

Pressure dependence of elastic constants and Debye temperature for $\text{Zr}_{50.5}\text{Ti}_{4.8}\text{Cu}_{19.0}\text{Ni}_{11.4}\text{Al}_{14.3}$ bulk metallic glass

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The microstructure of $\text{Zr}_{50.5}\text{Ti}_{4.8}\text{Cu}_{19.0}\text{Ni}_{11.4}\text{Al}_{14.3}$ bulk metallic glass (BMG) was investigated by high-resolution electron microscopy. The microstructure of the BMG is of homogeneous composition and short-range ordered microstructure. Using an ultrasonic technique with the pulse echo overlap method, the pressure-dependent acoustic velocities of the BMG have been measured up to 0.5 GPa. The elastic constants and their pressure dependence have been obtained. The isothermal equation of state (EOS) of the BMG is determined in terms of the Murnaghan form. With the results of the elastic constants and the EOS for those of its metallic components, the atomic configuration of the BMG is discussed.

I. INTRODUCTION

Mechanical properties, compared to other physical properties, are highly dependent on microstructure for a condensed matter. Studies on elastic constants and Debye temperature can provide important information about structural characteristics of metallic glasses (MGs).^{1–3} Many investigations on temperature-dependent physical properties in the MGs have been done, but little work involves the pressure-dependent properties because of the size limitations. The pressure-dependent acoustic velocities can provide critical information on the microstructural characteristics and thermal properties of the MG under pressure. Recently, the discovery of Zr-based multicomponent metallic glasses (BMGs)^{4–6} offers new opportunities on applications and fundamental research. Among the nonberyllium Zr-based BMGs, Zr–Ti–Cu–Ni–Al BMGs have the best glass-forming ability and can be prepared into glass with a thickness more than 10 mm at a cooling rate less than 100 K/s. The larger geometry of the BMGs is more suitable for *in situ* measurement of elastic wave propagation under high pressure using ultrasonic measurement.^{9,10} It is found that the mechanical properties of the BMGs are different from those of the conventional metallic glasses. On the other hand, the microstructure of the BMGs is dependent on the cooling rate.⁷ The degree of short-range order or medium-range order can be observed by high-resolution electron

microscopy (HREM),^{7,8} which is a powerful technique to obtain local structural information at an atomic level. In this work, the elastic constants and the Debye temperature have been determined by ultrasonic measurement of $\text{Zr}_{50.5}\text{Ti}_{4.8}\text{Cu}_{19.0}\text{Ni}_{11.4}\text{Al}_{14.3}$ BMG under high pressure. The microstructure is observed by HREM. With these results, we attempt to reveal the characteristic of the elastic behavior under high pressure and, furthermore, to investigate structural characteristics of the BMGs.

II. EXPERIMENTS

$\text{Zr}_{50.5}\text{Ti}_{4.8}\text{Cu}_{19.0}\text{Ni}_{11.4}\text{Al}_{14.3}$ BMG rods with a diameter of 4 mm were prepared by the copper mold sucking-cast method. The amorphous nature of the BMG was ascertained by x-ray diffraction, differential scanning calorimetry, and transmission electron microscopy. The sample for the ultrasonic measurements was cut into a length of 8 mm from the rods, and its ends were polished flat and parallel. Under the high pressure the acoustic velocities of the BMG were measured at room temperature by using the pulse echo overlap method.¹¹ The travel time of ultrasonic waves propagating through the sample with a 10-MHz carry frequency was measured by the MATEC 6600 ultrasonic system. The measuring sensitivity is 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. Density ρ was measured by the Archimedian principle. Upon pressure loading, the density and length of the

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sample were modified with the Cook method.¹² Elastic constants (e.g., Young's modulus, E , shear modulus, G , bulk modulus, K , and Poisson's ratio, σ) and Debye temperature, Θ_D , were derived from the acoustic velocities and the densities.¹² HREM samples were cut from the cross section of the same rod, polished mechanically with a Gatan polisher to a thickness of around 50 μm , dipped to 20 μm , and then ion-milled by a Gatan-691 PIPS ion miller. The HREM investigations were performed on a CM-200FEG (Japan) electron microscope operating at 200 kV.

