The equation of state and potential function of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass

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Abstract
Using a piston–cylinder displacement technique, the pressure–volume (P–V) relation of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass (BMG) has been measured up to a pressure of 4.5 GPa at room temperature. In the lower part of the high-pressure region the change of volume with pressure has remarkable non-linear characteristics indicating the existence of a large amount of free volume. A simple equation of state (EOS) with a cubic polynomial can be used to fit the experimental P–V data very well. From this, a potential function describing the EOS of the BMG has also been determined through combining experimental and theoretical analysis.

The behaviours of solids such as metallic or non-metallic crystals [1–4], oxide glasses [5, 6], polymer glasses, and ceramics under high pressure have been analysed by many authors on the basis of a model potential and the relationship between cold and thermal pressures [1–9]. However, studies on the equation of state (EOS) of metallic glass have been scant because of the inability to prepare bulk specimens. When a metal melt (liquid) is cooled, one of two events may occur. Either crystallization may take place at the melting point T_m, or else the melt will become 'supercooled' for temperatures below T_m, becoming more viscous with decreasing temperature, and may ultimately form an amorphous solid, i.e., a metallic glass. Thus, this solid or metallic glass state can be considered as the result of structural freezing of a melt or liquid. In the past, metallic glass was prepared in the form of thin strips due to its lack of glass formation ability, and thus many studies were restricted. The fundamental understanding of the microstructure and other properties of metallic glass is not as developed as that for crystalline solids [10–12]. The discovery of complex multicomponent bulk metallic glass (BMG) has stimulated great interest in various phenomena which were difficult to explain before. The large size and high

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thermal stability of BMGs allow a detailed and accurate study of their various properties over a large temperature and pressure range [11,13–15]. Typical examples include the investigation of pressure-assisted nanocrystallization and enthalpy change in Zr-based BMG [11,15]. However, the understanding of pressure effects in these processes still remains on a very qualitative level because of the lack of a quantitative description of the static and dynamic properties of the compressed metallic glassy state under high pressure. Using an EOS with a given potential function, one can distinguish between the possible contributions of cold and thermal pressure to structural relaxation or phase transition in the BMG during high-pressure annealing.

In this paper we show a measured pressure–volume (P–V) relation for $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG up to a pressure of 4.5 GPa at room temperature. In the lower part of the high-pressure region, the change of volume of the BMG with pressure has remarkable non-linear characteristics. A simple cubic polynomial equation can be used to fit the experimental P–V data very well, and the EOS of the BMG is determined, based on the Morse potential function, by a combination of experimental and theoretical analyses.

The measurements of the P–V relation were performed on $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG produced by cooling the alloy from the liquid to the glassy state in a quartz container. The amorphous nature of the as-quenched bar was confirmed by D/Max-2400 x-ray diffraction (XRD), differential scanning calorimetry, and transmission electron microscopy. The XRD pattern for this BMG shows a main diffuse peak located at about $2\theta = 38.6°$ and a second main diffuse peak located at about $2\theta = 66°$. The high-resolution transmission electron microscopy image exhibits a homogeneous hazy contrast, which is characteristic of amorphous materials where the atom arrangement is in the form of random close packing [16]. The amorphous substance was shaped into rods with a diameter of 4.13 mm and a length of 7 mm, to fit the tungsten carbide pressure cell. The P–V relation of the specimen was measured by a piston–displacement technique at room temperature up to 4.5 GPa. The density of the bulk metallic glassy specimen at room temperature was obtained by Archimedes' principle. The initial density was 6.125 g cm^{-3}. The constant-volume specific heat and bulk modulus of the specimen were calculated on the assumption of an isotropic homogeneous solid according to the density and acoustic velocity data measured by using a pulse-echo overlap method [15]. The low-temperature specific heat was measured in an adiabatic calorimeter between 1.8 and 20 K using a standard discontinuous heating method.

