

Elastic property and its response to pressure in a typical bulk metallic glass

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Abstract

Acoustic velocities, elastic constants and thermodynamic parameters upon pressure up to 2 GPa of typical $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass (BMG) have been studied by using a pulse echo overlap method. The results indicate that the glass forming ability (GFA) has a relation with the elastic constants for a glass forming system. The compression curve of the BMG is interposed among its components, and the BMG exhibits small volume changes upon pressure, confirming that the BMG has similar atomic close-packed configurations with elements which may closely related to the origin of its excellent GFA. © 2003 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Bulk metallic glasses; Equation of state; Acoustic method

1. Introduction

The acoustic, elastic and thermal properties of metallic glasses are closely related to their binding nature and vibrational characteristics [1–4]. The equation of state (EOS) of a solid (pressure–volume relation, P – V) plays an important role in condensed matter physics, because the knowledge of EOS is of importance for the general understanding of the behavior and the application of a condensed matter [5]. The physical properties and the EOS of crystalline solids have been long-standingly and deeply investigated, and a lot of interesting and important phenomena have been observed [5,6]. For many years, however, the very high cooling rate ($>10^5$ K/s) necessary to obtain the metallic glasses had limited their geometry to be very thin ribbons or wires. The difficulty to prepare bulky specimens makes the studies of intrinsic nature of the metallic glass and the measurements of many physical properties and EOS very difficult. The acoustic and elastic properties as well as the vibrational features in the metallic glasses are

poorly understood. A fundamental understanding of microstructural configuration in amorphous solids is not as developed as that in crystalline solids. The bulk metallic glasses (BMGs) make them in the form suitable for measurements of elastic wave propagation. The acoustic study of the new metallic glasses could get deep understanding of the structural and properties features. Since acoustic property is particularly sensitive to the microstructure, the acoustic study especially the P -dependent acoustic velocities can provide crucial information on the microstructural characteristics as well as the elastic and vibrational properties of the BMGs. On the other hands, the BMGs have been found to have a glass forming ability (GFA) close to oxide glasses, and are relative “strong” glasses [7–9], which means that they exhibit a large viscosity around the melting point and a large apparent activation energy for flow. From the different responses to pressure in elastic properties and structure of the BMG, it may provide more information for understanding the structural characteristics of the excellent glass forming alloys. In this paper, we present a systematic ultrasonic investigation on a typical $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG (vit1) that is an ideal model system for study of the nature and properties of the metallic glasses [10]. The density, and acoustic velocities,

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which can sensitively reflect the microstructural change, were measured in situ as functions of pressure up to 2 GPa. Some acoustic and elastic features are observed in the glass. The Murnaghan equation of the state of the BMG has been determined by ultrasonic measurements. The volume compression of the BMG is compared with those of its metallic components.

2. Experiments

Zr₄₁Ti₁₄Cu_{12.5}Ni₁₀Be_{22.5} BMG was prepared by water quenching method in a cylindrical rod with 12 mm diameter [11]. The amorphous nature as well as the homogeneity was ascertained by X-ray diffraction (XRD), differential scanning calorimeter (DSC), transmission electron microscopy (TEM) and small angle neutron scattering (SANS) [11]. The glassy rods were cut to a cylinder with a length of 8 mm for ultrasonic measurements. The ends of the cylinder were carefully polished flat and parallel before ultrasonic measurement. The acoustic velocities and their P -dependence were measured at room temperature by using a pulse echo overlap method [12,13]. The excitation and detection of the ultrasonic pulses were provided by X - or Y -cut (for longitudinal and transverse waves, respectively) quartz transducers. The frequency of the ultrasonic is 20 MHz, respectively. The transducers were bonded to the specimen for high-pressure experiments. Dow resin is used as bonding material for ultrasonic measurements under pressure, its effects on the ultrasonic velocities under pressure have been already determined, and can be ruled out. Its bond quality can be kept unchanged under pressure up to 2 GPa [14]. The travel time of ultrasonic waves propagating through the sample was measured using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. The ultrasonic velocity measurements under high pressure were calibrated by the known materials of Pb, Bi [14]. The pressure was applied using a piston–cylinder high-pressure apparatus, 1:1 pentane–isopentane was used for the pressure transmitting media, for which hydrostaticity has already been determined. The high-pressure measurements were performed for several pressure load–unload cycles to ex-

