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Predicting the eutectic compositions of four multicomponent alloy systems by a simple approach

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ABSTRACT

A simple approach based on the efficient cluster packing model (ECP model) was proposed to predict eutectic compositions in Ca–Mg–Zn, Mg–Cu–Y, Zr–Cu–Al ternary and Zr–Ti–Ni–Cu–Al quinary alloy systems. Predicted eutectic compositions are found to be in good agreement with experimental results. It may provide new insights into atomic packing of multicomponent eutectic alloy containing no more than four topologically different elements, and may be a new and simple way to obtain novel bulk metallic glasses in these alloy systems.

1. Introduction

As a novel material, metallic glass has been studied intensely in both theory and experiment, and has shown wide engineering applications. However, due to its limited size, the utilization of metallic glass as structural material is greatly limited. A general approach to predicting bulk metallic glass-forming compositions, however, is still not available, thus made the discovery of novel bulk metallic glasses trapped in the mire of trial-and-error.

It is observed in experiments that although not all eutectic compositions can easily form glasses with rapid cooling, most glass-forming alloys are near eutectic compositions [1]. The bulk metallic glass-forming compositions can be obtained in alloy systems with high glass-forming ability, when eutectic compositions are known. However, it becomes more and more difficult to obtain eutectic compositions of multicomponent alloy systems, due to the increasing difficulty of drawing equilibrium phase diagrams with increasing number of constituents. Therefore, other methods were used to obtain or predict eutectic compositions of multicomponent alloy systems. Yan et al. [2] and Cao et al. [3] identified compositions exhibiting low-lying liquidus surfaces, which are potential eutectic compositions, by a computational thermodynamic approach, in the quaternary Zr–Cu–Ni–Ti and the quinary Zr–Ti–Ni–Cu–Al alloy systems. Ma et al. [4] obtained the eutectic composition by drawing the liquidus temperature surface with DSC data in Mg–Cu–Y ternary alloy system. Cheney and Vecchio [5] found that the weighted liquidus temperature can be used as an indicator of the depth of the eutectic point in many alloy systems. Shi et al. [6] predicted the binary alloy compositions structurally favorable for the stability of metallic glass, direct correlation between the predicted compositions and eutectic compositions was found for symmetric eutectic systems, based on an idealized structural model proposed by Sheng et al [7].

Recently, Miracle [8,9] proposed an efficient cluster packing model (ECP model) for metallic glass, to explain some experimental observations on microstructure of metallic glasses, such as short-range atomic order (SRO), a surprising degree of medium range atomic order (MRO) and high density. Glass-forming compositions of almost all known metallic glasses were calculated based on the ECP model, and were found to be in good agreement with experimental results. Further, Yavari [1] explained eutectic compositions of binary alloys with the ECP model. It may be a new and simple way to obtain novel bulk metallic glasses, if we can predict eutectic compositions of multicomponent alloy systems with the ECP model. We have predicted bulk metallic glass-forming region of some alloy systems [10,11]. However, it is valid only for alloy systems containing no more than three topologically different constituents.

In the present study, eutectic compositions of well-studied Ca–Mg–Zn, Mg–Cu–Y, Zr–Cu–Al and Zr–Ti–Ni–Cu–Al multicomponent alloy systems were predicted by a simple approach based on the ECP model, and were compared with the experimental results. The predictability of this approach was also discussed.

2. Method

In the ECP model, solvent atoms Ω and solute atoms α form α clusters in the first coordination shell, solute atoms β and γ occupy cluster-octahedral interstices and

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Table 1
The predicted glass-forming compositions and eutectic compositions of four multicomponent alloy systems.