III. RESULTS AND DISCUSSION

Figure 1 exhibits the transmission electron microscopy images of the BMG. A nonuniform structure with the characteristic nonuniformity scale of approximately 3 nm can be observed from Fig. 1(a). It is reasonable to consider the nonuniformity as a characteristic of the

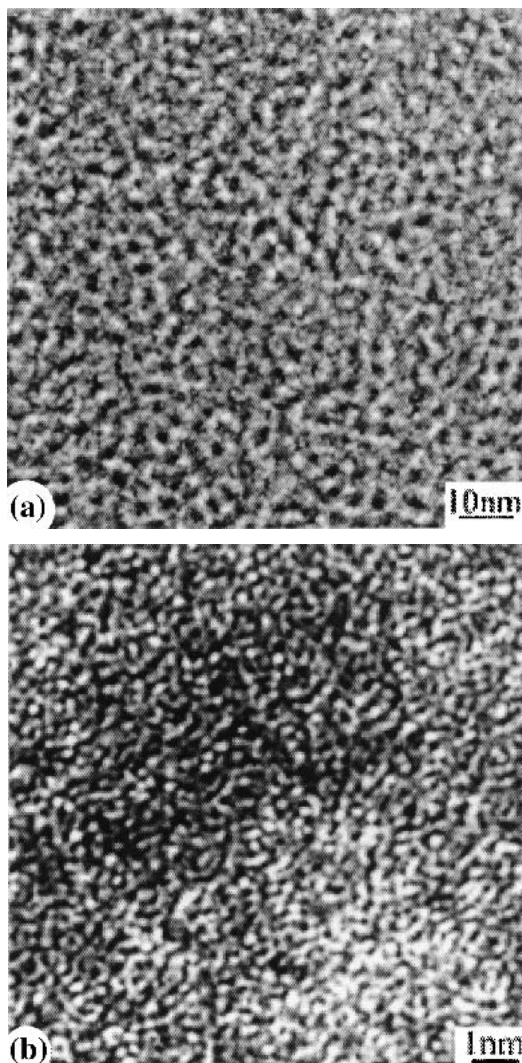


FIG. 1. HREM images for a $\text{Zr}_{50.6}\text{Ti}_{5.2}\text{Cu}_{18.8}\text{Ni}_{14.1}\text{Al}_{14.3}$ BMG rod with 4.0-mm diameter.

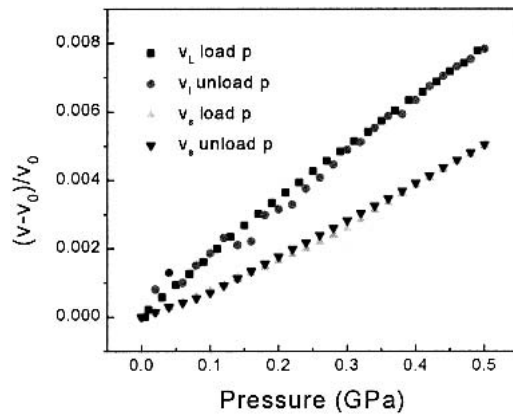
microstructure. The areas with different contrasts have the same microstructure features. Figure 1(b) shows the microstructure of the same sample with a different scale. It is clear that randomness is the common characteristic for the whole area observed, even though the contrast is different. There are no features suggestive of local ordering. These results indicate that the microstructure is only in short-range order and not even medium-range order exists.

The longitudinal, v_l , and transverse velocities, v_t , and the density ρ of the BMG at ambient condition are 4.890 km/s, 2.269 km/s, and 6.608 g/cm³, respectively. As shown in Table I, E , G , K , σ , and Θ_D are calculated to be 92.7, 34.0, 112.6 GPa, 0.362, and 291.2 K. The value of the Debye temperature is close to that of pure zirconium element, indicating no difference of the average atomic force between in the BMG and pure zirconium. Poisson's ratio σ contains more direct information on binding forces than any other elastic constant.¹³ $\sigma = 0.25$ is referred to as the typical value for isotropic materials with central interacting force, such as silicate glass.^{14,15} The value of σ (0.362) deviates from 0.25, meaning that the atoms in the BMG do not lie at centers of symmetry, or only rarely so, and noncentral forces contribute to a large extent. The main contribution is from the energy of the conduction electrons, which depends on the volume rather than on the exact position of the atoms.¹⁶ In contrast, the conventional MGs with poor glass-forming ability (GFA) have a high value of σ ($\sigma \approx 0.4$), indicating the ease of atomic rearrangement; it is responsible for the ductile plastic deformation of the material. For BMGs with better GFA, their value of σ is between that of the conventional MGs and oxide glasses. There is no obvious difference between the conventional metallic glasses and the BMGs, except for the microstructure. In the conventional metallic glasses medium-range order is prominent,¹⁷ while very little medium-range order exists in BMGs, as shown in Fig. 1. These results indicate that the value of σ is highly dependent on the microstructure for metallic glasses. Metallic glasses with medium-range order microstructure have an atomic rearrangement easier than those with little medium-range order microstructure.

