

On the Fragility of $\text{Al}_{70}\text{Ni}_{10}\text{Ti}_{10}\text{Zr}_5\text{Ta}_5$ Alloy Powder*

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ABSTRACT: In this study, the fragility index, m of Aluminium (Al) based $\text{Al}_{70}\text{Ni}_{10}\text{Ti}_{10}\text{Zr}_5\text{Ta}_5$ amorphous alloy powder was evaluated by using Vogel-Fulcher-Tammann (VFT) fit and Lasocka's functions. Activation energy (E_g) of the glass transition, (T_g) is determined by two methods, i.e., Augis & Bennett and Moynihan. The fragility index m , is also determined using T_g which is a measure of thermal stability and glass forming ability (GFA) of the system. The obtained value shows that the fragility index, m of the Al powder sample < 16 which is the lower limit of Angell's classification scheme. The result shows that the chosen system is a strong glass forming system than the rapidly quenched bulk metallic glass.

KEYWORDS: Fragility index, metallic glass powder, Activation energy, Glass transition temperature (T_g), VFT fit.

I. INTRODUCTION

Al based metallic glasses(MG) have evinced more attention towards the research due to their high tensile strength and high bending ductility[1,2].Al dominant metallic glasses are also light weight materials than the crystalline based Al alloys and also low specific weight[1,3].The main Al based MG are Al-TM(transition metal) system like Al-Ni-Ti ,as well as Al-Zr—LEM (LEM=Fe,Co,Ni and Cu) systems[2,4,5].Preparation of amorphous alloys by rapid cooling from liquid state produces limited alloys and small dimensional materials. These are also having limited glass forming ability (GFA) [2-6] and less usage as engineering materials due to their narrow super cooled liquid region. Efforts are in progress to attain wide super cooled liquid region $\Delta T = (T_g - T_x)$ in these materials, nevertheless the region reached is lesser than 50 K.

Mechanical alloying (MA) is another alternative method to rapid cooling to produce amorphous alloys. Since MA is a solid state process, high cooling rates are not required and the alloy composition can be easily altered [7].To understand the thermal stability of these Al based alloys, GFA is essential. The simplest and most widely used criteria for GFA are ΔT [8] and the fragility index m originally introduced by Angell [9, 10]. Fragility index m is also studied by the T_g dependent on heating rate (β) measured by differential scanning calorimetry (DSC) [11, 12]. The purpose of the present study is to understand the thermal stability in terms of fragility index m in the powder sample and compare with the available data of Al based amorphous alloys prepared by rapid cooling method.

*This paper was accepted in the International Conference on Materials Science and Technology (ICMSNT) 2016, 12th to 14th May, Seoul, Korea (south) but not published in any journal.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 9, September 2016

II. EXPERIMENTAL METHODS

Elemental Al, Ni, Ti, Zr and Ta powders with a purity of 99.9% and a mean diameter of 70 μm were used as the starting materials. The process of mechanical alloying (MA) and other details are taken from the Xiu Wei et al paper [13].

III. RESULTS

Four different methods are utilized to determine the fragility parameter, m and these are discussed in detail.

1. VFT fitting method

The dependence of the T_g with β is given in terms of VFT equation [11]

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

Here, C , 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. C has the dimension of a heating rate and D is the strength parameter. Simplifying the Eq.1, we get

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

Generally, the fragility can be classified in terms of the strength parameter D or the fragility parameter m defined as [17]

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

It is clear from Eq.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), and plotting $\ln \beta$ versus $1/(T_g - T_g^0)$, (Fig.1), the slope DT_g^0 is determined. DT_g^0 is substituted in Eq. 3, and the fragility parameter m is calculated. The value of T_g^0 is found to be 651.2 K and DT_g^0 is 177.42. $\ln C$, $D T_g^0$, T_g^0 values are given in the Table 1 and m values are in the Table 2 respectively.

2. Lasocka's method

The glass transition temperature, T_g as a function of heating rate, β is given by Lasocka's empirical relation [14]

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

Where A and B are empirical constants. The function T_g ($\ln \beta$) may be non linear for an extended range of data. However extrapolating the data to $\beta = 1 \text{ K/min}$, it is possible to obtain a tentative value $A = T_g^0$, which may be the lower limit of T_g [15]. Plotting T_g against $\ln \beta$, the value $A = T_g^0 = 640.89 \text{ K}$ is found. Substituting this value in Eq.2 and plotting $\ln \beta$ versus $1/(T_g - T_g^0)$, (Fig.2) the slope DT_g^0 is determined and substituted in Eq.3, hence the fragility parameter m is calculated. $\ln C$, $D T_g^0$, T_g^0 values are given in the Table 1 and m values are in the Table 2.

