



A new thermodynamic parameter G_{CE} for identification of glass forming compositions



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ABSTRACT

This work underlines the easy use of thermodynamics-based approach in identifying the glass forming systems. In this work, a simple and effective thermodynamic model named G_{CE} is devised to numerically predict easy glass forming compositions. Further, to validate its reliability, co-relation of G_{CE} with the Miedema model, P_{HSS} model, critical diameter, Turnbull's reduced glass transition temperature and Inoue supercooled liquid region in V–Ti–Cr, Zr–Cu–Ag, Mg–Zn–Ca, Ca–Mg–Cu and Cu–Zr systems respectively is demonstrated. The model co-related well, and therefore the calculations based on this model are well-capable of anticipating the glass forming compositions. With a proven accuracy for the prediction, this proposed model can be used as an efficient tool for alloy-designing.

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1. Introduction

Metallic glasses, by virtue of their random atomic arrangement, are regarded as promising materials for applications demanding extraordinary structural and functional properties. Since the discovery of bulk metallic glasses, many efforts have been taken to establish a universal parameter for identifying easy glass forming systems. Factors built on experimental data, such as $T_{rg} = \frac{T_g}{T_l}$ [1,2], $\Delta T_x = (T_x - T_g)$ [3], $\gamma = \frac{T_x}{T_g + T_l}$ [4], $\alpha = \frac{T_x}{T_l}$ and $\beta = \left(\frac{T_x}{T_g}\right) + \left(\frac{T_g}{T_l}\right)$ [5] have been suggested to numerically determine the glass forming ability of a system. The above parameters depend on the thermochemical properties, which can only be determined with the synthesis of glassy alloys. Thus, besides their inherent limitations and inaccuracy [6], the requirement for experiments fetters their popularity in prediction of glass forming systems.

Theoretical calculations to obtain thermodynamic properties have become more popular over experimental practices due to less time consumption, low cost and consistency in accuracy. Since entropy at low temperature contributes negligibly to Gibbs energy, enthalpy term is regarded as an indicator for the stability of a phase. A number of methods, both computational and experimental have been developed over the years to estimate the formation enthalpies of alloys [7].

Theoretical methods can be primarily classified into four types:

- first principles calculations, within the framework of density-functional theory,
- statistical mechanics based approaches, using atomistic simulation techniques like molecular dynamics,
- solution thermodynamics, based on extrapolation of experimental data, as in case of the CALPHAD method, and
- semi-empirical methods like Miedema's model, or the BFS (Bozzolo-Ferrante-Smith) model, which is in turn based on the equivalent crystal theory 3.

First principal calculation and atomistic simulation techniques bring with it high computational cost and time, which snags their use for predicting easy glass forming compositions. Similarly, the CALPHAD approach, which is based on the minimization of the Gibbs energy has not gained deserving popularity in the prediction of amorphous systems, due to the absence of either system database or inaccuracy in the interpolation of experimental results. Among the aforementioned methods, it is the Miedema's method, which has become the most used thermodynamic model for prediction of glass forming compositions. In situations where a large number of alloys have to be considered in the absence of a prior thermodynamic database, the Miedema model provides an excellent starting point. This model has been extensively used by Murty et al. [1], Basu et al. [8], and Takeuchi and Inoue [9] for predicting the glass forming abilities in various systems.

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In this work, a new thermodynamic model G_{CE} , for easy prediction of the glass forming ability is documented. The proposed model considers the implicit contribution of elastic enthalpy ($\Delta H^{elastic}$) for stabilization of the amorphous phase, which since inception of the Miedema model has been ignored or considered insignificant. Along with improving the accuracy in predicting the glass forming compositions, this model also brings to light the complexity of the semi-empirical Miedema model.

2. Thermodynamic model

2.1. G_{CE} parameter

In any system, binary or higher order, the elastic enthalpy and chemical enthalpy of mixing plays an imperative role in affecting the phase stability. Egami [10] proved that increasing the number of elements involved, increasing the atomic size ratio, increasing the attractive force between small and large atoms, and introducing a repulsive potential between small atoms will help the formation of bulk metallic glasses. In the same line, Murty et al. [11] documented that the elastic enthalpy, which is a manifestation of the topological instability existing in the host lattice, has a closer relationship with the T_{rg} and $\alpha = \frac{T_g}{T_f}$ models-used for studying the glass forming ability of a system. According to the Miedema model, for a given alloy, the amorphous phase is stable when $\Delta H^{amorphous} - \Delta H^{solidsolution} < 0$.

