Elastic Constants, Equation of State and Mechanical Relaxations of Some Metallic Glasses at High Pressure

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Abstract. One of the fundamental physical quantities necessary to describe the mechanical properties of the materials is the bulk modulus. In the present report, a simple method to estimate the values of the bulk modulus and its pressure derivative of metallic glasses is presented. The method which is based on a jellium model of metals provides a good agreement with measured data. The estimated values of the elastic constants have been used to determine the equation of state of bulk metallic glasses. It is found that the usual Murnaghan equation of state deviates considerably from the experimental results at high pressures. The deviation has been interpreted to arise from the structural relaxations. The effect of pressure on the fragility of bulk metallic glasses is discussed briefly.

Introduction

In recent years, multicomponent bulk metallic glasses have attracted considerable interest [1-5]. In contrast to traditional amorphous metals, these new alloys have low critical cooling rates and fully amorphous samples with one side dimension as large as 1 cm can be produced by conventional cooling processes. The bulk metallic glasses have unique properties such as extraordinary high strength, low ductility, high hardness, excellent corrosion resistance and high thermal stability of their supercooled liquids, which permit the study of thermophysical properties in the supercooled liquid state in addition to the amorphous solids [6-8]. To exploit the excellent properties of bulk metallic glasses, a good understanding on fundamental materials properties is indispensable. In the present study, a simple method to evaluate the bulk modulus and its pressure derivative of bulk metallic glasses is presented. The bulk modulus is a fundamental physical quantity that characterizes the mechanical properties of the materials. It is well known that the bulk modulus is related with the interatomic interactions. That is, valuable microscopic information to understand the origin of materials properties can be obtained from its study.

The equation of state is a fundamental relation that characterizes the material. Its knowledge is of primordial importance from both, fundamental and technological point of views. In this paper, the well known Murnaghan equation has been used to determine the equation of state of bulk metallic glasses. The bulk modulus and its pressure derivative are the input parameters needed. A comparison of the obtained equation of state with experimental data suggests that at high pressure, the effect of structural relaxation should be taken into account. As a related topic, the pressure dependence of the fragility has been studied. The result indicates that the fragility in bulk metallic system increases with pressure, although in the usual experimental conditions its variation is very small.

Bulk Modulus and its Pressure Dependence

As mentioned in the introduction, the evaluation of bulk modulus is of primordial importance to describe the mechanical properties of the materials. The calculation of bulk modulus through the use of traditional methods such as those based on electronic structure calculations could be accurate. However, it is technically too involved, time consuming and not appropriate to study the general trend of the materials in a simple way. Therefore, it will be valuable to develop a method to estimate

easily the physical quantities. Recently, it has been shown that the bulk modulus and its pressure derivative of bulk metallic glasses can be estimated from the values of the constituent elements and their compositions [9, 10]. The result shown in Fig. 1 indicates that the estimation is good. The result indicates also that the mechanical properties of bulk metallic glasses are determined essentially by the electron density analogously to the case of elementary metals [10].

