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Isothermal equation of state for Vetreloy glasses

Anjnai K. Pandey

Department of Applied Science, Sri Ram Murti Smarak College of Engineering and Technology , Unnao, India.

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ABSTRACT

The pressure – volume - temperature equation of state (EOS) of Vetreloy glasses is fundamental to high- pressure science because of its widespread use as an internal pressure standard. In the present work an attempt has been made to correlate Stacey K primed EOS (SRKP-EOS) with Kushwah EOS for calculating pressure at different compression ranges from (V/V_0 = 1.0 to V/V_0 = 0.5) for four different Zr based vetreloy glasses viz. $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$, $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$, $Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$, and $(Zr_{0.59}Ti_{0.06}Cu_{0.23}Ni_{0.13})_{85.7}$ and obtained result is compared with available theoretical data. The result shows that at compression range V/V_0=1.0 to V/V_0=0.6 both the EOS viz SRKP-EOS and Kushwah EOS cooperate well with available theoretical data proposed by Vinet but at compression V/V_0=0.5 they show a remarkable deviation.

Introduction

The equation of state (EOS) for solids plays an important role to describe their peculiar properties and applications in condensed matter physics and geophysics [1, 2]. However, little information about EOS has so for been obtained for Vitreloy glasses, because the measurements of EOS have been impeded mainly by the inability to prepare Vitreloy glassy specimens. Vitreloy is the commercial name of a series of Zr based metal alloys developed by a research team of California Institute of Technology. The Vitreloy BMG's are composed of five-six Zr based metallic components with large size difference in the atomic diameter. From glass point of view its microstructure is considered as a frozen one under cooled metal melt.

Therefore, the atomic arrangement in Vitreloy BMG's becomes random; due to the close packing of these atoms there exist free volume. Vitreloy BMGs were prepared by the water quenching method, and the details of the preparation can be seen in Refs. [3-6]. It has many desirable properties such as high specific strength and hardness, corrosion resistance, and near-net-shape casting ability [7-10]. It is being applied as a structural material in coatings, electronic packaging, sporting equipment, and defense purposes [10]. At elevated temperature and pressure near or above its glass transition temperature and critical pressure, Vitreloy exhibits nonlinear visco-elastic behavior, and its deformation behavior can be well characterized [11].

The deformation behavior of Zr based Vitreloy at higher pressure is directly related to the structural applications of the material which are commonly described in terms of the free volume model; it shows a significant increase in atomic mobility and a strong dependence of strain rate on slight changes of the local free volume. Due to their excellent physical, chemical, and mechanical properties, the Bulk Metallic Glasses (BMGs) have sparked wide range of interest in the past several decades. However, the understanding of pressure effects on Vitreloy BMG's is still remaining a subject of study at qualitative level because the qualitative properties of the compressed metallic glassy state under high pressure are yet to be explored.

In the field of EOS, Stacey [12-15] and Kushwah [16] have made an important development based on thermodynamics constraint in the limit of infinite pressure.

The variation of the pressure derivative of bulk modulus K with pressure in the limit of extreme compression (V→0) at infinite pressure (P→∞) provides the fundamental base for formulation of Stacey reciprocal K primed EOS [17], whereas, Kushwah etal. [16] have formulated the generalized equation using simple logarithmic function consistent with the infinite pressure extrapolation. Stacey [12] found the thermodynamic constraint $K'_\infty > \frac{5}{3}$ which is recognized as an important parameter for studies of high pressure properties of solids and it must be different for different materials. The above fact has also been verified by Kushwah EOS [17].

In our present work an attempt has been made to correlate Stacey reciprocal K primed EOS (SRKP-EOS) with Kushwah EOS for calculating pressure at different compression ranges from (V/V_0 = 1.0 to V/V_0 = 0.5) and obtained result is compared with available theoretical data. For our investigation we have taken four Zr based Vitreloy glasses viz. $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$, $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$, $Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$, and $(Zr_{0.59}Ti_{0.06}Cu_{0.23}Ni_{0.13})_{85.7}$ into the consideration.