Compared to the case for crystalline solids, compression of the amorphous solid, with the existence of free volume, is very sensitive to low pressure [2, 3, 17]. Figure 1 shows the P–V relation of the BMG under pressure at room temperature. It is clear that the change of volume with pressure is markedly non-linear and much larger than those for Cu, Ni, and other crystalline metallic solids below 1.5 GPa [16, 18]. This indicates there are microstructural differences among them. This non-linear behaviour has also been found in amorphous carbon [19], but the volume compression of amorphous carbon is much larger than that of the BMG, which confirms that the latter has a dense-packed atomic configuration compared to other amorphous materials [20, 21]. The Murnaghan, or Birch–Murnaghan, EOS and other equations that have been applied successfully to the isothermal compression of conventional solids cannot describe the experiment results for the metallic glass due to the drastic volume change at low pressure [22]. The P–V curve can be very well fitted by the Bridgman equation

$$P(V, T = 298 \text{ K}) = A_0 + A_3\left(\frac{V - V_{298}}{V_{298}}\right)^3 \tag{1}$$

where $V_0 = V_{298}$ is the specific volume at ambient pressure ($P = 1$ atm) and room temperature ($T = 298$ K), A_0 and A_3 are fitting constants, $A_0 = 10^{-4}$ GPa (1 atm) and $A_3 = -1.0771 \times 10^5$ GPa. In order to further study the compression behaviour of the BMG,
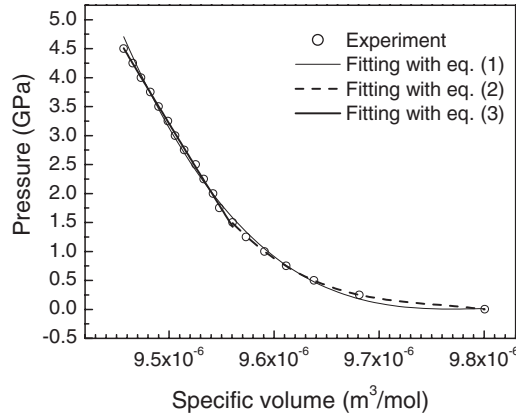
Figure 1. Experimental and fitted $P-V$ relations of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG under pressure at room temperature.

the $P-V$ curve of the BMG can be divided into two parts, i.e., one part for the drastic change of the compression (in the low-pressure region of about 0–1.5 GPa), and another for the section of the curve with less pronounced change (in the high-pressure region of about 1.5–4.5 GPa). A quadratic and a cubic polynomial are applied for the two parts, respectively. The section of the compression showing drastic change with increasing pressure can be expressed as (thick solid curve in figure 1)

$$P = 1.402\,29 \times 10^5 - 4.311\,831 \times 10^{10} V + 4.419\,56 \times 10^{15} V^2 - 1.510\,047 \times 10^{20} V^3. \quad (2)$$

The change in the second part can be written as (thick dashed curve in figure 1)

$$P = 8.704\,891 \times 10^2 - 1.528\,026 \times 10^8 V + 6.474\,716 \times 10^{12} V^2. \quad (3)$$

Comparing equation (2) with (3), we can see that the quadratic and cubic terms of V in equation (2) impose a non-linear behaviour upon the BMG in the low-pressure region because of the compression of the free volume. As we know, free volume is the space in which the atoms or molecules are free to move, and redistribution of the free volume occurs in liquids. As the temperature of the liquid is lowered, both the volume occupied by atoms or molecules and the free volume are expected to contract. In the free-volume model of atomic transport, the glass transition corresponds to the elimination of most of the free volume, and the remaining free volume is 'frozen in' in the glass. The primary term of V in equation (2) imposes a linear behaviour of the BMG in the high-pressure region. This is similar to the case for metals and crystalline alloys [16, 18], but markedly different from that in equation (2), which indicates that low pressure has a larger effect on the glassy state.

The EOS of a solid is generally described by a functional relationship between the thermodynamic variables defined for a system in equilibrium. Neglecting the electron–phonon interactions, the energy E and the pressure P of the system can be expressed as

$$E = E_C + E_{Ta} + E_{Te} \quad (4)$$
$$P = P_C + P_{Ta} + P_{Te} \quad (5)$$

where E_C and P_C are the energy and the pressure at $T = 0$ K, respectively, E_{Ta} and P_{Ta} correspond to the contributions from the atomic vibrations, and E_{Te} and P_{Te} correspond to the appropriate electron thermal contributions.