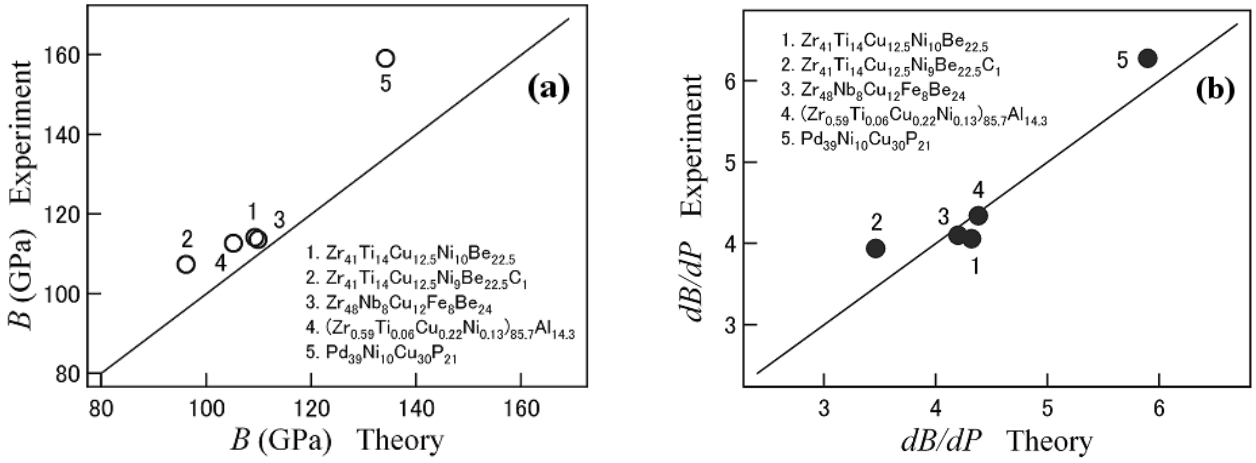

Fig. 1. Comparison between the calculated and the measured data of bulk modulus (a) and its pressure derivative (b).

The physical background of the estimation has been discussed based on the jellium model of metals that includes the kinetic, exchange and correlation energies of the electronic system [10]. According to the jellium model, the energy of the interacting electron gas is written as [11]

$$\varepsilon = \frac{3}{5\alpha^2 r_s^2} - \frac{3}{2\pi\alpha r_s}(1+\beta), \tag{1}$$

$$\alpha = \left(\frac{4}{9\pi}\right)^{1/3}, \tag{2}$$

$$\frac{1}{n} = \frac{4}{3}\pi r_s^3, \tag{3}$$

where β represents the contribution from the correlation energy and n is the electron number density. The bulk modulus and its pressure derivative are written as

$$B = \frac{1}{12\pi r_s}\left(\frac{\partial^2 \varepsilon}{\partial r_s^2} - \frac{2}{r_s}\frac{\partial \varepsilon}{\partial r_s}\right), \tag{4}$$

$$\frac{\partial B}{\partial P} = -\frac{1}{3}\frac{r_s}{B}\frac{\partial B}{\partial r_s}, \tag{5}$$

$$\frac{\partial B}{\partial r_s} = -\frac{5}{2\pi\alpha^2}\frac{1}{r_s^6} + \frac{2}{\pi^2\alpha}(1+\beta)\frac{1}{r_s^5}. \tag{6}$$

The above equations indicate that the values of B and dB/dP are obtained if the electron number density parameter r_s is available. Concerning the values of r_s for the elements, many researchers have

reported their own values based on different degree of sophistication [12, 13]. Although there are differences in details, all the results show the same behavior and trend along the periodic table of the elements. The result of a simple number of valence electrons counting method applied to the evaluation of bulk modulus is illustrated in Fig. 2. The calculation for the pressure derivative of the bulk modulus indicates that dB/dP ≈ 5 [10]. This value is close to the value reported for elemental metals. The experimental values reported for bulk metallic glasses are in the range dB/dP ≈ 4-6 [9].

