

Fragility of Zr based bulk metallic glass

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ABSTRACT: This study reports on the Fragility of Zr based $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk metallic glass utilizing differential scanning calorimetric (DSC) measurements of the glass transition at different heating rates ranging from 10 to 100 K/min. Vogel-Fulcher-Tammann (VFT) equation was fitted to the data recorded for the heating rate dependent shift of the glass transition temperature. The fragility of the amorphous alloy is determined in terms of fragility parameter. Different approaches are also utilized to determine the fragility parameter in addition to the VFT method. The fragility parameter decreases with increasing heating rate but remains constant at 69 for the heating rate 40 K/min. Bulk metallic glasses typically have the fragility parameter values range from 20 to 70 and, hence, can be classified in the intermediate strong glasses category according to the Angell's classification scheme. This indicates that $Zr_{55}Cu_{30}Al_{10}Ni_5$ behaves more like an intermediate strong glass.

KEYWORDS: Fragility, Bulk metallic glass, Glass transition, Activation energy, Kauzmann temperature.

I. INTRODUCTION

The synthesis of multicomponent bulk metallic glasses (BMGs) with excellent mechanical and chemical properties prompted more research in this field. Preparation of metallic glasses at low cooling rates as 1-100 K/s has accelerated more attention because these alloys can be manufactured in the form of thin ribbons, rods and also in the form of bulk materials known as BMGs [1]. To increase this possibility, more focused understanding of the concept called glass forming ability (GFA) of these materials is essential. The simplest and most widely used criteria for GFA are the reduced glass transition, T_{rg} and width of the super cooled liquid region, ΔT , given by Spaepen and Turnbull [2]. The T_{rg} is defined as the ratio of the glass transition temperature (T_g) to the liquidus temperature (T_l), and ΔT is defined as the temperature difference between the onset glass transition temperature, T_g and the onset crystallization temperature, T_x [3]. It has been proposed that the larger the ΔT and/or T_{rg} , hence higher the GFA [3]. But, to date, there is no single and unique criterion which can be effectively explain GFA.

To determine the GFA of glass forming liquids, the concept of fragility is originally introduced by Angell [4,5]. According to his concept, glass forming liquids are arranged in three categories, (1) strong glass formers, which obey an Arrhenian behavior in the Angell plot (2) fragile glass formers in which the viscosity dependent on temperature is of non-Arrhenian type but can be studied by Vogel-Fulcher-Tammann (VFT) relation and (3) intermediate glass formers which lie in between strong and fragile glass formers [5]. The fragility (Angell) graphs are generally evaluated using the viscosity data [5]. However, T_g dependent on heating rate, β measured by differential scanning calorimetry (DSC) can also adequately be utilized to elucidate the fragility [6,7]. There have been many research papers where the GFA of metallic glasses are explained in terms of fragility concept using DSC data. These research reports are mainly on Co-base [8], Pd-base [9], Ti-base [10], Fe-base [11,12], Mg-base [7,13], Ca-base [14] and Cu-base [15,16] metallic glasses. But so far there have been scanty investigations on the fragility of Zr-base metallic glasses.

Zr-based BMGs have been found in Zr-Cu [17-19], $Zr_{75-x}Ni_{25}Al_x$ ($x = 8-15$) [20], Zr-Cu-Ni-Al [21], Zr-Ti-Cu-Ni-Be [22] and Zr-Ti-Cu-Be [23] systems recently and have led to much interest because of their higher GFA as well as their mechanical properties. Our specific interest is the $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG. Tang *et al* reported fragility parameter of 62

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for the binary $Zr_{50}Cu_{50}$ BMG using DSC measurements [16]. In this paper, we report the fragility of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ alloy studied by DSC technique.

II. EXPERIMENTAL METHODS

$Zr_{55}Cu_{30}Al_{10}Ni_5$ amorphous alloy was prepared in Sendai, Japan, by casting the melt into a copper mould in Ar atmosphere. This sample appeared as plate like form with a thickness of 3 mm, and its amorphous nature was verified by X-ray diffraction (XRD). Table 1 shows the values of T_g , T_x and ΔT at different heating rates measured from DSC [24] and are utilized for the calculation of fragility.