Our fitting results show that only the Morse interatomic pair potential gives the proper description for interatomic interaction in the present glass. The cold energy of a metallic glass is of the form [23]

$$E_C(V) = P_{C0} V_0 \left(1 - \frac{V}{V_0} \right) + \frac{3}{2} \frac{A}{B} V_0 [\exp(B(1 - (V_0/V)^{-1/3})) - 1]^2. \quad (6)$$

The corresponding cold pressure is

$$P_C(V) = P_{C0} + A \left(\frac{V_0}{V} \right)^{2/3} [\exp(2B(1 - (V_0/V)^{-1/3})) - \exp(B(1 - (V_0/V)^{-1/3}))]. \quad (7)$$

Here A and B are potential parameters to be determined by fitting experimental results (equation (1)) at room temperature, V_0 is the specific volume of metallic glass at $T = 0$ K and $P = 0$ atm, and P_{C0} is an additional parameter to adjust for the zero-pressure point in fitting [24]. In equation (6) we have set the zero point of E_C to $V = V_0$.

On the basis of the Debye model of solids, the thermal energy and thermal pressure associated with lattice vibrations are expressed as

$$E_{Ta} = 3RT D \left(\frac{\theta_D}{T} \right) \quad (8)$$

$$P_{Ta} = 3RT \frac{K_{298} \alpha_{298}}{C_V} D \left(\frac{\theta_D}{T} \right) \quad (9)$$

where R is the universal gas constant, $D(\theta_D/T)$ the Debye function, θ_D the Debye temperature, γ_{298}, ρ_{298}, K_{298}, and α_{298} are, respectively, the thermodynamic Grüneisen parameter, metallic glass density, bulk modulus, and volume expansion coefficient at $T = 298$ K and $P = 1$ atm, and C_V is the constant-volume specific heat. As a suitable choice we have used an empirical approximation, $\gamma(V)/V = \gamma_{298}/V_{298}$, for the Grüneisen parameter γ [23].

The electronic contributions are given by

$$E_{Te} = \frac{1}{2} \beta_0 \left(\frac{V}{V_0} \right)^{2/3} T^2 \quad (10)$$

$$P_{Te} = \frac{\gamma_e}{V} \frac{1}{2} \beta_0 \left(\frac{V}{V_0} \right)^{2/3} T^2 \quad (11)$$

where β_0 is the electronic specific heat coefficient at $T = 0$ K and $P = 0$ atm, and can be obtained from the measurement of the constant-pressure specific heat at very low temperature. We take the electronic Grüneisen coefficient $\gamma_e = 2/3$ [23].

Substituting equations (6), (7), (10) and (11) into (4) and (5), we obtain a complete expression for the EOS of the BMG. In equations (6) and (7), the potential parameters A and B can be related to the expression $P_C = P - (P_{Ta} + P_{Te})$ by using the normal condition $V = V_{298}$ and total pressure $P = 1$ atm. ρ_0 (or V_0), V_{298}, α_T, K_{298}, C_V (or C_P), and β_0 can be obtained experimentally. The density (ρ_0) at 0 K is calculated from ρ_{298} and the thermal expansion coefficient (α_T) measured within the temperature range of 80–300 K and extrapolated to 0 K [25]. Thus in equations (6) and (7) only two adjustable parameters are to be determined by fitting the equations to the experimental results. The parameters involved in the EOS are given in table 1.

Figure 2 is a comparison of the calculated and experimental results. The agreement is very good. It can be seen that the thermal electronic contribution to the EOS is negligible although the specific heat of the BMG at low temperature is abnormal compared with those of normal metals and alloys in similar pressure regions [26, 27]. The thermal pressure does not change with applied pressure in our region of interest (equation (9)). Below the applied pressure of 0.7
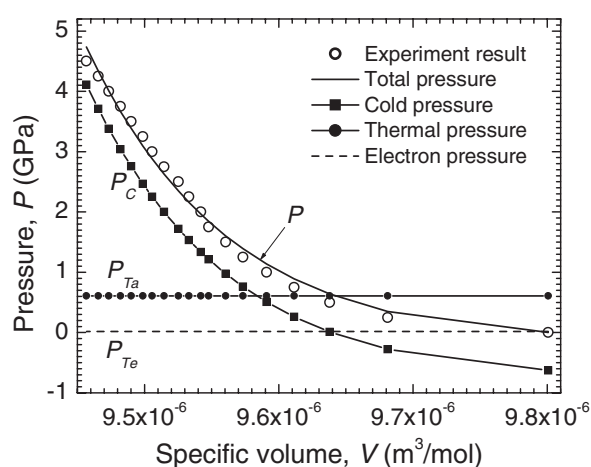
Figure 2. Comparison between the experimental and calculated results for the P–V relation of the BMG under pressure at room temperature. The contributions of cold and thermal pressure are also shown.