Figure 2 shows the pressure dependence of the reduced longitudinal and transverse velocities, $\delta v(P)/v(P_0) = [v(P) - v(P_0)]/v(P_0)$, for the $\text{Zr}_{50.5}\text{Ti}_{4.8}\text{Cu}_{19.0}\text{Ni}_{11.4}\text{Al}_{14.3}$ BMG at room temperature, where P_0 is the ambient pressure. Neither observable permanent changes in sound velocities with P up to 0.5 GPa nor density increase in the sample was found within experimental error after the testing. These results indicate the measurements are within the elastic region of the BMG, and no pressure-induced permanent structural relaxation existed. Upon pressure loading, v_l and v_s increase roughly linearly, and the pressure coefficients $(dv/dP)/v_0$ for v_l and v_s are to be approximately 0.013

TABLE I. The acoustic data and elastic constants for typical oxide glassed, conventional MG, BMGs, and $\text{Zr}_{50.6}\text{Ti}_{5.2}\text{Cu}_{18.8}\text{Ni}_{14.1}\text{Al}_{14.3}$ BMG at room temperature and ambient pressure.

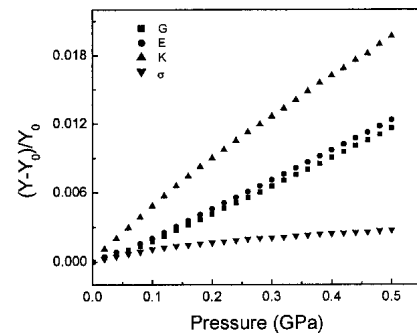
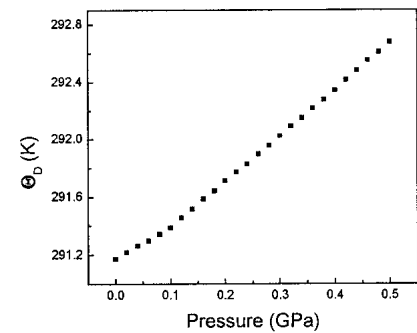
Sample	ρ (g/cm ³)	v_l (km/s)	v_s (km/s)	v_l/v_s	E (GPa)	G (GPa)	K (GPa)	σ	Refs.
$\text{Zr}_{50.6}\text{Ti}_{5.2}\text{Cu}_{18.8}\text{Ni}_{14.1}\text{Al}_{14.3}$	6.608	4.89	2.27	2.15	92.7	34.0	112.6	0.362	This paper
$\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_9\text{Be}_{22.5}\text{C}_1$	6.161	5.10	2.27	2.01	105.97	39.5	107.3	0.34	a
$\text{Pd}_{39}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{21}$	9.152	4.75	1.96	2.42	98.2	35.1	159.2	0.397	a
Water-white glass	2.479	5.84	3.42	1.70	71.92	29.06	45.71	0.238	b
Borosilicate glass	2.32	5.64	3.28	1.72	61.90	24.96	40.52	0.24	b
$\text{Pd}_{79.5}\text{Si}_{16.5}\text{Cu}_{60}$	10.52	4.6	1.80	2.56	92.9	32.9	174.6	0.411	c
$\text{Pt}_{60}\text{Ni}_{15}\text{P}_{25}$	15.71	3.97	1.48	2.70	96.1	33.8	201.9	0.420	c
$\text{Pd}_{64}\text{Fe}_{16}\text{P}_{20}$	10.04	4.53	1.816	2.49	93.0	33.1	161.9	0.404	c
$\text{Pd}_{32}\text{Ni}_{48}\text{P}_{20}$	9.19	4.93	2.02	2.44	104.9	37.5	173.5	0.399	c

^aReference 10.^bReference 15.^cReference 22.FIG. 2. Variation of longitudinal velocity v_l and transverse velocity v_s of the $\text{Zr}_{50.6}\text{Ti}_{5.2}\text{Cu}_{18.8}\text{Ni}_{14.1}\text{Al}_{14.3}$ BMG with pressure. v_0 is the velocity at ambient pressure P_0 .

and 0.007 GPa^{-1} , respectively. Therefore, the longitudinal velocity is slightly more sensitive to the pressure variation than the transverse one. In contrast, v_s of the silicate glasses and amorphous carbon decrease with increasing of P ,¹⁴ indicating the existence of the acoustic softening. However, the application of the pressure up to 0.5 GPa does not induce acoustic mode softening for the BMG.