Theory:

The variation of the isothermal pressure derivative of the isothermal bulk modulus K with pressure P, and in particular the behavior of K_0 in the limit of infinite pressure have provided the fundamental base for the formulation of the Stacey reciprocal K-primed EOS. The Stacey Reciprocal K-primed equation of state is written as (SRKP-EOS) [12-14]

Tele:

E-mail addresses: anjani_phys@yahoo.in

$$\frac{1}{K_T'} = \frac{1}{K_0'} + \left(1 - \frac{K_\infty'}{K_0'}\right)\frac{P}{K_T} \qquad (1)$$

Where, P is pressure, K_T is the isothermal bulk modulus at pressure P, K_0' is the first pressure derivative of K_T given as $K_T' = \left(\frac{\partial K_T}{\partial P}\right)$ at $P = 0$ and K_∞', is the value of K_T' at P= ∞ recognized as an important parameter for the analysis of EOS.

From a detailed analysis of seismic data for the lower mantle and core of Earth, it has been found empirically that the following relationship [13, 18-20] holds precisely well:

$$K_\infty' = \frac{3}{5}K_0' \qquad (2)$$

Equation (1) on integration can be reduced [24, 21] in terms of compression $\frac{V}{V_0}$, given

$$\ln\frac{V}{V_0} = \frac{K_0'}{K_\infty'}\ln\left(1 - K_\infty'\frac{P}{K_T}\right) + \left(\frac{K_0'}{K_\infty'} - 1\right)\frac{P}{K_T} \qquad (3)$$

. Kushwah et al formulated the generalized equation [16, 19] consistent with the infinite pressure extrapolation using a simple logarithmic function. The generalized logarithmic EOS formulated by Kushwah et al which shows agreement with the result based on the SRKP-EOS, obtained by fitting the seismological data can be given as

$$P(1-x)^{K_\infty'} = A_1\ln(1+x) + A_2[\ln(1+x)]^2 + A_3[\ln(1+x)]^3 \qquad (4)$$

Where, $x = \left(1 - \frac{V}{V_0}\right)$, V_0 is the volume at P=0.The constants A_1, A_2 and A_3 are determined by using the condition at P=0, i.e., $V=V_0$, bulk modulus $K=K_0$, $\frac{dK}{dP} = K_0'$, and $\frac{d^2K}{dP^2} = K_0''$.

The values of constants A_1, A_2 and A_3 are obtained in terms of K_0, K_0' and K_0'' from equation (3) given as,

$$A_1 = K_0 \qquad (5)$$

$$A_2 = \frac{K_0}{2}\left(K_0' - 2K_\infty' + 2\right) \qquad (6)$$

and

$$A_3 = \frac{K_0}{6}\left(K_0K_0'' + K_0'^2 - 3K_\infty'K_0' + 6K_0' + 3K_\infty'^2 - 12K_\infty' + 6\right) \qquad (7)$$

Values of K_0K_0'' are obtained from the Stacey relationship [12-13, 18], given as:

$$K_0K_0'' = -K_0'\left(K_0' - K_\infty'\right) = -0.4K_0'^2 \qquad (8)$$

By using equation (2) and (8) in equation (7), expression for A_3 can be written as,

$$A_3 = K_0\left(-\frac{K_0'^2}{50} - \frac{K_0'}{5} + 1\right) \qquad (9)$$

The expressions given by equations (1-3) based on Stacey Reciprocal K-Primed EOS whereas, equation (4-9) based on Kushwah EOS [16] which have been used in the present study to obtain pressure dependence of compressibility for Vetreloy glasses are discussed in the next section.

Result and Discussion:

In present work, the entire computational findings have been performed in two phases. In the first phase, the value of compression $\left(\frac{V}{V_0}\right)$ is calculated by using equation (3). The input value [22] for K_0 *and* K_0' displayed in table (1) along with calculated value of K_∞', calculated by using equation (2). The value of pressure P and corresponding isothermal bulk modulus K_T for various chosen bulk metallic glasses taken from literature [23] displayed in table (2-5) designated as initial P and initial K_T along with the compression ratio $\left(\frac{V}{V_0}\right)$ calculated by using equation (3) designated as cal. $\left(\frac{V}{V_0}\right)$. It is observed that in case of all four bulk metallic glasses, the result for volume compression ratio $\left(\frac{V}{V_0}\right)$ calculated by using SRKP-EOS, given in table (2-5) shows remarkably good agreement with those based on computed data of literature [23] up to the compression range V/V_0 =1 to V/V_0= 0.6

In the second phase of our work the pressure P is calculated by using equation (4-9) designated as cal. P, displayed in table (2-5). It is observed that the calculated values of pressure P for Kushwah EOS, obtained by using equation (4-9) with input value of compression resulted from equation (3) also shows good agreement with the input value of the pressure up to compression range V/V_0 =1 to V/V_0= 0.6. Graphs plotted between compression $\left(\frac{V}{V_0}\right)$ vs. pressure P (int. P and cal. P) as shown in fig.(1-4) leads to the following generalization.

