3.1 Introduction

Bulk metallic glasses have attracted significant interest in research as it has many applications. In order to make the best use of glassy materials with their excellent properties, there are two major problems which must be solved. The first one is the high glass forming ability (GFA) of the alloys, which is important for preparing glassy samples large enough for structural applications. The second is the thermal stability of the alloys, which provide information about the long-term stable structure and properties in the future. The principle scientific issue in the field of amorphous alloys is the characterization and prediction of GFA. Glass formation is an event of competition between super-cooled liquid and the related crystalline phases. The slowest a material can be cooled down to glass transition temperature (T_g) without crystallization the easiest it is vitrified, and this property has denominated glass forming ability [3.1]. GFA is a competition between cooling rate and the crystallization kinetics, which is closely related to structural, thermodynamic and kinetic characteristic. Knowledge of GFA of metallic glasses is of great importance as it gives an insight into better glass former.

To design an alloy having excellent GFA many empirical approaches have been proposed based on trial and error experiment but there are no justified theories and scientific rules [3.2-3.4]. Even if these empirical rules work for certain alloys but cannot be generalized for the whole class of glass forming systems. Inoue suggested a set of empirical rules for predicting GFA of different metallic glasses [3.5]. Different GFA parameters to find better glass forming systems have been put forward through criteria like reduced glass transition temperature (T_{rg}), order parameter(η), parameters Q, γ, γ_m and the Gibb's free energy difference (ΔG) between the super-cooled liquid and crystalline phases. In fact one of the most important features of BMGs with high GFA is their multi component compositions. According to the empirical multicomponent rule proposed by Inoue et al [3.5] minor addition of other element in glass forming alloys is regarded as effective and important way to improve the GFA and thermal stability of the BMGs. Minor substitution of some elements in amorphous alloys may strongly influence the GFA and crystallization of metallic alloys [3.6].

3.2 Different GFA Parameters

In order to predict the GFA of various metallic glass forming systems many parameters have been put forward which are important from theoretical and practical point of view. Most of the GFA parameters derived are based on the various characteristic temperatures like glass transition temperature (T_g), crystallization temperature (T_x), melting temperature (T_m), etc. To predict GFA of metallic glass most extensively used parameter are reduced glass transition temperature ($T_{rg}=T_g/T_l$), thermal stability parameter (ΔT_x), order parameter (η), critical cooling rate (R_c), $\gamma(=T_x/(T_g+T_l))$, $\beta(=1+(T_x/T_l))$, $\omega(=T_l(T_l+T_x)/(T_x(T_l-T_x)))$ etc. [3.7-3.8].

The thermal stability of various alloy compositions is studied by their under cooled liquid region, $\Delta T= T_x - T_g$ [3.9]. Large ΔT_x implies greater stability against crystallization of the amorphous structure. The parameter α $(=T_x/T_l)$ derived by Mondal et al [3.10] incorporates both the factors of stability of the liquid (a low

T_l) and the thermal stability of glass (a high T_x). The parameter Q [3.11] is derived based on consideration of liquid phase stability, resistance to crystallization and enthalpy of crystallization. The GFA criterion T_{rg} was introduced for purely kinetic reasons associated with the need to avoid crystallization. The GFA of glass forming liquids is considered to be better if they follow Turnbull's criterion [3.4] of $T_{rg} \geq 2/3$.

3.3 Thermodynamics of Metallic Glasses

A quantitative measure of the stability of a glass as compared to its corresponding crystalline state can be obtained by calculating the thermodynamic parameters such as the Gibbs free energy difference (ΔG), entropy difference (ΔS) and the enthalpy difference (ΔH) between the super-cooled liquid and the corresponding crystalline phase. ΔG plays an important role in the analysis of the kinetics of crystallization at high undercooling. For the multicomponent metallic glass during crystallization event nucleation of crystals take place, in which ΔG is considered to be an important parameter. The nucleation frequency has an exponential dependence on ΔG and so the estimation of ΔG as a function of temperature is often critically important in the analysis of nucleation phenomena. ΔG is known as the driving force of crystallization. ΔG is a function of the heat capacity difference between metastable liquid and crystalline solid. So, it becomes important to study the thermodynamic properties of glasses specially the specific heat difference which gives the measure of glass formation. The driving force of crystallization (ΔG) provides very important information about the glass forming ability (GFA) of metallic glasses. Lesser the driving force of crystallization more is the glass forming ability. Decreasing ΔG acts as a driving force for nucleation causing an increase in critical nucleation work and a reduction in nucleation rate.

ΔG plays an important role in predicting GFA of metallic alloys. Driving force for crystal nucleation can be estimated by the calculation of a thermodynamic parameter i.e ΔG. The value of ΔG increases with lowering of temperature due to decrease in entropy of metallic alloy. It indicates that at lower temperature ample amount of driving force is available for crystallization. Hence nucleation starts at lower temperature is followed by growth of crystal. As temperature increases growth of stable nuclei takes place. At glass transition temperature (T_g), the driving force is maximum which allows the amorphous alloy to move towards crystallization. With further increase in temperature, ΔG approaches towards zero. Hence crystallization event ends due to increase in entropy of the alloy resulting in melting of alloy. So estimation of ΔG at T_g becomes important to study the GFA of metallic alloys.

The value of ΔG can be calculated by measurement of specific heat difference ΔC_p, between super cooled liquid and corresponding crystalline phase. But due to non availability of the experimental ΔC_p data, different theoretical approximations of ΔC_p results in variety of expressions of ΔG.

3.4 Different expressions of ΔG & ΔS

The general equation for ΔG between the undercooled liquid and corresponding crystalline phase is given by:

$$\Delta G = \Delta H - T\Delta S \tag{3.1}$$

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \tag{3.2}$$

and $$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \tag{3.3}$$

where, ΔS_m, ΔH_m and T_m are the entropy, enthalpy and temperature of fusion, respectively. They are related to each other by the relation:

$$\Delta S_m = \Delta H_m / T_m \tag{3.4}$$

ΔC_p, defined as $C_p^l - C_p^x$, is the difference in specific heats of the liquid and corresponding crystalline phases of metallic alloy.

So the equation becomes,

$$\Delta G = \Delta S\left(T_m - T\right) - \int_T^{T_m} \Delta C_p dT + T\int_T^{T_m} \Delta C_p d(\ln T) \tag{3.5}$$

From the above eq.(3.5) the experimental value of ΔG can be obtained provided the value of ΔC_p is available for the undercooled and the crystal phases. But the experimental determination of ΔC_p is difficult because the metallic liquids are generally not stable over an extended temperature range in the supercooled liquid. Thus different theoretical expressions of ΔC_p that effectively represent the temperature dependence of $\varDelta C_p$ is considered. Hence, approximating the values of $\varDelta C_p$, the correct evaluation of $\varDelta G$ is possible.

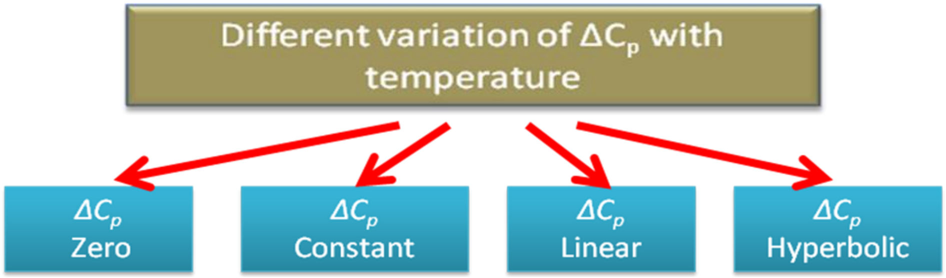

Fig 3.1 Different variation of $\varDelta C_p$ with temperature.