Postulated by Takeuchi and Inoue [12], the contribution of elastic enthalpy to the glass forming ability (GFA) of a system can be explained through Eq. (1).

$$\Delta H^{amorphous} - \Delta H^{solidsolution} = (\Delta H^{chemical}(amorphous) - \Delta H^{chemical}(solidsolution)) + \Delta H^{topological} - \Delta H^{elastic} \quad (1)$$

The amorphous phase is stable for a negative value of the difference in the left hand side (LHS) of the aforementioned Eq. (1). Thus, to arrive at stabilization of the amorphous phase, it is required to learn the contribution of individual terms on the right hand side (RHS) of Eq. (1). In order to aid stabilization of the amorphous phase through retarded diffusion of the constituent elements, the chemical enthalpy of mixing must be a negative term. This indicates that the difference $\Delta H^{chemical}(amorphous) - \Delta H^{chemical}(solidsolution)$ has to be negative for stabilizing the amorphous phase. Further, the second term $\Delta H^{topological} -$ enthalpy of fusion/topological enthalpy of individual components – unlike the first term, by virtue of its positive sign and contribution promotes stabilization of the solid solution phase. Thus, it leaves researchers with the less explored, elastic enthalpy, to explain the relative stabilities between the solid solution and amorphous phase. The effect of elastic enthalpy ($\Delta H^{elastic}$) term, on the glass forming ability can be easily related to the negative sign on it. The negative sign positively contributes to glass formation. This means that the bigger the value for elastic enthalpy, the higher shall be the stabilization of the glassy phase. To summarize, it is a negative contribution from the first and the third term on the RHS of Eq. (1), which forms the ground for predicting the glass forming ability of a system.

An extension of the previous expression is the G_{CE} parameter. G_{CE} parameter is explicitly based on the difference between $\Delta H^{chemical}(amorphous)$ and $\Delta H^{elastic}$, and can be expressed as

$$G_{CE} = \Delta H^{chemical}(amorphous) - \Delta H^{elastic} \quad (2)$$

The more negative the difference is, the higher will be the propensity of the system to form glass.

2.2. Calculation of chemical enthalpy: ($\Delta H^{chemical}$)

Change in the chemical enthalpy during mixing depends upon three parameters: molar volume, electronegativity and the electron density of the constituent elements [13]. For a binary system, a negative contribution to the chemical enthalpy comes from the electronegativity difference between the two constituents, and a positive contribution comes from their difference in the electron density [14]. To stabilize an amorphous phase, this enthalpy term must be negative.

The chemical enthalpy, which influences the degree of mixing for a binary system is usually based on the extended regular solution model [1]. It is written as

$$\Delta H^{chemical} = \sum_{i=1, i \neq j}^n x_i x_j (x_j \Delta H_{inj}^c + x_i \Delta H_{jmi}^c) \quad (3)$$

where X_A and X_B represent the mole fraction of A and B atoms; ΔH_{inj}^c and ΔH_{jmi}^c are the enthalpies of solution of one element in another, at infinite dilution.

The interfacial enthalpy of atomic cells ΔH_{inj}^c and ΔH_{jmi}^c can be calculated from the Miedema's semi-empirical model [15]. In the present work, the values of ΔH_{inj}^c and ΔH_{jmi}^c have been taken from Niessen et al. [15].

$$\Delta H_{inj}^c = \frac{2V_i^{2/3}}{[n_i^{-1/3} + n_j^{-1/3}]} * [-P(\Delta\phi)^2 + Q(\Delta n^{1/3})^2 - R^*] \quad (4)$$

$$\Delta H_{jmi}^c = \frac{2V_j^{2/3}}{[n_i^{-1/3} + n_j^{-1/3}]} * [-P(\Delta\phi)^2 + Q(\Delta n^{1/3})^2 - R^*] \quad (5)$$

where V_i and V_j is the molar volume of i^{th} and j^{th} element respectively; n_i and n_j are the electron density of i^{th} and j^{th} element respectively; P and Q are constants which depend on the type of metals forming the alloy or an intermetallic compound. The value of P is taken as 14.2 for metals with valency higher than 2, and 10.7 for metals with valency of 1 or 2 [16]. The $\frac{P}{Q}$ ratio is maintained as 9.4 [17,18]; $\Delta\phi$ the difference of the modified electronegativities between dissimilar atomic cells of i^{th} and j^{th} elements; Δn the difference in the electron density of i^{th} and j^{th} elements and R^* is the correction value of an alloy of a transition metal with one of the polyvalent non-transition metals.

