STUDY OF GLASS FORMING ABILITY PARAMETERS OF Mg-Ni-Pr-BASED METALLIC GLASSES*

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Knowledge of Glass forming Ability (GFA) of metallic glasses is of great importance as it gives an insight of a better Glass former. Number of GFA parameters like Gibb's free energy difference ΔG , ΔS , ΔH , η , γ , γ_m , Q , T_g ($=T_g/T_l$) etc. are calculated and compared for Mg-Ni-Pr-based metallic glass forming alloys to predict which parameter describes the best GFA criterion. On the basis of these parameters the excellent glass forming composition is identified. Also the GFA parameters of Mg-Ni-Pr-based alloys are studied in air and argon atmosphere. Present work suggests that ΔG is the best GFA criterion and Mg-Ni-Pr-based metallic glassy alloys can be successfully fabricated in air due to its high oxidation resistance ability.

Keywords: Bulk Metallic Glasses, Gibb's Free Energy, GFA.

Introduction

Bulk metallic glasses have found significant interest in research as it has many applications. Various parameters and criteria have been proposed to predict GFA. Glass formation is a competition process between super-cooled liquid and the related crystalline phases.¹ In order to find better glass forming metallic glass many theoretical approaches 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. A large number of systems follow these all criteria with some exceptions. The driving force of nucleation is given by

thermodynamic factor i.e. Gibb's free energy difference ΔG . Lower the value of ΔG lesser will be the driving force of nucleation which degrades the crystallization hence better will be the GFA.²

In the present work different GFA criteria for Mg-Based metallic alloys with different composition and in different atmosphere are calculated. The thermodynamic properties like ΔG and ΔS are also determined.

Formulation of Theoretical Expression

The Gibbs free energy difference gives a qualitative measure of the stability of the glass compared to the crystalline state. The difference in Gibbs free energy between the liquid and crystalline phases is given by

$$\Delta G = \Delta H - T\Delta S. \quad (1)$$

Where,
$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT. \quad (2)$$

And

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \quad (3)$$

Where, T_m is the melting temperature, ΔS_m is the entropy of fusion and ΔH_m is the enthalpy of fusion. They are related to each other by the following relation:

$$\Delta S_m = \frac{\Delta H_m}{T_m}. \quad (4)$$

ΔC_p , defined as $C_p^l - C_p^x$, is the difference in specific heat of liquid and the corresponding crystalline phases of metallic alloy. The most common linear expression is given by

$$\Delta C_p = AT + B. \quad (5)$$

Substituting Eq. (5) in Eqs. (2) and (3), Eq. (1) can be simplified to

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \frac{1}{2} A (\Delta T)^2 + B \left(T \ln \frac{T_m}{T} - \Delta T \right). \quad (6)$$

Considering large undercooled region of the multicomponent metallic alloys Lad et al.³ obtained the following expression.

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(1 - \frac{\Delta T}{2T} \right). \quad (7)$$

Considering logarithmic term in eq. (6) and taking the Taylor series expansion up to second order gives the following approximation:

$$\ln \left(\frac{T_m}{T} \right) \cong \frac{4T\Delta T}{(T + T_m)^2}. \quad (8)$$

Substituting Eq. (8) in Eq. (6) Lad et al.⁴ obtained the following equation for the Gibb's free energy difference

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} \left(\frac{4T^2}{(T + T_m)^2} \right). \quad (9)$$

The entropy difference can be obtained by taking partial derivative of ΔG w.r.t to T :

$$\Delta S = - \frac{\partial(\Delta G)}{\partial T}. \quad (10)$$

Substituting Eq. (7) & (9) in (10) we get the following equation,

$$\Delta S_1 = \frac{\Delta H_m}{2T_m} \left(\frac{3T^2 - T_m^2}{T^2} \right). \quad (11)$$

$$\Delta S_2 = \frac{4\Delta H_m T}{T_m} \left(\frac{T^2 - 2T_m^2 + 3TT_m}{(T + T_m)^3} \right). \quad (12)$$

Results and Discussion

Many criteria have been predicted for finding the GFA of metallic glasses like $\gamma_m (= 2T_x - T_g/T_l)$, $Q (= (T_g + T_x)/T_l)$, $\eta (= 1 - \Delta H_x/\Delta H_m)$, $\gamma (= T_x/(T_g + T_l))$, $T_{rg} (= T_g/T_l)$ etc. where, T_b , T_x , T_g are liquidus, crystallization, and glass transition temperature respectively. All parameters are calculated in Table-1 which shows that T_{rg} , γ , γ_m gives constant value which cannot give idea about variation in GFA for the given compositions. One can see 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.