Firstly, Turnbull [3.4] assumed $\varDelta C_p$ to be zero and derived the following equation of $\varDelta G$:

$$\Delta G = \Delta H_m \left(\frac{\Delta T}{T_m} \right) \tag{3.6}$$

The expression given by Turnbull shows very large deviation as it is evident that $\varDelta C_p$ will never be zero.

Further assuming ΔC_p = constant, one gets

$$\Delta G = \Delta S_m \left(T_m - T \right) + \Delta C_p \left[T \ln\left(\frac{T_m}{T} \right) - \left(T_m - T \right) \right]$$

To simplify the above equation, Thomson and Spaepen (TS) [3.12] used the following approximation:

$$\ln \frac{T_m}{T} \cong \frac{2\Delta T}{T_m + T}$$

And they derived an expression given as

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(\frac{2T}{T_m + T} \right) \tag{3.7}$$

This equation is only valid for small ΔT, and leads to error in calculations of ΔG values at larger undercooling. Generally, multicomponent metallic glasses exhibit larger undercooling range. Hence, eq. (3.7) cannot be used for a wide range of metallic glasses.

Lad et al. [3.13] assumed $\Delta C_p = \Delta H_m/T_m$ and used Taylor series expansion of $\ln(T_m/T) = \ln(1+\Delta T/T) = \Delta T[1-\Delta T/2T] / T$, retaining terms upto second order and derived the following expression of ΔG:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(1 - \frac{\Delta T}{2T}\right) \text{ [Lad-1]} \qquad (3.8)$$

This expression provides good result to estimate ΔG for various metallic glass forming alloys. But, it was found that the calculated values of ΔG showed deviation a large undercooling for the alloys which possess very high glass forming ability.

Again, considering Taylor series expansion of $\ln(T_m/T) = \ln(1 + \Delta T/(T_m+T)/2)$ and retaining up to second order terms i.e, $\ln(T_m/T) = 4T\Delta T / (T_m+T)^2$.

Lad et al. [3.14] gave another expression of ΔG:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{4T^2}{\left(T + T_m\right)^2}\right) \quad \text{[Lad-2]} \qquad (3.9)$$

Eq. (3.9), gives good account of ΔG in most of the systems. But, since the derivation again involves the approximation of the logarithmic term, the results obtained are not in excellent agreement with the experimental points for all the metallic glasses.

As stated by Hoffmann [3.15]

$$\ln\frac{T_m}{T} = 2\frac{T_m - T}{T_m + T}$$

With this approximation equation becomes

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{T}{T_m}\right) \tag{3.10}$$

According to Battezatti and Garone [3.16] the expression for ΔG is given as follows:

$$\Delta G = \Delta S(T_m - T) - \gamma \Delta S_m \left[\left(T_m - T \right) - T \ln(T_m / T) \right] \tag{3.11}$$

The γ parameter in above equation is represented as:

$$\gamma = \frac{(1 - \Delta H_x / \Delta H_m)}{(1 - \Delta T_x / \Delta T_m)} \tag{3.12}$$

Where, ΔH_x denotes the enthalpy difference at crystallization.

Normally, the value of γ in the above expression (Eq.(3.11)) has been taken to be 0.8 for glass forming liquids. Using $\gamma = 0.8$ in Eq.3.11, ΔG has been reported for multicomponent amorphous alloys [3.17] and even for bulk metallic glass [3.18].

Singh and Holz (S & H) [3.19] used the above approximation and gave the following expression:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left(\frac{7T}{T_m + 6T}\right) \tag{3.13}$$

Ji & Pan [3.20] considered hyperbolic variation of ΔC_p with T ($\Delta C_p = \Delta H_m / T$) and derived the following expression:

$$\Delta G = \frac{2\Delta H_m \Delta T}{T_m}\left(\frac{T}{T_m + T} - \frac{\Delta T^2 T_m}{3\left(T_m + T\right)^3}\right) \tag{3.14}$$

The values obtained using Ji & Pan approach under estimate ΔC_p and also at $T = T_m$, $\Delta C_p^m = \Delta H^m / T_m$ provides the reference values of ΔC_p^m which is much below the experimental values. Eventually the expression derived for ΔG does not account well for bulk glass forming alloys.

Dubey and Ramchandrarao [3.21] derived expression for ΔG based on the hole theory of liquids given as:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \frac{\Delta C_p^m \left(\Delta T\right)^2}{2T}\left(1 - \frac{\Delta T}{6T}\right) \tag{3.15}$$

Finally Lele et al [3.22] derived an expression of ΔG to study its temperature dependence for the entire undercooled region represented as

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \frac{\Delta C_p^m \left(\Delta T\right)^2}{\left(T_m + T\right)} \tag{3.16}$$

The entropy difference between the super cooled liquid and crystalline phase can be obtained by taking partial derivative of ΔG w.r.t to T:

$$\Delta S = -\frac{\partial\left(\Delta G\right)}{\partial T} \tag{3.17}$$

Substituting Eq. (3.8) & (3.9) in (3.17) we get the following equation,

$$\Delta S_1 = \frac{\Delta H_m}{2T_m}\left(\frac{3T^2 - T_m{}^2}{T^2}\right). \tag{3.18}$$

$$\Delta S_2 = \frac{4\Delta H_m T}{T_m}\left(\frac{T^2 - 2T_m^2 + 3TT_m}{\left(T + T_m\right)^3}\right) \tag{3.19}$$

3.5 Results and Discussion

3.5.1 Gibbs free energy difference for different multicomponent amorphous alloys.

To study glass forming ability, ten different metallic glass forming systems all with different composition are taken into consideration. ΔG is calculated to understand the glass formability of various metallic glasses i.e $Ca_{50}Mg_{25}Cu_{25}$ [3.23], $Mg_{65}Cu_{25}Y_{10}$ [3.24-3.25], $Mg_{65}Cu_{20}Zn_{5}Y_{10}$ [3.26], $Mg_{59.5}Cu_{22.9}Ag_{6.6}Gd_{11}$ [3.27-3.28], $Fe_{41}Co_{7}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2}$ [3.29-3.30], $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [3.30-3.31], $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$ [3.30, 3.32-3.33], $Pd_{40}Ni_{40}P_{20}$ [3.30,3.32,3.34], $Pd_{40}Ni_{10}Cu_{30}P_{20}$ [3.30,3.32,3.35], $Au_{76.9}Ge_{13.65}Si_{9.45}$ [3.34,3.36] by different expressions. Thermodynamically, smaller Gibbs free energy difference ΔG, is expected to stabilize the undercooled melt against crystallization. Basically, ΔG is the driving force for crystallization and as a result, it is a reliable indicator for GFA. As discussed earlier, estimation of ΔG at T_g is important to study the GFA of metallic alloys. So, in present case ΔG (T_g) has been calculated by the various theoretical expressions given by Turnbull, T&S, S&H, Ji & Pan, Lad et al, Hoffmann, Battezzati and Garrone i.e. (eq.(3.6) to eq.(3.11) and eq.(3.13) to eq.(3.16)). Here all expressions of ΔG are based on different temperature dependence of ΔC_p. All these expressions estimate ΔG (T_g) with minimum experimental data available. The calculated values of ΔG (T_g) are shown in table-3.1.