Table 1. Values of T_g , T_x and ΔT for $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG [24]

Heating rate β (K/min)	T_g (K)	T_x (K)	ΔT (K)
10	678.35	754.65	76.3
20	680.65	763.85	83.2
40	683.25	775.05	92.0
60	685.25	781.05	95.8
80	686.25	792.35	106.2
100	688.45	801.75	113.3

III. RESULTS

Five different methods are utilized to determine the fragility parameter, m and these are enumerated below.

1. VFT fitting method

The dependence of the T_g with β is given in terms of VFT equation [6]

$$\beta(T_g) = B \exp[D T_g^0 / (T_g^0 - T_g)] \quad (1)$$

Here, B , D and T_g^0 are adjustable VFT parameters and T_g^0 is the asymptotic value of T_g , which is generally approximated as the onset of T_g at the limit of infinitely slow cooling rate. B has the dimension of a heating rate and D is the strength parameter. Simplifying the equation 1, we get

$$\ln \beta(T_g) = \ln B - (D T_g^0) / (T_g - T_g^0) \quad (2)$$

From the VFT fits the fragility parameter (m) at a particular T_g can be calculated from the Equation (3) [25]:

$$m = D T_g^0 T_g / (T_g^0 - T_g)^2 \ln 10 \quad (3)$$

It is clear from Equation (3) that the value of m depends on the value of T_g . Substituting T_g and adjusting T_g^0 value (by checking maximum regression value), plotting $\ln \beta$ versus $1 / (T_g - T_g^0)$, (Fig.2), the slope $D T_g^0$ is determined and substituted in Equation 3, hence the fragility parameter m is calculated. The value of T_g^0 is found to be 662 K and $\ln B$ is 8.50. The $\ln B$ and T_g^0 values are shown in the Table 2 and m values are in Table.3.

2. Using Kauzmann Temperature T_K

T_g^0 and T_K refer to the kinetic and thermodynamic instability points and it has been empirically established that the relation $T_K \approx T_g^0$ holds for many glass-forming liquids [26]. The β dependence of T_g and T_x is plotted by a linear fit and extrapolation of both the curves to lower temperature as well as heating rates leads to a point of intersection. The temperature that corresponds to this point of intersection is Kauzmann Temperature [27]. The $T_K \approx T_g^0$ value is found to

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be 658 K. Substituting this value in Equation 2 and plotting $\ln \beta$ versus $1/(T_g - T_g^0)$, (Fig.1) the slope $D T_g^0$ is determined and substituted in equation 3, and hence the fragility parameter m is calculated. $\ln B$ and T_g^0 values are shown in the Table 2.

3. Lasocka's method

The glass transition, T_g as a function of heating rate, β is given by Lasocka's empirical relation [28]

$$T_g = A + E \ln \beta \quad (4)$$

Where A and E are empirical constants. The function $T_g(\ln \beta)$ may be non-linear for an extended range of data. However extrapolating the data to $\beta = 1$ K/min, it is possible to obtain a tentative value $A = T_g^0$, which may be the lower limit of T_g [29]. Plotting T_g against $\ln \beta$, the value $A = T_g^0 = 668.26$ K is found. Substituting this value in equation 2 and plotting $\ln \beta$ versus $1/(T_g - T_g^0)$, (Fig.2) the slope $D T_g^0$ is determined and substituted in equation 3, and hence the fragility parameter m is calculated. $\ln B$ and T_g^0 values are shown in the Table 2 and m values in Table 3.