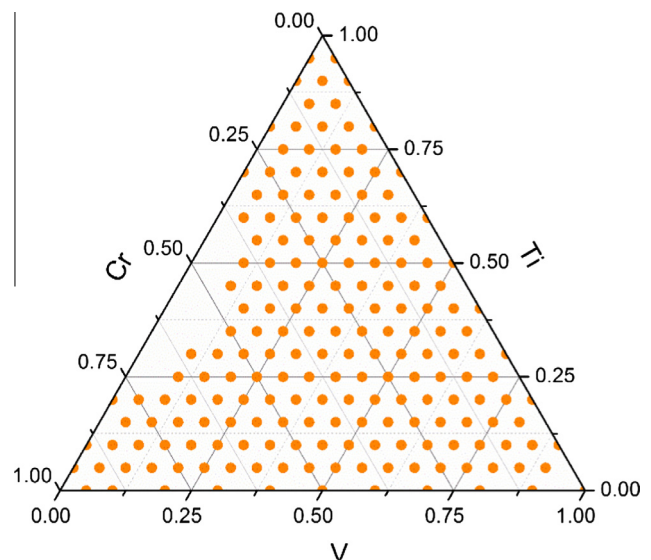


Fig. 1. Solid solution forming composition ranges in ternary V–Ti–Cr alloy system: Reproduced from Basu et al. [22].

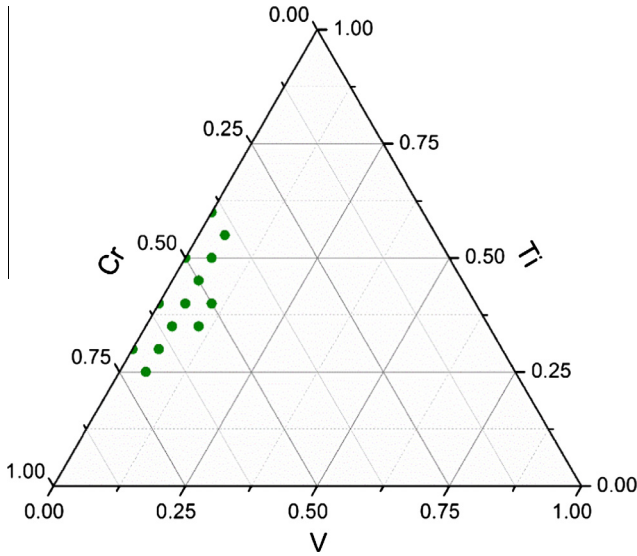


Fig. 2. Glass forming composition ranges in ternary V–Ti–Cr alloy system determined using G_{CE} .

Table 1
Comparison of Miedema and G_{CE} model based glass forming compositions in V–Ti–Cr system.

Compositions	Miedema [22] (kJ/mol)	G_{CE} (kJ/mol)
V ₁₀ Ti ₄₀ Cr ₅₀	–0.05791	–13.1861
V ₀ Ti ₅₀ Cr ₅₀	–2.1520	–16.8708
V ₀ Ti ₆₀ Cr ₄₀	–1.1904	–15.3787
V ₀ Ti ₃₀ Cr ₇₀	–1.6580	–15.6017
V ₅ Ti ₅₀ Cr ₄₅	–0.8369	–14.6076
V ₁₀ Ti ₃₅ Cr ₅₅	–0.0142	–13.0586
V ₅ Ti ₄₀ Cr ₅₅	–1.1764	–15.0370

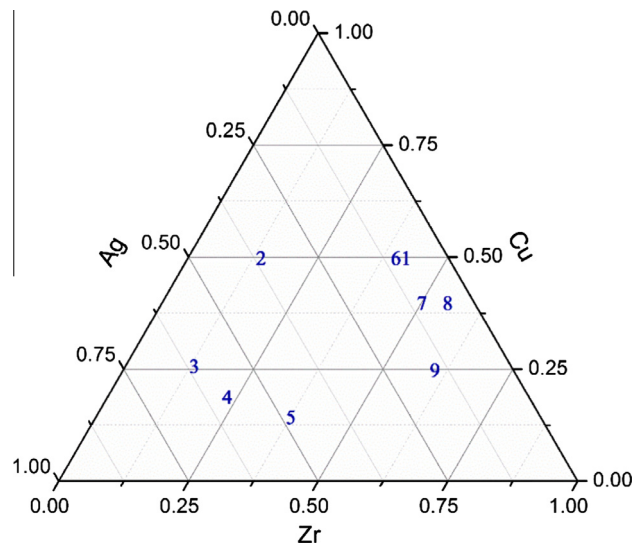


Fig. 3. Glass forming composition ranges in the Zr–Cu–Ag alloy system determined using G_{CE} .

Expression for the chemical enthalpy of mixing of a solid solution, for a ternary alloy, as modified by Gallego et al. [19], can be expressed as

$$\Delta H_{ABC}^{\text{chemical}} = \Delta H_{AB}^{\text{chemical}} + \Delta H_{BC}^{\text{chemical}} + \Delta H_{CA}^{\text{chemical}} \quad (6)$$

2.3. Calculation of elastic enthalpy: ($\Delta H^{\text{elastic}}$)

In solid solutions, where atoms of different sizes have to occupy equivalent lattice positions, an additional positive contribution to the alloying enthalpy arises due to the lattice deformations, which is necessary to accommodate atoms of different sizes [13].