Table3.1 Thermodynamic parameter ΔG by different theoretical expressions

Systems	**d_c (mm)**	**$\Delta G(T_g)$ by different expression (kJ/mol)**			
		Lad-I	**Lad-II**	**Hoffman**	**Turnbull**
$Ca_{50}Mg_{25}Cu_{25}$	9	2.287	1.938	2.037	3.193
$Mg_{65}Cu_{25}Y_{10}$	4	2.317	1.961	2.117	3.697
$Mg_{65}Cu_{20}Zn_5Y_{10}$	6	2.082	1.760	1.898	3.289
$Mg_{59.5}Cu_{22.9}Ag_{6.6}Gd_{11}$	27	1.791	1.515	1.599	2.555
$Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$	16	2.375	2.004	2.134	3.535
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	25	2.065	1.760	1.836	2.774
$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	16	2.754	2.324	2.487	4.198
$Pd_{40}Ni_{40}P_{20}$	10	2.417	2.050	2.151	3.335
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	72	1.536	1.337	1.373	1.905
$Au_{76.9}Ge_{13.65}Si_{9.45}$	0.04	2.466	2.302	2.642	5.597

Table 3.1 Continued…..

Systems	**d_c (mm)**	**$\Delta G(T_g)$ by different expression (kJ/mol)**				
		Ji & Pan	**S & H**	**T&S**	**B&G**	**γ (eq.3.12)**
$Ca_{50}Mg_{25}Cu_{25}$	9	2.424	2.954	2.487	2.339	1.29
$Mg_{65}Cu_{25}Y_{10}$	4	2.576	3.341	2.692	2.718	1.05
$Mg_{65}Cu_{20}Zn_5Y_{10}$	6	2.308	2.984	2.410	2.000	1.57
$Mg_{59.5}Cu_{22.9}Ag_{6.6}Gd_{11}$	27	1.912	2.354	1.967	1.805	1.35
$Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$	16	2.572	3.232	2.661	2.087	1.78
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	25	2.163	2.585	2.209	2.134	1.2
$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	16	3.008	3.822	3.124	2.880	1.31
$Pd_{40}Ni_{40}P_{20}$	10	2.552	3.092	2.615	2.604	1.08
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	72	1.576	1.805	1.596	0.994	3.09
$Au_{76.9}Ge_{13.65}Si_{9.45}$	0.04	3.263	4.826	3.589	4.124	0.8

The metallic alloy is considered to be a good glass former if the value of ΔG is low. The multicomponent alloy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ has an exceptionally low Gibbs free energy difference ΔG and hence an outstanding high glass forming ability (GFA). This system falls under the category of such glass forming alloys which show appreciable increase in ΔC_p with increased undercooling. Pd-based metallic alloys are found to have highest GFA, having minimum critical cooling rate [3.37]. Also as suggested by Inoue [3.5] increasing the number of components in the metallic alloys increases the GFA but from the table-3.1 it can be observed that for the present case it is not true. $Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$ metallic glass constitutes the greatest number of components among all the metallic systems but its GFA is not highest.

As stated by Battezzati and Garrone [3.16] the value γ should be equal to 0.8 for all metallic glasses, but from the table-3.1 it can be observed that it varies for different metallic glasses. The reason for variation of γ is due to the difficulty in choosing suitable crystallization step in multistep crystallization process for multicomponent metallic glasses. Moreover T_x and ΔH_x are also heating rate dependent [3.38]. So γ cannot be considered as constant and it is calculated by the equation (3.12) and the results are obtained accordingly.

The experimental values of $\Delta G(T_g)$ for $Mg_{65}Cu_{25}Y_{10}$ [3.24], $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [3.31], $Pd_{40}Ni_{40}P_{20}$ [3.34], $Pd_{40}Ni_{10}Cu_{30}P_{20}$ [3.33] and $Au_{76.9}Ge_{13.65}Si_{9.45}$ [3.34] are as shown in table 3.2. Based on the experimental data available in literature for few metallic glasses, it is observed from the calculated values of ΔG (T_g) by different expressions provide accurate values of ΔG at T_g for all systems.

Table 3.2 Thermodynamic parameter ΔG for different metallic glasses

Systems	**$\Delta G(T_g)$ (kJ/mol)**	**$\Delta G(T_g)$ by different expression (kJ/mol)**	
	Experimental	Dubey & Ramchandrarao	Lele et al
$Mg_{65}Cu_{25}Y_{10}$	2.761	2.601	2.787
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	2.190	2.361	2.414
$Pd_{40}Ni_{40}P_{20}$	2.953	2.573	2.677
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	1.378	1.386	1.440
$Au_{76.9}Ge_{13.65}Si_{9.45}$	4.486	4.638	4.841

For $Pd_{40}Ni_{40}P_{20}$ the experimental results lie close to the values obtained by S & H expression, whereas for $Pd_{40}Ni_{10}Cu_{30}P_{20}$ alloy Hoffman and Lad-II expressions show better agreement. Also it was found that T&S and B&G provide good results for other BMGs. Also thermodynamic analysis is carried out by expressions of ΔG given by Lele et al [3.22] and Dubey & Ramchandrarao [3.21] which are found to be in close agreement with the experimental results. The values of ΔG (T_g) as calculated by both expression are shown in table 3.2.

There are some more expressions available in literature [3.39-3.41] to determine ΔG which requires more experimental parameters to obtain exact values. Hence, these expressions may give accurate results for few BMGs, but it may not be true for all the cases. So, one cannot predict which equation gives better result for evaluation of ΔG, for a wide range of metallic glasses with different compositions.

Therefore, in the absence of experimental knowledge of the temperature dependence of ΔC_p, there is no universal expression for the estimation of ΔG in the undercooled liquid region. Hence, along with the exact variation of ΔC_p the evaluation of the constants existing in ΔC_p expressions are also important in deriving the expression for ΔG. So, for estimation of ΔG in the undercooled region there is a need to minimize the approximations used in the derivation of expression for ΔG.

3.5.2 Calculation of GFA parameters for different multicomponent amorphous alloys.

Different GFA criteria laid down by different workers are calculated for the multicomponent amorphous alloys and given in table 3.3. It can be observed from table 3.3 that different GFA parameters do not show any systematic variation in the glass forming tendency for various compositions of these multicomponent amorphous alloys.

Table3.3 Different GFA parameters

Systems	Different GFA parameters					
	ΔT_x	T_{rg}	Q	Υ_m	α	β
$Ca_{50}Mg_{25}Cu_{25}$	39	0.547	0.705	0.654	0.601	1.645
$Mg_{65}Cu_{25}Y_{10}$	50	0.566	0.748	0.701	0.633	1.685
$Mg_{65}Cu_{20}Zn_5Y_{10}$	52	0.555	0.532	0.698	0.626	1.684
$Mg_{59.5}Cu_{22.9}Ag_{6.6}Gd_{11}$	47	0.579	0.716	0.707	0.643	1.6
$Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$	37	0.583	0.412	0.635	0.609	1.627
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	60	0.624	0.878	0.745	0.685	1.721
$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	75	0.577	0.675	0.709	0.643	1.691
$Pd_{40}Ni_{40}P_{20}$	80	0.582	0.891	0.746	0.664	1.723
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	85	0.688	0.687	0.89	0.789	1.835
$Au_{76.9}Ge_{13.65}Si_{9.45}$	5	0.454	0.535	0.469	0.462	1.471

All the parameters almost show constant values and do not vary appreciably. ΔT_x represent the stability of glass i.e., how far is crystallization from glass transition. A greater value of ΔT_x represents greater stability of glass against crystallization.

Here $Pd_{40}Ni_{10}Cu_{30}P_{20}$ metallic glass has highest value of ΔT_x indicating better stability against crystallization and having GFA among all other compositions. Also parameter Q by Suo et al [3.11] seems to be a sensitive parameter showing variation with change in composition. However, it may be noted that the evaluation of Q essentially requires the knowledge of crystalline enthalpy ΔE. The parameter α derived is independent of T_g, so for metallic alloys for which distinct T_g is not observed the GFA can be estimated which proves its applicability.

