Elastic constants and their pressure dependence of $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ bulk metallic glass

Wei-Hua Wang,[a] R. J. Wang, F. Y. Li, D. Q. Zhao, and M. X. Pan
Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, People's Republic of China

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The acoustic velocities and their pressure dependence of bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ metallic glass (MG) have been measured up to 0.5 GPa by using a pulse echo overlap method. The elastic constants and thermodynamic parameters as well as their pressure dependence of the MG have been determined. The obtained elastic constants were compared to that of other kinds of glasses. More information about the microstructure, elastic properties, and glass forming ability of the MG was obtained. © *1999 American Institute of Physics.* [S0003-6951(99)00313-7]

There has been long-standing interest in the elastic properties of metallic glasses (MGs) because the studies can provide important information about the structural and vibrational characteristics of MGs.[1–4] However, the understanding of the glassy metallic state has been impeded, in large part, by the inability to prepare bulk specimens of MGs. Recently, multicomponent Zr-based glass forming systems with a larger three-dimensional size have been developed by the conventional casting process at a low cooling rate.[5–9] The obtained bulk MGs make them in the forms suitable for measurements of elastic wave propagation. On the other hand, there have been some investigations of the temperature dependence of the physical properties in the bulk MGs, but little work has been done about the pressure dependence of the physical behaviors of MGs. In this work, we present an ultrasonic study on the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ MG which exhibits excellent glass forming ability (GFA) and properties.[8,9] The elastic constants and the Debye temperature of the MG have been determined by ultrasonic measurements under high pressure. The purpose of the study is to understand the glassy metallic state and the effects of high pressure on the microstructure and elastic properties.

$Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ ingots were prepared by inductive levitation melted under a Ti-gettered Ar atmosphere with oxygen partial pressure of 10^{-9} Pa. The ingots were remelted together in a silica tube and quenched in water to get a cylindrical rod with 12 mm diameter. The details of the experimental procedure can be seen in Refs. 8 and 9. The amorphous nature as well as the homogeneity of the MG was ascertained by x-ray diffraction, differential scanning calorimetry, transmission electron microscopy, and small angle neutron scattering.[8,9] The amorphous rod was cut to a length of about 10 mm, and its ends were carefully polished flat and parallel. The acoustic velocities and their pressure dependence of the bulk MG were measured at room temperature by using the pulse echo overlap method.[10] The travel time of ultrasonic waves propagating through the sample with a 10 MHz carry frequency was measured using the MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. The high pressure was performed using a piston-cylinder high-pressure apparatus, and electric insulation oil was used for the pressure transmitting media, for which hydrostaticity has already been determined. The measurements were performed for several pressure load–unload cycle times to examine the reproducibility. Density ρ was measured by the Archimedian principle. The elastic constants (e.g., bulk modulus K, Young's modulus E, shear modulus G, and Poisson's ratio σ) and the thermodynamic parameters (e.g., Debye temperature θ_D,) of an isotropic homogeneous solid are derived from the acoustic velocities and density.[10–14]

The longitudinal, transverse velocities and density at ambient condition were 5.096 ± 0.001 km/s, 2.533 ±0.003 km/s, and 6.1608 ± 0.0001 g/cm^3, respectively. The moduli and the thermal parameters of the bulk MG calculated from the acoustic data and the moduli parameters of other solids are listed in Table I. The Poisson's ratio σ characterizes the relative value of the compressive and shear deformation of a solid. As shown in Table I, the nonmetallic glasses (e.g., oxide glass), whose σ is less than 0.25, are brittle, since atoms or molecules can hardly rearrange themselves to shear strains without a drastic disturbance in bonding configurations. In contrast, the conventional MGs with poor GFA have a high value of σ ($\sigma\approx0.40$), indicative of the ease of atomic rearrangement; it is responsible for the ductile plastic deformation of the materials. For bulk MGs with excellent GFA, its value of σ is between that of the conventional MG and oxide glasses. Previous studies show that the bulk MG consisting of a mixture of atoms with different atomic size has highly dense random packed structure compared to conventional MG.[15,16] The closer packed structural characteristic of the MG makes the redistribution of atoms extremely difficult, and leads to a larger value of σ. The comparison indicates that σ has a correlation with the atomic configuration in these amorphous materials. On the other hand, the GFA of bulk MG is much better than the conventional MG and approaches that of oxide glass. The relation of σ and the critical cooling rate for glass formation of the oxide glasses, bulk MG, and conventional MGs are shown in Fig. 1. It is shown that σ has a correlation with the GFA (The critical cooling rate represents the GFA of a glass forming system) of the three kinds of glasses. The glass with a small value of σ has higher GFA. This indicates that the

[a]Corresponding author. Electronic mail: whw@aphy.iphy.ac.cn

TABLE I. The acoustic data and elastic constants for typical oxide glasses, conventional MG, and bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ MG.