Table 1. Different GFA Criteria

Systems. ⁵	ΔT_x (K). ⁵	Q	T_{rg} ⁵	η	γ ⁵	γ_m	$\Delta G_1(T_g)$ (Lad-1) kJ/mol	$\Delta G_2(T_g)$ (Lad-2) kJ/mol	$\Delta G_1(T_g)$ $/\Delta H_m$	$\Delta G_2(T_g)$ $/\Delta H_m$	$\Delta S_1(T_g)$ (Lad-1) kJ/mol	$\Delta S_2(T_g)$ (Lad-2) kJ/mol
Mg ₄₈ Ni ₃₁ Pr ₂₁	47	0.451	0.570	0.627	0.403	0.695	2.92	2.47	0.265	0.249	1.77	1.45
Mg ₆₃ Ni ₂₂ Pr ₁₅	52	0.803	0.574	0.339	0.407	0.708	1.35	1.14	0.265	0.224	0.53	0.51
Mg ₆₅ Ni ₂₁ Pr ₁₄	42	0.907	0.569	0.238	0.396	0.675	1.38	1.17	0.264	0.224	0.91	0.72
Mg ₆₅ Ni ₂₁ Pr ₁₄ (air)	41	0.814	0.574	0.322	0.397	0.678	1.50	1.26	0.265	0.223	0.93	0.75

ΔG is calculated for the entire undercooled region, from Lad-1 & Lad-2 equations. Figure -1 shows ΔG variation with temperature for Mg₄₈Ni₃₁Pr₂₁ and Mg₆₃Ni₂₂Pr₁₅ metallic glasses. Lower the value of $\Delta G(T_g)$ indicates better GFA and hence Mg₆₃Ni₂₂Pr₁₅ is better glass former.

Figure 1. Gibb's free energy difference with Temperature for $\text{Mg}_{48}\text{Ni}_{31}\text{Pr}_{21}$ and $\text{Mg}_{63}\text{Ni}_{22}\text{Pr}_{15}$

Figure 2. Gibb's free energy difference with Temperature for $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ in air and argon atmosphere.

Figure 3. Entropy Difference with Temperature for $\text{Mg}_{63}\text{Ni}_{22}\text{Pr}_{15}$ and $\text{Mg}_{48}\text{Ni}_{31}\text{Pr}_{21}$.

Figure 4. Entropy Difference with Temperature for $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ in air and argon atmosphere.

Lower value of $\Delta G(T_g)$ indicates higher GFA and hence $\text{Mg}_{63}\text{Ni}_{22}\text{Pr}_{15}$ is better glass former. Lad-2 gives smaller value of $\Delta G(T_g)$ than Lad-1 for both the systems as given in table-1 which indicates that it is good approximation. $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ metallic glass produced in argon is better glass former than $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ produced in air as $\Delta G(T_g)$ is lower for sample prepared in argon as shown in figure-2. Mg-Ni-Pr system has high oxidation resistance ability so it can be prepared in air but for other BMGs it is not possible as in air they favour crystallization. The entropy difference, ΔS , between the undercooled liquid and the corresponding crystalline phase has also been calculated from Eq. (11) & (12), and plotted in fig. (3) & (4), for all the four composition i.e. $\text{Mg}_{48}\text{Ni}_{31}\text{Pr}_{21}$, $\text{Mg}_{63}\text{Ni}_{22}\text{Pr}_{15}$, $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$, $\text{Mg}_{65}\text{Ni}_{21}\text{Pr}_{14}$ (air).

Conclusion

It can be concluded that $\text{Mg}_{63}\text{Ni}_{22}\text{Pr}_{15}$ is the best glass former among all composition as the driving force of crystallization; ΔG is very low for it which indicates excellent GFA.

Mg₆₅Ni₂₁Pr₁₄ 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 Mg₆₅Ni₂₁Pr₁₄ metallic glass which is prepared in air has comparatively smaller value of $\Delta G (T_g)$ which indicates that Mg₆₅Ni₂₁Pr₁₄ is also a good glass former.

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