amine the reproducibility and minimize error. Pressure induced changes in the sample dimensions were accounted for by using Cook's methods [15]. The elastic constants, e.g. bulk modulus K , Young's modulus E , shear modulus G , and Poisson's ratio σ , the Debye temperature θ_D of the BMG is derived from the acoustic velocities and density, ρ [12,16–19]. Density was measured by the Archimedian principle and the accuracy was evaluated to be 0.005 g/cm³.

3. Results and discussions

3.1. Acoustic and elastic properties of the vit1 BMG

The values of ρ , v_l , and v_s of the Zr₄₁Ti₁₄Cu_{12.5}Ni₁₀Be_{22.5} BMG at ambient pressure are listed in Table 1. For the BMG, the ρ , v_l , and v_s are 6.125 g/cm³, 5.174, and 2.472 km/s, respectively. E , G , K , and σ , and θ_D calculated from the acoustic data are 101.2, 37.4, 114.1 GPa, 0.35, and 326.8 K, respectively. The obtained elastic data are in good agreement with those of the BMGs measured by different methods [10]. Table 1 also lists the acoustic and elastic data of a series of other BMGs [13,20], and the elastic data are agreement with those of the BMGs measured by different methods [21–25]. σ characterizes the relative value of the compressive and shear deformation of a solid [12]. The values of σ for various BMGs listed in Table 1 range from 0.3 to 0.4, which is close to those of metals [26], e.g. Cu (0.37) and crystalline alloys, e.g. Monel (0.33). The conventional metallic glasses available have higher value of σ ($\sigma \approx 0.40$) [27]. The conventional metallic glasses have poor GFA (the critical cooling rate, R_c for the glass formation, which represents the GFA of an alloy, is from 10⁴ to 10⁷ K/s). The GFA of the BMGs (R_c ranges from 1 to 100 K/s, for vit1, its R_c is even lower than 1 K/s [7,28]) is much better than that of the conventional metallic glasses. The above results show that the glass with higher GFA has small value of σ . This indicates that the GFA has relation with the value of σ for a glass forming system. The nature of the chemical bond in a solid determines the microstructure which has close relation with the excellent GFA of an alloy [21], thus the

Table 1
The acoustic data and elastic constants for typical BMGs at ambient pressure

Sample	ρ (g/cm ³)	v_l (km/s)	v_s (km/s)	E (GPa)	G (GPa)	K (GPa)	σ	θ_D (K)	v_l/v_s	K/G
Zr ₄₁ Ti ₁₄ Cu _{12.5} Ni ₁₀ Be _{22.5}	6.125	5.174	2.472	101	37.4	114.1	0.35	327	2.09	3.06
Zr _{46.75} Ti _{8.25} Cu _{7.5} Ni ₁₀ Be _{27.5}	6.014	5.182	2.487	100.5	37.2	111.9	0.350	327	2.08	3.01
Zr _{45.4} Ti _{9.6} Cu _{10.15} Ni _{8.6} Be _{26.25}	6.048	5.171	2.485	100.9	37.3	111.9	0.350	327	2.08	3.00
Zr ₄₈ Nb ₈ Cu ₁₂ Fe ₈ Be ₂₄	6.436	4.994	2.338	95.7	35.2	113.6	0.359	306	2.13	3.22
(Zr _{0.59} Ti _{0.06} Cu _{0.22} Ni _{0.13}) _{85.7} Al _{14.3}	6.608	4.890	2.269	92.7	34.0	112.6	0.363	291	2.15	3.31
Cu ₆₀ Zr ₂₀ Hf ₁₀ Ti ₁₀	8.315	4.620	2.108	101.1	36.9	128.2	0.368	282	2.02	3.47
Pd ₃₉ Ni ₁₀ Cu ₃₀ P ₂₁	9.152	4.74	1.96	98.2	35.1	159.1	0.40	280	2.42	4.52

difference in microstructure will influence the mechanical properties of a solid and then result in the variation of the acoustic parameters and elastic constants. For various BMGs listed in Table 1 the values of K/G are from 3.0 to 4.5, which is similar to metals, such as Cu and steel (K/G is about 2.5) [26], which may indicate the similar bonding nature of the BMG and metals, and the metallic bond remains after amorphization [29].

