

Pressure dependence of the fragility in metallic glass forming liquids: Predictions from a theoretical model and materials properties correlations

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Abstract. By studying the pressure dependence of the fragility, it is expected that new horizons will open to understand the relaxation behaviour of supercooled liquids. However, as far as the authors are informed, no study has been performed on pressure dependence of the fragility in bulk metallic glass forming systems. In the present study, such dependence is investigated based on materials properties correlations. It is suggested that the effect of pressure on the fragility of bulk metallic glasses is very small. Our analysis indicates also that the fragility of metallic glasses will increase with the application of pressure. This behaviour contrasts with the behaviour observed in molecular systems, where the fragility remains almost constant or decreases slightly with the application of pressure. The result found is discussed in terms of the bond strength-coordination number fluctuation model of the viscosity.

1. Introduction

The temperature dependence of the viscosity or relaxation time for various glass forming materials can be characterized by using the concept of fragility, which quantifies the degree of deviation from the Arrhenius behaviour [1]. The concept of fragility has been used widely and has played a fundamental role in understanding the relaxation behaviour of supercooled liquids [2-7]. Some years ago, one of the authors derived an expression for the fragility based on a simple model of the melt [8]. According to the model, the fragility is determined by the relaxation of structural units that form the melt and is described in terms of the bond strength, coordination number and their fluctuations of the structural units. Previous studies have shown that the model describes quite well the fragility behaviour of many kinds of materials that include oxides, chalcogenides, molecular and metallic systems [8-11].

Bulk metallic glasses are characterized by the high thermal stability of their supercooled liquids, which permit the study of thermophysical properties in the supercooled liquid in addition to the amorphous solids [12]. By studying the pressure dependence of the fragility, it is expected that new horizons will open to understand the relaxation behaviour of supercooled liquids. Concerning the pressure dependence of the fragility, some works have been done in molecular and polymeric liquids [13, 14]. In mono-component metallic fluid systems, the effect of pressure on some physical quantities has been done [15]. However, as far as the authors are informed, no study has been performed on pressure dependence of the fragility in bulk metallic glass forming systems. In the present paper, such

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dependence is investigated based on materials properties correlations. The obtained result indicates that the effect of pressure on the fragility of bulk metallic glass forming systems is very small, but the sign of the pressure derivative is opposite to those reported in molecular and polymeric systems.

2. Bulk modulus and fragility

2.1. Pressure dependence of the bulk modulus

One of the fundamental physical quantities necessary to describe the mechanical properties of materials is the bulk modulus. 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 [16,17]. There it has been shown that the predicted values from the model are in good agreement with the experimental data [17]. 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. From the study, it was concluded that the mechanical properties of bulk metallic glasses are determined essentially by the electron density analogously to the case of elementary metals [16]. The same picture has been presented in [18]. The model predicts also that for bulk metallic glasses, the pressure derivative of the bulk modulus is positive and $dB/dP \cong 5$. This value is close to the value reported for elemental metals. The experimental values reported for bulk metallic glasses are in the range $dB/dP \cong 4-6$ [17]. Therefore, for the metallic systems, we can adopt $dB/dP \cong 5$ as a typical value.

2.2. Correlation between fragility and bulk modulus

Recently, it was shown that the fragility of simple nonmetallic and metallic glass forming systems increases with the increase in the Poisson's ratio [19]. This relationship has attracted much attention because it provides a connection between the elastic property and the structural relaxation behavior. In Fig. 1, a similar correlation is shown. Here we have plotted the fragility vs. the bulk modulus instead of Poisson's ratio. The trend and the degree of dispersion of the data are similar to those reported in previous works. 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

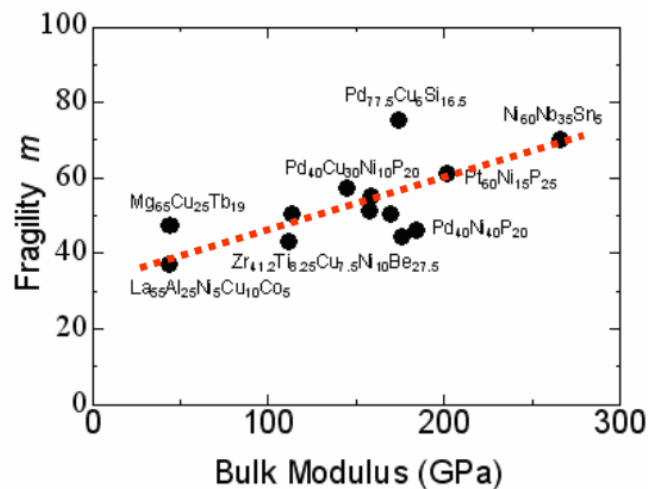


Figure 1. Correlation between the fragility and the bulk modulus in some bulk metallic glass forming systems. Values of the fragility and bulk modulus are taken from [18].