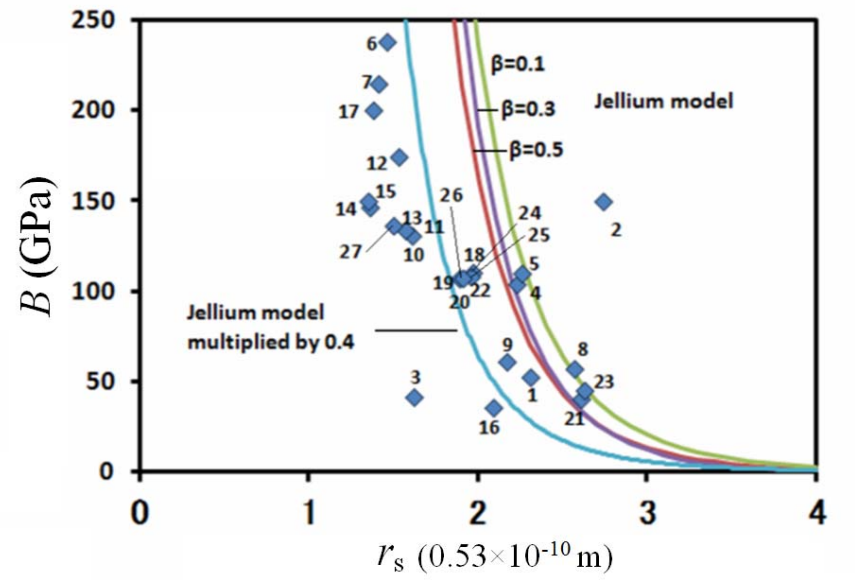

Fig. 2. The predicted values of the bulk modulus are shown as a function of the electron density parameter r_s. The numbers in the figure indicate the glasses given in Table 1. The symbols represent the estimated values from the values of the constituent elements and their compositions [9, 10].

Table 1. List of metallic glasses shown in Fig. 2.

No.	Glasses	No.	Glasses	No.	Glasses
1	$La_{55}Al_{25}Ni_5Cu_{10}Co_5$	10	$Ni_{40}Cu_5Ti_{17}Zr_{28}Al_{10}$	19	$Zr_{55}Al_{19}Co_{19}Cu_7$
2	$Au_{55}Cu_{25}Si_{20}$	11	$Ni_{45}Ti_{20}Zr_{25}Al_{10}$	20	$Zr_{57.5}Cu_{15.4}Ni_{12}Al_{10}Nb_5$
3	$Ce_{70}Al_{10}Ni_{10}Cu_{10}$	12	$Ni_{60}Nb_{35}Sn_5$	21	$Mg_{70}Zn_{25}Cu_5$
4	$Cu_{46}Zr_{42}Al_7Y_5$	13	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	22	$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$
5	$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	14	$Pd_{60}Fe_{20}P_{20}$	23	$Mg_{65}Cu_{25}Tb_{10}$
6	$Fe_{53}Cr_{15}Mo_{14}Er_1C_{15}B_6$	15	$Pd_{64}Ni_{16}P_{20}$	24	$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$
7	$Fe_{61}Mn_{10}Cr_4Mo_6Er_1C_{15}B_6$	16	$Pr_{60}Cu_{20}Ni_{10}Al_{10}$	25	$Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$
8	$Mg_{65}Cu_{25}Gd_{10}$	17	$Pt_{60}Ni_{15}P_{25}$	26	$(Zr_{0.59}Ti_{0.06}Cu_{0.22}Ni_{0.13})_{85.7}Al_{14.3}$
9	$Nd_{60}Al_{10}Fe_{20}Co_{10}$	18	$Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$	27	$Pd_{39}Ni_{10}Cu_{30}P_{21}$

Equation of State and Structural Relaxation

The evaluated bulk modulus and its pressure derivative can be used to determine the equation of state. As an example, the equation of state of $Pd_{39}Ni_{10}Cu_{30}P_{21}$ has been calculated by employing the Murnaghan equation which is used widely in the literature. It is written as

$$P = \frac{B_0}{B_0'}\left[\left(\frac{V_0}{V(P)}\right)^{B_0'} - 1\right], \tag{7}$$

where B_0 and $B_0^{'}$ are the bulk modulus and its pressure derivative at ambient pressure, $V(P)/V_0$ denotes the relative volume change under compression. The result is shown in Fig. 3.