3.2. Pressure dependence of elastic properties and EOS

The EOS and the response in elasticity of the glasses to pressure can provide crucial information about the microstructural features of different glasses[30]. Fig. 1 presents the pressure variations $\Delta v(P)/v(P_0) = [v(P) - v(P_0)]/v(P_0)$ of v_l , and v_s , (at 20 MHz) of the BMG, where P_0 is the ambient pressure. To determine P -dependence of the elastic moduli exactly, Cook's method [15], by which the elastic constants and sample dimensions can be calculated simultaneously and self-consistently, was used for the correction. When using Cook's method, a mesh of 0.1 GPa pressure intervals and a value for the quantity $1 + \Delta$ of 1.01, which is the ratio of the adiabatic to the isothermal bulk moduli, were used. The data of v_l and v_s are reproducible and show no measurable hysteresis effects in the pressure loading and release cycle. It seems that there are no observable permanent changes in acoustic velocities up to 2.0 GPa. No detectable density increase in the sample after testing was found. These results indicate the elastic behavior in the BMG under hydrostatic compression up to 2.0 GPa. The change of v_l upon pressure is two times larger than that of the v_s . Both v_l and v_s increase smoothly with increasing pressure and show an approximately linear P -dependence.

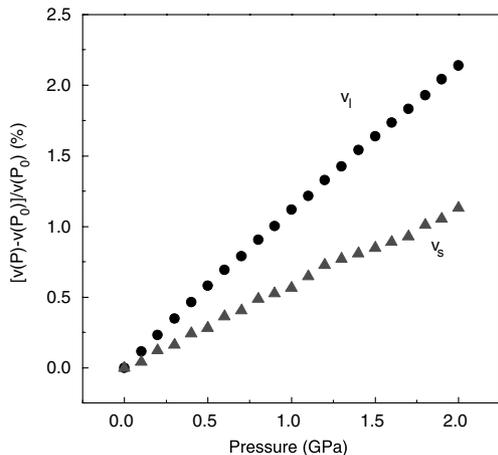


Fig. 1. Variation of longitudinal and transverse velocities ($v = v_l, v_s$) of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG upon pressure at room temperature. v is normalized by $\Delta v/v_0 = (v - v_0)/v_0$, where v_0 is a normal velocity at ambient pressure P_0 .

The corresponding P -dependence of elastic constants Y ($Y = E, G, K, \sigma$) calculated from the velocities for vit1 is shown in Fig. 2. Y is normalized by $\Delta Y/Y_0 = (Y - Y_0)/Y_0$, where Y_0 is a normal modulus at P_0 . For the BMG, E, G, K , and σ monotonically and linearly increase with increasing pressure. In the absence of phase changes, such an increase with increasing pressure is generally expected as a consequence of the vibrational anharmonicity of the BMG [31]. As shown in Fig. 2, the value of dK/dp of vit1 is positive, the elastic constants exhibit a positive deviation with pressure from linearity showing that the modulus stiffens under pressure. The monotonically increases of K can be attributed to the denser packing of the BMG [28]. The application of pressure does not induce acoustic mode softening for the BMG. It worth noting that the pressure-induced changes of v_l, v_s, G , and K for vit1 are different from the changes of these parameters induced by crystallization [32]. The pressure leads to a smaller change of v_s (1.2%) and G (4.1%), and relatively larger changes of v_l (2.2%) and K (7.1%) (listed in Table 2). This result means that pressure has larger effect on the longitudinal acoustic phonons than the transverse phonons in the BMG. Meanwhile, crystallization causes a striking stiffening of transverse acoustic phonons relative to the BMG [32].