3.5.3 Regression Analysis

All GFA parameters are correlated with critical cooling rate (R_c) or with critical size (d_c) in order to interpret its sensitivity towards the GFA of metallic glasses. The reliability of GFA criteria is evaluated by linear regression analysis and hence these criteria are correlated to their corresponding d_c. The GFA criterion is considered to be better, if the coefficient of correlation R^2 is large. The GFA parameters are calculated based on the available experimental data of characteristic temperatures, crystallization enthalpy and fusion enthalpy of BMGs. The advantage of doing such a regression analysis lies in the fact that it provides consideration to select GFA criteria and this study is useful to get a quantitative idea about how different GFA parameters reflect the GFA of different metallic alloys. Critical size (d_c) is a conclusive criterion for measuring GFA of BMGs. So, d_c is related with other parameter to check whether these parameters can be used to evaluate the GFA. A statistical correlation factor, R^2 have been evaluated from the plots of d_c versus GFA parameter for various BMGs.

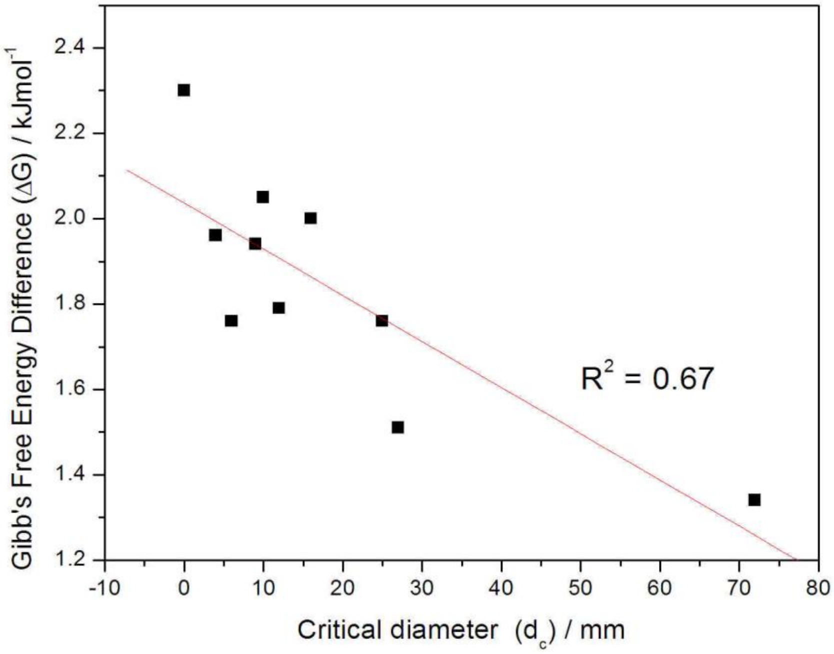

Fig.3.2 Variation of Gibbs free energy difference (ΔG) with critical diameter (d_c)

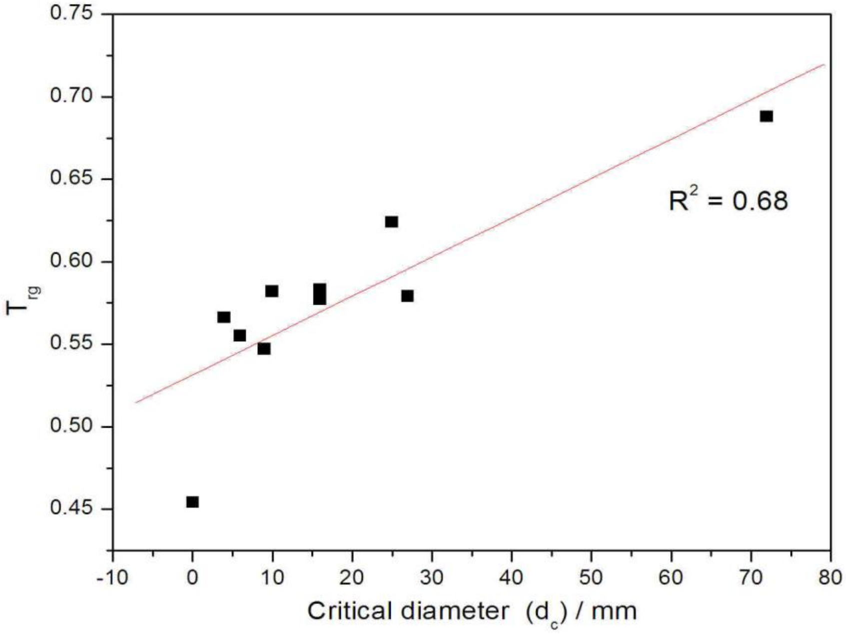

Fig.3.3 Variation of T_{rg} parameter with critical diameter (d_c).

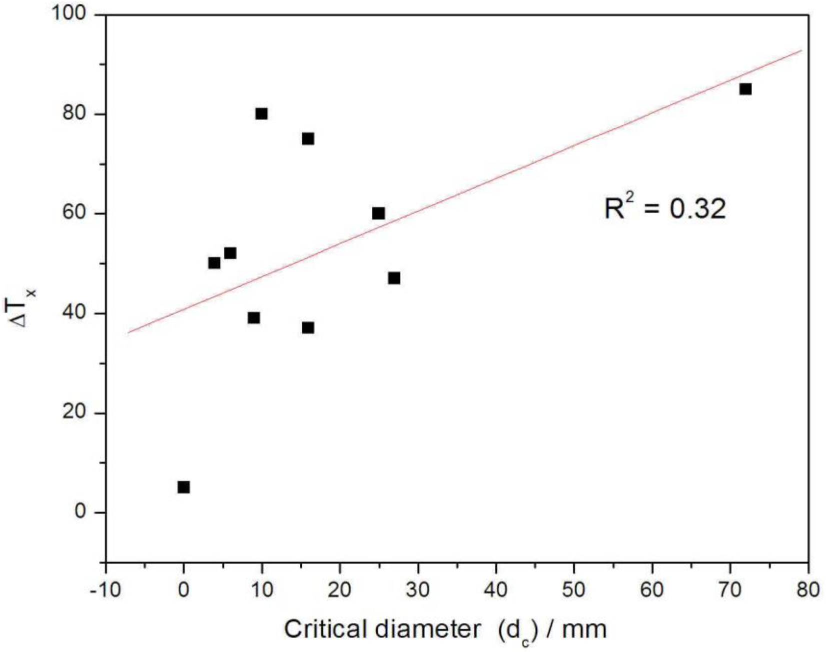

Fig.3.4 Variation of ΔT_x parameter with critical diameter (d_c).

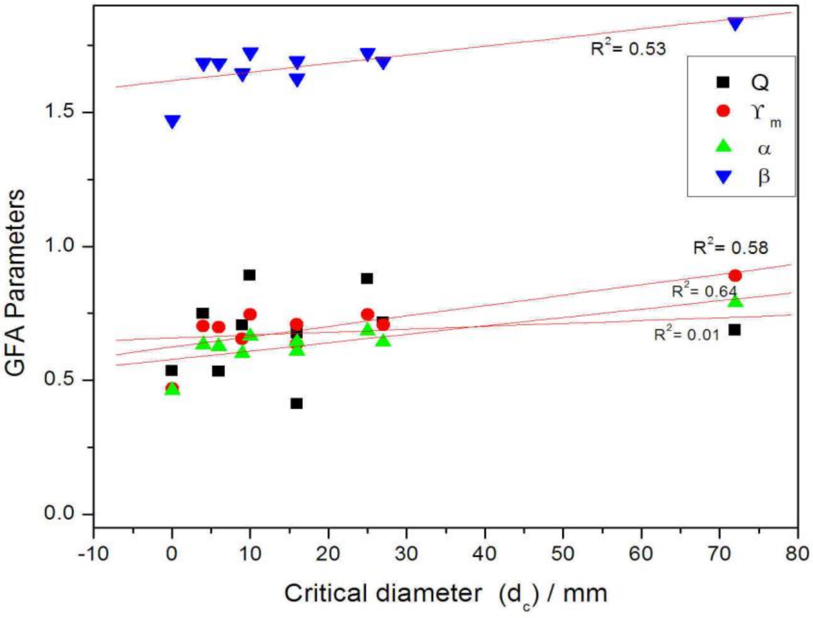

Fig.3.5 Variation of different GFA parameters with critical diameter (d_c).

