The Interstitialcy theory is grounded on two main assumptions. First, a relation between the instantaneous shear modulus G and the defect concentration c is exponential, that is [10, 24]

$$\mathrm{G} = \mu \exp\left(-\alpha\beta c\right) \tag{1}$$

where μ is the instantaneous shear modulus of the maternal crystalline state of the glass. The dimensionless quantity α is related to the interstitialcy defect stain field [24], and is taken to be $\alpha \approx 1$ according to a numerical fit for copper performed by Granato [10]. The dimensionless parameter β accounts for the shear susceptibility, and for metallic glasses its value lies in the range 15-20, depending on their chemical composition [25]. With an increase of temperature, mechanical relaxation (α relaxation and β relaxation processes) occurs in metallic glasses, resulting in a change of defect concentration c. After full crystallization, the defect concentration c drops to zero, and the shear modulus G equals to μ as described by Eq. (1).

The second assumption relates the interstitialcy formation enthalpy H with the shear modulus[10, 26]

$$H = \alpha\Omega G \tag{2}$$

where α is the same parameter as in Eq. (1) and Ω is the volume per atom. According to Eq. (1), the increase or decrease of defect concentration c changes the shear modulus G, which modifies the interstitialcy formation enthalpy H in Eq. (2). Therefore, any change of the instantaneous shear modulus G results in a heat release or heat absorption. Then, differential scanning calorimetry (DSC) data can be correlated to the instantaneous shear modulus.

In this framework, the specific heat flow (rate of enthalpy changes per unit times and unit mass) caused by the change of defect concentration is given as [20, 27]

$$W = \frac{\dot{T}}{\rho\beta}\left[\frac{G(T)}{\mu(T)}\frac{d\mu}{dT} - \frac{dG}{dT}\right] \tag{3}$$

where $\dot{T} = dT/dt$ is the heating rate and ρ is the density of glass, $G(T)$ and $\mu(T)$ are the instantaneous shear modulus of glass and maternal crystal (i.e. the one, which was used for glass production), respectively.

Therefore, the relationship between the heat flow of the metallic glass and shear modulus changes (both due to the relaxation and anharmonicity) upon temperature scanning and thermal effects is revealed in Eq. (3). It was found that Eq. (3) shows a good characterization of the heat release in the as-produced glass below T_g and the heat absorption in the relaxed state near the glass transition in different metallic glasses [8, 21-23, 27]. Although the shear modulus of metallic glasses changes very quickly in the crystallization state, it was recently found that Eq. (3) can be also applied to the temperature range above T_g and the whole crystallization range [26]. We noticed that the Interstitialcy theory fits properly all the thermal effects of amorphous alloys upon heating: heat release below the T_g to structural relaxation, heat absorption in the glass transition region due, and heat release upon crystallization state.

3. Experimental procedure

The $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG studied in this work was produced by melt suction and all samples were checked to be entirely amorphous by X-ray diffraction. Differential scanning calorimetry (DSC) measurements were completed on a Hitachi DSC 7020 instrument in flowing high purity (99.99%) N_2. Measurements of the heat flow were performed in initial states – as quenched glass, relaxed states and fully crystallized states. In order to eliminate the uncertainty of the baseline in the DSC measurement, the heat flow of the fully crystalline sample was subtracted from the heat flow of the initial glassy sample.

The principle of shear modulus measurements performed in this work consists in the Lorentz interaction of the alternating surface current induced by the exciting coil with the external permanent magnetic field leading to the resonant shear vibrations of the sample. This electromagnetic acoustic transformation (EMAT) allows to determine temperature dependences of the shear modulus. The advantage of this method is that no direct acoustic contact between the sample and the exciting/signal coil is needed. The transverse resonance frequency f corresponding to the maximum shear amplitude during frequency scanning (about 450-550 kHz depending on heat treatment) was measured by the EMAT automatic system on 5×5×2 mm^3 samples. Measurements were automatically executed every 10-30 seconds as the temperature changed.

