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Atomic-scale structural heterogeneity and elastic modulus for metallic glasses

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ABSTRACT

The role of atomic-scale structural heterogeneity (ASSH) in the elastic modulus for metallic glasses (MGs) is investigated. A strategy for estimating the strength of ASSH in MGs is proposed and then the fraction of ASSH is obtained. It is found that the fraction of ASSH could be the basic entities responsible for the change of elastic modulus during the change of composition and structure relaxation in MGs.

1. Introduction

As promising functional and structural materials, metallic glasses (MGs) possess excellent mechanical, magnetic, and chemical properties; and these unique properties are believed to be closely related to their disordered atomic structures [1–3]. It is, therefore, essential to study this disordered structure for better understanding and then tailoring these materials with desired properties [4]. Although MGs are isotropic and homogeneous on macroscale, recent studies have found the existence of the loose or weakly bound atoms in the oversized cages, voids, or similar defects, named as atomic-scale structural heterogeneity (ASSH) [5] besides short- and medium-range order clusters [6]. Such microstructure may affect the elastic deformation of MGs as well [7]. Some of the studies also suggest that the elastic deformation in MGs mainly occurs at solvent–solvent junctions among solute-centered clusters; and the elastic modulus is essentially determined by solvent–solvent bonding [8,9]. However, extensive experiments illustrate that the elastic modulus is very sensitive to the minor change of composition which may lead to the appearance of ASSH in MGs [10]. This induces the following interesting question: how does the ASSH affect the elastic modulus of MGs? It has been proven that the excess low frequency vibrational contribution appears as a bump in $C_{p,Latt}/T^3$–T curves ($C_{p,Latt}$ is the lattice specific heat and T is the temperature), which is significantly affected by structural heterogeneity in MGs [11–13]. Thus, the study of the excess low frequency vibrations may help understand the role of ASSH in elastic modulus for MGs. In this paper, we study $(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ ($x = 0.1$, 0.3, 0.5, and 0.7) to investigate the role of ASSH in elastic modulus for MGs. It will provide guidance for the substitution of an element for varying mechanical properties in MGs.

2. Experimental

$(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ ($x = 0.1$, 0.3, 0.5 and 0.7) and $(Fe_{0.5}Co_{0.5})_{72}B_{20}Si_4Nb_4$ MGs are prepared by arc melting the mixture of Fe (99.99%), Co (99.99%), Nb (99.99%) metals and B (99.50%), Si (99.99%) crystals in an argon atmosphere, $(Fe_{0.5}Co_{0.5})_{72}B_{20}Si_4Nb_4$ MG is annealed at 823, 873, and 923 K for 0.5 h in vacuum. Cylindrical alloy rods are produced by copper mold casting method [14]. The glassy nature is ascertained by X-ray diffraction (XRD), differential scanning calorimeter (DSC) and transmission electron microscopy (TEM). The isobaric low temperature specific heat C_p of as-cast $(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ ($x = 0.1$, 0.3, 0.5, and 0.7) MGs and annealed $(Fe_{0.5}Co_{0.5})_{72}B_{20}Si_4Nb_4$ metallic glass (MG) are measured by the Physical Property Measurement System (PPMS6000) with disk shape (~0.5 mm in thickness). The relative error for the specific heat measurements is less than 2%. Elastic modulus is measured using ultrasonic method. The rods (~3.0 mm) are cut to 6.0–

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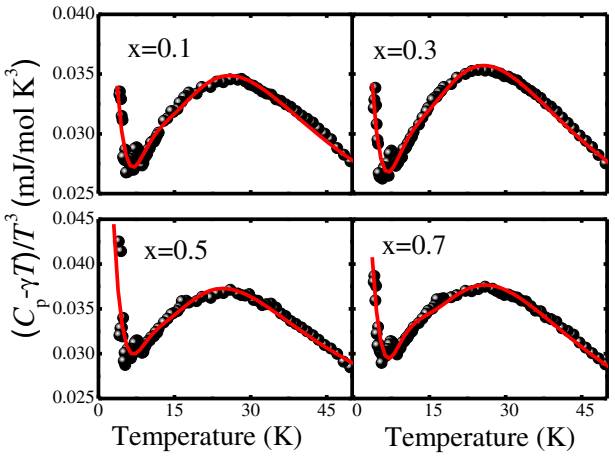

Fig. 1. Standard plotting of $(C_p - \gamma T) / T^3$ versus T for $(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ ($x = 0.1, 0.3, 0.5$ and 0.7) MGs. The fitting lines from experimental data with Eq. (3) are also shown.

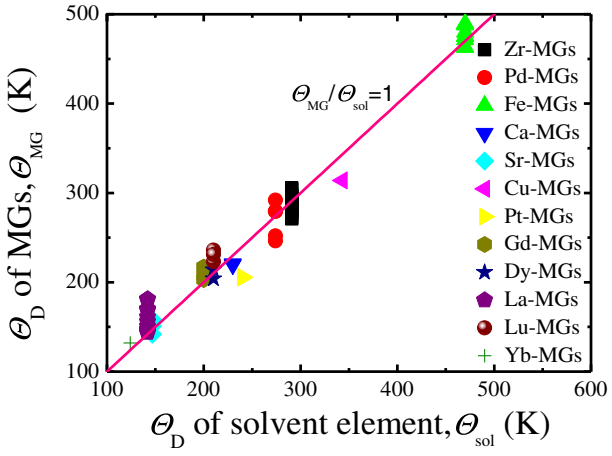

Fig. 2. The average ratio of θ_D for various MGs and their solvent. Data are taken from Ref. [18,23].

