

Equation of state of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass

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The pressure-volume (P - V) relation of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass (BMG) at room temperature has been studied using a piston-cylinder high-pressure apparatus up to 4.5 GPa. The equation of state of the BMG is determined. As the first equation of state of the BMG, it is compared with other crystalline solids, and the differences are phenomenologically explained. The experimental results indicate the BMG contains a large amount of vacancylike free volume.

The equation of state (EOS) of compressed solids (pressure-volume relation) plays an important role in many fields, such as condensed-matter physics and geophysics, because the knowledge of the EOS and the compressibility of a solid is of central importance for the general understanding of the behavior and the application of a condensed matter.¹ The EOS and the compressibility of crystalline solids have been long standing and deeply investigated, and a lot of interesting and important phenomena have been observed.¹⁻² However, up to now, no EOS is obtained for the metallic glasses, because the measurements of the volume-pressure (P - V) relation of the metallic glasses have been impeded mainly by the inability to prepare bulk specimens. A fundamental understanding of microstructural configuration under high pressure in amorphous solids is not as developed as that in crystalline solids. Recently, multicomponent glass forming systems with a larger three-dimension size have been developed by the conventional casting process at a low cooling rate.³⁻⁷ The obtained bulk metallic glasses (BMG's) are suitable for measurements of the P - V relation. In this paper, we present the first volume compression measurements on a metallic glass. A $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG which exhibits excellent glass forming ability (GFA) and properties^{3,7} is chosen as a representative BMG for investigations. The P - V isotherm of the BMG is obtained, and the P - V relation is markedly affected by the structural relaxation induced by pressure. The EOS of the BMG is determined from the fit of the P - V relation and compared with other crystalline solids. The differences are phenomenologically explained.

$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ ingots were prepared by inductive levitation melting 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 cylindrical rods 12 mm in diameter and several cm long. The details of the experimental procedure are given in Ref. 7. The amorphous nature as well as the homogeneity of the BMG was ascertained by x-ray diffraction (XRD), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and small-angle neutron scattering (SANS).^{7,8} The amorphous rods were machined down to 4.13 mm in diameter and cut to a length of 7 mm which fit the tungsten carbide pressure cells. By grinding off the outer

surface, any remaining oxide materials from the quartz container were removed. The P - V relation of the sample was measured by a piston-displacement technique developed by Bridgman⁹ at room temperature up to 4.5 GPa. The volume change of the sample under high pressure was determined by the linear compressibility of the solid, and from this the change of the volume was calculated. The linear change of dimension of the BMG was measured by a digital displacement meter, and the pressure was monitored by a pressure meter. The volume change of the sample as well as the piston and pressure cell, and the pressure measurements were calibrated by the known P - V relation of pure Bi and Fe metals. The corrections were applied to remove the frictional effects and the distortion of the vessel in which the sample was contained according to Refs. 10 and 11. The sample was first precompressed at room temperature to 4.5 GPa to eliminate the gap between the sample and the pressure cell. The precompression has no obvious effect on the volume change of the sample. The P - V measurements were performed on several samples cut from the same amorphous rod. For each sample, four to six pressure load-unload cycles were performed to examine the reproducibility and minimize errors. The diagram of the P - V measuring system and the details of the measurement procedure can be seen in Ref. 10. X-ray-diffraction experiments indicate that no crystallization of any kind was observed for the sample after pressuring. The as-prepared BMG samples were annealed or pressure annealed at various temperatures and pressures (annealing time 2 h) for density (ρ) measurements. The high pressure was performed in an apparatus with six anvil tops. The accuracy for measuring the temperature of the sample itself under applied pressure was about ± 1.5 K. After the annealing or pressure annealing, the density of the samples was measured by the Archimedian principle, and the accuracy was evaluated to be 0.005 g/cm³.

Figure 1 shows the relative volume change $\Delta V/V_0$ upon pressure at room temperature of the BMG after precompression. The dotted line in Fig. 1 is the P - V relation of the first compression run after precompression under high pressure, and the solid curve is the P - V relation of the second compression run. There is a remarkable difference between the two curves. No obvious difference for the P - V curves can be

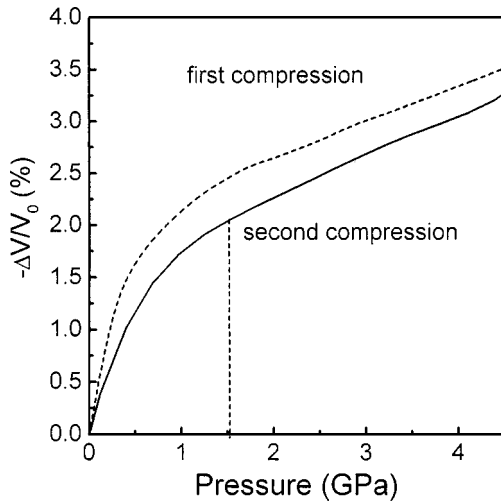


FIG. 1. The relative volume change $\Delta V/V_0$ of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG for the first (dashed curve) and second (solid curve) compression run (after precompression). A marked difference between the two P - V curves can be seen.

observed for more than two times compression. The P - V data are reproducible under pressure and show no measurable hysteresis effects after two pressure load and unload cycles. This kind of phenomenon has been generally observed in porous materials, resulting from the disappearance of the pores under pressure.¹¹ The difference between the P - V curves of the first and second compression indicates that a large amount of free volume exists in the as-prepared BMG, and the free volume is removed through the structural relaxation under high pressure. The result provides direct evidence for pressure-induced structural relaxation in the BMG.