The absolute shear modulus was calculated as

$$G = G_0 \left[1 + g(T) \right] \tag{4}$$

where G_0 is the initial (i.e. at room temperature) shear modulus for $Ti_{20}Zr_{20}Hf_{20}Be_{20}(Cu_{10}Ni_{10})$ HEBMG taken from [28], $g(T)$ is the relative change of the shear modulus calculated as

$$g(T) = f_2 / f_0^2 - 1 \tag{5}$$

where f_0 and f are the resonant vibration frequencies at room temperature and current temperature T, respectively.

The absolute shear modulus *G(T)* calculated by Eq. (4), neglects the density variation (up to 1 %) that may occur during heating. The relative error of the absolute shear modulus *G(T)* obtained by this calculation method changed from about 5 ppm well below T_g to about 100 ppm at, near and above T_g. The heat flow was calculated by Eq. (3). The density of the glass $\rho = 8026 \frac{\mathrm{kg}}{\mathrm{m}^3}$ was determined experimentally with a Radwag AS 60/220/C/2 analytical balance. Shear modulus measurements were carried out in a vacuum of about 0.1 Pa. Both the heating/cooling rates of DSC and shear modulus measurements were $\dot{T}$=3 K/min.

The thermal processing protocol consisted in the following. DSC and EMAT measurements were initially performed on two as quenched samples heated up to 687 K, and these measurements are identified as the initial state or as quenched glass. The samples were then cooled to room temperature, but as a consequence of this first heating process the samples became thermally relaxed. DSC and EMAT measurement were then subsequently performed on these "relaxed" samples up to 870 K to ensure full crystallization. Measurements were eventually repeated on fully crystallized samples.

4. Results and discussion

Fig. 1(a) displays temperature dependences of the shear modulus G of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG in the initial, relaxed states and fully crystalline states. As temperature rises from room temperature to ≈500 K, the shear modulus G decreases linearly due to the anharmonicity of interatomic interaction. With a further increment of temperature, the shear modulus G tends to remain constant and next shows an increase due to structural relaxation, which corresponds to the heat release in Fig. 2. At about the glass transition temperature T_g =667 K (shown by the arrow in Fig. 2), the shear modulus G speedily decreases, as found also for other amorphous alloys [8, 23, 27]. The shear modulus G increases rapidly as crystallization begins at about T_x =706 K. Structural relaxation performed by heating up to 687 K (supercooled liquid state) results in about 6.6% increase of the room-temperature G upon subsequent heating (run 2). In the relaxed state, the behavior is reversible upon thermal cycling.