Alloy system	Predicted composition	Eutectic composition
Ca–Mg–Zn	$Ca_{53}Mg_{12}Zn_{35}$ (β and γ filled) $Ca_{69}Mg_{15.5}Zn_{15.5}$ (γ vacant) $Ca_{60}Mg_{13}Zn_{27}$ (β vacant)	$Ca_{64}Mg_{14}Zn_{22}$
Mg–Cu–Y	$Mg_{68}Cu_{24}Y_8$ (β and γ filled) $Mg_{80}Cu_{10}Y_{10}$ (γ vacant) $Mg_{73.6}Cu_{17.6}Y_{8.8}$ (β vacant)	$Mg_{65}Cu_{25}Y_{10}$
Zr–Cu–Al	$Zr_{60}Cu_{30}Al_{10}$ (β and γ filled) $Zr_{75}Cu_{12.5}Al_{12.5}$ (γ vacant) $Zr_{67}Cu_{22}Al_{11}$ (β vacant)	$Zr_{52}Cu_{38}Al_{10}$; $Zr_{48}Cu_{38}Al_{14}$; $Zr_{45}Cu_{49}Al_6$
Zr–Ti–Ni–Cu–Al	$Zr_{60}(CuNi)_{30}(AlTi)_{10}$ (β and γ filled) $Zr_{75}(CuNi)_{12.5}(AlTi)_{12.5}$ (γ vacant) $Zr_{67}(CuNi)_{22}(AlTi)_{11}$ (β vacant)	$Zr_{51}(CuNi)_{35}(AlTi)_{14}$; $Zr_{47.9}(CuNi)_{42.4}(AlTi)_{19.7}$; $Zr_{51.1}(CuNi)_{34.2}(AlTi)_{14.7}$; $Zr_{44.8}(CuNi)_{44.7}(AlTi)_{20.5}$; $Zr_{59.3}(CuNi)_{28.9}(AlTi)_{11.9}$

cluster-tetrahedral interstices, respectively. The convention chosen here is that the largest solute atom is α, and β and γ solute atoms are progressively smaller. There are S_j sites per α site. For face-centered cubic (fcc) cluster packing, which is adopted in the present work, there is one β site and two γ sites for each α site, so that $S_\beta = 1$ and $S_\gamma = 2$. α clusters share common vertices, so that the number of Ω atoms in the first shell of an α cluster $N_{\alpha\text{-}\Omega}$ are shared between that cluster and φ overlapping nearest-neighbor α clusters. Thus the total number of Ω sites per α site is

$$S_\Omega = \left[\frac{N_{\alpha-\Omega}}{\left(1+\left(\frac{\varphi}{N_{\alpha-\Omega}}\right)\right)}\right] \quad (1)$$

where $N_{\alpha\text{-}\Omega}$ is specified by R^* [9]. The total number of structural sites is $\sum S = \sum S_i$. The total number of species i per α site is $S_i = \sum jS(i_j)$, where $S(i_j)$ is the number of species i that occupy j sites per α site.The concentration of species i can be obtained as

$$C_i = \frac{100S_i}{\sum S} \quad (2)$$

For a ternary alloy system, there are three atom species: solvent atoms Ω and solute atoms α and β. We can expect that there are mainly three packing schemes in the tetrahedral and octahedral interstices: (1) β and γ sites are filled with β solute atoms (β and γ filled); (2) β sites are filled with β solute atoms with γ sites being vacant (γ vacant); (3) γ sites are filled with β solute atoms with β sites being vacant (β vacant).

3. Results and discussions

In the Ca–Mg–Zn ternary alloy system, the atomic radius of constituents Ca, Mg and Zn are 0.197, 0.160, 0.138 nm [9], respectively. The chemical mixing enthalpies between constituents are −6 kJ/mol (Ca–Mg), −4 kJ/mol (Mg–Zn), −22 kJ/mol (Ca–Zn) [12]. The largest Ca atoms occupy Ω sites, and α sites are filled with Mg atoms, to form efficient packed (The solute to solvent radius ratio R_α is 0.812, which is close to the specific value 0.799) α clusters. Solute atoms Zn may occupy β and γ sites, or occupy β sites with γ sites being vacant, or occupy γ sites with β sites being vacant. The corresponding calculated glass-forming compositions are $Ca_{53}Mg_{12}Zn_{35}$, $Ca_{69}Mg_{15.5}Zn_{15.5}$ and $Ca_{60}Mg_{13}Zn_{27}$.