Bridgman presented the EOS as follows:¹⁰

$$-\Delta V/V_0 = a_0 + aP + bP^2 + cP^3, \quad (1)$$

where $\Delta V = V - V_0$, V_0 is the volume at zero pressure, and a_0 , a , b , and c are constants. Equation (1) has been applied successfully to the isothermal compression of a lot of classes of solids in the nonphase transitional case.¹⁰ However, Eq. (1) cannot be successfully applied to fit the compression curve of the BMG at least in the range of 0 to 4.5 GPa. Figure 2 shows a comparison of the P - V relations of Cu, Ni,¹² stainless steel ($Cr_{18}Ni_{82}$), and the BMG. It can be clearly seen that the change of $\Delta V/V_0$ of the BMG with increasing pressure is markedly different from those of Cu, Ni, and stainless steel. On one hand, the volume compression of the BMG is much larger than that of crystalline alloy and metals, indicating that a microstructural difference exists among them. On the other hand, $\Delta V/V_0$ increases much faster with pressure in the low-pressure range of 0–1.5 GPa, which indicating the compression is more sensitive to low-pressure. This phenomenon has also been found in amorphous carbon¹³ as shown in Fig. 3. Figure 3 presents a comparison of the P - V relation of the BMG and amorphous carbon. Similar change tendency of $\Delta V/V_0$ can be seen for the BMG and amorphous carbon, but the volume compression of the amorphous carbon is much larger than that of the BMG, confirming that the BMG has a dense packed atomic configuration compared to other amorphous materials.^{4,5,8}

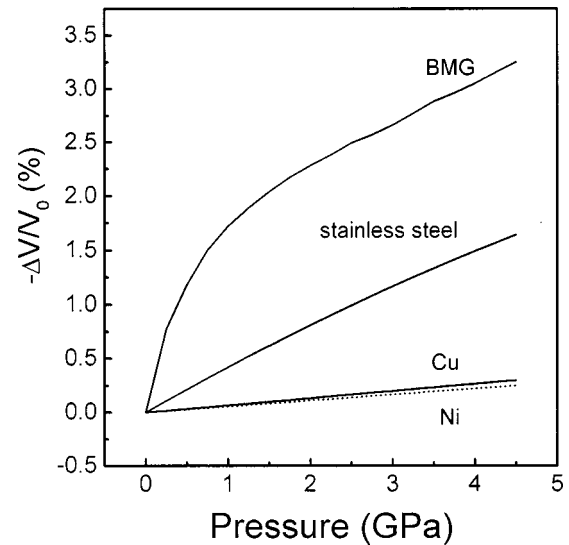


FIG. 2. A comparison of the P - V relations for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG and other solids. The volume compression of the BMG is much larger than that of crystalline alloy and metals. The $\Delta V/V_0$ of the BMG increases more drastically upon pressure in the low pressure range of 0 to 1.5 GPa.

The $\Delta V/V_0$ change of the BMG can be divided into two parts, and Eq. (1) can be applied to the two parts, respectively. In the first part (0–1.5 GPa) the compression changes drastically with increasing pressure and can be expressed as

$$-\frac{\Delta V}{V_0} = 0.034P - 0.0238P^2 + 0.0068P^3. \quad (2)$$

The change in the second part (1.5–4.5 GPa) is smaller and can be expressed as

$$-\frac{\Delta V}{V_0} = 0.0145 + 0.02425P - 5.874 \times 10^{-5}P^2. \quad (3)$$

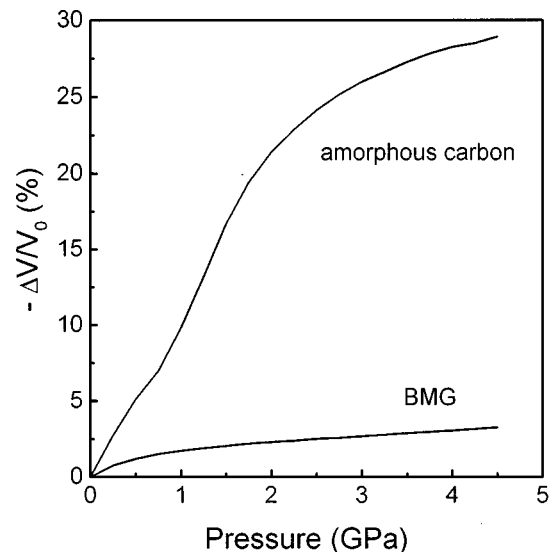


FIG. 3. A comparison of the P - V relation between amorphous carbon and the BMG. The $\Delta V/V_0$ of the BMG and amorphous carbon shows similar change tendency, but the volume compression of the amorphous carbon is much larger than that of the BMG.