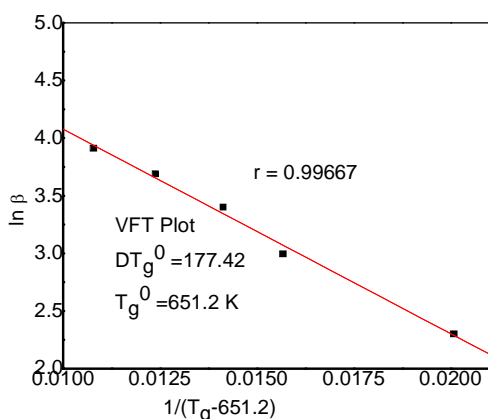


Fig.1 VFT Plot

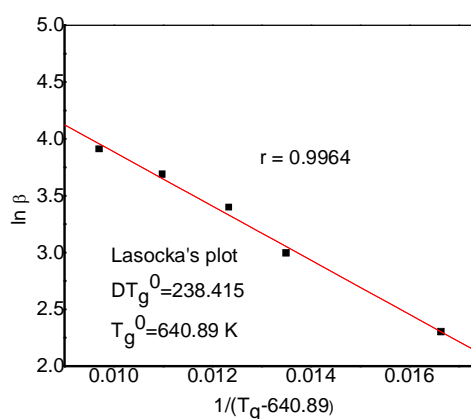


Fig.2. Lasocka's plot

Table 1. Thermal stability data and VFT parameters for the best fit in the DSC data according to Eq.2.

Method	ln C	$D T_g^0$	T_g^0 (K)
Lasocka	6.27	238.41	640.89
VFT	5.85	177.42	651.2

3. Augis & Bennett method

The fragility parameter, m also could be estimated using the Eq. 5 [16]

$$m = E_g / 2.303RT_g \quad (5)$$

Where E_g the activation energy of glass transition and R is is gas constant. The E_g can be determined from the well known Augis & Bennett Eq.6 [17].

$$\ln(\beta/T_g) = - E_g / R T_g + C_1 \quad (6)$$

C_1 is a constant. Fig.3 shows the graph of $\ln(\beta/T_g)$ versus $1000/RT_g$. The plot gives slope E_g/R . Substituting R value the activation energy $E_g = 159.01 \text{ kJ/mol}$ is obtained. Substituting this E_g value in Eq.5, the m values are determined and are given in the Table 2.

4. Moynihan method

According to this method [18], the E_g is calculated using the following expression

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

From the Fig.4, $\ln(\beta)$ versus $1000/RT_g$, the slope E_g/R found. Substituting R value, $E_g = 165.02 \text{ kJ/mol}$ is obtained. Substituting this value in Eq. 5, the m values are determined and are given in the Table 2.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 9, September 2016

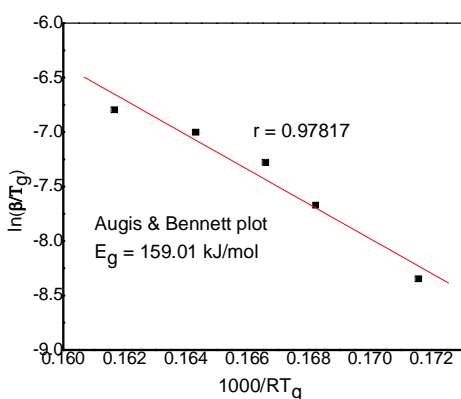


Fig.3. Augis & Bennett plot

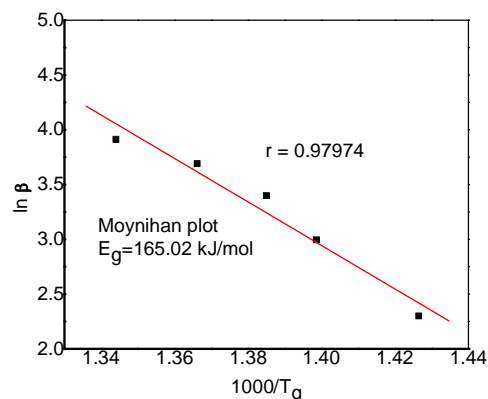


Fig 4. Moynihan plot

Table 2. Fragility parameter, m from various methods

Heating rate, β (K/min)	T_g (K)	Fragility parameter, m			
		VFT	Lasocka	Augis & Bennett	Moynihan
10	701	21.78	19.49	11.85	12.30
20	715	13.53	13.08	11.61	12.06
30	722	11.10	11.02	11.5	11.94
40	732	8.64	8.86	11.35	11.78
50	744	6.66	7.03	11.16	11.59

Table 3. Fragility parameter, m for various Al based amorphous alloys

Amorphous alloys composition	m	Reference
$Al_{70}Ni_{10}Ti_{10}Zr_5Ta_5$	11	Present study
$Al_{84}Ni_{10}Pr_6$	18	26
$Al_{87}Ni_9Nd_4$	18	26
$Al_{88}Ni_6La_6$	21	26
$Al_{84}Ni_8Ce_5Si_3$	24	27
$Al_{87}Co_8Ce_5$	34	28