Higher the value of R^2, better is the correlation between d_c and GFA parameters. The value of R^2 can give idea about how efficient are the different GFA parameters to evaluate GFA of metallic glasses. The value of R^2 determines the relationship between GFA criteria and d_c. It should reflect one to one correspondence between the two variables. If the value of R^2 is around unity it is considered to be highly correlated and have exact linear relationship. Fig.3.2-3.5 show the plots of d_c versus thermodynamic parameter ΔG, and other parameters T_{rg}, ΔT_x, Q, α, β, γ_m respectively for the BMGs listed in the table 3.1. By using the linear regression method a linear relationship can be obtained between d_c and GFA parameters. From the plots it can be observed that all GFA parameters show a correlation with d_c, indicating that all these parameters, to a certain range reflect GFA of alloys. The values of correlation coefficient R^2 were computed to be 0.67 for the d_c- ΔG plot, 0.01, 0.58, 0.64, 0.53 for the d_c -Q, γ_m α, β plot, 0.68 for d_c-T_{rg} plot and 0.32 for d_c- ΔT_x plot respectively. From the values of R^2, it can be observed that ΔG, which is the driving force of crystallization and reduced glass transition temperature T_{rg} better represents GFA of different metallic glasses. ΔG (T_g) varies inversely with d_c and hence it shows a negative correlation with d_c. As $\Delta G(T_g)$ increases, d_c decreases and hence GFA decreases. Lower the value of ΔG, lesser will be the driving force of nucleation which degrades the crystallization, hence better will be the GFA. So thermodynamically the GFA of metallic alloys can be understood by ΔG (T_g). Other GFA parameters show a reasonable linear relation with d_c, except for T_{rg}. As T_{rg} increases GFA also increases and it show a positive correlation with d_c. GFA of metallic glass is considered to be high if the value of T_{rg} lies in the range 0.66-0.69. In the present case $Pd_{40}Ni_{10}Cu_{30}P_{20}$ has T_{rg} value of 0.68 indicating that it is best glass former among all. From the fig.3.4 it can be seen that there exists a weak correlation between ΔT_x and d_c which implies that GFA is not closely related to ΔT_x. d_c represents GFA of metallic glasses, as d_c increases, GFA increases. A good GFA parameter is expected to show one-to-one correspondence with d_c. So for the same value of d_c a good GFA parameter should have same values. But for the parameter ΔT_x few metallic glasses with same value of d_c have different ΔT_x values. Though GFA and glass thermal stability are related properties, but ΔT_x cannot be used to understand both of them. Weinberg [3.42] found that a high GFA does not always indicate a high thermal stability. Hence, GFA and thermal stability can be different for few metallic glasses. Therefore ΔT_x cannot be used as GFA parameter. In the present case correlation between GFA criteria and d_c gives lower value of R^2 .This may be due to the fact that the compositions of metallic alloys used in this study are significantly different from each other. The metallic glasses having slight variation in composition show high value of R^2. Cai et al [3.43] studied GFA of Zr-Al-Ni-Cu based bulk metallic glasses and found that GFA parameters show strong correlation with critical size.

From the fig.3.2-3.5 it can also be observed that different GFA parameters deviate from the fitted line. For some GFA criteria, the deviation from fitted line is quite large as the regression analysis is based on dispersed data on different metallic systems. The values of R^2 for α and β are found to be higher than that of ΔT_x which implies that they are strongly correlated and better indicator of GFA. The weak correlation of ΔT_x is due to the fact that it can only reflect the stability of glass whereas α and β combine both the properties i.e. thermal stability of glass and ease of glass formation. It is reported in literature that some glass forming criteria such as ΔT_x and T_{rg}, when correlated with R_c or d_c show a high degree of diversion in number of cases [3.44-3.45]. So analyzing data which is highly distributed may not provide accurate results. The value of R^2 for the plots of different GFA parameter with d_c is not so high because d_c is also dependent on different casting condition used by different researchers. In the present case metallic glasses with large variation in composition are taken into consideration. Hence metallic glasses with different composition will have different GFA. Also the characteristic temperatures for all the glasses will be different. Here correlation between d_c and different GFA parameters is obtained. A higher value of R^2 corresponds to better correlation between d_c and different GFA parameters. In the present case, lower value of R^2 is obtained which may be due to following reasons:

1. The regression analysis is carried out for a much dispersed data. Hence one-to-one correspondence between d_c and different GFA parameters is not observed.
2. Since d_c is affected by number of other factors like alloy preparation route, hence the accurate value of d_c is hard to obtain, which probably accounts for weak correlation between d_c and GFA parameters.
3. GFA parameters used for analysis have been derived using different approximation. Here the value of R^2 for ΔT_x is 0.32, indicating poor

correlation with d_c, because it represents only thermal stability of metallic glass. Results indicate that compositions possessing same d_c value have different ΔT_x values. This infers that ΔT_x cannot give a clear indication of GFA of metallic glasses.

3.5.4 Glass forming ability of Mg-Ni-Pr based metallic glasses

Among various amorphous alloys, Mg-based alloys are of prime interest due to their high strength to weight ratio and relatively low price. Also, Mg-based BMGs are potential candidate for hydrogen storage material [3.46]. So, in the present study the glass forming ability of Mg-based metallic glass is studied and to identify the best glass former among all the four composition i.e. $Mg_{48}Ni_{31}Pr_{21}$, $Mg_{63}Ni_{22}Pr_{15}$, $Mg_{65}Ni_{21}Pr_{14}$ and $Mg_{65}Ni_{21}Pr_{14}$ (air) different GFA criteria are calculated. The thermodynamic properties like ΔG and ΔS are also determined. Many GFA criteria have been used for finding the GFA of metallic glasses like $\gamma_m(=2T_x\text{-}T_g/T_l)$, $Q(=(T_g+T_x)/T_l)$, η $(=1-\Delta H_x/\Delta H_m)$, $\gamma(=T_x/(T_g+T_l))$, $T_{rg}(=T_g/T_l)$ etc. where T_l, T_x, T_g are liquidus, crystallization, and glass transition temperature respectively.

Table3.4 Different GFA criteria for Mg-Ni-Pr based metallic glasses

Systems [3.47]	**Different GFA parameters**					
	ΔT_x [3.47]	T_{rg} [3.47]	Q	Υ_m	γ [3.47]	η
$Mg_{48}Ni_{31}Pr_{21}$	47	0.570	0.451	0.695	0.403	0.627
$Mg_{63}Ni_{22}Pr_{15}$	52	0.574	0.803	0.708	0.407	0.339
$Mg_{65}Ni_{21}Pr_{14}$	42	0.569	0.907	0.675	0.396	0.238
$Mg_{65}Ni_{21}Pr_{14}$ (air)	41	0.574	0.814	0.678	0.397	0.322

Different GFA parameters are calculated and listed in table 3.4. It can be observed from the table 3.4 that none of the GFA parameter gives clear indication of the better glass former. The parameters $\underline{T_{rg}}$, γ, γ_m gives constant value which cannot give idea about variation in GFA for the given compositions.