From the graph (1-4), a plot between P vs $\left(\frac{V}{V_0}\right)$, it is observed that up to the pressure corresponding to compression range V/V_0 =1 to V/V_0= 0.6, the SRKP-EOS along with Kushwah et al EOS is showing complete agreement with the available data but at compression $\left(\frac{V}{V_0}\right) = 0.5$ both the EOS shows remarkable deviation with available theoretical data predicted by Vinet.

It is clear from the graph (1-4) that Kushwah-EOS is in fact mimicking the SRKP-EOS, for vetreloy glasses at different compressions upto compression range V/V_0 =1 to V/V_0= 0.6. The results obtained in the present study support the validity of the SRKP-EOS for investigating the volume expansion of bulk metallic glasses at compression range V/V_0 =1 to V/V_0= 0.6. The same is applicable for the Kushwah-EOS, which predicts the value of pressure at high temperature, and that is also in agreement with available data. Kushwah-EOS is blindly following the SRKP-EOS because both of them are consistent with equation (2) and (8). It is also noticed that the Kushwah-EOS can conveniently be used only for determining the pressure values if the volume expansion data are available.

Fig. 1

$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$

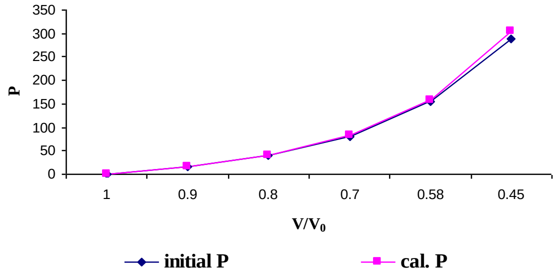

Fig. 2

$Zr_{41}Ti_{14}Cu_{12.5}Ni_{9}Be_{22.5}C_{1}$

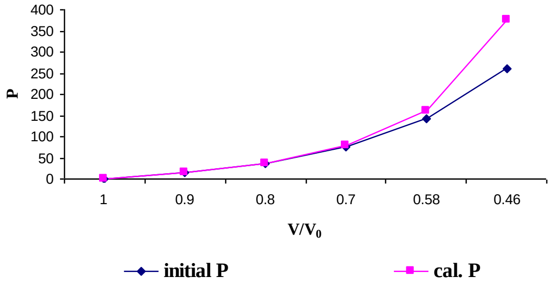

Fig. 3

$Zr_{48}Nb_{8}Cu_{12}Fe_{8}Be_{24}$

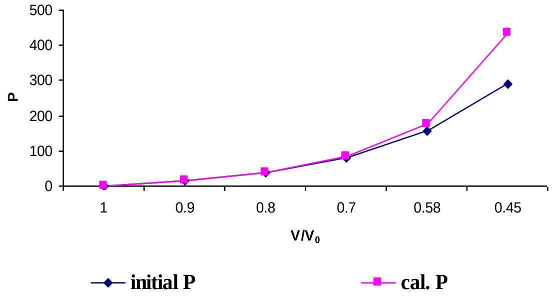

Fig. 4

$(Zr_{0.59}Ti_{0.06}Cu_{0.22}Ni_{0.13})_{85.7}Al_{14.3}$

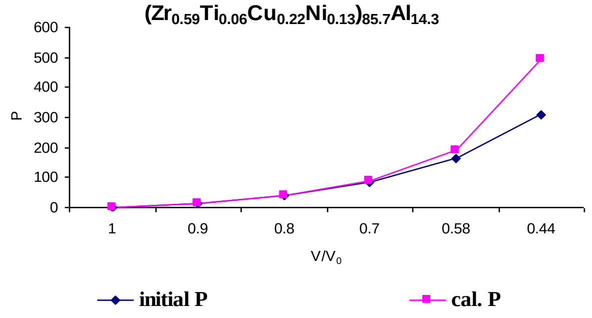

Fig. (1-4): Variation of initial P and calculated P with V/V_0 for Vetreloy glass