The elastic enthalpy, which attributes to the degree of mixing for a binary system is usually based on the extended regular solution model [20]. It is written as

$$\Delta H^{\text{elastic}} = \sum_{i=1, i \neq j}^n x_i x_j (x_j \Delta H_{ijn}^e + x_i \Delta H_{jii}^e) \quad (7)$$

ΔH_{ijn}^e can be obtained by using the elastic continuum approximation as defined by Eshelby [20].

$$\Delta H_{ijn}^e = \frac{2\mu_j(V_i - V_j)^2}{V_j(3 + 4\mu_j K_i)} \quad (8)$$

where μ_j is the shear modulus of the solvent, and K_i is the compressibility of the solute.

Expression for the elastic enthalpy of mixing of a solid solution, for a ternary alloy, as modified by Gallego et al. [19], can be expressed as

$$\Delta H_{ABC}^{\text{elastic}} = \Delta H_{AB}^{\text{elastic}} + \Delta H_{BC}^{\text{elastic}} + \Delta H_{CA}^{\text{elastic}} \quad (9)$$

The G_{CE} parameter through elastic enthalpy brings into account, the topological instability or the frustration caused by the addition of elements with differing atomic size [21]. Taking into the equation the decisive factors, and considering the need for calculation of the ignored terms as inconsequential, the G_{CE} parameter thus facilitates easy prediction of the glass forming alloys.

It must be understood that $\Delta H^{\text{elastic}}$ contributes to glass forming ability by destabilizing the Ordered or solid solution phase. According to the Hume-Rothery's rule, an atomic size difference of 15% or more prevents the formation of extensive solid solutions. This is due to the elastic strains generated when atoms of different sizes are introduced substantially in the lattice of the host. In physical terms, the numerical value for elastic enthalpy would implicitly correspond to a larger distortion of the lattice due to the larger atomic size differences. This value attaches to itself a quantitative measure to predict the disorder rendered to the lattice, which otherwise could only be determined in terms of mismatch entropy. However, entropy is a statistical concept, and hence gives no quantitative measure of energy, which on the other hand can be obtained through the elastic enthalpy. The significance of elastic enthalpy can be further correlated to the Atomistic mechanism proposed by Egami [10], which states that the atomic misfit generates micro strain that exceeds the threshold value of the ordered phase, and thus results in the formation of disordered phase. This predicament when coupled with high chemical enthalpy of mixing further aid to stabilization of the amorphous phase. Takeuchi and Inoue [12] have in past performed calculations on various systems to realize and prove the positive effect of elastic enthalpy on glass forming ability.

3. Validation of the G_{CE} parameter

To justify accuracy of the proposed model in predicting glass forming systems, a comparison of the reported and reproduced results with the G_{CE} parameter-identified, easy glass forming compositions, is carried out in V–Ti–Cr [22], Zr–Cu–Ag [1], Mg–Zn–Ca [23,24], Cu–Zr [26] and Ca–Mg–Cu [27] metallic systems.

Table 2
Comparison of P_{HSS} and G_{CE} model based glass forming compositions in Zr–Cu–Ag system.

S. no.	Compositions	P_{HSS} [1] (kJ/mol)	P_{HSS} reproduced (kJ/mol)	G_{CE} (kJ/mol)
1	Zr ₄₂ Cu ₅₀ Ag ₈	-4.52	-4.52	-38.9895
2	Zr ₁₄ Cu ₅₀ Ag ₃₆	-0.82	-0.82	-14.3055
3	Zr _{13.2} Cu _{25.9} Ag _{60.9}	-0.54	-0.54	-10.3082
4	Zr ₂₃ Cu ₁₉ Ag ₅₈	-1.00	-1.00	-15.2377
5	Zr _{37.5} Cu _{14.5} Ag ₄₈	-1.45	-1.45	-20.5145
6	Zr ₄₀ Cu ₅₀ Ag ₁₀	-	-4.21	-37.1027
7	Zr ₅₀ Cu ₄₀ Ag ₁₀	-	-3.96	-35.7886
8	Zr ₆₀ Cu ₂₅ Ag ₁₅	-	-2.56	-27.7666

Table 3
Comparison of critical diameter and G_{CE} model in Mg–Zn–Ca system's glass forming compositions.