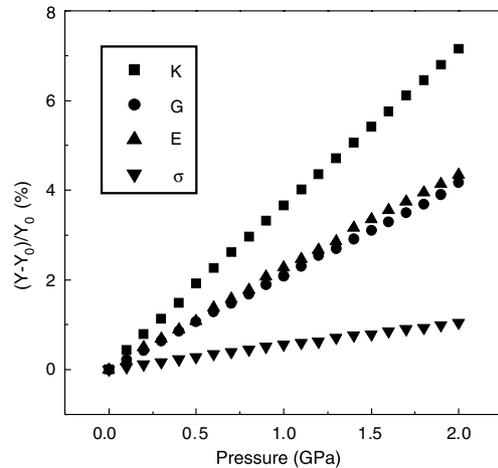


Fig. 2. The variation of elastic constants Y of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG ($Y = E, G, K, \sigma$) with pressure, Y is normalized by $\Delta Y/Y_0 = (Y - Y_0)/Y_0$, where Y_0 is a normal modulus at P_0 .

Table 2

The properties at ambient state (Y_0) and under high pressure (Y_p) of the vit1

Property	Ambient pressure	2 GPa	$(Y_p - Y_0)/Y_0$ (%)
v_l (km/s)	5.174	5.297	2.2
v_s (km/s)	2.472	2.501	1.2
K (GPa)	114.1	122.9	7.1
G (GPa)	37.4	39.0	4.1
θ_D (K)	326.8	332.8	1.8

The Debye temperature θ_D can also be determined from acoustic data by [33]

$$\theta_D = \frac{h}{k} \left(\frac{4\pi}{9} \right)^{-1/3} \rho^{1/3} \left(\frac{1}{v_l^3} + \frac{2}{v_s^3} \right)^{-1/3}, \quad (1)$$

where k is Boltzmann constant, h Planck constant. θ_D represents the temperature at which nearly all modes of vibrations in a solid are excited [33]. The pressure variation of θ_D reflects the rigidity change upon pressure of a solid. Fig. 3 shows the pressure variation of θ_D for vit1 in the range of 0–2 GPa. For the BMG, the pressure variation of θ_D increases monotonically and slightly with increasing P , implying that an increase in rigidity of the BMG upon pressure [34].

The Grueneisen constant γ , which is related to the pressure derivative of K , can be estimated by using of Slater's equation [35]

$$\gamma = \frac{1}{2} \left(\frac{\partial K}{\partial p} \right)_T, \quad (2)$$

the value of γ of vit1 is 2.0 estimated from the fit of Fig. 2. The values are close to the reported values of fused silica (–2.9) [36], etched soda glass (2.5) [36], iron (3.4) [37], and silicon (0.8 to –1.5) [38]. The values of the Grueneisen constant for usual metallic components [39], such as Cu(1.93), Ni (2.77), and Zr (2.18) are close to the BMG. This classifies the BMG among the solids with larger anharmonicity [2]. On the other hand, this indicates that the microstructure of the BMG has close correlation with the atomic configurations in their metallic components.

From the data of K_0 and K'_0 (K_0 and K'_0 are the bulk modulus and its pressure derivative at P_0 , respectively), the volume compression $V_0/V(P)$ and their pressure dependence, or the EOS of the BMG in the non-phase transitional case is obtained with the Murnaghan form [40]

$$P = \left(\frac{K_0}{K'_0} \right) \left[\left(\frac{V_0}{V(P)} \right)^{K'_0} - 1 \right] \text{ GPa}. \quad (3)$$

From the acoustic data in Fig. 2, K_0 and K'_0 are obtained to be 114.8 GPa, 4.06 for vit1, respectively. The P – V relation of the BMG is plotted in Fig. 4. The obtained EOS of vit1 is close to that obtained by direct P – V measurements at room temperature [41].