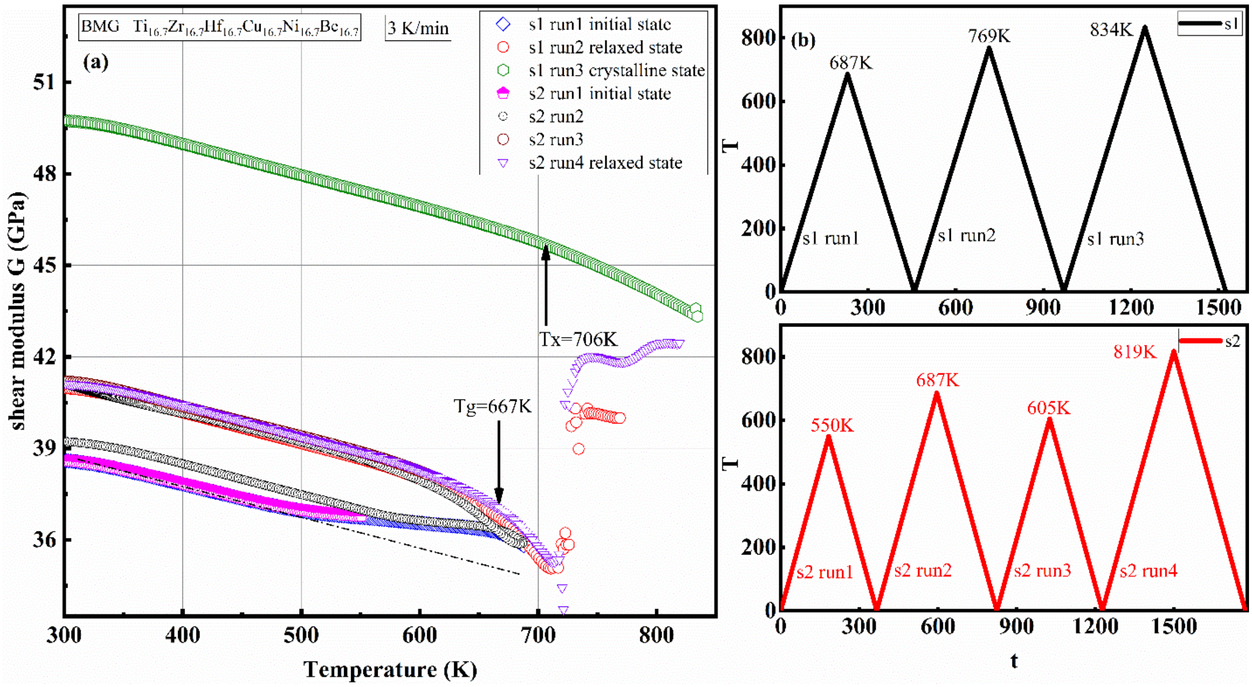

Fig.1 Experimental temperature dependences of the shear modulus G of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG in the initial states, relaxed states and crystalline states (a) and the corresponding annealing protocols for the samples 1 and 2 (b).