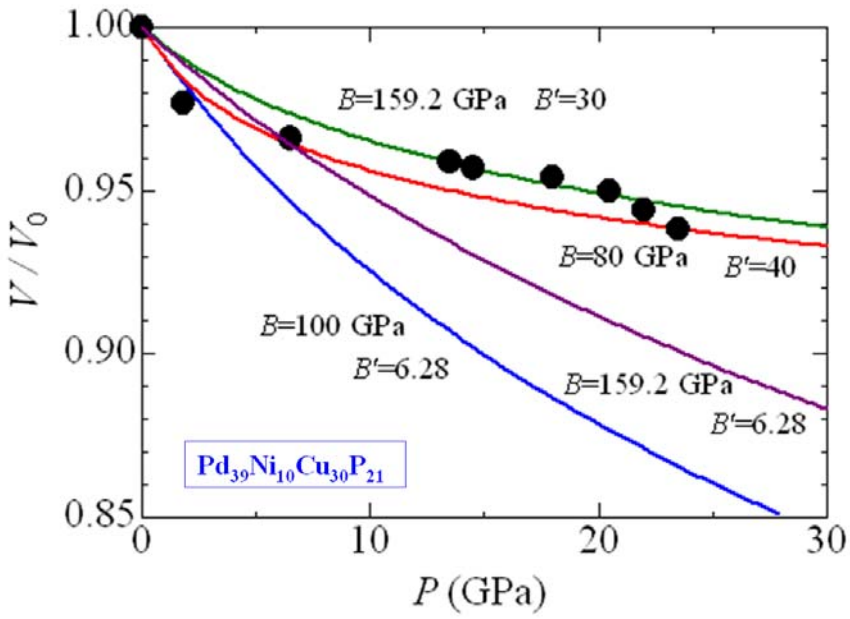

Fig. 3. The relative volume change under compression in $Pd_{39}Ni_{10}Cu_{30}P_{21}$ calculated by the Murnaghan equation of state. The experimental values are from [14].

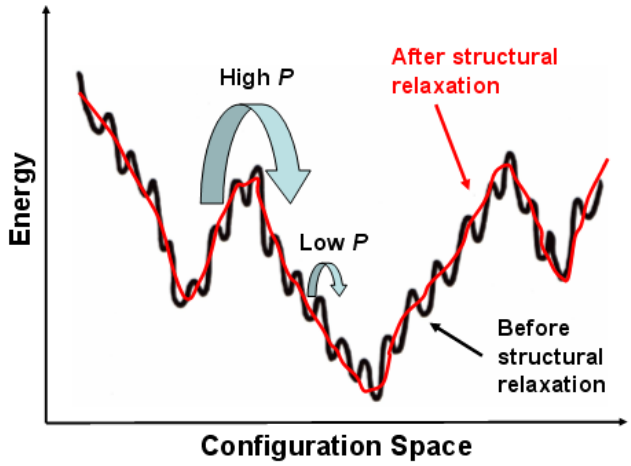

Fig. 4. Energy profile represented in the configuration space. The effect of pressure on the smoothing of energy profile is illustrated.

From Fig 3 it is noted that by using the values of the parameters B_0 = 159.2 GPa and dB/dP = 6.28 determined at ambient pressure [14] does not reproduce the behavior of $V(P)$ observed experimentally at high pressure. The result is interesting, because, the Murnaghan equation of state has been used successfully to evaluate the thermal and mechanical properties of crystalline materials. Analysis using another equation of state gives similar result to that shown in Fig. 3 [14]. These results suggest that at high pressure, the effect of structural relaxation should be taken into account [14]. In Fig. 3, the curves calculated by varying the values of B and dB/dP are shown. The curves reveal that the agreement with the experimental data at high pressure is improved by adopting a large value of dB/dP. This behavior could be explained as a change in the energy profile in the configuration space reflecting the structural relaxations. The idea is illustrated in Fig. 4. A metallic glass is thermodynamically in a metastable state. It occupies one of the many local minima configurations.

The difference in energy between these local minima arises mainly from the disorder related energy, which is governed by angular interactions between the structural units that form the system. Since in metallic systems these interactions are weak, the energy difference is overcome easily by the application of pressure. In other words, the energy profile in the configuration space is smoothed by the application of pressure. As shown in Fig. 3, the rapid decrease of V/V_0 at low pressure is probably due to this effect. After the small energy difference is overcame, further change in the configuration space is difficult, because in metallic systems, the interactions have spherical symmetry and the structural units can be represented by effective hard spheres occupying close packed like structures. The smooth change of V/V_0 observed at high pressure in Fig. 3 supports this conjecture.