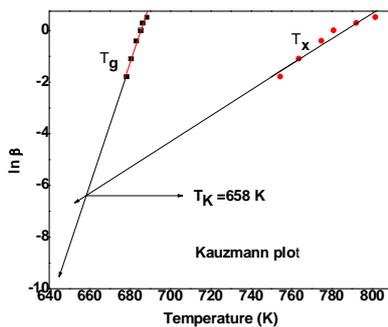


Fig.1: Plot of T_g and T_x versus $\ln \beta$

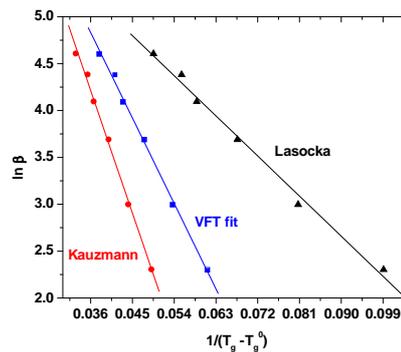


Fig.2: Plot of VFT, Kauzmann and Lasocka

Table 2. The values of $\ln B$ and T_g^0

Method	$\ln B$	T_g^0 (K)
VFT	8.50	662
Kauzmann	9.44	658
Lasocka	6.94	668.26

4. Kissinger method

The fragility parameter, m also could be estimated using the relation [30]

$$m = E_g / RT_g \ln 10 \quad (5)$$

where E_g is the activation energy of glass transition and R is a gas constant. The E_g can be determined from the well known Kissinger equation [31]. Even though, Kissinger equation is used to determine the activation energy of crystallization, recently on the basis of free volume model of glass transition, Ruitenberg [32] showed that the Kissinger method can also be used to determine E_g . According to the Kissinger method, the E_g can be obtained using the following relation:

$$d \ln(\beta/T_g^2) / d(1/T_g) = -E_g/R \quad (6)$$

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From the Kissinger plot $\ln(\beta/T_g^2)$ versus $1000/T_g$, (Fig.3) the $E_g = 894.34$ kJ/mol is found. Substituting this value in equation 5, the m values are determined and are given in the Table 3.

5. Moynihan method

According to this method [33], the E_g is calculated using the following expression

$$d \ln(\beta)/d(1/T_g) = -E_g/R \quad (7)$$

From the plot $\ln(\beta)$ versus $1000/T_g$ (Fig.4) the $E_g = 905.70$ kJ/mol is found. Substituting this value in Equation 5, the m values are determined and are given in the Table 3.

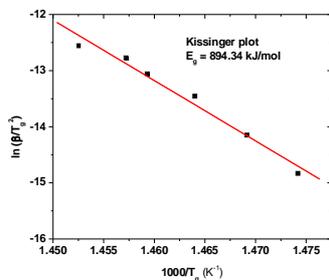


Fig.3: Plot of $\ln(\beta/T_g^2)$ versus $1000/T_g$

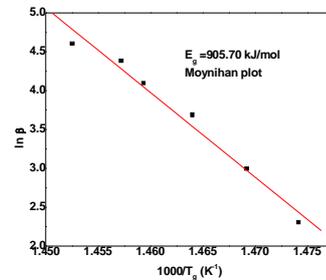


Fig.4: Plot of $\ln(\beta)$ versus $1000/T_g$

Table 3. Fragility parameter, m from different methods

Heating rate, β	T_g (K)	Fragility parameter, m				
		VFT	Kauzmann	Lasocka	Kissinger	Moynihan
10	678.35	111.6	103.3	137.6	68.9	69.7
20	680.65	86.1	83.7	91.5	68.6	69.5
40	683.05	67.8	68.6	64.5	68.4	69.3
60	685.25	55.86	58.2	49.0	68.2	69.0
80	686.25	51.3	54.2	43.8	68.1	68.9
100	688.45	43.3	46.8	34.9	67.9	68.7

