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Identifying non-equiatomic high entropy bulk metallic glass formers through thermodynamic approach: A theoretical perspective

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ABSTRACT

Identifying high entropy bulk metallic glasses (HEBMGs) through high entropy alloy philosophy has the potential to avert complications inherent to pinpointing bulk metallic glass forming compositions. Currently, the mixing enthalpy and topological strain parameter of a multicomponent alloy is a popular guideline to demarcate glass forming alloys from solid solution and intermetallic phase forming high entropy alloys. However, the discovered HEBMGs have relatively inferior glass forming ability (GFA) in comparison to the best glass former in a particular alloy system. The origin of such low glass forming ability can be traced back to their moderately higher liquidus temperature. Therefore there exists an opportunity to engineer non-equiatomic HEBMGs through modifying the composition of the constituent alloying elements. In this work, based on the thermodynamic modeling of two quinary alloy systems we demonstrate that the existence of large atomic size difference over broad compositional region is necessary condition for enhancing GFA in non-equiatomic HEBMGs. In addition, it is proposed that figuring out the prominent binary chemical interactions in the near equiatomic alloy composition is an effective approach to enhance GFA in these complex alloy systems.

1. Introduction

High entropy bulk metallic glasses (HEBMGs) are emerging as new materials based on the simplified alloying concept proposed by Yeh et al. [1,2]. Though originally intended for developing solid solutions, it was shown that alloy design strategy based on HEA philosophy can be utilized for the synthesis of complex materials of great diversity [2,3]. Interestingly, the devitrification of HEBMGs predominantly resulted into formation of F.C.C and B.C.C phases [4–7] contrary to conventional BMGs which crystallize into complex intermetallic phases. This indicates that the metastable solid solution phases preferentially form due to their lower Gibbs energy (in multi principal element alloys) at high temperatures and govern an important role in vitrification of HEBMGs and subsequent SRO formation. In fact for PdPtCuNiP HEBMG, its higher glass forming ability (GFA) has been ascribed to the formation of configurationally frozen solid solution that minimizes liquidus temperature [4]. However, Gong et al. have shown that the origin of low GFA of equiatomic Zr-Ti-Cu-Ni-Be HEBMG in comparison to Vit.1 glassy alloy ($Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$) is its higher melting temperature [5]. The high melting temperature of Ti-Zr-Cu-Ni-Be HEBMG was opined to culminate into poor stability of supercooled liquid [5]. Therefore, large configurational entropy obtained due to alloying elements in equiatomic concentration does not always result into lowering the liquidus temperature of the melt and enhance GFA.

Among the HEBMGs reported recently, TiZrHfCuNiBe HEBMG has moderate liquidus temperature (1100 K) [8] in comparison to TiZrCuNiBe (1176 K) [5], TiZrHfBeCu (1164 K) [9] and TiZrHfCuNi (1149 K) [10]. Low liquids temperature of TiZrHfCuNiBe might have contributed to its superior GFA among the equiatomic HEBMGs discovered till date. Furthermore decrease in liquidus temperature of non equiatomic TiZrHfCuNiBe BMG resulted in improved GFA [6]. The best glass forming composition in this system, $Ti_{20}Zr_{20}Hf_{20}Be_{20}Cu_{7.5}Ni_{12.5}$, has the lowest liquidus temperature (1040 K) [6] and further variation in composition of Cu and Ni resulted in decreased GFA and concomitantly increased liquidus temperature [6]. Similar phenomenon has also been observed in Ti-Zr-Be-Ni and Ti-Zr-Be-Cu medium entropy BMGs, which exhibit optimal GFA at the compositions that have the lowest liquidus temperatures [11,12]. The minor compositional variation in Ni and Cu might have altered local SRO by fine tuning the strong chemically attractive binary bond pairs [13] and resulted into enhanced GFA of non equiatomic Ti-Zr-Hf-Cu-Ni-Be HEBMGs [6].

Such marginal compositional adjustment also resulted in significant variation in GFA for Zr-Cu-Ni-Al quaternary system (medium entropy BMG according to Ref. [2]) [14]. The origin of this enhancement in GFA is the increase in Cu concentration at the expense of Ni [14]. Hence a precise understanding of chemical effects aids to tailor GFA of off

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eutectic BMGs and HEBMGs through compositional substitutions that minimize liquidus temperature [6,8,11,12,and]. The augmentation in GFA for HEBMGs [6,8] due to decrease in liquidus temperature bears striking similarity with conventional BMGs that usually form near deep eutectic compositions [15]. The mechanism for decrease in liquidus temperature for HEBMGs in Refs. [6, 8], must be originated from the complex interplay of topological and chemical contributions of constituent elements [16].