Figure 3 shows that the variations $(Y - Y_0)/Y_0$ upon pressure, where Y_0 is a normal modulus at ambient P_0 , of the elastic constants E , G , K , and σ calculated from the ultrasonic velocities. The elastic constants increase with pressure, indicating the denser packing of the MG under high hydrostatic pressure. The increasing of K with pressure is highest, while that of G and E is relatively smaller. The change of σ is the smallest within the experimental range, indicating little structural change. Considering the BMG as a monatomic lattice with an average cellular volume, the Debye temperature Θ_D can be calculated from acoustic velocities with the following equation:

$$\Theta_D = \frac{h}{k_B} \left(\frac{9}{4\pi\Omega_0} \right)^{1/3} \left(\frac{1}{v_l^3} + \frac{2}{v_s^3} \right)^{-1/3}, \quad (1)$$

FIG. 3. Variation of elastic constants Y ($Y = E, G, K, \sigma$) of the $\text{Zr}_{50.6}\text{Ti}_{5.2}\text{Cu}_{18.8}\text{Ni}_{14.1}\text{Al}_{14.3}$ BMG with pressure. Y is normalized by $(Y - Y_0)/Y_0$, where Y_0 is a normal modulus at ambient P_0 .FIG. 4. Pressure dependence of Debye temperature for the $\text{Zr}_{50.6}\text{Ti}_{5.2}\text{Cu}_{18.8}\text{Ni}_{14.1}\text{Al}_{14.3}$ BMG.

where h and k_B are the Planck constant and the Boltzman constant, respectively. Ω_0 is the atomic volume. As shown in Fig. 4, Θ_D almost increases linearly with the pressure up to 0.5 GPa, indicating that an increase in the rigidity of the BMG with P .¹⁸ These results mean that the atomic force in the BMG increases with pressure up to 0.5 GPa and no structural change occurs.

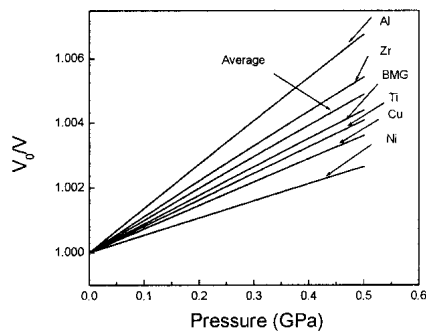


FIG. 5. Volume compression curves for the $\text{Zr}_{50.6}\text{Ti}_{5.2}\text{Cu}_{18.8}\text{Ni}_{14.1}\text{Al}_{14.3}$ BMG and its elements.

On the basis of bulk modulus and its pressure dependence, an isothermal equation of state (EOS) can be established in the Murnaghan form,^{19,20}

$$P = \frac{K_0}{K_0'} \left[\left(\frac{V_0}{V(P)} \right)^{K_0'} - 1 \right], \quad (2)$$

where K_0 and K_0' are the bulk modulus and its pressure derivative at zero P , respectively, and V_0 is the volume at zero pressure. From Fig. 3 K_0 and K_0' is derived to be 112.6 and 4.341, respectively. Accordingly, the isothermal EOS of the BMG is described as

$$P = 25.97 \left[\left(\frac{V_0}{V(P)} \right)^{4.341} - 1 \right]. \quad (3)$$

The compressibility of a solid is determined by the nature of the interatomic potential and the atomic configurations.²¹ Figure 5 shows the volume compress curves $V_0/V(P)$ of the BMG and its elements up to 0.5 GPa. It is seen that the compression curve of the $\text{Zr}_{50.5}\text{Ti}_{4.8}\text{Cu}_{19.0}\text{Ni}_{11.4}\text{Al}_{14.3}$ BMG is interposed among those of its metallic components Zr, Ti, Cu, Ni, and Al. The $V_0/V(P)$ of the BMG is near that of the average results of its metallic components. A similar result is found in the $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_9\text{Be}_{22.5}\text{C}_1$ and $\text{Pd}_{39}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{21}$ BMGs.¹² The results indicate that the BMGs have dense atomic packing.

IV. CONCLUSION

For BMG with the size of a 4.0-mm diameter, the microstructure is only of short-range order and no medium-range order exists. Decomposition is found with the HREM images. Young's modulus, E , shear modulus, G , bulk modulus, K , Poisson's rate, σ , and Debye temperature, Θ_D , of the $\text{Zr}_{50.5}\text{Ti}_{4.8}\text{Cu}_{19.0}\text{Ni}_{11.4}\text{Al}_{14.3}$ BMG

are calculated to be 92.70, 34.01, 112.6 GPa, 0.363, and 291.2 K by ultrasonic measurements at ambient pressure and room temperature. In the elastic region the elastic constants and Debye temperature all increase with pressure. Their pressure dependence is different from that of the nonmetallic glasses. The isothermal equation of state of the BMG is established in terms of the Murnaghan form with pressure up to 0.5 GPa.

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