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A thermodynamic approach towards glass-forming ability of amorphous metallic alloys

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Abstract. 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 is known as the driving force of crystallization. The driving force of crystallization (ΔG) provides very important information about the glass-forming ability (GFA) of metallic glasses (MGs). Lesser the driving force of crystallization more is the GFA. The ΔG varies linearly with the critical size (d_c). According to Battezzati and Garonne the parameter $\gamma (= (1-(\Delta H_x/\Delta H_m))/(1-(T_x/T_m)))$ in the expression for ΔG should be a constant (i.e., 0.8), but its uniqueness is not observed for all MGs. The thermal stability of various alloy compositions is studied by their undercooled liquid region ($\Delta T = T_x - T_g$). Large ΔT_x implies greater stability against crystallization of the amorphous structure. Other GFA parameters are also calculated and correlated with critical size (d_c).

Keywords. Metallic glass; Gibbs free energy; critical size.

1. Introduction

Metallic alloys can be converted into metallic glasses by cooling their melt at a high rate, i.e., 10^5–10^6 K s^{-1}, such that their molecules does not get sufficient time to occupy stable configuration, thereby suppressing their crystallization event. These supercooled metallic alloys with a disordered atomic scale arrangement and connected by metallic bonds are known as 'metallic glasses (MGs)'. Metallic alloys which fail to crystallize during solidification even at low critical cooling rate, i.e., less than 100 K s^{-1}, form 'bulk metallic glasses (BMGs)' with thickness ranging from 1 mm to several centimetres due to smaller cooling rates. MGs and BMGs are prepared by different synthesis routes. Melt spinning technique is used to prepare amorphous ribbons of metallic alloys, which involves rapid cooling. On the other hand, BMGs are formed by different methods such as copper mould casting, arc melting, which require comparatively low cooling rate. These metastable materials possess excellent properties, such as high strength, high hardness, exhibit good corrosion resistance and attractive soft magnetic behaviour.[1,2] This inspires us to study the thermal properties of MGs in the undercooled region. To design an alloy having excellent glass-forming ability (GFA), many empirical approaches have been proposed based on trial and error experiments,[3–5] but there are no justified theories and scientific rules. The GFA of alloys may be characterized by the Gibbs free energy

difference (ΔG). Decreasing ΔG acts as a driving force for nucleation causing an increase in critical nucleation work and a reduction in nucleation rate. Lele et al[6] studied the temperature dependence of free energy of crystallization. It provides an insight for understanding the effect of heating rate on nucleation in undercooled region. The value of ΔG can be calculated by the measurement of specific heat difference ΔC_p, which is difficult to attain experimentally. So, different theoretical approximations of ΔC_p results in a variety of expressions of ΔG.[7,8] To understand glass formation and to predict GFA, Guo et al[9] have imposed physically accepted boundary conditions to evaluate the GFA criteria, and performed statistical analysis in order to identify the best GFA criterion. Recently, Tang et al[10] have studied the GFA of Ce-based alloys, using different GFA parameters.

All GFA parameters are correlated with in order to interpret its sensitivity towards the GFA of MGs. Senkov[11] introduced GFA parameter based on fragility of MG and found a good correlation with critical cooling rate. Also Xiu-lin and Ye[12] formulated a new GFA parameter based on thermodynamic analysis and found a good correlation with d_c for Ca-Mg-Cu BMGs. In the present work, ΔG and other GFA parameters[5,13–16] for different MGs are calculated and are correlated with critical size to study the GFA of metallic alloys. ΔG is evaluated by different theoretical expressions. We have calculated ΔG to understand the glass formability of various MGs, i.e., $Ca_{50}Mg_{25}Cu_{25}$,[17] $Mg_{65}Cu_{25}Y_{10}$,[18,19] $Mg_{65}Cu_{20}Zn_5Y_{10}$,[20] $Mg_{59.5}Cu_{22.9}Ag_{6.6}Gd_{11}$,[21,22] $Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$,[23,24] $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$,[24,25] $Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$,[24,26,27] $Pd_{40}Ni_{40}$

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$P_{20},$[24,26,28] $Pd_{40}Ni_{10}Cu_{30}P_{20},$[24,26,29] and $Au_{76.9}Ge_{13.65}$ $Si_{9.45}$[28,30] by different expressions.