Though previous arguments indicate that multi component alloys with low melting point tend to have supreme GFA, it has been proved that to have maximum GFA, the melt should exhibit strong liquid nature along with proximity to deep eutectic compositional regions [17]. For instance, in Zr-Ti-Cu-Ni-Al system, the superior BMG former $Zr_{51}Ti_5Cu_{25}Ni_{10}Al_9$ is not reported to be the one with locally lowest liquidus temperature in deep eutectic region [18]. Similarly, Ma et al. [19] located many low melting quaternary eutectic compositions in Zr-Ti-Cu-Ni system but noted that only Zr-Cu rich compositions and one Ti-Cu rich composition form BMGs. Therefore, minimizing liquidus temperature is necessary but not sufficient criterion to enhance GFA. Along with liquidus temperature, how the chemical interactions between the elements contribute to strong melt [17] need to be probed to understand the variation in GFA among various low melting alloys. It is further noteworthy that the GFA of HEA composition, $Zr_{30}Ti_{23}Cu_{15}Ni_{22}Al_{10}$ (Φ 0.7 mm) [20] is low as compared to Zr-Cu rich deep eutectic glass formers in this quinary system [18]. In Zr-Ti-Cu-Ni-Al system at constant Al concentration ~10%, increase in Ti and Ni along with concomitant decrease in Zr and Cu from $Zr_{44.8}Ti_{0.2}Cu_{40}Ni_{4.7}Al_{10.3}$ up to $Zr_{30}Ti_{23}Cu_{15}Ni_{22}Al_{10}$ resulted into decrease of GFA [18,20]. This phenomenon can be explained from the perspective of large negative heat of mixing between Zr-Ni and Ti-Ni pairs [21]. Significantly large negative heat of mixing between Zr-Ni and Ti-Ni pairs leads to suppression of icosahedral order during super cooling [22]. Similar analysis holds true as regards to formation of ordered pairs (between elements with significant negative heat of mixing) in ZrTiCuNiBe as against $Ti_{32.8}Zr_{30.2}Cu_{5.3}Ni_9Be_{22.7}$ (here at Be concentration of ~20% Cu and Ni concentration increase at expense of Ti and Zr).

As GFA of a multi component alloy is a piecewise continuous function exhibiting exponential variation with composition [23], HEBMGs in general must correspond to the compositional regions farther from the hypercusps in the compositional landscape of GFA (of a particular alloy system) [23]. Hence it can be deduced that many potential HEBMG formers with varying GFA exist in near equi-atomic compositions, and their GFA can be maximized as peaks in compositional space – GFA map are approached through compositional optimization [23]. Evidently in such case, vast permutations of non equiatomic HEBMG compositions are available for GFA optimization. In this scenario, identifying compositions possessing largest topological strain [24] that causes melt to become deep eutectic [25] along with negative heats of mixing between constituent elements (which favor MG formation) [16] becomes primary criterion to locate potential HEBMG formers.

As the above arguments underscore the simultaneous importance of chemical, topological and configurational parameters in influencing HEBMG formation, we took Ti-Zr-Cu-Ni-Be and Ti-Zr-Cu-Ni-Hf as the model quinary systems for theoretical study. We initially computed P_{HSS} parametric values [26] that describe the combined effect of chemical enthalpy of mixing, topological and configurational entropy on GFA for certain simulated compositions. It is deduced that a unified parameter like P_{HSS} [26] can explain GFA of Zr-Ti-Cu-Ni-Be better in comparison to Zr-Ti-Cu-Ni-Hf system. The subsequent independent statistical analysis of ΔH_{mix} and $\Delta S_\sigma/k_B$ for both these alloy systems reveal that $\Delta S_\sigma/k_B$ of Zr-Ti-Cu-Ni-Be has distinct larger magnitude in comparison to Zr-Ti-Cu-Ni-Hf over broad compositional region. On the contrary ΔH_{mix} of both these systems has similar statistical range. Specifically we highlight that, prominent binary chemical interactions of elements bring down the liquidus temperature in Zr-Ti-Cu-Ni-Be system. We later extend this approach to Zr-Ti-Cu-Ni-Hf system.

1.1. Modeling premises and assumptions

There are multiple factors for choosing Zr-Ti-Cu-Ni-Be and Zr-Ti-Cu-Ni-Hf alloy systems for the present study. Existing literature reveals that non equiatomic HEBMGs are being developed either through varying an elemental pair from equiatomic composition [8] or through multiple substitution of elements that have similar atomic radius and properties [27]. However, it is evident that multiple substitutions do not necessarily increase GFA [27] in comparison to single element substitution [8]. The current work is an extension of our previous investigation [28] in which Al was substituted into fifteen quaternary eutectics of Zr-Ti-Cu-Ni system. The simulated compositions in this study (supplementary data) were obtained by substituting Be and Hf into each of those fifteen quaternary eutectic compositions of Ti-Cu-Ni-Zr in exactly similar manner as mentioned in supplementary data of Ref. [28]. The ΔH_{mix}, $\Delta S_\sigma/k_B$, $\Delta S_c/R$ and P_{HSS} values of the fifteen quaternary eutectics of Zr-Ti-Cu-Ni system is calculated and depicted in Table.1.