Sample	ρ (g/cm^3)	V_1 (km/s)	V_s (km/s)	V_1/V_s	E (GPa)	G (GPa)	K (GPa)	σ	θ_D (K)	K/G	Refs.
$Zn_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ MG	6.161	5.10	2.53	2.01	105.97	39.54	107.31	0.34	335	2.71	This work
Ni	8.9				239	92.9	188	0.288	450	2.02	a
Cu	8.93	5.01	2.27	2.21	~126	~46	~163	0.37	343	3.54	a
Monel	8.84	5.35	2.72	1.97	174.58	65.84	166.94	0.33		2.53	a
Stainless steel	7.91	5.79	3.1	1.87	197.50	76.10	163.82	0.30		215	a
Water-white glass	2.479	5.836	3.423	1.70	71.924	29.055	45.707	0.238		1.57	b
Borosilicate glass	2.32	5.64	3.28	1.72	61.90	24.96	40.52	0.24		1.6	b
Amorphous carbon	1.56	3.88	2.407	1.61	21.4	9.01	11.4	0.187	338	1.26	b
Fused quartz	2.201	5.96	3.75	1.59	72.7	31.0	36.9	0.17	496	1.2	d
$Pd_{79.5}Si_{16.5}Cu_6$	10.52	4.6	1.797	2.56	92.9	32.9	174.6	0.411	250	5.3	c
$Pt_{60}Ni_{15}P_{25}$	15.71	3.965	1.467	2.70	96.1	33.8	201.9	0.421		5.97	c
$Pd_{64}Fe_{16}P_{20}$	10.04	4.53	1.816	2.49	93.0	33.1	161.9	0.404		4.98	c
$Pd_{32}Ni_{48}P_{20}$	9.19	4.93	2.02	2.44	104.9	37.5	173.5	0.399		4.63	c

[a]Reference 17.
[b]Reference 18.
[c]Reference 19.
[d]Reference 22.

GFA is closely related to the microstructure of a glass forming system. A decreasing σ may result in high GFA in a glass forming system. The value of σ of bulk MG is close to those of metals and crystalline alloys listed in Table I, indicating that the bulk MG has a good plastic deformation similar to that of Cu. The nature of the chemical bond in a solid determines the microstructure of the solid, thus the difference in local structure will influence the mechanical properties of a solid and then result in the variation of the acoustic parameters. For the covalent bond solid such as silicate glasses, amorphous carbon as shown in Table I, $K/G=(\nu_l/\nu_s)^2-4/3$ is about 1.7.[17] For conventional MG listed in Table I K/G is about 5.2, while the K/G of the Zr-based bulk MG is 2.71, which is markedly different from the conventional MG. This result also indicates the different microstructural characteristics between the two kinds of MGs. The relative larger value of G for the bulk MG compared to other MGs and oxide glasses means that the bond angle of the structure of the MG cannot be changed easily. The K/G of the bulk MG is similar to metals, such as Cu and steel (K/G is about 2.5). The results indicate that the metallic bond is retained in the bulk MG even if the MG lacks long-range order. In fact, the MG does have some isotropic metallic properties.[6]

In Fig. 2, we have plotted the pressure variations $\delta\nu(p)/\nu(p_0)=[\nu(p)-\nu(p_0)]/\nu(p_0)$ of the longitudinal velocity, ν_l, and transverse velocity, ν_s, for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ MG at room temperature, where p_0 is the ambient pressure. The data are reproducible under p cycling and show no measurable hysteresis effects. It seems that there are no observable permanent changes in sound velocities with p up to 0.5 GPa. The changes in both ν_l and ν_s are reproducible for repeated compression as shown in Fig. 2. The change of ν_l with pressure of the MG is two times larger than ν_s. No density increase in the sample after testing was found here within experimental error. These results indicate the elastic behavior in the bulk MG under hydrostatic compression up to 0.5 GPa. It is shown that both of ν_l and ν_s increase smoothly with the increase of pressure in loading and unloading processes and shows an approxi-

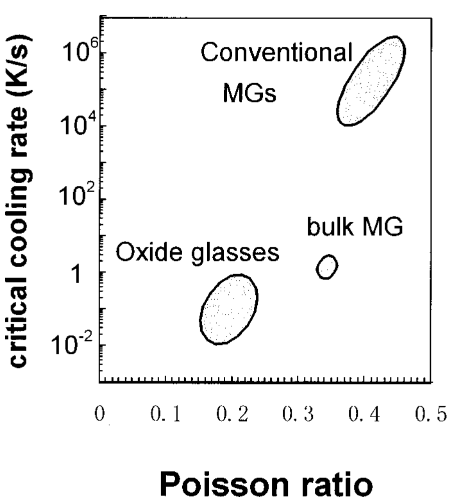

FIG. 1. The relation of critical glass formation cooling rate and the Poisson's ratio σ for oxide glasses, conventional MG, and bulk MG.