2. Theory

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

$$\Delta G = \Delta H - T \Delta S \tag{1}$$

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \tag{2}$$

$$\text{and} \quad \Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \tag{3}$$

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:

$$\Delta S_m = \Delta H_m / T_m \tag{4}$$

So the equation becomes,

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

Turnbull[5] assumed ΔC_p to be zero. So ΔG can be written as

$$\Delta G = \Delta H_m \left(\frac{\Delta T}{T_m} \right). \tag{5}$$

Assuming $\Delta C_p = $ constant, one gets

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

To simplify the above equation, Thompson and Spaepen[7] (T–S) used the following approximation:

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

And they derived an expression given as

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(\frac{2T}{T_m + T} \right). \tag{6}$$

This equation is only valid for small ΔT, and leads to error in calculations of ΔG values at larger undercooling.

Generally, multicomponent MGs exhibit larger undercooling range. Hence, equation (6) cannot be used for a wide range of MGs.

Lad *et al*[8] 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 up to second order and derived the expression:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(1 - \frac{\Delta T}{2T} \right) \text{[Lad-I]} \tag{7}$$

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*[31] gave the expression:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(\frac{4T^2}{(T + T_m)^2} \right) \text{[Lad-II]} \tag{8}$$

As stated by Hoffman[32]

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

With this approximation equation becomes

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(\frac{T}{T_m} \right). \tag{9}$$

According to Battezatti and Garone[33] the expression for ΔG is given as follows:

$$\Delta G = \Delta S(T_m - T) - \gamma \Delta S_m \left[(T_m - T) - T \ln(T_m/T) \right]. \tag{10}$$

The γ-parameter in the above equation is represented as:

$$\gamma = \frac{(1 - \Delta H_x / \Delta H_m)}{(1 - \Delta T_x / \Delta T_m)}, \tag{11}$$

where ΔH_x denotes the enthalpy difference at crystallization.

Singh and Holz[34] (S and H) gave the following expression for linear variation of ΔC_p with T:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(\frac{7T}{T_m + 6T} \right). \tag{12}$$

Ji and Pan[35] considered hyperbolic variation of ΔC_p with $T (\Delta C_p = \Delta H_m / T)$ and derived the following expression:

$$\Delta G = \frac{2\Delta H_m \Delta T}{T_m} \left(\frac{T}{T_m + T} - \frac{\Delta T^2 T_m}{3 (T_m + T)^3} \right). \tag{13}$$

Dubey and Ramchandrarao[36] derived expression for ΔG based on the hole theory of liquids given as:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \frac{\Delta C_p^m (\Delta T)^2}{2T} \left(1 - \frac{\Delta T}{6T} \right). \tag{14}$$

Finally Lele *et al*[6] derived an expression of ΔG to study its temperature dependence for the entire undercooled region represented as:

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \frac{\Delta C_p^m (\Delta T)^2}{(T_m + T)}. \tag{15}$$

3. Results and discussion

3.1 *Regression analysis*

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 larger. The GFA parameters are calculated based on the available experimental data of characteristic temperatures, crystallization enthalpy and fusion enthalpy of BMGs in the literature. Critical size is a conclusive criterion for measuring GFA of BMGs. So d_c is related with other parameters 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 *vs.* GFA parameter for various BMGs. 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 MGs. 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 having exact linear relationship. 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.