Compositions	Critical diameter [23,24] (mm)	References	G_{CE} (kJ/mol)
Mg ₆₀ Zn ₃₅ Ca ₅	2	23	-10.2748
Mg ₆₆ Zn ₃₀ Ca ₄	5	24	-8.98594
Mg ₆₇ Zn ₂₈ Ca ₅	4	23	-8.92677
Mg _{67.5} Zn _{27.5} Ca ₅	4	23	-8.82824
Mg ₇₀ Zn ₂₅ Ca ₅	3	23	-8.33262
Mg ₇₁ Zn ₂₅ Ca ₄	2	24	-7.88954
Mg ₇₅ Zn ₂₀ Ca ₅	1	23	-7.33234
Mg ₆₅ Zn ₃₀ Ca ₅	-	-	9.31839
Mg ₆₆ Zn ₂₉ Ca ₅	-	-	-9.12312
Mg ₆₈ Zn ₂₈ Ca ₄	-	-	-8.84748

3.1. Miedema model vs G_{CE} parameter

Attempting for alloy designing, Basu et al. [22] used the Miedema model for eliminating the glass forming compositions in the V–Ti–Cr system.

According to the Miedema model, for a given phase, the formation enthalpy of a ternary alloy can be expressed in general through Eq. (10) or Eq. (11).

Solid solution phase

$$\Delta H_{ABC}^{solid\ solution} = \Delta H_{ABC}^{chemical} + \Delta H_{ABC}^{elastic} + \Delta H_{ABC}^{structure} \quad (10)$$

where $\Delta H_{ABC}^{chemical}$ and $\Delta H_{ABC}^{elastic}$ is calculated as described in Sections 2.2 and 2.3 respectively.

Amorphous phase

$$\Delta H_{ABC}^{amorphous} = \Delta H_{AB}^{chemical} + \Delta H_{BC}^{chemical} + \Delta H_{CA}^{chemical} + X_A \alpha T_{f,A} + X_B \alpha T_{f,B} + X_C \alpha T_{f,C} \quad (11)$$

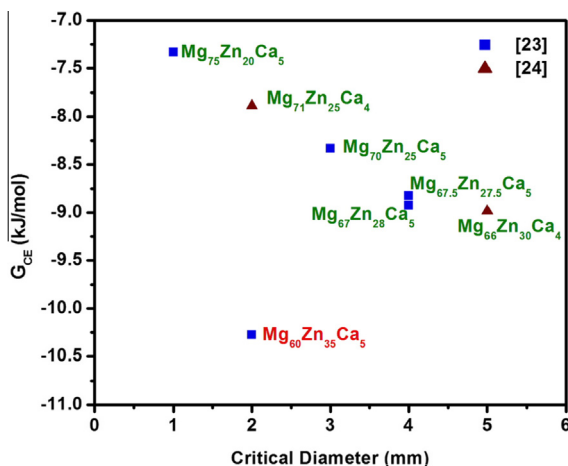


Fig. 4. Comparison between critical diameter and G_{CE} model in Mg–Zn–Ca system.

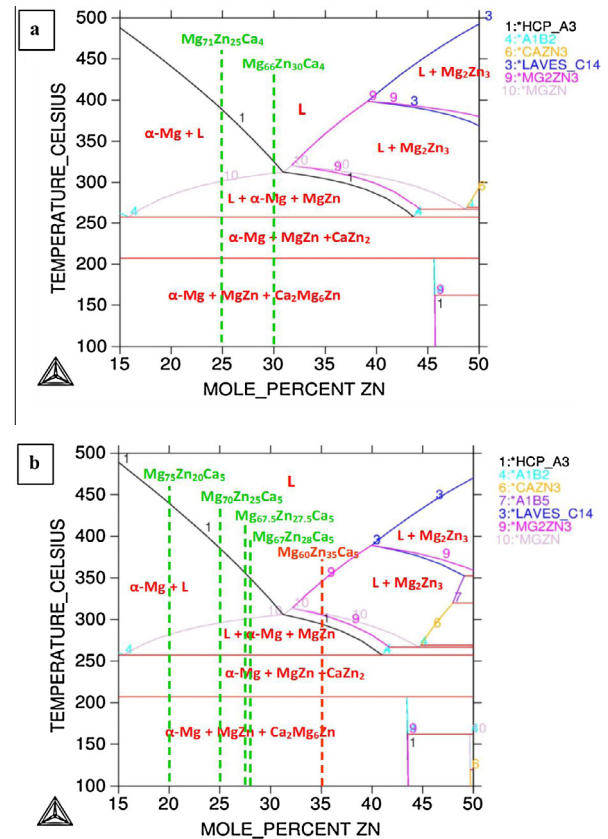


Fig. 5. Vertical section of (a) Mg–xZn–4Ca and (b) Mg–xZn–5Ca phase diagram generated based on CALPHAD approach using ThermoCalc software.

