International Journal of Materials Science ISSN 0973-4589 Volume 12, Number 1 (2017)


# High Pressure Isothermal Equation of State for Bulk Metallic glasses

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**Abstract**: Studies on the equation of state for metallic glasses have been secant, because of the inability to prepare bulk specimen Solid-state materials with the major bonding types including ionic, covalent, van der-Waals, hydrogen and metallic can be made by various ways into amorphous solid forms. Metallic amorphous alloys (i.e. metallic glasses) are comparatively newcomers to the amorphous materials group. In the present work, the pressure of two different structured BMGs viz. Water-white glass and Fused quartz, have been calculated at different compression's using four different nature of equation of state (EOS), out of which two EOS's based on interaction potential model viz. Brennan Stacey EOS and Shanker EOS and other two based on logarithmic opotential model viz Poirier- Tarantola EOS and Freund & Ingalls EOS. A comparative studies have been made among the calculated values of pressure for different BMG's at different compressions ranging from V/V0 = 1.00 to V/V0 = 0.40 to test the validity of these different nature equation of state's.. On critical analysis of calculated results shows that Shanker EOS gives the better agreement than other three equation of states. Poirier-Tarantola EOS. Freund Ingalls EOS and Brennan Stacey EOS gives better agreement with Shanker EOS upto $V/V_0$=0.6 and after that it deviates sharply and show high pressure values and also Brennan-Stacey and Poirier-Tarantola equation of state shows abrupt deviation. It is observed that one equation of state shows deviation in upward direction, where as other shows a linear type projection.

Key word: BMG's. EOS, Interaction Potential model, Logarithmic Potential model

**Theory:** Metallic glasses differ in structure and properties from metals. Metals normally have a crystalline structure with atoms in periodic arrays called lattice. In contrast, atoms in glassy metals do not form periodic arrays; their distribution is random. Originally devised a quarter of a century ago, the technique to produce amorphous or glassy metals required cooling of the molten metal about one hundred thousand times faster than had previously been possible.

Rapid cooling was the only way to prevent mobile atoms in the molten metal from rearranging themselves into crystal lattice. Recently [1] it has been discovered, that metallic glasses can be synthesized at low temperatures without quenching by directly introducing certain rapidly diffusing species into crystalline materials. Systems studied so far include hydrogen diffusion in some intermetallic compounds, gold diffusion in lanthanum, nickel diffusion in zirconium metal and others. The common process in all of these systems is that one of the elements, viz., hydrogen, gold and nickel in the above examples, diffuses very rapidly in the other at low temperatures. The rapidly diffusing species induces a phase instability which, because of the low temperatures, results in an amorphous structure rather than a crystalline structure.

However, the understanding of pressure effect in these processes is still remaining on a very qualitative level because of the lack of quantitative properties of the compressed metallic glassy state under high pressure. A fundamental understanding of micro structural configuration properties in amorphous solid is not developed in comparison to that of crystalline. Due to large size and high thermal stability of BMGs, detailed and accurate study of various properties over a wide temperature and pressure ranges becomes possible. The studies of the acoustic, elastic and thermal properties of metallic glasses can provide important information about the structural and vibrational characteristics [2-4].

The equation of state (EOS) of a solid (pressure–volume relation) plays an important role in condensed matter physics, because the knowledge of the EOS is of central importance for the general understanding of the behaviour and the application of condensed matters [5]. The EOS of crystalline solids has been a long-standing topic and extensively investigated. A lot of interesting and important phenomena have been observed [5]. For many years, however, the very high cooling rate (>105 K/s) necessary to obtain metallic glasses limits their geometry to very thin ribbons or wires and makes the studies of intrinsic nature of the glass and glass transition as well as the measurements of many physical properties for establishing the EOS very difficult.

. In the present work, the pressure of two different structured BMGs viz. Water-white glass and Fused quartz, have been calculated at different compression's using four different nature of equation of state (EOS), out of which two EOS's based on interaction potential model viz. Brennan Stacey EOS and Shanker EOS and other two based on logarithmic opotential model viz Poirier- Tarantola EOS and Freund & Ingalls EOS. A comparative study has also been made among the calculated values of pressure to test the validity of these equation of states.