In the Mg–Cu–Y ternary alloy system, the atomic radius of constituents Mg, Cu and Y are 0.160, 0.127, 0.180 nm [9], respectively. The chemical mixing enthalpies between constituents are −3 kJ/mol (Cu–Mg), −6 kJ/mol (Mg–Y), −22 kJ/mol (Cu–Y) [12]. Mg atoms with medium size are selected to occupy Ω sites, and α sites are filled with Y, to form efficient packed (the solute to solvent radius ratio R_α is 1.125, which is close to the specific value 1.116) α clusters. The β and γ sites may be filled with Cu atoms, or β sites are filled with Cu atoms with γ sites being vacant, or γ sites are filled with Cu atoms with β sites being vacant. The corresponding calculated glass-forming compositions are $Mg_{68}Cu_{24}Y_8$, $Mg_{80}Cu_{10}Y_{10}$ and $Mg_{73.6}Cu_{17.6}Y_{8.8}$.

In the Zr–Cu–Al alloy system, the atomic radius of constituents Cu, Zr and Al are 0.127, 0.158, 0.143 nm [9], respectively. The chemical mixing enthalpies between constituents are −44 kJ/mol (Zr–Al), −23 kJ/mol (Zr–Cu), −1 kJ/mol (Cu–Al) [12]. Zr is chosen to occupy Ω sites, and α sites are filled with Al, to form efficient packed (the solute to solvent radius ratio R_α is 0.905, which is close to the specific value 0.902) and strong bonding (the chemical mixing enthalpies between Zr and Al is as large negative as −44 kJ/mol) α clusters. Solute atoms Cu may occupy β and γ sites, or occupy β sites with γ sites being vacant, or occupy γ sites with β sites being vacant. The corresponding calculated glass-forming compositions are $Zr_{60}Cu_{30}Al_{10}$, $Zr_{75}Cu_{12.5}Al_{12.5}$ and $Zr_{67}Cu_{22}Al_{11}$.

The Cu–Zr–Ni–Al–Ti alloy system is a pseudo-ternary Cu(Ni)–Zr–Ti(Al) alloy system, due to the equivalent atomic radius between Cu and Ni, and Ti and Al. The efficient cluster packing in it is expected to be similar to that in the Cu–Zr–Al system, due to the large negative chemical mixing enthalpy between Zr and Al, that is, Ω sites are filled with Zr atoms, α sites are filled with Al or Ti atoms to form α clusters. Solute atoms Cu or Ni may occupy β and γ sites, or occupy β sites with γ sites being vacant, or occupy γ sites with β sites being vacant. Therefore, the calculated glass-forming compositions are $Zr_{60}(CuNi)_{30}(AlTi)_{10}$, $Zr_{75}(CuNi)_{12.5}(AlTi)_{12.5}$ and $Zr_{67}(CuNi)_{22}(AlTi)_{11}$, respectively.

Table 1 lists the calculated glass-forming compositions and eutectic compositions for these four multicomponent alloy systems. It can be seen in Table 1 that the calculated glass-forming compositions composition corresponding to β vacant defects is close to the eutectic composition [13], in the Ca–Mg–Zn ternary alloy system, and the calculated ones corresponding to β and γ filled scheme are also close to the eutectic compositions [3,14,15], in other three alloy systems.It was pointed out by Yavari that binary eutectic compositions can be obtained based on the ECP model with proper filling and vacancy in Ω, α, β and γ sites [1]. The present results indicate that calculated glass-forming compositions also could be used to predict eutectic compositions of multicomponent alloy systems containing no more than four topologically different elements. The efficient atomic packing, which results in difficulty in long-range rearranging of different constituents, combining with the strong chemical bonding between constituents (especially what is in the first coordination shell), which stabilizes the undercooled melt, in the alloys at the calculated compositions have similar effect on glass formation as eutectic reaction.

For these ternary or pseudo-ternary alloy systems, there are four different sites (Ω, α, β and γ) and three species in the ECP model. The predicted compositions obtained with β and γ sites filled with β solute atoms are in better agreement with eutectic compositions in the Zr–Cu–Al, Mg–Cu–Y and Cu–Zr–Ni–Al–Ti alloy systems. It indicates that β and γ sites filled scheme can help to increase the packing efficiency for most ternary alloy system. However, it is strange that β vacant scheme produce more efficient packing in the Ca–Mg–Zn alloy system. It should be noted that Ca and Mg atoms have relatively large size, which results in larger size of α clusters.