Table 1. Experimental data necessary for solving the EOS, and values of the potential parameters A, B, and P_{C0}.

V_{298} (m^3 mol^{-1})	9.8007×10^{-6}
V_0 (m^3 mol^{-1})	9.783×10^{-6}
α_T (K^{-1})	2.61×10^{-5}
K (GPa)	114.1
C_V (J mol^{-1})	23.5
θ_D (K)	327.8
β_0 (J mol^{-1} K^{-2})	6.372×10^{-3}
A (GPa)	0.408 12
B (dimensionless)	121.8
P_{C0} (GPa)	-0.601 95

GPa the cold pressure becomes negative, and $P_C \approx -P_{Ta}$ at $T = 298$ K and $P = 1$ atm. The proportion of the negative cold pressure decreases with increase in temperature. Corresponding to zero cold pressure (0.7 GPa), there is a minimum in the cold energy. Hence, it can be deduced that the structural phase transition and relaxation of the BMG can occur when the applied pressure exceeds 0.7 GPa and there is an increase of temperature. Correspondingly, the change of the cold energy in this pressure region is about 3×10^{-3} eV/atom in the BMG (figure 3). This estimate is in the range of 10^{-2}–10^{-4} eV/atom from the stored energy calculation [28], which is small compared with the bond energy (2–4 eV) and the activation energy of diffusion (1 eV) in BMGs. However, it is important to note that the effect of the temperature on the thermal contribution is very obvious. For example, its thermal effect can supply an additional energy of about 0.1 eV to each atom when the temperature is increased to 573 K (see equation (9) and figure 3). The apparent structural change in the BMG can occur when the specimen is relaxed below the calorimetric glass transition temperature and under pressure [29].

Originally, the Morse potential was used to describe the interaction in molecular crystals and liquids, where the binding force between molecules is of dispersion or dipole–dipole type. The structure and interactions between atoms in metallic glass are markedly different from
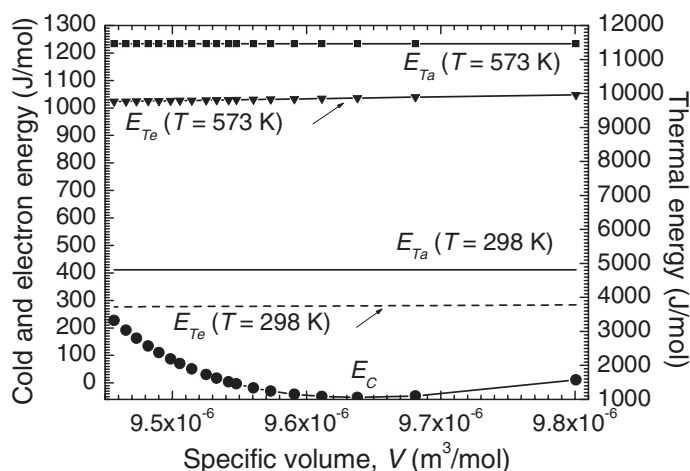
Figure 3. Contributions of the cold, thermal, and electronic energies at room temperature and 573 K in the BMG.

those for ionic and covalent or metallic crystals. The BMG alloy is composed of five metallic components with large size differences in the atomic diameter, and the glass from the point of the view of microstructure is considered as a frozen undercooled metal melt; thus the atomic arrangement is random close packing. The interactions between atoms are non-directional and weaker than those of crystals due to the packing and the existence of the free volume. In fact, the resistance of the BMG is about two orders higher than that of metal crystals. Thus, the Morse potential is more suitable for describing the interaction between atoms in the BMG.