IV. DISCUSSION

The fragile/strong nature of the super cooled liquid can be categorized by the fragility parameter (m) [19,20]. Strong liquids, SiO_2 and GeO_2 behave an Arrhenius type temperature dependence and exhibit m values in the region of $16 \leq m \leq 30$ [4,5]. Whereas, fragile liquids like ionic melts and polymers display large values ($m \geq 100$) [4,5]. Bulk metallic glasses typically have m values in the range of $32 \leq m \leq 70$ and hence are classified in the intermediate category according to Angell's classification.[34]. It is clear from the equation (3) and (5) the fragility parameter, m depends on T_g . In order to make uniform comparison with fragility data found in the literature, m , has been evaluated at T_g corresponding to a particular heating rate. Table 3 gives the fragility parameter, m determined from various methods and at different heating rates. It is evident from the Table 3, the corresponding m value is 69 for the metallic glass $Zr_{55}Cu_{30}Al_{10}Ni_5$ for the heating rate 40 K/min. Fig.5 shows the variation of m with heating rate. $m=69$ is the fragility value for the studied sample at 40 K/min value (intersecting point). The composition $Zr_{55}Cu_{30}Al_{10}Ni_5$ shows in the intermediate category according to the Angell's scheme. When the composition is slightly changed to $Zr_{55}Cu_{17.5}Al_{7.5}Ni_{10}$ and $Zr_{65}Cu_{15}Al_{10}Ni_{10}$ then the m value obtained is 35. And also for the system $Zr_{75-x}Ni_{25}Al_x$ ($x = 8-$

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24) and for $Zr_{50}Cu_{50}$ the m values are 40 and 62. This nature is evident from the Table.4. This clearly indicates the m value is dependent on the specific composition of the Cu. However, more information and further research is necessary to validate this proposition in a more quantitative way. The evaluated m values give the information regarding the kinetic fragility. So, it can be said that, there exists a relation between the kinetic and thermodynamic fragility. Indeed, it was shown from the literature that there exists a close correspondence between kinetic and thermodynamics in the calculation of the fragility parameter for the metallic glasses [35,36]. However, recently, Battezzatti[37] reported that both the kinetic and thermodynamic fragilities are not same, even though there exists a closer connection between them. This fact is due to the uncertainties in the measurement of thermodynamic parameters. Hence, it is obvious that both the kinetic and thermodynamic contributions contribute essential part in the fragility of glass forming metallic glasses.

Table 4. Fragility parameters for the various Zr based BMGs

BMG composition	m
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$	34
$Zr_{42.1}Ti_{12.9}Cu_{11.5}Ni_{10.2}Be_{23.3}$	31
$Zr_{41.2}Ti_{13.8}Cu_{12.8}Ni_{10}Be_{22.5}$	39
$Zr_{35}Ti_{30}Cu_{8.25}Be_{26.75}$	66
$Zr_{75-x}Ni_{25}Al_x$ (x = 8-24)	40
$Zr_{65}Cu_{15}Al_{10}Ni_{10}$	35
$Zr_{55}Cu_{17.5}Al_{7.5}Ni_{10}$	35
$Zr_{55}Cu_{30}Al_{10}Ni_5$	69
$Zr_{50}Cu_{50}$	62

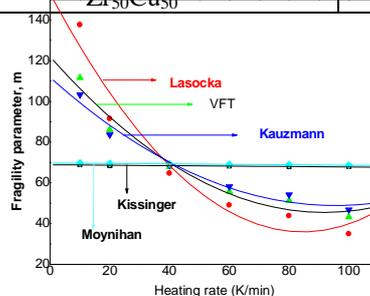


Fig.5: Plot of m versus heating rate (β)

V. CONCLUSION

The thermal stability of BMG $Zr_{55}Cu_{30}Al_{10}Ni_5$ prepared by casting the melt into a copper mould in Ar atmosphere has been evaluated in terms of fragility parameter (m) using five different methods based on the glass transition temperature (T_g) determined from DSC runs. Table 2 shows the consistency of $\ln B$ and T_g^0 values determined from three different approaches namely, VFT, Kauzmann and Lasocka. The fragility parameter, m is 69 and this reflects the Zr based $Zr_{55}Cu_{30}Al_{10}Ni_5$ behaves like an intermediate strong glass.

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