Larger α clusters may occupy space with more overlapping area and less β sites, thus Zn atoms fill γ sites with β sites being vacant.

As pointed out by Fan et al. [16], in liquid alloys, large negative mixing enthalpy produces SRO, which remains in the amorphous phase during rapid quenching. For example, they confirmed the existence of Zr–Al and Zr–Cu SRO in bulk metallic glass $Zr_{55}Cu_{35}Al_{10}$. In the Ca–Mg–Zn alloy system, Ca–Zn atom pairs exist in amorphous alloy due to the large negative mixing enthalpy between them (−22 kJ/mol). They form densely packed Zn-centered γ clusters (R_γ is 0.701, which is close to the specific value 0.710) in the ideal ECP model discussed above. In the Mg–Cu–Y alloy system, Cu–Y atom pairs exist in amorphous alloy due to the large negative mixing enthalpy between them (−22 kJ/mol). However, they cannot form densely packed clusters in the ideal ECP model. In the Zr–Cu–Al and Cu–Zr–Ni–Al–Ti alloy systems, Zr–Al (−44 kJ/mol) atom pairs form Al-centered α clusters, Zr–Cu (−23 kJ/mol) and Zr–Ni (−49 kJ/mol) atom pairs form Cu-centered or Ni-centered β and γ clusters, while other atom pairs with large negative mixing enthalpy can not form SRO in the ideal ECP model. The strongly attractive (with a large negative mixing enthalpy of −23 kJ/mol) and densely packed (R is 1.244, which is very close to the specific value 1.248) Zr-centered Zr–Cu clusters may also appear in the Zr–Cu–Al and Cu–Zr–Ni–Al–Ti alloy systems, which results in larger discrepancy between the predicted compositions and eutectic compositions than that in Ca–Mg–Zn and Mg–Cu–Y alloy systems.

Table 1 shows that predicted eutectic compositions are not exactly at the experimental ones, and the concentrations of the solvent species of actual eutectic compositions are lower than the predicted ones in all cases where the discrepancies are significantly large. It has been widely accepted that the optimum glass formation actually occurs at off-eutectic compositions [17]. On the other hand, there will be other defects in the ECP model [8,9]. They may be the main reasons resulting in the discrepancies between predicted compositions and equilibrium phase eutectic compositions for these four multicomponent alloy systems. Miracle et al. [18] found that antisite defects (solute atoms occupy solvent sites) are important in the glass-forming ability of the most stable glasses in 175 binary glass systems. It could be concluded that antisite defects, which results in large differences between the actual eutectic compositions and the predicted ones, are also important for the stability of multicomponent metallic glasses.

It should be pointed out that a special element was chosen as Ω atom to construct an ideal ECP model, because only Ca, Mg and Zr-rich eutectic compositions are available in the literature for these four alloy systems. Other elements in an alloy system also can be chosen as Ω atom, which indicates that other eutectic compositions at the chosen atom-rich corner may also exist.

We have predicted bulk metallic glass-forming region of some alloy systems in our previous works [10,11]. However, it is valid only for alloy systems containing no more than three topologically different constituents. For alloy systems containing up to four topologically different constituents, eutectic compositions can be predicted based on the ECP model. Therefore, novel bulk metallic glasses can be found in a narrow composition region near predicted eutectic composition. On the other hand, it may provide new insights into atomic packing of eutectic alloys.

4. Conclusion

Eutectic compositions in Ca–Mg–Zn, Mg–Cu–Y, Zr–Cu–Al ternary and the Zr–Ti–Ni–Cu–Al quinary alloy systems were predicted based on the efficient cluster packing model proposed by Miracle. It is found that the predicted compositions are in good agreement with experimental eutectic compositions. This simple approach may be used to predict eutectic compositions and to obtain novel bulk metallic glasses in multicomponent alloy systems containing no more than four topologically different constituents. It also may provide new insights into atomic packing of eutectic alloys.

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