Table3.5 Thermodynamic parameters of Mg-Ni-Pr based metallic glasses

Systems	ΔG_1 (Lad-1) kJ/mol	ΔG_2 (Lad-2) kJ/mol	$\Delta G_1/\Delta H_m$	$\Delta G_2/\Delta H_m$	$\Delta S_1(T_g)$ (Lad-1) kJ/mol	$\Delta S_2(T_g)$ (Lad-2) kJ/mol
$Mg_{48}Ni_{31}Pr_{21}$	2.92	2.47	0.265	0.249	1.77	1.45
$Mg_{63}Ni_{22}Pr_{15}$	1.35	1.14	0.265	0.224	0.53	0.51
$Mg_{65}Ni_{21}Pr_{14}$	1.38	1.17	0.264	0.224	0.91	0.72
$Mg_{65}Ni_{21}Pr_{14}$ (air)	1.50	1.26	0.265	0.223	0.93	0.75

The GFA of Mg-Ni-Pr based alloys for all four different composition is evaluated by ΔG in the entire undercooled region. Thermodynamic parameters ΔG and ΔS at T_g along with $\Delta G(T_g)/\Delta H_m$ are given in table 3.5. It can also be observed from the table-3.5 that there is a significant variation in ΔG values which can predict better glass forming composition. ΔG is the driving force for crystallization. Lower the value of ΔG, higher is the GFA of metallic alloys. Thus, $Mg_{63}Ni_{22}Pr_{15}$ appears to have the highest glass forming tendency having lowest ΔG value of 1.35 and 1.14 by Lad-1 and Lad-2 expressions of ΔG respectively. It can also be observed from table 3.5 that value of $\Delta G(T_g)/\Delta H_m$ for the alloys with four different compositions lie around 0.2 by both the expression of ΔG. This constant value of 0.2 of the ratio indicates that lower the value of $\Delta G(T_g)$, lower the value of the corresponding ΔH_m and better is the glass forming ability.

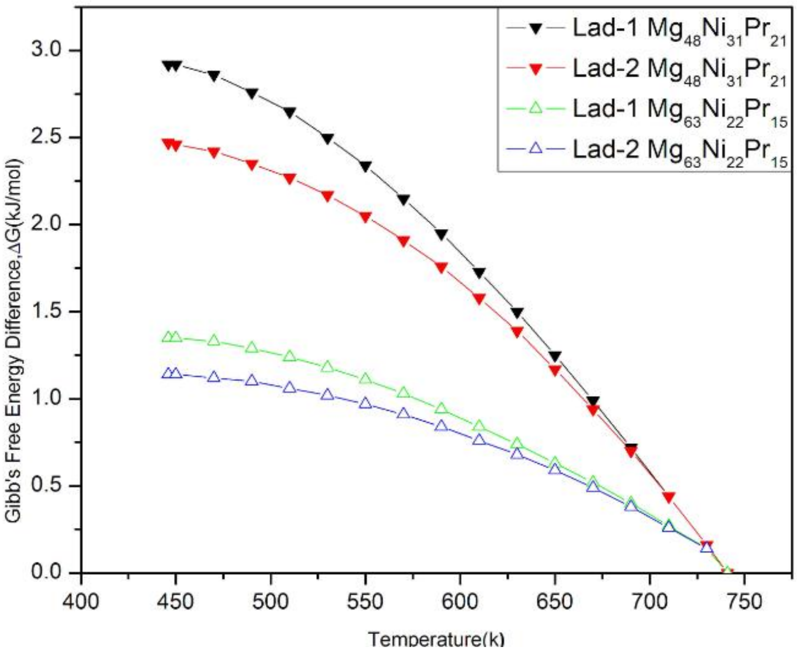

Fig 3.6 Gibbs free energy difference with temperature for $Mg_{48}Ni_{31}Pr_{21}$ and $Mg_{63}Ni_{22}Pr_{15}$

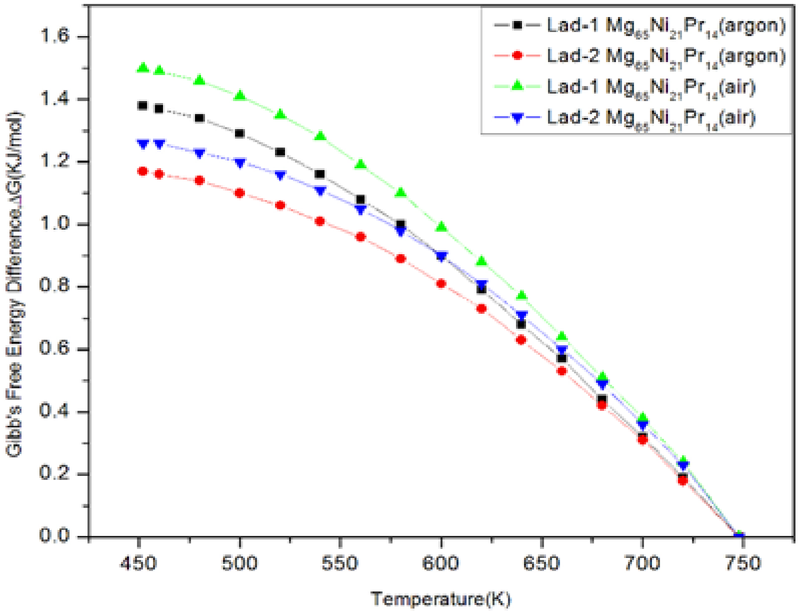

Fig. 3.7 Gibbs free energy difference with temperature for $Mg_{65}Ni_{21}Pr_{14}$ in air and argon atmosphere. .

ΔG is calculated for the entire undercooled region, from Lad-1 &Lad-2 (Eq.(3.8) & Eq.(3.9)) equations. Lad-1 and Lad-2 expressions are used to evaluate ΔG as it requires minimal experimental parameters. These expressions are derived approximating ΔC_p to be constant.

Figure-3.6 shows ΔG variation with temperature for $Mg_{48}Ni_{31}Pr_{21}$ and $Mg_{63}Ni_{22}Pr_{15}$ metallic glasses. Lad-2 gives smaller value of $\Delta G(T_g)$ than Lad-1 for all the systems as given in table-3.5 which indicates that it is a good approximation. $Mg_{65}Ni_{21}Pr_{14}$ metallic glass produced in argon is better glass former than $Mg_{65}Ni_{21}Pr_{14}$ produced in air as $\Delta G(T_g)$ is lower for sample prepared in argon as shown in fig.3.7. The entropy difference, ΔS, between the undercooled liquid and the corresponding crystalline phase has also been calculated from Eq. (3.18) & (3.19), and plotted in fig. (3.8) & (3.9), for all the four composition i.e. $Mg_{48}Ni_{31}Pr_{21}$, $Mg_{63}Ni_{22}Pr_{15}$, $Mg_{65}Ni_{21}Pr_{14}$ and $Mg_{65}Ni_{21}Pr_{14}$ (air).

Fig. 3.8 & 3.9 shows the entropy difference between liquid and crystal, ΔS as a function of the temperature. ΔS between the undercooled liquid and corresponding crystalline solid has been obtained from the derivative of ΔG expression. Here ΔS expressions are derived using only Lad et al expressions for ΔG. The entropy of the Mg-Ni-Pr based metallic glasses decreases with increasing undercooling.