Our prime objective is to probe whether statistical heterogeneities in ΔH_{mix} and $\Delta S_\sigma/k_B$ values that get generated through different chemical species substitution can provide insight into the difference in GFA of these systems. Furthermore it is interesting to verify how such knowledge of diversified values in ΔH_{mix} and $\Delta S_\sigma/k_B$ helps to design non equiatomic HEBMGs. It is noteworthy that Be and Hf atoms has large difference in atomic diameters and provide an ideal case to probe the heterogeneities induced in ΔH_{mix} and $\Delta S_\sigma/k_B$. Since the previous study involved Al [28] which is of intermediate atomic diameter between Be and Hf, this work completes a systematic study encompassing substituent atoms of smaller, medium and larger atoms.

1.2. Description of thermodynamic and topological parameters used in modeling

1.2.1. Enthalpy of chemical mixing (ΔH_{mix})

The ΔH_{mix} of a quinary alloy is calculated based on the summation of each of the binary ΔH_{mix} of the constituent pairs. The binary ΔH_{mix} values have been taken from Ref. [21] in which Miedema's approach was utilized to derive ΔH_{mix} of a liquid phase. Therefore calculated ΔH_{mix} values of all the alloys in this work are for liquid phase. According to Ref. [21], the ΔH_{mix} of a binary pair can be expressed as

$$\Delta H^c_{AB} = 4\left[\Sigma^3{}_{k=0}\Omega_k(c_A \backslash c_B)^k\right]c_A c_B \quad (1)$$

where Ω_k ($k = 0, 1, 2, 3$), an interaction parameter, approximates ΔH_{mix} through the sub regular solution model. c_A, c_B is the composition of A and B elements respectively. The ΔH_{mix} for quinary composition is arrived at by extending the approach mentioned in Ref. [21] for ternary

Table. 1
Composition of Zr-Ti-Cu-Ni quaternary eutectics and their P_{HSS} values.

	Composition [19]	ΔH_{mix} (kJ/mol)	$\Delta S_\sigma/k_B$	$\Delta S_c/R$	P_{HSS} (kJ/mol)
1	$Zr_{49.9}Ti_{19.8}Cu_{13.7}Ni_{16.6}$	−25.6	0.21	1.24	−6.67
2	$Zr_{44.8}Ti_{5.1}Cu_{37.9}Ni_{12.2}$	−25.74	0.28	1.14	−8.22
3	$Zr_{48.3}Ti_{8.5}Cu_{33.8}Ni_{9.4}$	−23.97	0.26	1.15	−7.17
4	$Zr_{20.5}Ti_{19.5}Cu_{1.4}Ni_{58.6}$	−42.31	0.26	1.02	−11.22
5	$Zr_{46.6}Ti_{14.2}Cu_{13.8}Ni_{25.4}$	−32.5	0.26	1.25	−10.56
6	$Zr_{15.4}Ti_{41.4}Cu_{25.7}Ni_{17.5}$	−21.72	0.18	1.31	−5.12
7	$Zr_{10.4}Ti_{37.1}Cu_{43.6}Ni_{8.9}$	−15.92	0.16	1.18	−3.01
8	$Zr_{21}Ti_{43.7}Cu_{24.7}Ni_{10.6}$	−18.28	0.17	1.27	−3.95
9	$Zr_{15.2}Ti_{47.4}Cu_{10.4}Ni_{27}$	−28.24	0.18	1.23	−6.25
10	$Zr_{13.3}Ti_{54.4}Cu_9Ni_{23.3}$	−25.56	0.15	1.15	−4.41
11	$Zr_{4.6}Ti_{23.5}Cu_{70.4}Ni_{1.5}$	−10.1	0.12	0.79	−0.96
12	$Zr_{24.2}Ti_{7.9}Cu_{14.3}Ni_{53.6}$	−35.61	0.28	1.16	−11.57
13	$Zr_{25.9}Ti_{6.6}Cu_{30.5}Ni_{37}$	−29.18	0.28	1.26	−10.29
14	$Zr_{10}Ti_{4.6}Cu_{19.2}Ni_{66.2}$	−19.77	0.18	0.96	−3.42
15	$Zr_{49}Ti_{17}Cu_{14}Ni_{20}$	−28.6	0.23	1.25	−8.22