Figure 1a–d shows the plots of d_c *vs.* thermodynamic parameter ΔG, and other parameters T_{rg}, ΔT_x, Q, α, β, γ_m, respectively, for the BMGs listed in table 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 plots, 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 MGs. $\Delta G(T_g)$ 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.
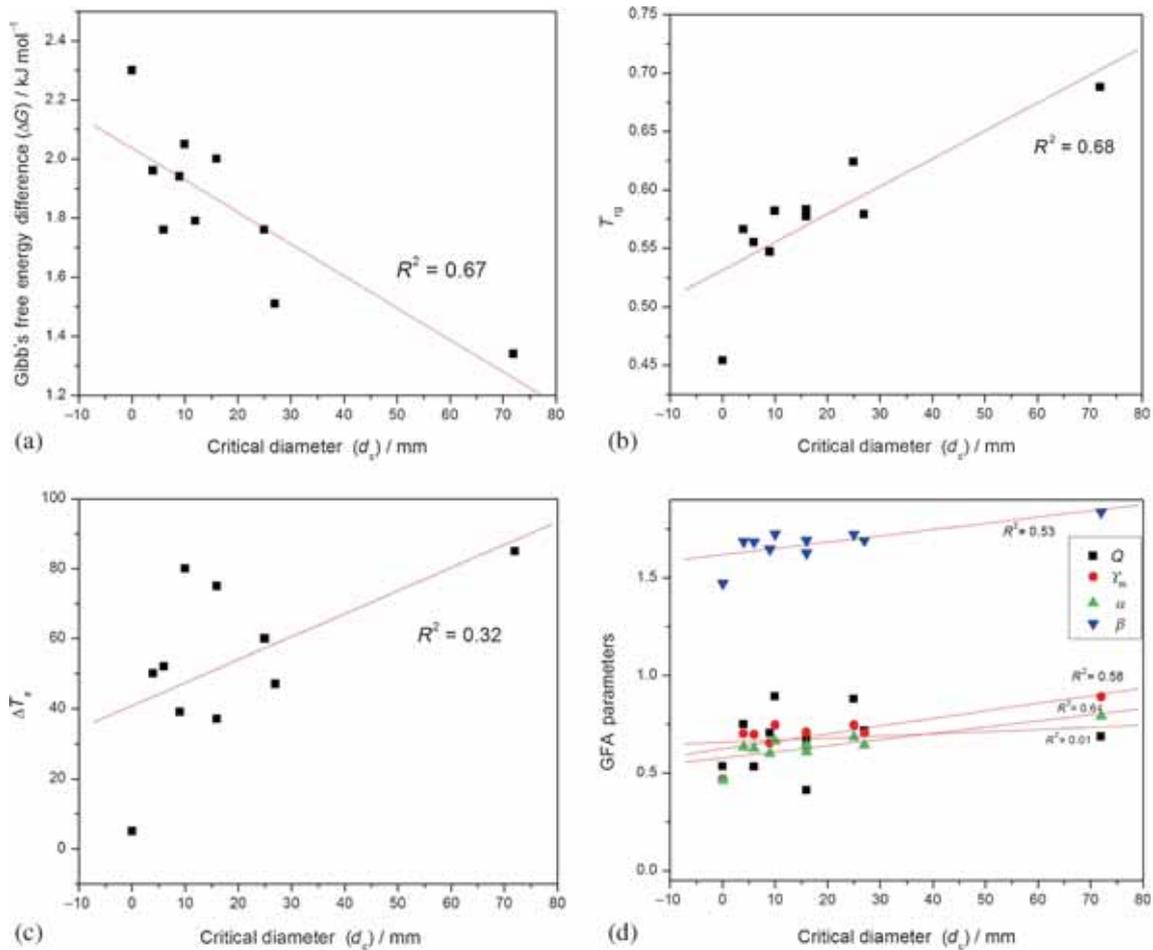

Figure 1. Variation of Gibb's free energy difference ΔG, T_{rg}, ΔT_x and other GFA parameters with critical diameter (d_c).

Table 1. Thermodynamic parameter ΔG by different theoretical expressions.

Systems	d_c (mm)	$\Delta G(T_g)$ by different expressions (kJ mol^{-1})								
		Lad-I	Lad-II	Hoffman	Turnbull	Ji and Pan	S and H	T and S	B and G	γ (equation 11)
$Ca_{50}Mg_{25}Cu_{25}$	9	2.287	1.938	2.037	3.193	2.424	2.954	2.487	2.339	1.29
$Mg_{65}Cu_{25}Y_{10}$	4	2.317	1.961	2.117	3.697	2.576	3.341	2.692	2.718	1.05
$Mg_{65}Cu_{20}Zn_5Y_{10}$	6	2.082	1.760	1.898	3.289	2.308	2.984	2.410	2.000	1.57
$Mg_{59.5}Cu_{22.9}Ag_{6.6}Gd_{11}$	27	1.791	1.515	1.599	2.555	1.912	2.354	1.967	1.805	1.35
$Fe_{41}Co_7Cr_{15}Mo_{14}C_{15}B_6Y_2$	16	2.375	2.004	2.134	3.535	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	2.065	1.760	1.836	2.774	2.163	2.585	2.209	2.134	1.2
$Zr_{65}Cu_{17.5}Ni_{10}Al_{7.5}$	16	2.754	2.324	2.487	4.198	3.008	3.822	3.124	2.880	1.31
$Pd_{40}Ni_{40}P_{20}$	10	2.417	2.050	2.151	3.335	2.552	3.092	2.615	2.604	1.08
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	72	1.536	1.337	1.373	1.905	1.576	1.805	1.596	0.994	3.09
$Au_{76.9}Ge_{13.65}Si_{9.45}$	0.04	2.466	2.302	2.642	5.597	3.263	4.826	3.589	4.124	0.8