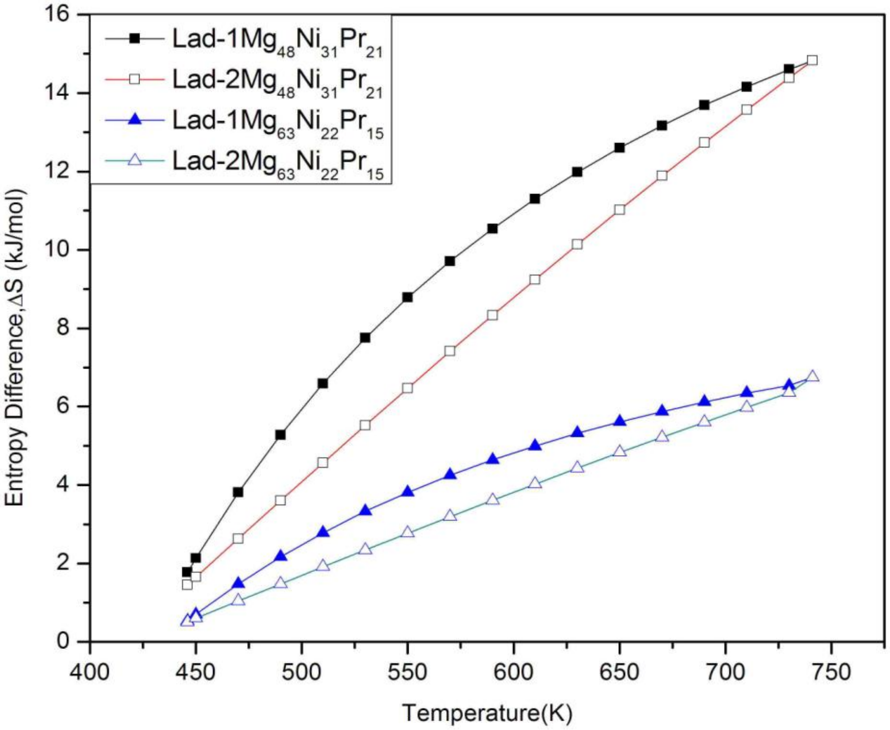

Fig. 3.8 Entropy Difference with temperature for $Mg_{63}Ni_{22}Pr_{15}$ and $Mg_{48}Ni_{31}Pr_{21}$.

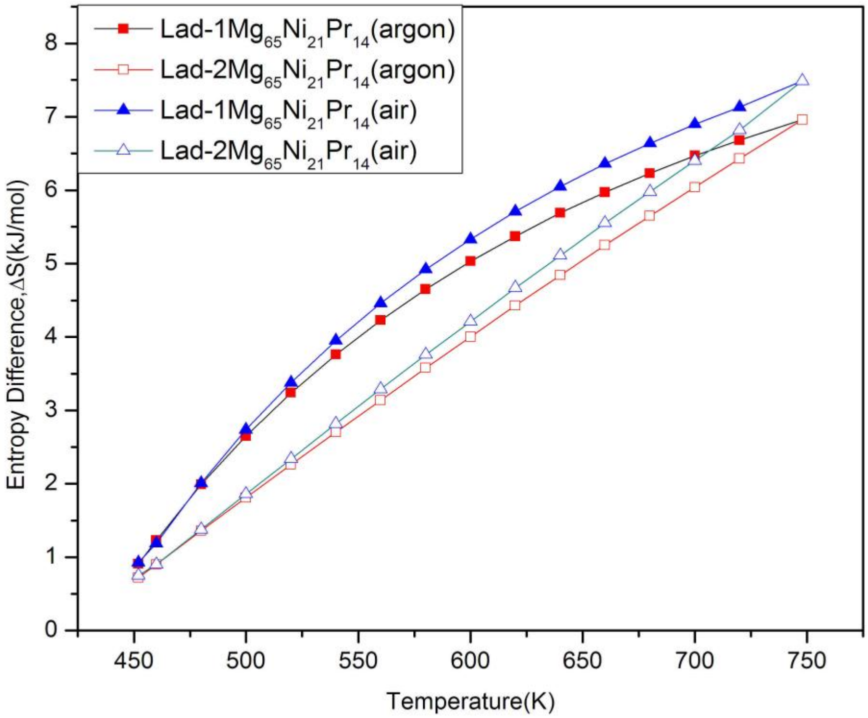

Fig 3.9 Entropy Difference with temperature for $Mg_{65}Ni_{21}Pr_{14}$ in air and argon atmosphere

3.5.5 Glass forming ability and Thermal Stability of Cu-Pr Based Metallic Alloys

The driving force for nucleation and the free energy of activation for the crystal growth depends on the Gibb's free energy difference (ΔG) between super cooled liquid and corresponding crystalline phase. In the present case two Cu-Pr based alloys are taken into consideration i.e. $Cu_{50}Pr_{30}Ni_{10}Al_{10}$ and $Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$ [3.48]. The glass forming ability of $Cu_{50}Pr_{30}Ni_{10}Al_{10}$ and $Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$ metallic glass is studied through different GFA parameters and by ΔG. The aim of the work is to study the effect of minor substitution of Ti and B on GFA and thermal stability of Cu-Pr based metallic alloy. The minor addition of Ti & B in Cu-Pr based alloy decreases the glass transition temperature (T_g), crystallization temperature (T_x) and liquidus temperature (T_l) but increases the melting temperature which result in an increase of bulk glass formation ability [3.48]. The most frequently used parameters are the reduced glass transition temperature, T_{rg}, super cooled liquid range, ΔT_x, parameter γ and Hurby parameter (H_r) [3.49] are evaluated for Cu-Pr based amorphous alloys. ΔG, which is the driving force of nucleation, is one of the dominating factors that affect kinetics of crystallization. Further, ΔG is calculated and compared with other GFA parameters. The thermal stability of the two alloys is studied through their supercooled liquid region i.e. ΔT_x ($=T_x-T_g$). Table 3.4 reports various GFA parameters for both alloy compositions.

Table3.6 Gibbs free energy difference (*ΔG*) and GFA parameters for Cu-Pr based metallic glasses

GFA parameters	**Compositions**	
	$Cu_{50}Pr_{30}Ni_{10}Al_{10}$	**$Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$**
$\Delta G(T_g)$/kJmol^{-1}	1.79	1.61
$\Delta T_x(=T_x-T_g)$ /K	115	114
$T_{rg}(=T_g/T_l)$	0.37	0.37
$\Upsilon(=T_x/(T_g+T_l)$	0.34	0.34
$\Upsilon_m(=(2T_x-T_g)/T_l)$	0.56	0.56
$\delta(=T_x/(T_l-T_g)$	0.75	0.74
$\alpha(=T_x/T_l)$	0.47	0.46
$H_r(=(T_x-T_g)/(T_m-T_x))$	0.25	0.24

ΔG is the driving force of crystallization and is a vital factor in nucleation rate and crystal growth rate. Less value of *ΔG* means the less driving force of crystallization, the smaller nucleation rate in supercooled liquid and the better GFA. So, the GFA of Cu-Pr based amorphous alloy after microalloying can be investigated from the thermodynamic point of view. $\Delta G(T_g)$ and other GFA parameters are evaluated and reported in table 3.6. It is evident from the table 3.6, that Ti and B addition improves the glass forming ability. ΔG (T_g) varies significantly for both the alloy compositions. A lower value of ΔG implies greater GFA. It can be seen that ΔG for $Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$ is less than that of $Cu_{50}Pr_{30}Ni_{10}Al_{10}$, it indicates that among the both metallic alloys $Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$ is the better glass former. Other parameters, ΔT_x, T_{rg}, γ γ_m, *α*, *δ,* show almost same values for both the alloy compositions. The larger value of ΔT_x indicates the better thermal stability of the alloys. However, ΔT_x could not reflect better thermal stability among the two alloys as the values of ΔT_x for both the alloys vary in very small magnitude.