TABLE I. The constants a_0 , a , b , c of the Bridgman equation for the BMG and other solids.

Solid	Range (GPa)	a_0	a (GPa ⁻¹)	b (GPa ⁻²)	c (GPa ⁻³)
BMG	0–1.5		0.034	-0.0238	0.00676
BMG	1.5–4.5	0.0145	0.02425	-5.874×10^{-5}	
Cu	0–4.5		6.621×10^{-4}	1.098×10^{-8}	
Ni	0–4.5		5.547×10^{-4}	2.704×10^{-8}	
Stainless steel	0–4.5		4.365×10^{-3}	-1.603×10^{-4}	

The constants a_0 , a , b , and c of the Bridgman equation for the BMG and other solids are listed in Table I. As shown in Table I, the EOS of the second part of the BMG is similar to that of metals and crystalline alloys, but markedly different from that of the first part, indicating that low pressure has a larger effect on the glassy state.

Pressure is expected to be sensitively related to the evolution of free volume, reducing voids through compressing the glassy structure during relaxation. Experimental studies and numerical modeling demonstrate that low pressure promotes a short-range rearrangement of the atoms in the supercooled liquid region of the metallic glasses.^{14,15} The structural relaxation causes annihilation of the free volume. Low pressure results in the collapse of the free volume and reconstruction of the atomic configuration in the BMG.¹⁴ The effects of pressure on metallic glass during static relaxation have also been computed.^{14–17} An explicit feature is the noticeable shrinkage of volume at low pressure, implying a significant degradation of the free volume during pressurization. Similar changes of parameters of magnetic Curie temperature and electrical resistivity of metallic glasses upon low-pressure relaxation have also been observed, these changes are related to the contraction of the free volume under pressure.¹⁴

To confirm the existence of vacancylike free volume in the BMG, the density change of the BMG treated under vari-

ous pressures and temperatures were measured. Figure 4 contrasts the density change of the BMG treated at various temperature with or without applied pressure. The densities of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG in the as-prepared state and compressed state (after exposure of the sample to 4.5 GPa for 2 h) at room temperature were measured to be 6.162 and 6.180 g/cm³ respectively. The increase in density due to applied pressure is about 0.31%. This result further confirms that the high pressure does remove the free volume to some extent and induces structural relaxation in the BMG. When the BMG is annealed near glass transition temperature (623 K) and in supercooled liquid region, 653 K [the supercooled liquid region is from 623 to 683 K (Ref. 7)] the applied low-pressure induced larger change of density compared with that of sample annealed at the same temperature without applied pressure (as shown in Fig. 4). Even if the BMG is in crystallization process (annealed at 723 K), low-pressure results in larger change of density. The P - V relation and density measurements as well as others' theoretical and experimental results^{14–17} concerning the strong change of physical parameters upon low-pressure relaxation indicates that the as-quenched BMG, which has more packed atomic configurations compared to conventional binary metallic glasses,^{8,18} also contains a distinct amount of vacancylike free volume.

In conclusion, the equation of state obtained for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG in the non-phase-transitional case is

$$-\frac{\Delta V}{V_0} = 0.034P - 0.0238P^2 + 0.0068P^3 (0 < P < 1.5 \text{ GPa})$$

$$-\frac{\Delta V}{V_0} = 0.0145 + 0.02425P$$

$$-5.874 \times 10^{-5}P^2 (1.5 < P < 4.5 \text{ GPa})$$

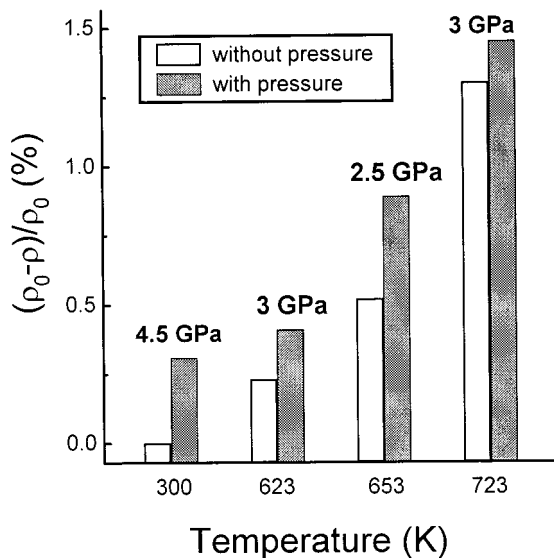


FIG. 4. The relative change of density (ρ) of the BMG treated at various temperatures with and without applied pressure. ρ_0 is the density of the as-prepared BMG.

The volume change under pressure is much larger than that of the crystalline materials which indicates that the BMG contains a large amount of vacancylike free volume. Low pressure induces the collapse of the free volume and reconstruction of the atomic configuration in the BMG.

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