The deviation between the compression $\left(\frac{V}{V_0}\right)$ calculated by using SRKP-EOS and theoretically predicted data and also the deviation between pressure P calculated by Kushwah EOS and theoretically predicted by Vinet is due to the difference between calculated and predicted values of K'_∞. The theoretically predicted data for the compression ratio is obtained according to the Vinet, who has considered $K'_\infty \approx \frac{2}{3}$, that is characteristic of EOS [24] while in the present calculation $K'_\infty \geq \frac{5}{3}$ is characteristic of the material decided by equation (2). Since, the input values of pressure P and corresponding isothermal bulk modulus K_T are taken from Vinet-Rydberg EOS [23] so, it always supports $K'_\infty \approx \frac{2}{3}$. Stacey has generalized the Rydberg-Vinet EOS [12] to make it consistent with the infinite pressure extrapolation. The generalized Rydberg-EOS, however could not resolve the problem [17, 25] of K'_∞ of Vinet-EOS, its value remains less than $\frac{5}{3}$. Thus the above study support the conclusion that the generalized *Vinet-Rydberg EOS does not follow the thermodynamic constraint [12], according to which* $K'_\infty \geq \frac{5}{3}$.

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Table-1: Input Value of K_0 (GPa) and K'_0 [22] along with calculated value of K'_∞ calculated by using equation (2)

S.No.	Sample	K_0(GPa)	K'_0	K'_∞
1	$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	114.10	4.06	2.44
2	$Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$	107.30	3.94	2.36
3	$Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$	113.60	4.10	2.46
4	$(Zr_{0.59}Ti_{0.06}Cu_{0.22}Ni_{0.13})_{85.7}Al_{14.3}$	112.60	4.34	2.60

Table 2: Initial V/V_0 and Initial P taken from literature [23] along with calculated value of V/V_0 and P calculated by using equation (2-9) for $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$

Initial V/V_0	Initial P (GPa)	Initial K_T(GPa)	cal.V/V_0	cal.P(GPa)
1	0	114.1	1	0
0.9	14.85	170.29	0.9	14.84
0.8	39.57	253.37	0.8	39.54
0.7	81.42	379.85	0.7	81.79
0.6	154.56	580.05	0.58	157.74
0.5	288.96	914.1	0.45	304.82

Table 3: Initial V/V_0 and Initial P taken from literature [23] along with calculated value of V/V_0 and P calculated by using equation (2-9) for $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$

Initial V/V_0	Initial P (GPa)	Initial K_T(GPa)	cal.V/V_0	cal.P(GPa)
1	0	107.3	1	0
0.9	13.88	158.35	0.9	13.85
0.8	36.73	233.17	0.8	36.77
0.7	75.04	346.88	0.7	77.3
0.6	141.31	523.17	0.58	159.26
0.5	261.83	815.82	0.46	374.99

Table 4: Initial V/V_0 and Initial P taken from literature [23] along with calculated value of V/V_0 and P calculated by using equation (2-9) for $Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$

Initial V/V_0	Initial P (GPa)	Initial K_T(GPa)	cal.V/V_0	cal.P(GPa)
1	0	113.6	1	0
0.9	14.81	170.19	0.9	14.77
0.8	39.56	254.08	0.8	39.59
0.7	81.61	382.19	0.7	84.25
0.6	155.34	585.58	0.58	177.08
0.5	291.27	926.06	0.45	434.17

Table 5: Initial V/V_0 and Initial P taken from literature [23] along with calculated value of V/V_0 and P calculated by using equation (2-9) for $(Zr_{0.59}Ti_{0.06}Cu_{0.22}Ni_{0.13})_{85.7}Al_{14.3}$

Initial V/V_0	Initial P (GPa)	Initial K_T(GPa)	cal.V/V_0	cal.P(GPa)
1	0	112.6	1	0
0.9	14.87	172.52	0.9	14.83
0.8	40.24	262.91	0.8	40.26
0.7	84.22	403.4	0.7	87.23
0.6	162.9	630.57	0.58	189.02
0.5	310.97	1018.2	0.44	495.3