(0.1-0.2) GPa⁻¹. For the sake of comparison, it should be interesting to mention that, among the data collected by the authors, no clear correlation between the fragility and bulk modulus was found for nonmetallic molecular systems. Concerning this point however, a further study is required in order to make some conclusive statement.

3. Interpretation based on the bond strength-coordination number fluctuation model of the viscosity

Form the correlation shown in Fig. 1 and the value of dB/dP evaluated in section 2.1, 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. For the case of molecular and polymeric systems, it has been shown that, depending on the system, the fragility remains invariable or decrease slightly with the application of pressure [13,14]. It is interesting to note that, although small, the pressure seems to act differently in these two kinds of materials. The fragility in metallic systems increases, whereas in molecular and polymeric systems decreases with the application of pressure.

In the following, the above observation is interpreted in the light of the bond strength-coordination number fluctuation (BSCNF) model of the viscosity [8]. According to this model, the viscosity η and the fragility index m is described in terms of the mean values of the bond strength E_0 , the coordination number Z_0 , and their fluctuations ΔE , ΔZ of the structural units that form the melt. Specifically, these are written as

$$\eta = \frac{\eta_0}{\sqrt{1-Bx^2}} \exp \left[\frac{Cx + Cx^2 \left[\ln \left(\frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1-B) \right] \left(\frac{1-B}{C} - 1 \right)}{1-Bx^2} \right], \quad (1)$$

$$m = \lim_{T \rightarrow T_g} \frac{d \log \eta}{d(T_g/T)} = \frac{1}{\ln(10)} \left\{ \frac{B-C + 2 \left[\ln \left(\frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1-B) \right]}{1-B} \right\}, \quad (2)$$

where

$$B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2}, \quad C = \frac{E_0 Z_0}{RT_g} \quad \text{and} \quad x = T_g/T. \quad (3)$$

Here T_g is the glass transition temperature, $\eta_{T_g} = 10^{12}$ Pa·s and $\eta_0 = 10^{-5}$ Pa·s are respectively, the values of the viscosities at T_g and at the high temperature limit, and R is the gas constant. It should be noted that C gives the average total bond strength between the structural units and B gives its fluctuation. Fig. 2 shows the application of this model. (a) shows the case for metallic glass forming systems at $P=0$. Here, we have compared our model with the result of VFT fitting which is known as an expression that reproduces the experimental behavior. (b) shows the case for molecular systems with varying pressure. We can note that the fragility of this system decreases with the application of pressure. Fig. 2 indicates that the model reproduces quite well the experimental behavior by choosing appropriately the values of B and C .