where X_A , X_B , X_C are the mole fraction of A, B and C. $T_{f,A}$, $T_{f,B}$, $T_{f,C}$ are the melting points of pure A, B, C and $\alpha = 3.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

For glass formation in a ternary system,

$$\Delta H_{ABC}^{amorphous} - \Delta H_{ABC}^{solid\ solution} < 0 \quad (12)$$

The $\Delta H^{structure}$ contribution appears, according Miedema, in the solid solutions and reflects the preference for the transition metals in the 3d series to crystallize in one of the main crystallographic structures Body-Centered Cubic (BCC), Face-Centered Cubic (FCC) or Hexagonal Closely Packed (HCP), depending on Z, the number of valence electrons per atom [13]. It is expected to have only a minor effect when compared with the elastic energy contribution. Therefore, as a first approximation, this term is generally not considered in calculations [1].

It is thus understood that for any system, be it binary or multi-component, a great deal of calculations must be carried out in the Miedema model to predict glass forming ability in various compositions. Basu et al. [22] generated a ternary Isoleth to discover the

Table 4
Comparison of the empirical rules and G_{CE} in Cu–Zr system's glass forming compositions.

Alloy	T_g (K)	T_x (K)	T_l (K)	$T_x - T_l$ (K) [26]	$T_{rg} = T_g/T_x$ [26]	Critical thickness (mm) [26]	G_{CE} (kJ/mol)
Cu ₄₆ Zr ₅₄	696	746	1201	50	0.58	2	–25.3334
Cu ₆₄ Zr ₃₆	787	833	1233	46	0.64	2	–26.2435
Cu ₆₆ Zr ₃₄	787	841	1263	54	0.62	2	–25.8572

solid solution forming compositions using the Miedema model (Fig. 1).

To investigate its accuracy and identify the glass forming composition ranges in the V–Ti–Cr system, the G_{CE} parameter is deployed. A ternary isopleth is generated to show the composition exhibiting propensity for glass formation (Fig. 2). Table 1 is generated to compare the reported and predicted glass forming compositions. It should be understood that the larger the negative value of G_{CE} parameter, easy will be the glass formation. With juxtaposition of Figs. 1 and 2, and with a reference to Table 1, it can be clearly inferred that the G_{CE} parameter based predictions agree well with the reported compositions. This comparison with the Miedema model reflects the aptness of the proposed model in predicting glass forming compositions and alloy designing. It can also be observed that the G_{CE} parameter undermines the need for calculating the chemical enthalpy and topological enthalpy for the amorphous phase as required in the Miedema model. In essence, it ignores the calculation of $\Delta H^{amorphous}$, thus simplifying computation (see Fig. 3).

3.2. P_{HSS} model vs G_{CE} parameter

Murty et al. [1], postulated and employed the thermodynamic and topological parameters based P_{HSS} model in predicting the best glass forming compositions in Zr–Cu–x (Ag, Al, Ti, Ga) systems. P_{HSS} parameter can be described as

$$P_{HSS} = (\Delta H^{chem}) \left(\frac{\Delta S_{config}}{R} \right) \left(\frac{\Delta S_{\sigma}}{R} \right) \quad (13)$$

where configurational entropy (ΔS_{config}), which is based on the atomic fraction [1] is expressed as

$$\Delta S_{config} = -R \sum_{i=1}^n x_i \ln x_i \quad (14)$$

where x_i and x_j are the atomic fractions of the i^{th} and j^{th} element.

Boltzman's constant normalized mismatch entropy (ΔS_{σ}) is the measure of the randomness and can be calculated using the Mansoori approach [1], which is given by

$$S_{\sigma} = k_B \left(\frac{3}{2}(\zeta^2 - 1)y_1 + \frac{3}{2}(\zeta^2 - 1)y_2 - \left\{ \frac{1}{2}(\zeta - 1)(\zeta - 3) + \ln \zeta \right\} (1 - y_3) \right) \quad (15)$$

where d_i and d_j are the atomic diameters of i^{th} and j^{th} elements; k_B is Boltzmann's constant and parameter ζ is defined as $\zeta = 1/(1 - \xi)$, ξ is the packing fraction. In the present study ξ is taken as 0.64, which

implies dense random packing and y_1, y_2 and y_3 are dimensionless constants, and have a relation, $y_1 + y_2 + y_3 = 1$.