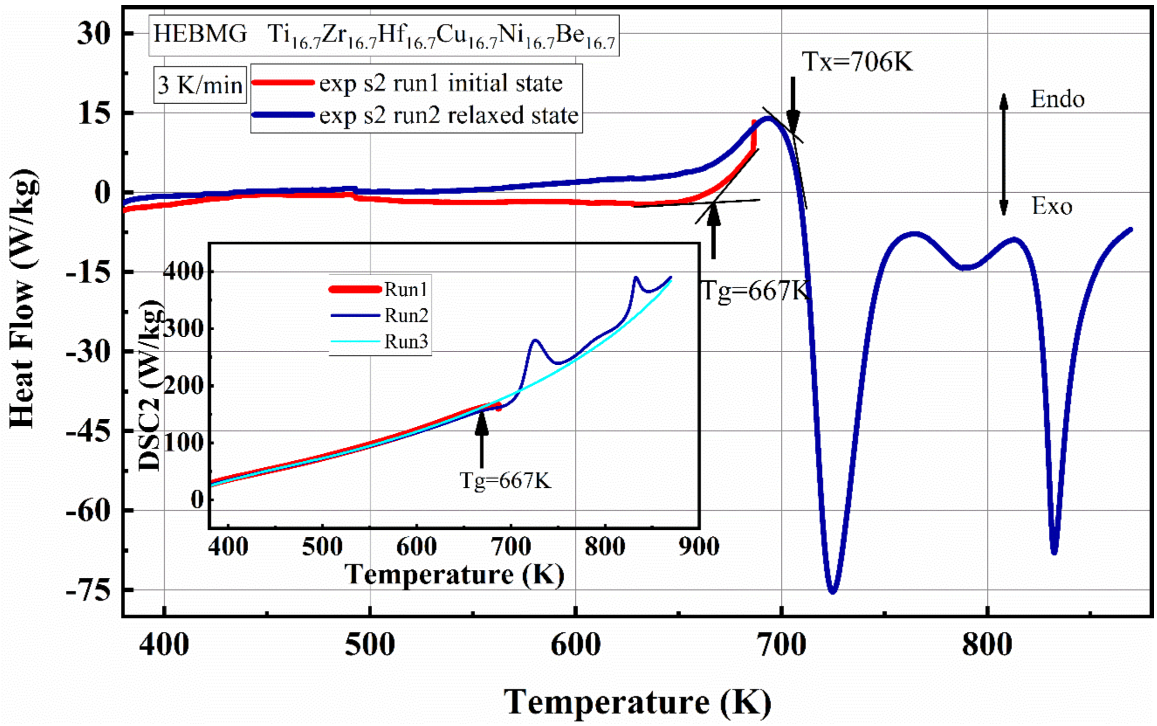

Fig.2 DSC traces of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG after the subtraction of the heat flow the fully crystallized sample. s2 run1: as produced sample; s2 run2: relaxed sample. The calorimetric temperatures T_g and T_x are indicated by the arrows. The inset presents the experimental DSC trails of the as-quenched glass (run 1), relaxed glass (run 2) and after full crystallization (run 3).

Fig. 2 shows the differential scanning calorimetry of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG for the as quenched state (run 1) and after relaxation (run 2). The inset in the figure shows the original DSC traces of both samples and also that of the fully crystallized sample (run 3). The as produced and relaxed glass show the typical features of amorphous alloys, while the fully crystallized sample is featureless. Therefore, the heat flow corresponding to the transformations of the glassy state is obtained by subtracting the thermal response of the fully crystallized sample. These heat flows are used for comparison with Eq. (3).

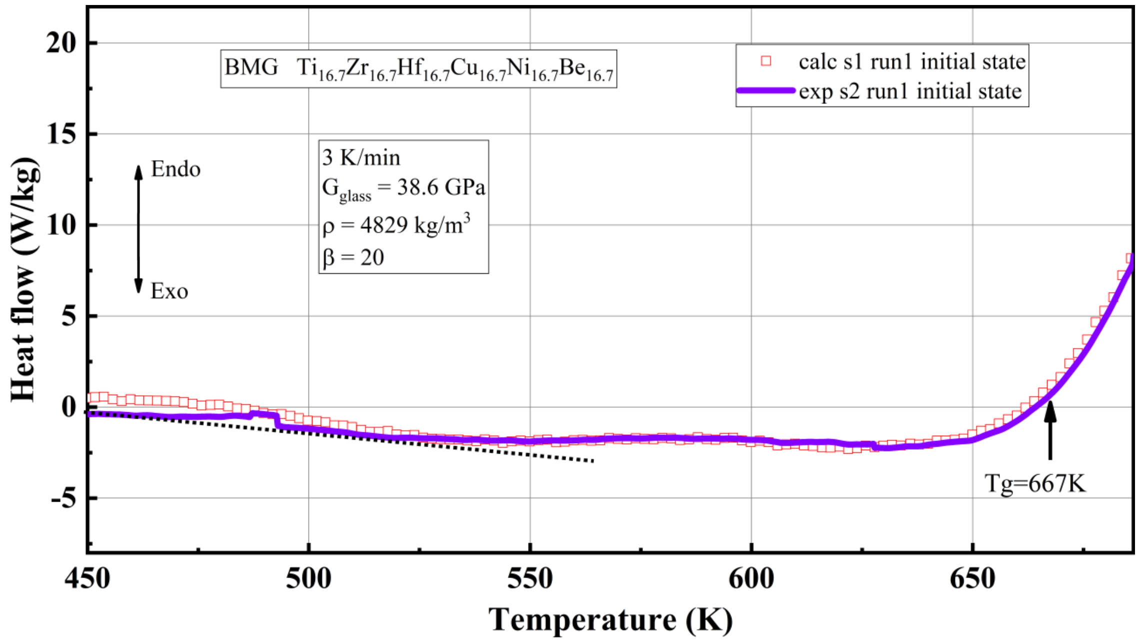

Fig. 3 Experimental and calculated using Eq. (3) temperature dependences of the heat flow of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG in the as quenched glass. The glass transition temperature is shown by the arrow.