## Formulation of equation of state

An Equation of state can be derived from the volume derivative of lattice potential energy [6, 7] by using the relation

$$P = -\left(\frac{dW}{dV}\right)_T \tag{1}$$

where W for an ionic crystal can be written as the sum of electrostatic energy and short range overlap repulsive energy

$$W = -\alpha_M \frac{Z^2 e^2}{V^{1/3}} + \Phi(V) \tag{2}$$

### *Brennan-Stacey Equation of State*

Using the free volume formula [8] for the Grüneisen parameter $\gamma$ and assuming that the Grüneisen parameter $\gamma$ is proportional to volume, Brennan and Stacey obtained an EOS [9] which is given as

$$P = \frac{3K_0\left(\frac{V}{V_0}\right)^{-4/3}}{\left(3K_0^{'} - 5\right)}\left[\exp\left\{\frac{\left(3K_0^{'} - 5\right)\left(1 - \frac{V}{V_0}\right)}{3}\right\} - 1\right] \tag{3}$$

## *Shanker Equation of State*

On the basis of Born lattice theory [10] taking the volume derivative of short range force constant, Shanker obtained a equation of state known as Shanker EOS [11, 12] which are as

$$P = \frac{\left[K_0\left(\frac{V}{V_0}\right)^{-4/3}\right]}{t}\left[\left(1-\frac{1}{t}+\frac{2}{t^2}\right)\{\exp(ty)-1\}+y\left(1+y-\frac{2}{t}\right)\exp(ty)\right] \quad (4)$$

where

$$y = 1-\frac{V}{V_0} \qquad \text{and} \qquad t = \left(K_0^{'}-\frac{8}{3}\right)$$

$K_0$ is isothermal bulk modulus and $K_0^{'}$ is the first derivative of isothermal bulk modulus at zero pressure.

## *Freund - Ingalls Equation of State*

The modification in the basic assumption of Kumari et al [13] EOS can be written as

$$P = \frac{K_0}{\left(K_0^{'}+\alpha\right)}\frac{\exp\left\{-\left(K_0^{'}+\alpha\right)\right\}}{\alpha}\left[\left\{\left(\frac{V}{V_0}\right)^{\alpha}-1\right\}-1\right]$$

This equation can also be written as

$$\frac{V}{V_0} = \left[1-\frac{\alpha}{\left[K_0^{'}+\alpha\right]}\ln\left\{1+\frac{K_0^{'}+\alpha}{K_0}P\right\}\right]^{1/\alpha}$$

where $\alpha$, $K_0$ & $\mathbf{K_0^{'}}$ are adjustable parameters.

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By Substituting the adjustable parameter α=1/3 Freund and Ingalls introduced a new EOS known as Freund & Ingalls EOS [14] given by

$$P = \frac{K_0}{\left(K_0^{'} + 1/3\right)} \frac{\exp\left\{-\left(K_0^{'} + 1/3\right)\right\}}{1/3} \left[ \left\{ \left( \frac{V}{V_0} \right)^{1/3} - 1 \right\} - 1 \right] \qquad (5)$$

### *Poirier-Tarantola Equation of State*

Poirier and Tarantola [15] derived an equation define strain as Є= log($l_0$/l) and derived an equation of state given as

$$P = K_0 \left( \frac{V_0}{V} \right) \left[ \ln\left( \frac{V_0}{V} \right) + \left\{ \left( \frac{K_0^{'} - 2}{2} \right) \right\} \left\{ \ln\left( \frac{V_0}{V} \right)^2 \right\} \right] \qquad (6)$$

## Results and Discussion

The pressure have been calculated at different compression ranges (from $V/V_0$=1.0 to 0.40) for two different BMGs viz. Water-white glass and Fused quartz, four different equation of states viz. Brennan-Stacey EOS, Shanker EOS, Poirier-Tarantola EOS and Freund-Ingalls EOS from equation (3-6). The calculated values are displayed in table (2-5). The input value of isothermal bulk modulus $K_0$ and its first pressure derivative $(\mathbf{K_0^{'}})$ at zero pressure are taken from the literature [16], displayed in table (1). The logarithmic values of calculated pressure obtained by different EOS have been plotted against the logarithmic values of unit cell volume ratio ($V/V_0$) and shown graphically, displayed in fig. (1-2). The result thus obtained show that the values of

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pressure of Water-white glass shows liner characteristic whereas Fused quartz shows non linear characteristic [Fig. (1-2)],

Another remarkable characteristic is observed that the variation in value of pressure from compression range $V/V_0$= 1.0 to 0.4 are minimum. When we consider about the success of equation of state derived from certain scientists, we have observed that three of state show very good agreement with each other except Poirier-Tarantola EOS. The Brennan-Stacey shows an abrupt deviation.