8.0 mm in length and their ends are carefully polished flat and parallel. The acoustic longitudinal and transverse velocities are measured using pulse echo overlap method by a MATEC 6600 model ultrasonic system [9]. The final data were obtained by averaging 3 experimental results. The relative error for the ultrasonic measurements is less than 5%. The densities of the specimens are measured using Archimedes's method with an accuracy of about 2%.

3. Results and discussion

Fig. 1 exhibits $(C_p - \gamma T) / T^3$ vs T for $(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ ($x = 0.1$, 0.3, 0.5, and 0.7) MGs, where, C_p is the low temperature specific heat, and γ is the electronic specific heat coefficient with values 6.96, 6.26, 5.92, and 5.72 mJ/mol K^2 for $(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ ($x = 0.1$, 0.3, 0.5, and 0.7) MGs, respectively, depending linearly on the temperature [15]. From Fig. 1, it can be seen that there exists excess peaks of specific heat in 10–50 K temperature regions in the metallic glassy systems.

According to the solid state theory, the low temperature specific heat C_p can be assumed to be consisted of three terms

$$C_p = C_e + C_M + C_L \tag{1}$$

where $C_e = \gamma T$ represents the electronic contribution to C_p, $C_M = \delta T^{3/2}$ the magnetic contribution [16], and C_L the lattice specific heat, which originates from the Debye oscillator and Einstein oscillators. Here Einstein oscillators are mainly responsible for ASSH in MGs, such as the loose or weakly bound atoms in the oversized cages, voids, or similar defects in the case of complex materials [17]. It seems that the experimental curves presented in Fig. 1 have two minimums, which mean that two distinct Einstein-type vibration modes exist in the MGs [15]. However, the second Einstein-type vibration mode is relatively small [19], and then it can be ignored in this work. Then, the lattice specific heat C_L can be expressed as

$$C_L = (1-f)C_D + fC_E \tag{2}$$

where f is the fraction of ASSH in the glassy state; $C_D = 3R(\frac{T}{\theta_D})^3 \int_0^{\theta_D/T} \frac{\xi^4 e^\xi}{(e^\xi-1)^2} d\xi$, the contribution of Debye term, with θ_D the Debye temperature; and $C_E = R(\frac{\theta_E}{T})^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}$, the contribution of Einstein mode, with θ_E the Einstein temperature, and R the gas constant.

Then the relationship between $(C_p - \gamma T) / T^3$ and T can be drawn as

$$\frac{C_p-\gamma T}{T^3} \approx \frac{234R(1-f)}{\theta_D^3} + \frac{fR\theta_E^2}{T^5}\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2} + \delta T^{-3/2}. \tag{3}$$

The comparisons of theoretical values and experimental data of $(C_p - \gamma T) / T^3$ vs T for $(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ ($x = 0.1$, 0.3, 0.5, and 0.7) MGs are also shown in Fig. 1. It can be seen that the theoretical lines are consistent with the experiments. The values of Debye temperature θ_D, Einstein temperature θ_E and magnetic specific heat coefficient δ obtained from the least-squares fit of the present data to Eq. (3) are summarized in Table 1. The presence of the relatively large δ coefficient means a substantial deviation of magnetic ions from the lattice specific heat C_L, occurring at relatively low temperatures for $(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ MGs. It can be also seen from Table 1 that the ratio of θ_D to θ_E is around 5. These results are in good agreement with Ref. [19]. The expression of θ_D and θ_E can be unified as

$$\theta_i = \frac{\hbar\omega_i}{k_B} \tag{4}$$

Table 1
Terms from fits to Eq. (3) for the low temperature specific heat of $(Fe_{1-x}Co_x)_{72}B_{20}Si_4Nb_4$ ($x = 0.1$, 0.3, 0.5 and 0.7) MGs. The Debye temperatures of solvent components are also listed.

Metallic glasses	Base metal	θ_D[a]	θ_D (K)	θ_E (K)	δ (mJ/mol K$^{5/2}$)
$(Fe_{0.9}Co_{0.1})_{72}B_{20}Si_4Nb_4$	Fe	470	480 ± 10	90 ± 5	0.103
$(Fe_{0.7}Co_{0.3})_{72}B_{20}Si_4Nb_4$	Fe	470	475 ± 5	93 ± 3	0.116
$(Fe_{0.5}Co_{0.5})_{72}B_{20}Si_4Nb_4$	Fe/Co	470/445	460 ± 10	95 ± 5	0.147
$(Fe_{0.3}Co_{0.7})_{72}B_{20}Si_4Nb_4$	Co	445	450 ± 15	100 ± 5	0.165

[a] Reference [18].