The solid purple line in Fig. 3 shows the experimental heat flow obtained by DSC on the as quenched $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG. It can be clearly observed that the structural relaxation leads to the heat release corresponding to an increase of the shear modulus in the same range of 520 K < T < 660 K. The dotted red line in Fig. 3 displays the heat flow $W(T)$ computed by with Eq. (3) using the values indicated in the Experimental section and the data of $G(T)$ shown in Fig. 1. The shear susceptibility was obtained by a least-squares fit to the experimental heat flow curve resulting in a value of β=20 . This value is quite close to experimentally determined shear susceptibilities for other metallic glasses [21-23, 25, 27].

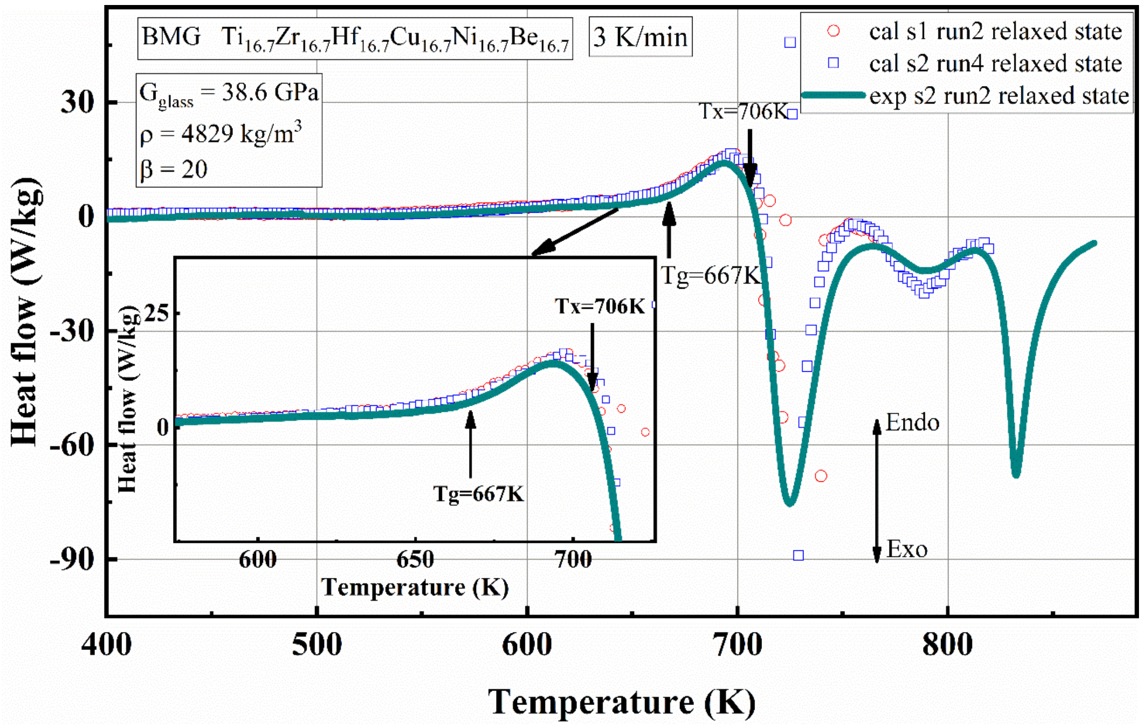

Fig. 4 Experimental and calculated using Eq. (3) temperature dependences of the heat flow for $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG in the relaxed states. The glass transition temperature is given by the arrow.

In contrast to Fig. 3, the solid dark cyan line in Fig. 4 illustrates the experimental heat flow of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG of the relaxed sample up to the complete crystallization. In this case, no exothermal heat flow is observed, as one would expect. The heat flow gradually changes to a strong heat absorption above T_g, and finally forms the crystallization heat release above T_x, which is a typical characteristic of metal glasses [29].