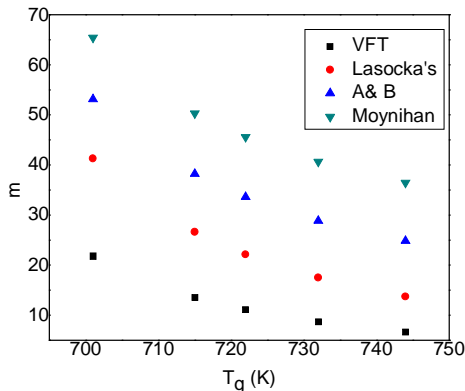


Fig.5. Variation of m with T_g

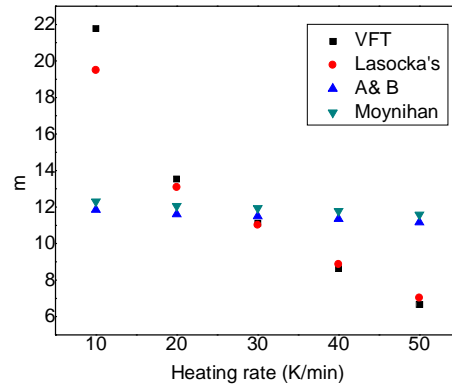


Fig.6. Variation of m with heating rate

IV. DISCUSSION

Fragility index, m is used to calculate the GFA or thermal stability of metallic glasses. According to Angell's theory [9, 10] glass forming materials can be categorized into three groups based on the value of fragility index, m , namely, strong, intermediate and fragile. For strong materials, m is less than 30 with a lower limit of 16, while for fragile materials $m \geq 100$. For an intermediate materials like bulk metallic glasses, the value of m lies in the range $32 \leq m \leq 70$.

Since T_g depends on the heating rate, the fragility parameter, m can be calculated from the Eq.5 for various heating rates. Table 2 summarizes the results obtained from VFT, Lasocka, Augis & Bennett and Moynihan methods. Table 2 also gives the fragility parameter, m at different heating rates. The dependence of m with T_g and heating rate are shown in Fig 5 & 6. The nature of decreasing m with T_g is also consistent in other bulk metallic glasses [19]. The calculated m value is 11 for $Al_{70}Ni_{10}Ti_{10}Zr_5Ta_5$ amorphous powder prepared by mechanical alloying method for the heating rate 30 K/min. This is evident from the Fig.6 (intersecting point) and are selected in bold in Table.2. The value $m = 11$ which is less than 16 confirms that the given system is a strong glass and having an excellent GFA. The scaling parameter for temperature in the non-Arrhenius version of the strong/fragile scheme is T_g . So the departure from Arrhenius behavior, fragility is also a function of T_g^0/T_g [20,21]. This ratio lies between 0 (strong) and 1 (fragile) and is related to fragility and suggested by Donth [22], Ikeda et al [23] also noted recently the same interesting observation that m increases by increasing the value of T_g^0/T_g in bulk metallic glasses. This is evident in our present work and shown in the plot of m versus T_g^0/T_g in the Fig.7. Table 3 gives the increase of the m value for different Al alloy compositions [24-26]. This shows the dependence of m on the preparation, composition and heating rate. Except the first Al based amorphous material, all the materials are rapidly quenched. This is quite evident that the MA prepared amorphous metallic powder behaves strong glass forming system than the rapidly quenched metallic ribbons.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 9, September 2016

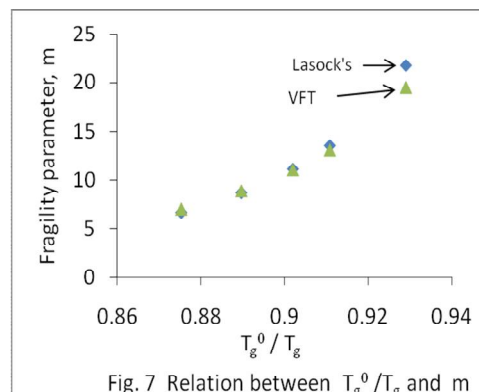


Fig. 7 Relation between T_g^0/T_g and m

V. CONCLUSION

Fragility index, m of Al based amorphous alloy powder prepared by MA is evaluated. The main results are summarized as follows:

- (1) Activation energy, E_g corresponding to the glass transition, T_g is determined by Augis & Bennett and Moynihan method. The E_g values are 159.01 and 165.02 kJ/mol respectively. These are in accordance with the Xui Wei et al value 153.15 kJ/mol.
- (2) Fragility index, m is calculated by four methods, namely VFT, Lasocka, Augis & Bennett and Moynihan and found to be consistent. The value comes out to be 11 at the heating rate 30 K/min.
- (3) From the evaluated m value, Al based amorphous alloy classified into “strong glass” with high GFA when compared to the rapidly quenched metallic glasses.

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