The volume compressibility of metallic elements can be expressed as [42]

$$\Delta V/V_0 = -aP + bP^2, \quad (4)$$

where a and b are constants, volume compression $\Delta V = V(P) - V_0$. For comparison, the compression curves of Zr, Ti, Cu, Ni, and Be obtained by directly volume and pressure measurements [35] are also plotted in Fig. 4. The compression curves of the BMG is interposed among their metallic components, e.g. the compression curve of the $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ BMG is interposed among Zr, Ti, Cu, Ni, and Be. To understand the phenomenon, the volume compression of the BMG is calculated as a mean value of all elements based on the atomic percents of constituent elements. The calculated result is also shown in Fig. 4. The calculated EOS for vit1 in terms of Eq. (4) is consistent well with its EOS derived from the Murnaghan form and experimental data (Eq. (3)). This indicates that the compression curves of the BMG has correlation with that of their metallic components and exhibit roughly an average value of these elements. Since the compressibility of a solid is determined by the nature of the interatomic potential and the atomic configurations [43], the total compression of BMG may be ascribed to individual metallic elements. Thus above results imply that the short-range order structure of the BMG has close correlation with the atomic configurations in their metallic components. Since those metallic components are of cubic close-packed structures, it is very likely that the similar atomic close-packed configurations

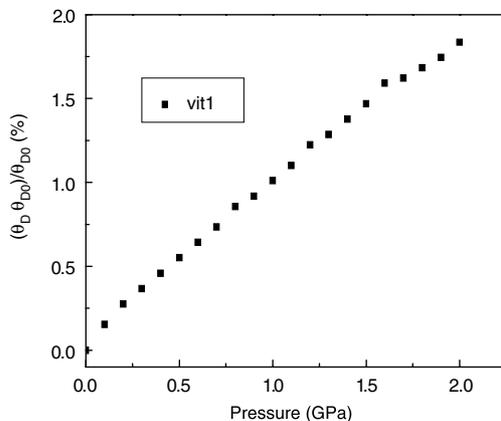


Fig. 3. The relative variation of the Debye temperature, θ_D of vit1 with pressure, θ_D is normalized by $\Delta\theta_D/\theta_{D_0} = (\theta_D - \theta_{D_0})/\theta_{D_0}$, where θ_{D_0} is a normal Debye temperature at P_0 .

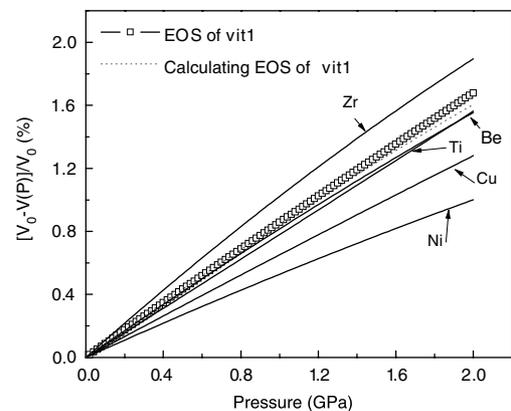


Fig. 4. The pressure and volume relation of the BMG got from acoustic measurement, a comparison of the EOS of vit1 and its crystalline components.

dominate the short-range structure of the BMG. These highly packed structures have also been confirmed by density measurements. The relative density change of the BMGs between amorphous and fully crystallized states is about 1.0% [32]. The highly random packed structure in BMG forming alloys could lead to a high fluid viscosity and the crystallization in liquid state is difficult and controllable; these have close relation with its excellent glass forming ability [28].

4. Conclusions

The elastic constants of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG as well as their P -dependence change have been determined by ultrasonic measurements. The elastic properties of the BMG have a correlation with its excellent GFA. The applied pressure results in relatively larger change of the longitudinal velocity and bulk modulus than that of the transverse velocity and shear modulus. The hydrostatic-pressure derivative $\partial K/\partial p$, $\partial G/\partial p$ are positive, showing modulus stiffening for the BMG. The EOS of the BMG is determined. The compression curve of the BMG is interposed among its components, and the BMG exhibits much small volume changes upon pressure comparing with oxide glass, indicating that the BMG has similar atomic close-packed configurations with elements.

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