In summary, in the lower part of the high-pressure region, the change of volume of the BMG with pressure has remarkable non-linear characteristics indicating the existence of a large amount of free volume. A simple cubic polynomial equation can be used to fit the experimental P–V data very well. This is also the first time that the EOS of a BMG with the Morse potential function and the Debye model of solids have been determined by a combination of experimental and theoretical analyses. This equation can be used to analyse the characteristics of the interatomic action and structural phase transition caused by pressure and heat relaxation in the BMG.

Acknowledgments

References

[1] Bundy F P and Strong H M 1962 *Solid State Physics* vol 13, ed F Seitz and D Turnbull (New York: Academic) p 81
[2] Otto J W, Vassiliou J K and Frommeyer G 1997 *J. Mater. Res.* **12** 3106
[3] Zhang J and Guyot F 1999 *Phys. Chem. Minerals* **26** 206
[4] Lundin A, Soldatov A, Sundqvist B, Strongin R M and Brard L 1996 *Carbon* **34** 1119
[5] Bridgman P W, Simon I and Little A D 1953 *J. Appl. Phys.* **24** 405
[6] Tsiok O B, Brazhkin V V, Lyapin A G and Khvostantsev L G 1998 *Phys. Rev. Lett.* **80** 999

[7] Rehage G and Oels H-J 1977 *High Temp.–High Pressures* **9** 545
[8] Roy S B and Roy P B 1999 *J. Phys.: Condens. Matter* **11** 10 375
[9] Hama J and Suito K 1996 *J. Phys.: Condens. Matter* **67–8** 67
[10] Eliezer S, Ghatak A, Hora H and Teller E 1986 *An Introduction to Equations of State: Theory and Application* (Cambridge: Cambridge University Press)
[11] Samwer K, Busch R and Johnson W L 1999 *Phys. Rev. Lett.* **82** 580
[12] Ruitenberg G, Hey P D, Sommer F and Sietsma J 1997 *Phys. Rev. Lett.* **79** 4830
[13] Peker A and Johnson W L 1993 *Appl. Phys. Lett.* **63** 2342
[14] Ehmler H, Heesemann A, Raetzke K and Faupel F 1998 *Phys. Rev. Lett.* **80** 4819
[15] Wang W H, Wang R J, Li F Y, Zhao D Q and Pan M X 1999 *Appl. Phys. Lett.* **74** 1803
[16] Wang W H, Wang R J, Zhao D Q, Pan M X and Yao Y S 2000 *Phys. Rev.* B **62** 11 292
[17] Bernardes N and Swenson C A 1963 *Solids Under Pressure* ed W Paul and D M Warschauer (New York: McGraw-Hill) p 101
[18] Bao Z X and Zhang Z T 1990 *Chin. J. High Pressure Phys.* **4** 78
[19] Bao Z X, Gu H C and Zhang Z T 1988 *J. High Pressure Phys.* **2** 179 (in Chinese)
[20] Johnson W L 1996 *Mater. Sci. Forum* **225–7** 35
[21] Inoue A 1995 *Mater. Trans. JIM* **36** 866
[22] Spain I L and Paauwe J 1977 *High Pressure Technology: Equipment Design, Materials and Properties* vol 1 (New York: Dekker)
[23] Xu X S and Zhang W X 1986 *Introduction to Practical Equations of State* (Beijing: Academic)
[24] Tang W H and Zhang R Q 1999 *Theory of States of Solids and an Introduction to Calculations* (Chang Sha: National Defence University Press)
[25] He Y, Schwarz R B, Mandrus D and Jacobson L 1996 *J. Non-Cryst. Solids* **205–7** 602
The averaged values are 3.83×10^{-5} and 3.0×10^{-5} K^{-1}; see
Ohsaka K, Chung S K, Rhim W K, Peker A, Scruggs D and Johnson W L 1997 *Appl. Phys. Lett.* **70** 726
[26] Obi Y, Wang L C, Motsay R and Onn D G 1982 *J. Appl. Phys.* **53** 2304
[27] Caudron R, Meunier J J and Costa P 1974 *Solid State Commun.* **14** 975
[28] Chen H S 1983 *Amorphous Metallic Alloys* ed F E Luborsky (London: Butterworth) p 169
[29] Pan M X, Wang J G, Yao Y S, Zhao D Q and Wang W H 2001 *Appl. Phys. Lett.* **78** 601