Brennan-Stacey EOS is based on assumption that Grüneisen parameter is proportional to volume and equation is obtained on account of free volume formula. The metallic crystals have a packed arrangement, where as BMGs have random close packing with the existence of free volume. Due to this reason Brennan EOS in case of bulk metallic glasses fails hopelessly.

The Poirier-Tarantola proposed a equation of state derived using Hencky logarithmic strain [17] equivalent to the Eulerian strain for small strain and better behaved for large strain. The reference strain is neither the initial nor the final configuration, but the instantaneous configuration of the body being deformed. In uniaxial deformation as the instantaneous volume (V) of the body is increased by an infinitesimally small increment dV, the ratio (dV/V) is considered as an increment of the current state of strain

$$dE=(dV/V)$$

When the solid goes from volume $V_0$ to V the total finite strain or normal strain also called the Hencky measure of strain.

$$E_H=(1/3)\log(V/V_0)$$

It has been observed that Hencky strain is as a function of the ratio ($V_0$/V) and in this way what we find that as the compression increases this potential deviates from other potential and successively it shows a pseudo linear characteristic in fig. (1-9). The conclusion is very interesting and it requires a critical and comprehensive study for further research work.

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International Journal of Materials Science ISSN 0973-4589 Volume 12, Number 1 (2017)


**Table-1**

**The input values of isothermal bulk modulus ( $K_0$ ) & its first pressure derivative ( $K_0'$ ) at zero pressure**

| S.No. | Sample | $K_0$ (GPa) | $K_0'$ (GPa) |
|---|---|---|---|
| 8. | Water-white glass | 45.70 | 1.78 |
| 9. | Fused quartz | 36.90 | -4.67 |

**Table-2**

**Calculated values of pressure (P) in GPa as a function of $V/V_0$ at different compressions using different equation of state from equations (3-6) for bulk metallic glass "Water white glass"**

| $V/V_0$ | P (GPa) Brennan- Stacey EOS (3) | P (GPa) Shanker EOS (4) | P (Gpa) Freund- Ingalls EOS (5) | P (GPa) Poirer -Tarantola EOS (6) |
|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 |
| 0.9 | 5.29 | 5.3 | 5.29 | 4.76 |
| 0.8 | 12.45 | 12.51 | 12.44 | 9.95 |
| 0.7 | 22.43 | 22.68 | 22.38 | 15.66 |
| 0.6 | 36.94 | 37.6 | 36.7 | 22.02 |
| 0.5 | 59.21 | 60.7 | 58.3 | 29.24 |
| 0.4 | 96.2 | 99.34 | 92.97 | 37.61 |
| 0.3 | 165.63 | 172.24 | 153.94 | 47.65 |
| 0.2 | 326.84 | 342.11 | 278.41 | 60.37 |
| 0.1 | 931.75 | 980.97 | 622.42 | 78.23 |

**Table-3**
**Calculated values of pressure (P) in GPa as a function of $V/V_0$ at different compressions using different equation of state from equations (3-6) for bulk metallic glass "Fized Quartz"**

| $V/V_0$ | P (GPa) Brennan- Stacey EOS (3) | P (GPa) Shanker EOS (4) | P (Gpa) Freund- Ingalls EOS (5) | P (GPa) Poirer -Tarantola EOS (6) |
|---|---|---|---|---|
| 1 | 0 | 0 | 0 | 0 |
| 0.9 | 3.15 | 3.15 | 3.08 | 2.52 |
| 0.8 | 5.64 | 5.66 | 5.16 | 2.11 |
| 0.7 | 7.97 | 8.03 | 6.53 | -2.49 |
| 0.6 | 10.6 | 10.69 | 7.4 | -13.25 |
| 0.5 | 14.06 | 14.21 | 7.93 | -33.53 |
| 0.4 | 19.33 | 19.56 | 8.24 | -69.48 |
| 0.3 | 28.67 | 29.03 | 8.4 | -133.91 |
| 0.2 | 49.51 | 50.15 | 8.48 | -259.29 |
| 0.1 | 125.12 | 126.77 | 8.51 | -567.32 |

Fig. (1-2): **The logarithmic graph between calculated values of pressure (P) against $V/V_0$ of bulk metallic glass " Water white glass " and " Fuzed Quartz" using different equation of state from equations (3-6)**