Where,

$$y_1 = \frac{1}{\sigma^3} \sum_{j>i=1}^3 (d_i - d_j)(d_i - d_j)c_i c_j \quad (16)$$

$$y_2 = \frac{\sigma^2}{(\sigma^3)^2} \sum_{j>i=1}^3 d_i d_j (d_i - d_j)^2 c_i c_j \quad (17)$$

$$y_3 = \frac{(\sigma^2)^3}{(\sigma^3)^2} \quad (18)$$

$$\sigma^k = \sum_{i=1}^3 c_i d_i^k \quad (k = 2, 3) \quad (19)$$

According to the authors, P_{HSS} parameter requires generation of Isometric contours [1] for $\frac{\Delta S_{config}}{R}$, $\Delta H^{chemical}$ and $\frac{\Delta S_{\sigma}}{R}$ values, and it is the identification of the intersecting points in the range 0.9–1.0 of $\frac{\Delta S_{config}}{R}$, of the superimposed contours, which forms the basis for the determination of easy glass forming compositions.

In this section, we have compared the reproduced P_{HSS} model results for the Zr–Cu–Ag system with those obtained using the proposed G_{CE} parameter. Table 2 highlights the analyzed and newly identified glass forming compositions.

As observed from Table 2, the resulting inclination of compositions as reported by the P_{HSS} model moves parallel with the G_{CE} anticipated trend. This brings into the picture, the positive connecting relationship between the P_{HSS} model and the G_{CE} parameter. Also, it must be valued that less effort is required in determining the G_{CE} values over P_{HSS} , as the requirement for normalized mismatch entropy is made obsolete.

3.3. Critical diameter vs G_{CE} parameter

Owing to their superior strength, elasticity and higher corrosion resistance than their crystalline counterparts, Mg based metallic glasses are gaining considerable attention as biodegradable implant materials. There exists a direct relationship between the critical diameter and the GFA of a system, i.e. the larger the GFA, larger shall be the critical diameter. In this section, a comparison of the experimentally observed best glass forming compositions in Mg–Zn–Ca system with their corresponding G_{CE} values is carried out. This is represented in Table 3.

It can thus be observed from the comparison in Table 3 that the trend G_{CE} parameter projected closely matches with that of the reported experimental outcomes. Among the reported and predicted Mg–Zn–Ca compositions, it is the Mg₆₀Zn₃₅Ca₅ composition

Table 5
Comparison of the empirical rules and G_{CE} in Ca–Mg–Cu system's glass forming compositions.

Compositions	T_g (°C)	T_x (°C)	T_l (°C)	T_m (°C)	Critical thickness (mm) [27]	G_{CE} (kJ/mol)
<i>Near eutectic</i>						
Ca ₅₀ Mg ₂₀ Cu ₂₀	128	169	417	355	8	–31.5803
Ca ₅₃ Mg ₂₃ Cu ₂₄	133	166	382	354	7	–25.8076
<i>Near peritectic</i>						
Ca ₇₀ Mg ₂₀ Cu ₁₀	83	112	429	386	0.5	–14.3802
Ca ₇₀ Mg ₁₀ Cu ₂₀	112	134	440	397	1	–24.1731

Table 6
Comparison of the critical diameter and G_{CEE} in Cu–Zr–Ag–Hf system's glass forming compositions.

Alloy [29]	Critical thickness (mm) [29]	Configurational entropy [29]	G_{CE} (kJ/mol)	G_{CEE} (kJ/mol)
Cu _{51.2} Zr _{32.2} Ag _{4.6} Hf ₁₄	–	1.12	–34.1521	–38.2503
Cu ₄₅ Zr ₃₅ Ag ₁₀ Hf ₁₀	4	1.18	–30.8176	–36.3648
Cu ₄₅ Zr ₂₅ Ag ₁₀ Hf ₂₀	3	1.25	–27.2336	–34.0420
Cu ₄₅ Zr ₁₅ Ag ₁₀ Hf ₃₀	2	1.24	–26.0868	–32.6085
Cu ₄₅ Zr ₅ Ag ₁₀ Hf ₄₀	<2	1.10	–27.3770	–30.1147

that shows deviation from the expected trend (Fig. 4). Though Mg₆₀Zn₃₅Ca₅ exhibited the lowest G_{CE} value, its GFA was not the highest. This can be attributed to the eutectic point phenomenon i.e., the value of the Turnbull's T_{rg} parameter; this value proportionally aids to the stabilization of glassy phase, and decreases as one moves further away from the eutectic point. The Mg₆₆Zn₃₀Ca₄ composition, which exhibits highest glass forming ability lie very close to the eutectic point of the Mg–xZn–4Ca phase diagram as represented in the diagram (Fig. 5(a)), generated using the Thermo Calc software-based on CALPHAD approach; computation for Mg–Zn–Ca phase diagram was done based on thermodynamic assessment proposed by Zhong [25] for Mg–Al–Ca–Sr–Zn system. In contrast, the Mg₆₀Zn₃₅Ca₅ composition lies far away, and on the hypereutectic side of the Mg–xZn–5Ca phase diagram (Fig. 5(b)). This explains its poorer glass forming tendency. Thus a high negative G_{CE} value and closeness to the eutectic point in this system, justify the relative divergence of GFA for various compositions.