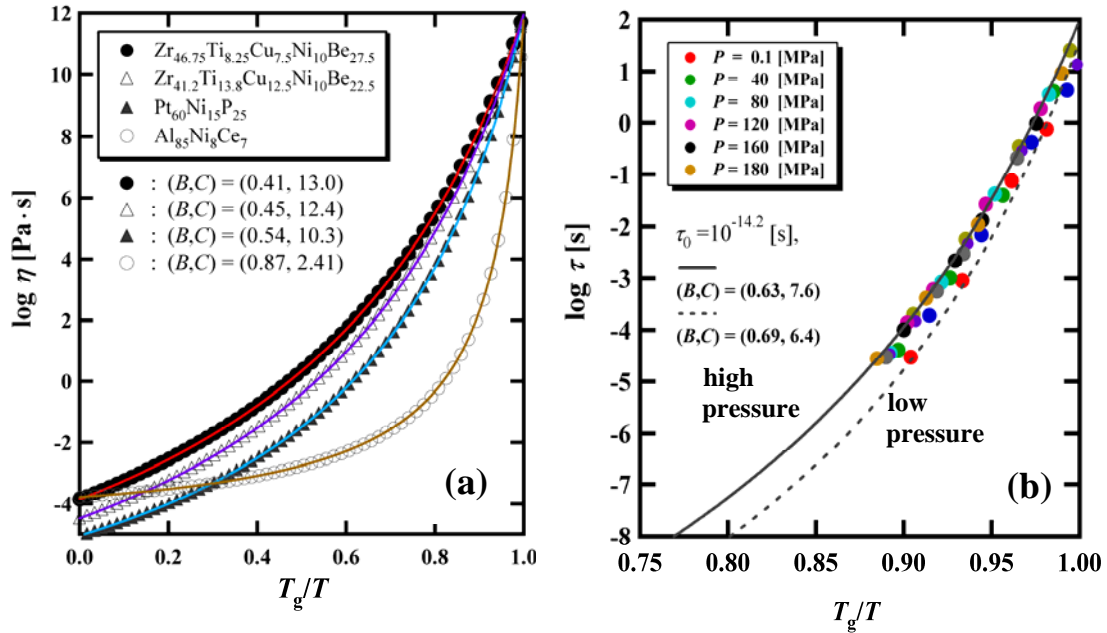


Figure 2. (a) Temperature dependence of the viscosity in metallic systems. (b) Temperature dependence of the relaxation time in an organic system 1,1'-di(*p*-methoxyphenyl)cyclohexane at different pressures. The relaxation time is calculated by $\tau = \eta / G_\infty$, where G_∞ is the shear modulus at high frequency. Full and broken lines denote the theoretical curves and symbols are the experimental data (b) or the VFT fitting (a). Materials data of (a) and (b) are taken from [20] and [14], respectively.

In a previous study, it was shown that strong systems have large values of C and small values of B , whereas fragile systems have small values of C and large values of B [9]. The values of B and C shown in Fig. 2 are consistent with this trend of the parameters. For the system shown in Fig. 2(b), the total bond strength C increases and the fluctuation B decreases with the application of pressure. In other words, the pressure strengthens the connectivity and decreases the fluctuations between the structural units. This behavior can be interpreted to arise from the increase in the overlap of the wave functions between the adjacent molecules with the application of pressure. This view is consistent with the result of study done in some polymers, where the interchain coupling is reported to increase with pressure [21].

For the case of metallic systems, we have predicted that the fragility will increase with the application of pressure. According to the BFCNF model, this may arise from the decrease of the bond strength C or by the increase of its fluctuation B . The effect of pressure on the nature of chemical bonding in metallic systems is small when compared with nonmetallic systems. In addition, metallic systems are characterized by their close packed structure. Therefore, a drastic change in the bond strength E_0 , and coordination number Z_0 with the application of pressure is not expected. Moreover, the glass transition temperatures T_g of bulk metallic glasses exhibit only a weak pressure dependence [22]. Therefore, the quantity C is expected to be almost pressure insensitive. On the other hand, in metallic systems, the angular force is weak. This implies that the structural units may slide with the application of pressure, which results in the increase of the fluctuation described by the parameter B .

In this way, the different behavior that the metallic and the nonmetallic materials exhibit under pressure can be traced back to the different nature of the chemical bonding and connectivity of the

structural units that exist in these two types of materials. In our model, such information is incorporated in the quantities B and C .

4. Conclusion

The pressure dependence of the fragility in metallic glass forming systems has been studied by joining the result of the elastic properties calculation based on the jellium model, or the values of reported experimental data on the pressure dependence of bulk modulus, and the result of the correlation between the fragility and the bulk modulus. The study has indicated that in the usual experimental conditions, the variation of the fragility with pressure is very small. The study has also shown that the fragility of metallic glassy systems will increase with the application of pressure. This behavior contrasts with the behavior reported in molecular or polymeric systems, where the fragility remains almost constant or decreases slightly with the application of pressure. According to the BSCNF model of the viscosity, the difference arises from the different nature of the chemical bonding and connectivity of the structural units that exist in these two types of materials. As far as the authors are informed, measurement of the pressure dependence of the fragility in metallic glassy systems is not available. Experimental studies or simulation studies are necessary to verify the prediction given in the present study.

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