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 $\Delta G(T_g)$. Other GFA parameters show a reasonable linear relation with d_c, except for T_{rg}. As T_{rg} increases GFA also increases and it shows a positive correlation with d_c. GFA of MG 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 a best glass former among all. The parameter α derived by Mondal and Murty[37] 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. The parameter Q is derived based on consideration of liquid-phase stability, resistance to crystallization and enthalpy of crystallization, which is heating rate dependent. So it may not be sufficient to study the GFA of metallic alloys. ΔT_x represents the stability of glass, i.e., how far is the crystallization from glass transition. A greater value of ΔT_x represents greater stability of glass against crystallization. But from figure 1c 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 MGs, 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 MGs with same value of d_c have different ΔT_x values. Although GFA and glass thermal stability are related properties, ΔT_x cannot be used to understand both of them. Weinberg[38] found that a high GFA does not always indicate a high thermal stability. Hence, GFA and thermal stability can be different for few MGs. Therefore ΔT_x cannot be used as a 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 MGs having slight variation in composition show high value of R^2. Cai et al[39] studied GFA of Zr-Al-Ni-Cu-based bulk MGs and found

that GFA parameters show strong correlation with critical size.

From figure 1 it can be observed that different GFA parameters deviate from the fitted line. For some GFA criteria, the deviation from the 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 imply 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.[40,41] So analysing 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 conditions used by different researchers.

3.2 *Estimation of Gibbs free energy difference*

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 followed by the 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.

Table 2. Thermodynamic parameter ΔG for different metallic glasses.

| | | $\Delta G(T_g)$ by different expressions (kJ mol^{-1}) | |
Systems	$\Delta G(T_g)$ (kJ mol^{-1}) Experimental	Dubey and 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

In the present case, $\Delta G(T_g)$ has been calculated by the various theoretical expressions given by Turnbull, T and S, S and H, Ji and Pan, Lad *et al*, Hoffman, Battezzati and Garonne. Here all expressions of ΔG are based on different temperature dependence of ΔC_p. All these expressions estimate $\Delta G(T_g)$ with minimum experimental data available. The calculated values of $\Delta G(T_g)$ are shown in table 1. Based on the experimental data available in literature for few MGs, it is observed from the above calculated values of $\Delta G(T_g)$ by different expressions that provide accurate values of ΔG at T_g for all systems. The experimental values of $\Delta G(T_g)$ for $Mg_{65}Cu_{25}Y_{10}$,[18] $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$,[25] $Pd_{40}Ni_{40}P_{20}$,[28] $Pd_{40}Ni_{10}Cu_{30}P_{20}$[27] and $Au_{76.9}Ge_{13.65}Si_{9.45}$[28] are as shown in table 2. For $Pd_{40}Ni_{40}P_{20}$ the experimental results lie close to the values obtained by S and 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 and S as well as B and G provide good results for other BMGs. 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 results for evaluation of ΔG, for a wide range of MGs with different compositions. As stated by Battezzati and Garonne[33] the value γ should be equal to 0.8 for all MGs, but from the table 1 it can be observed that it varies for different MGs. The reason for variation of γ can be the difficulty to choose suitable crystallization step in multistep crystallization process for multicomponent MGs. Moreover T_x and ΔH_x are also heating rate dependent.[42] So γ cannot be considered as constant and it is calculated by using equation (11). There are some more expressions available in literature[43–45] to determine ΔG, which require more experimental parameters to obtain exact values.

Also thermodynamic analysis is carried out by the expressions of ΔG given by Lele *et al*[6] and Dubey and Ramchandrarao,[36] which are found to be in close agreement with the experimental results. The values of $\Delta G(T_g)$ as calculated by both expressions are shown in table 2.

The metallic alloy is considered to be a good glass former if the value of ΔG is low. Pd-based metallic alloys are found to have highest GFA, having minimum critical cooling rate.[46] Here the value of ΔG of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ composition was found to be the lowest ($= 1.378$ kJ mol^{-1}) among all composition indicating its higher GFA.

4. Conclusion

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 MGs. T_{rg} also show a high correlation with d_c, hence it is a 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 $Pd_{40}Ni_{10}Cu_{30}P_{20}$ has high GFA among all as it has lowest value of ΔG and large stability against crystallization, indicated by greater value of ΔT_x ($= 85$ K).

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