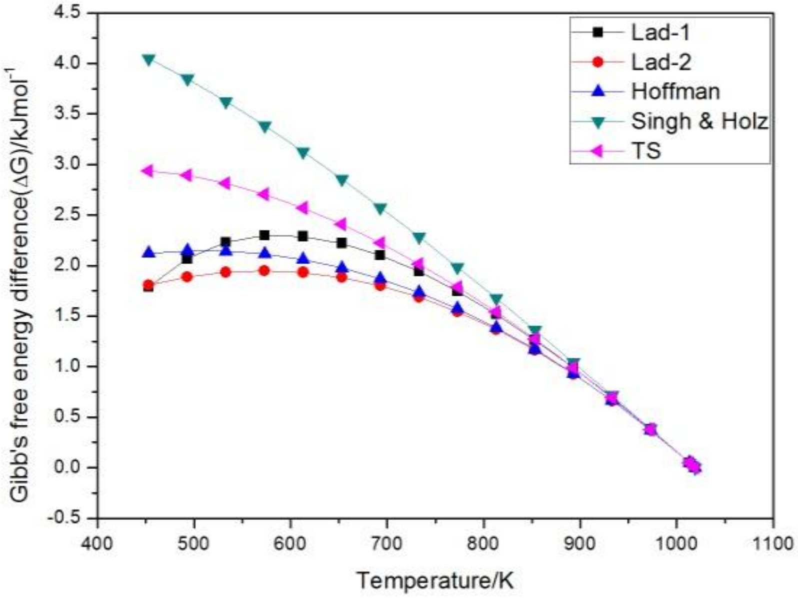

Fig. 3.10 Variation of Gibbs free energy difference with temperature, for $Cu_{50}Pr_{30}Ni_{10}Al_{10}$ alloy

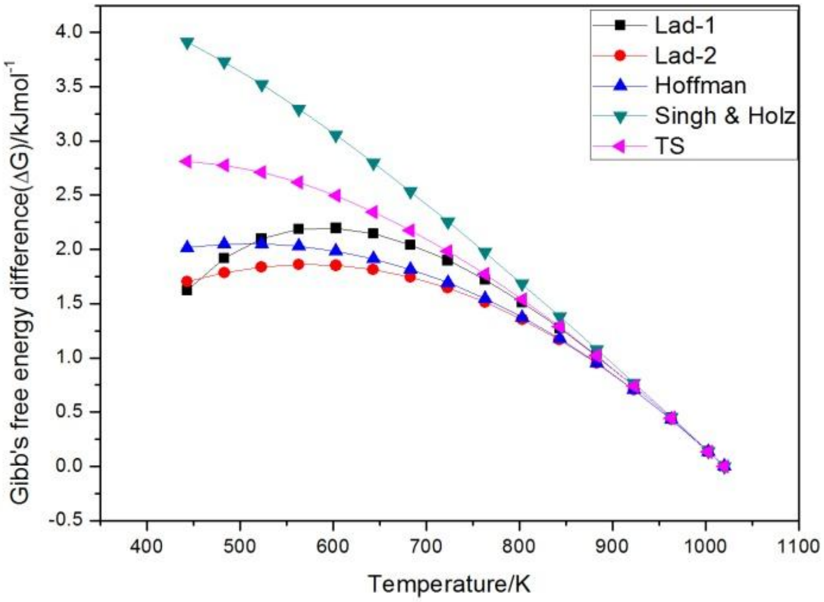

Fig 3.11 Variation of Gibbs free energy difference with temperature for $Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$

The variation of ΔG between glass transition temperature (T_g) and melting temperature (T_m) have been shown in fig. 3.10 & 3.11 respectively for $Cu_{50}Pr_{30}Ni_{10}Al_{10}$ and $Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$ alloys. In the absence of experimental ΔG data, various expressions of ΔG derived using different ΔCp approximations are used to evaluate ΔG in the entire undercooled region. The so obtained ΔG values are plotted against temperature to study the glass forming tendency for both the alloy compositions. Different expressions of ΔG give different values of $\Delta G(T_g)$. The plot clearly indicates that the value of ΔG at T_g, obtained by eq. (3.8) and (3.9) are lowest as compared to that obtained by other expressions. As seen from the fig. 3.10 & 3.11 that at high temperatures all formulae give ΔG values basically identical, but marked differences arise when the melt is brought to low temperatures. The parameter H_r gives the probability of obtaining glass which increases as T_m-T_x decreases and T_x-T_g increases.

3.6 Conclusions

Based on the results discussed in this chapter, the following conclusions can be drawn regarding the role of kinetic and thermodynamic properties on the glass-forming ability of bulk metallic glass-forming alloys.

Glass forming ability is an important parameter for understanding the origin of glass formation and it is very crucial parameter for designing and developing new BMGs. The knowledge of the thermodynamics of the undercooled melts is required to understand the glass formation. Many GFA parameters and thermodynamic parameter, ΔG were calculated to understand the GFA of multicomponent amorphous alloys. Based on reasonably good correlation with d_c, thermodynamic parameter ΔG reflects the GFA of metallic alloys. ΔG shows a negative correlation with d_c whereas other parameters show a positive correlation. The correlation of d_c with other parameters also shows linear dependence, suggesting that they are equally important to predict GFA of all metallic glasses. T_{rg} also shows a high correlation with d_c hence it is good GFA indicator. So thermodynamically the GFA of the metallic alloys can also be predicted and alloy with higher GFA can be designed. By comparing the values of GFA parameters of glass forming alloys, one can conclude that $Pd_{40}Ni_{10}Cu_{30}P_{20}$ have high GFA among all, as it has the lowest value of ΔG and large stability against crystallization, indicated by greater value of ΔT_x (=85 K).

The thermodynamic analysis for the metallic glasses is represented by Gibbs free energy difference (ΔG). Different expressions of ΔG have been discussed in order to get a clear idea of the best glass former. Different models of ΔG, taken for calculations, have been derived using different variation of ΔC_p with temperature. Hence they provide values of ΔG different from each other. On comparing theoretical and available experimental ΔG values for few metallic glasses, all models of ΔG satisfactorily explain the variation of GFA among various metallic glasses. From this it is quite clear that in order to achieve accurate values for ΔG; one has to consider an appropriate variation of ΔC_p. $Pd_{40}Ni_{10}Cu_{30}P_{20}$ has been found to be the best glass former among all metallic glasses under consideration. Furthermore, there are few other expressions which provide very accurate values of ΔG, but they involve experimental values of ΔC_p. However in absence of sufficient experimental data one cannot utilize those expressions for all metallic glasses. Only those expressions of ΔG are considered that involve minimum experimental data.

According to Battezzati and Garrone the parameter γ (= $(1-(\Delta H_x/\Delta H_m))/(1-(T_x/T_m))$) in the expression for ΔG should be a constant (i.e., 0.8), but its uniqueness is not observed for all metallic glasses.

It can be concluded that $Mg_{63}Ni_{22}Pr_{15}$ is the best glass former among all compositions as the driving force of crystallization; ΔG is very low for it which indicates excellent GFA. $Mg_{65}Ni_{21}Pr_{14}$ though has better GFA in argon atmosphere, but it can also be successfully prepared in air which is not possible for synthesis of other BMG's. ΔG value for $Mg_{65}Ni_{21}Pr_{14}$ metallic glass which is prepared in air has comparatively smaller value of ΔG (T_g) which indicates that $Mg_{65}Ni_{21}Pr_{14}$ is also a good glass former.

Glass forming ability of $Cu_{50}Pr_{30}Ni_{10}Al_{10}$ was investigated on addition of minor alloying elements Ti and B. It is observed that 0.05% of Ti and 0.05% of B addition enhances the GFA of $Cu_{50}Pr_{30}Ni_{10}Al_{10}$. ΔG values for $Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$ is lower that indicate $Cu_{50}Pr_{30}Ni_{10}Al_{9.9}Ti_{0.05}B_{0.05}$ is the better glass former. The driving force of crystallization has been calculated by various methods available in literature. Expressions given by Lad et al. provide lower ΔG values than other expressions.

It can be concluded that the driving force plays an important role in predicting the glass forming ability of alloys.

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