The calculation of heat flow of $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG in all temperature ranges is shown by the dotted lines in Fig. 4. The computation was performed using the same values for the parameters as in Fig. 3. It is seen that the calculation of heat flow using Eq. 3 provides a good description of experimental heat release below T_g, heat absorption in the glass transition region as well as the release upon crystallization. In particular, the temperature of crystallization heat release peak is consistent with the experiment, showing a difference of less than 4 K. As illustrated by Fig. 4, the calculation results also approximately represent the heat release on the second stage of crystallization at about 789 K.

In general terms, the Interstitialcy theory offers a promising verifiable method for the understanding of shear elasticity changes, heat effects as well as other relaxation phenomena occurring upon annealing below Tg, in the supercooled liquid state as well as upon crystallization (the latter can be also considered as a relaxation change of the structure) [30]. The method assumes that the melting of metallic crystals is related to the quick increase of dumbbell interstitials.

Interstitialcy defects constitute special "elastic dipoles" with local symmetry, which is lower than the local symmetry of the surrounding matrix [31]. These defects create internal stresses which interact with the external stress and determine a certain frozen-in elastic energy. In the liquid state, the defects keep their own characteristics and become an inherent part rather than a defect of the structure. Crystallization of the glass results in the reduction of "defect" concentration and corresponding dissipation of their elastic energy, which is detected as an enthalpy in DSC experiments. Therefore, the alteration of "defect" concentration i) can be precisely monitored by measurements of the shear modulus and ii) leads to temperature dependent heat flow. This is the main physical picture controlling the relaxation dynamics in metallic glasses within the framework of the Interstitialcy theory. A simple mathematical expression of the Interstitialcy theory in Eq. (1) constitutes a direct relationship between the interstitialcy defect concentration and the shear modulus of the glass and maternal crystal. The results show that this connection is consistent with the experimental data. The general heat flow law Eq. (3) of Interstitialcy theory directly shows that the temperature dependent heat flow is controlled by the evolution of the shear modulus, which in turn is driven by the concentration of the interstitialcy defects.

The experimental results of EMAT and DSC show that there is a fundamental relationship between the shear modulus and heat flow in $Ti_{16.7}Zr_{16.7}Hf_{16.7}Cu_{16.7}Ni_{16.7}Be_{16.7}$ HEBMG, both in the as quenched, relaxed, supercooled liquid and fully crystalline states. The valuable agreement of the temperature dependent heat flow with the temperature dependence of the shear modulus G gives the evidence that the heat flow during structural relaxation and crystallization of metallic glass are intrinsically linked to the relaxation of frozen-in interstitialcy defects. The heat release below T_g is caused by a decrease of shear concentration c, which corresponds to the increase of shear modulus of metallic glasses. The heat absorption above T_g is due to the growth of defect concentration, which is manifested as shear softening towards the metastable equilibrium [8]. The obvious decrease of the defect concentration at the first crystallization stage indicates the major heat release. However, since only a small part of interstitialcy defects in metallic glasses remain after that, there is a rather poor correspondence between the experimental and calculated heat flow data for the second crystallization stage.

5. Conclusions

Based on the Interstitialcy theory, an approach to reveal a relationship between the heat flow and shear modulus changes occurring upon structural relaxation and crystallization of metallic glasses is analyzed. All thermal effects of high entropy metallic alloy - heat release due to structural relaxation below the T_g, heat absorption in the glass transition region, and heat release in the crystallized state - are related to the alteration of shear modulus of metallic glass and the reference crystal during heating. The underlying physical reason can be understood as the relaxation of the internal dumbbell interstitial-type "defects" system. Since the shear susceptibility β entering the calculation of the heat flow using Eq.(3) is essentially anharmonic quantity, the Interstitialcy theory clearly indicates that the anharmonicity of the interatomic potential plays a critical role in the thermal flow and shear softening of high entropy amorphous alloys.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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