Pressure dependence of the Fragility

The concept of fragility has been used widely and has played a fundamental role in understanding the relaxation behavior of glass forming liquids [15]. Some years ago, it was shown that the fragility of simple nonmetallic and metallic glass forming systems increases with the increase in the Poisson's ratio [16]. This relationship has attracted much attention because it provides a connection between the elastic property and the structural relaxation behavior. In Fig. 5, a similar correlation is shown. Here, instead of Poisson's ratio, the relation between fragility and bulk modulus is shown. From this correlation we recognize that in bulk metallic glass forming systems, the fragility increases as the bulk modulus increases. The estimated value of dm/dB from the correlation is (0.1-0.2) GPa^{-1} [17].

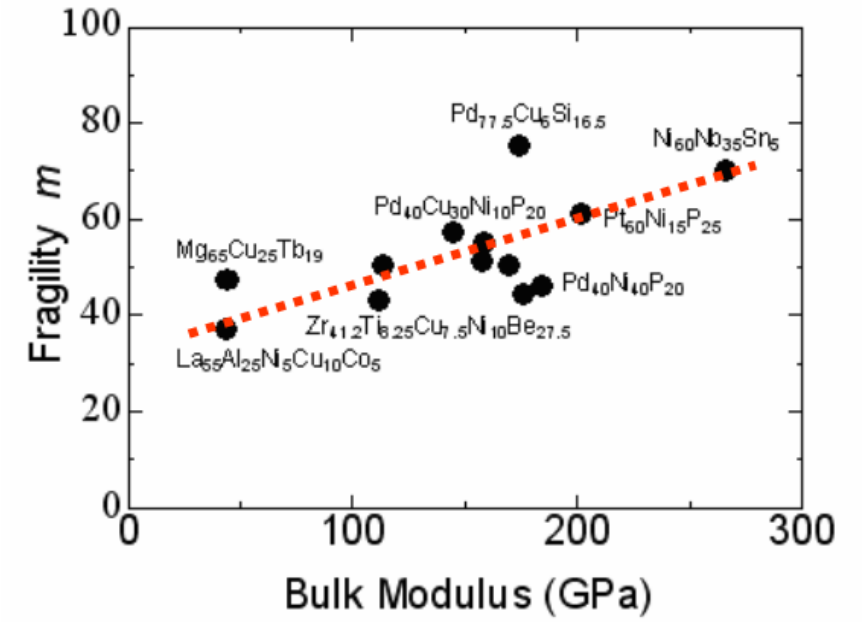

Fig. 5. Correlation between the fragility and the bulk modulus in some bulk metallic glass forming systems. Values of the fragility and bulk modulus are taken from [18].

In the above section, it was shown that for the metallic systems, the typical value is dB/dP ≈ 5. From the correlation shown in Fig. 5 and this value of dB/dP, we can estimate the following value for the pressure derivative of the fragility in metallic glass forming systems, dm/dP = (0.5-1.0) GPa^{-1}. This quantity is very small and difficult to detect precisely in the usual experimental conditions. Since the fragility gives a measure on the degree of how easy the structural relaxation occurs, the result found indicates that it is difficult to induce changes in structural relaxation processes with the application of pressure in metallic glass forming systems. This observation seems consistent with the hard sphere like picture of metallic systems discussed above. However, further high pressure study is required to make a conclusive statement.

Conclusion

A simple method to estimate the values of the bulk modulus and its pressure derivative from the values of the constituent elements and their compositions has been presented and applied to bulk metallic glasses. The physical background of the estimation has been investigated based on the jellium model of metals. The result reveals that the mechanical properties of bulk metallic glasses are determined essentially by the electron density analogously to the case of elementary metals The estimated values of the elastic constants have been used in the Murnaghan equation to state to calculate the volume change under compression. A comparison of the obtained results with experimental data indicates that the effect of structural relaxation should be taken into account. A discussion on the pressure effects in structural relaxation has been given using the concepts of configuration space and fragility. The analysis indicates that the pressure derivative of the fragility in metallic glass forming systems is small.

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