3.4. Empirical rules vs G_{CE} parameter

By identifying the best near eutectic glass forming compositions in Cu–Zr and Cu–Hf binary alloy systems, Xu [26] contradicted the validity of the multicomponent component rule as postulated by Inoue [28]. It can be observed from Table 4 that the two empirical factors – ΔT_x and T_{rg} , although to some extent explains the good glass forming compositions in the Cu–Zr system, does not move in hands with each other, as a whole. Thus, solely relying on these empirical rules may not be a good choice, especially when fine optimization of glass forming composition within the given system is concerned.

It can be perceived from Table 4 that the estimated G_{CE} values are in good agreement with the reported experimental results, and the T_{rg} values. It must be noted that ΔT_x considers the thermal stability of the system against recrystallization, and not the easy glass forming ability [6]. Since T_{rg} implicitly forms its base on the concept of viscosity and closeness to the deep eutectic regions, it fits well in predicting the glass forming ranges. One can thus appreciate the potential of the G_{CE} parameter in predicting best glass forming ranges, as it requires no mind numbering thermal analysis for monitoring the glass transition and crystallization behavior among the studied systems.

Ca-based metallic glasses have unique properties. For example, they have low density (2.0 g/cm³), low Young's modulus (17–20 GPa), which is comparable to the modulus of human bones, low glass transition temperature (T_g – 110 °C) and a wide temperature range of super-cooled liquid (ΔT_x – 30–70 °C). While most Ca-based crystalline alloys oxidize in air in a matter of days, many Ca-based metallic glasses (i.e. Ca–Mg–Cu, Ca–Mg–Al) have satisfactory oxidation resistance and retain shiny surfaces long after casting. Senkov et al. [27] by correcting the Ca–Mg–Cu phase diagram, projected the best glass forming composition to be near eutectic, and the poor ones with a long freezing range to be near peritectic. Table 5 displays the reported experimental results, and their subsequent comparison with the theoretically determined values through the G_{CE} parameter.

From Table 5 as reference, it can be concluded that the calculated G_{CE} values agree well with the segregated near eutectic and those near peritectic regions. This comparison further advocates and supplements to the reliability of the G_{CE} parameter in predicting glass forming compositions.

4. Extension of G_{CE} to higher order system

Though, the G_{CE} parameter promises to be a reliable tool in predicting glass forming compositional ranges, its accuracy may negatively digress for higher order systems (more than 3 constituent elements). This can be attributed to the upsurge in the contribution of the configurational entropy term in deciding the phase stabilities. To address this situation, one can make use of the following expression.

$$G_{CEE} = (G_{CE})(\Delta S_{config}) \quad (20)$$

The importance of the G_{CEE} parameter in predicting glass forming ability in higher order systems, can be realized through Table 6. The Cu₄₅Zr₅Ag₁₀Hf₄₀ composition, as understood from the critical diameter values, exhibits poorest glass forming ability. However, as observed from Table 6, the G_{CE} based predictions contradict the experimental results. This inconsistency in the prediction can be mitigated through the introduction of the decisive configurational entropy term in the proposed model. Multiplication of G_{CE} with the easier to calculate, unbiased ΔS_{config} term befits accurately as observed in Table 6 for predicting the relative propensities of compositions toward glass formation. This proves that for the higher order systems, the G_{CEE} parameter can be an effective model in predicting the easy glass forming compositional ranges.

The ability of an alloy to form glass can thus be verified solely with the chemical and elastic enthalpy values. This model can be successfully extended to higher order systems by inclusion of the configurational entropy term.

5. Conclusion

The present work identifies a simple and effective parameter $G_{CE}(\Delta H^{chem} - \Delta H^{elastic})$, where easy glass forming composition ranges are foretold by incorporating thermodynamic parameters such as enthalpy of chemical mixing and the much ignored elastic enthalpy. This model was evaluated by carrying out comparisons with five select systems: V–Ti–Cr, Zr–Cu–Ag, Mg–Zn–Ca, Cu–Zr and Ca–Mg–Cu. Collation with Miedema model, P_{HSS} model, critical diameter, Turnbull's reduced glass transition temperature and Inoue supercooled liquid region criteria. The modeling predictions are in good agreement with the reported literature and reproduced results. More negative G_{CE} value supports easy glass formation, provided the composition falls closer to the eutectic point in the phase diagram. Unexplored Zr–Cu–Ag and Mg–Zn–Ca glass forming compositions have also been identified. Thus, alongside making the requirement for experimental data and complex thermodynamic calculations obsolete, the G_{CE} parameter ascertains itself as a reliable parameter in predicting glass forming compositions. The documented results corroborate to be of substantial significance in the field of alloy designing.

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