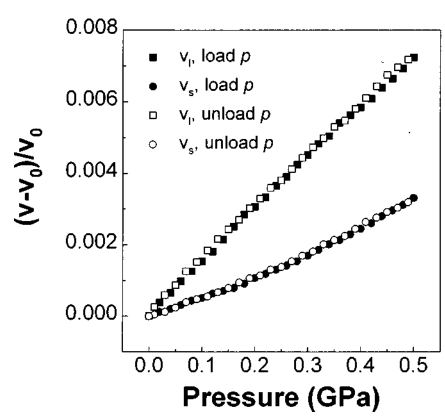

FIG. 2. Variation of longitudinal and transverse velocities of the bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ MG with pressure $p(\nu=\nu_l,\nu_s)$, ν is normalized by $(\nu-\nu_0)/\nu_0$, where ν_0 is a normal velocity at ambient p_0.

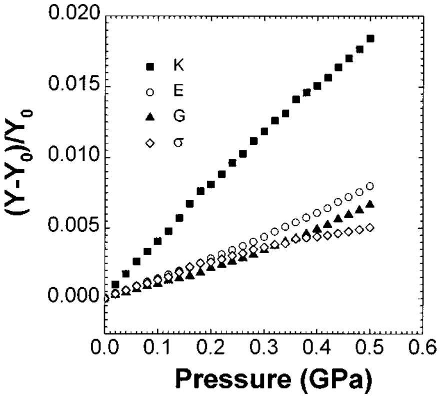

FIG. 3. Variation of elastic constants Y of the bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ MG ($Y=E,G,K,\sigma$) with pressure p. Y is normalized by $(Y-Y_0)/Y_0$, where Y_0 is a normal modulus at ambient p_0.

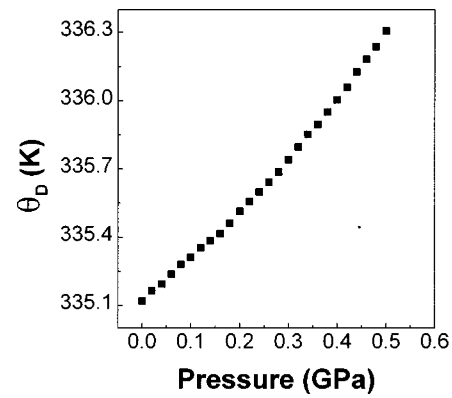

FIG. 4. Dependence of Debye temperature on the pressure in the bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ MG.

mately linear p dependence over a range of p up to 0.5 GPa, whereas v_s of the silicate glasses and amorphous carbon decrease with increasing of p.[18] The MG has similar p dependence of sound velocities to steel and tungsten carbide.[18]

The pressure variations $\delta Y(p)/Y(p_0)=[Y(p)-Y(p_0)]/Y(p_0)$ of the elastic constant E, G, K, and Poisson ratio σ calculated from the ultrasonic velocities for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ MG at room temperature are shown in Fig. 3. The elastic constants increase with increasing p at room temperature. The increase in elastic constants can be attributed to the denser packing of the MG.[19] As shown in Fig. 3, dK/dp and dG/dp of the bulk MG are positive, and the elastic constants exhibit a positive deviation with p from linearity, showing the modulus stiffness under hydrostatic pressure. The application of pressure does not induce acoustic mode softening for the bulk MG.

In calculating θ_D, we treat the amorphous alloy as a monatomic lattice with an average cellular volume. Using elastic data, the Debye temperature of the MG can be represented as[14]

$$\theta_D(\text{elastic})=\frac{h}{k_B}\left(\frac{9\Omega_0}{4\pi}\right)^{1/3}\left(\frac{1}{\nu_l^3}+\frac{2}{\nu_s^3}\right)^{-1/3}, \tag{1}$$

where h and k_B are the Planck constant and the Boltzman constant, respectively, Ω_0 is the atomic volume. In general, the value of θ_D calculated from acoustic measurements agrees well with the thermal values. The pressure dependence of the θ_D calculated from Eq. (1) is shown in Fig. 4. A monotonic increase of θ_D is shown in Fig. 4. θ_D represents the temperature at which nearly all modes of vibrations in a solid are excited, and its increase implies an increase in the rigidity of the MG with the p.[20]

The volume compression $V_0/V(p)$ and their hydrostatic-pressure dependence using an equation of state such as that of Murnaghan[21] which in logarithmic form is

$$\ln\left(\frac{V_0}{V(p)}\right)=\frac{1}{K_0'}\ln\left(\frac{K_0'}{K_0}p+1\right), \tag{2}$$

where K_0 and K_0' are the bulk modulus and its pressure derivation at zero p, respectively. For the inspection of the data for K in Table I and Fig. 3, we obtain $K=3.924p+107.37$ for the bulk MG by assuming the linear relationship between sound velocities and p in the MG. By substituting the data of K_0 and K_0' into Eq. (2), the obtained equation of the state for the MG in the nonphase transitional case is

$$p=27.35\left[\left(\frac{V_0}{V(p)}\right)^{3.924}-1\right]. \tag{3}$$

In conclusion, the elastic constants and Debye temperature of the bulk $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ metallic glass as well as their pressure dependence, and the equation of the state of the MG have been determined by ultrasonic measurements. It is found that the elastic properties of the MG have a good correlation with its excellent glass forming ability and microstructural characteristics.

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