Letter

Characteristics of cluster formulas for binary bulk metallic glasses

A B S T R A C T

Compositions of typical bulk metallic glasses (BMGs) and boron-containing eutectics have been previously interpreted by cluster formulas issued from the cluster-plus-glue-atom model. In the present work, binary BMG composition formulas are established via dissociating dual-cluster formulas for their relevant eutectics. It is unveiled that BMG formulas satisfy three ubiquitous rules: cluster formula of the form [cluster](glue atom)$_{1 \text{ or } 3}$ with 24 valence electrons per unit formula, the center and the glue sites occupied by the same atomic species, and the BMG composition falling within the eutectic zone. These characteristics may serve as the finger prints for good glass formers and eventually the BMG design tool.

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1. Introduction

A metallic glass is formed by continuous cooling of a liquid below the glass transition temperature T_g, during which detectable crystallization is avoided [1]. Since the first report of Au–Si metallic glasses made by splat quenching [2], the glass-forming ability (GFA) of an alloy has been one of the most intriguing issues, and the search for alloys with high GFAs in a huge number of candidates has been extensively conducted. However, the correlation between alloy composition and GFA remains an open issue [3].

Ideal metallic glasses that comply fully with the Hume-Rothery stabilization mechanism generally have high GFAs [4]. The cluster-plus-glue-atom model [5] proposed by us allows pinpointing the compositions of ideal metallic glasses by establishing cluster formulas. The cluster formula for an ideal metallic glass, termed "ideal cluster formula" in this letter, is formulated as [cluster](glue atom)$_{1 \text{ or } 3}$ [5], and the valence electron number per unit formula, e/u, is approximately 24 [6]. Here the cluster refers to a nearest neighbor coordination polyhedron. The cluster that formulates an ideal cluster formula is the principal cluster derived from a devitrification phase. Though many binary and ternary bulk metallic glasses (BMGs) have been explained by the ideal cluster formulas [6], there was a missing point, i.e., the characteristics of the ideal cluster formulas for BMGs, in contrast to those for weak glass formers. The answer should be implied in the form of BMG formulas as well as in their relevant eutectic points.

Recently, binary boron-containing eutectic compositions have been addressed via dual-cluster formulas [cluster$_\alpha$ + cluster$_\beta$](glue atoms)$_{2, 4, 6}$, assuming that a eutectic liquid is composed of two stable subunits, each formulated as an ideal cluster formula [cluster$_{\alpha \text{ or } \beta}$](glue atom)$_{1 \text{ or } 3}$, where the cluster is the principal cluster derived from the eutectic phase α or β [7]. With the help of eutectic formulas, it might be possible to uncover

more details about the ideal cluster formulas for good glass formers.

In this letter, the dual-cluster composition formulas for binary eutectics in systems Cu-(Zr, Hf, Ti), Ni-(Nb, Ta), and Al–Ca will be further analyzed, with the objective of revealing the characteristics of the BMG formulas.

2. Eutectic composition interpretation

The Cu$_{61.8}$Zr$_{38.2}$ eutectic system, schematically shown in Fig. 1, is taken as an example to demonstrate the process of establishing the BMG formula out of the dual-cluster formula for this eutectic.

This eutectic zone is bounded by eutectic phases Cu$_8$Zr$_3$ (structure type Cu$_8$Hf$_3$) and Cu$_{10}$Zr$_7$ (Ni$_{10}$Zr$_7$). Their crystal structures can be found in Pearson's handbook [10]. Following the criteria of atomic dense packing and cluster isolation, already stated in Ref. [11], the principal clusters are first selected from the two phases.

In the unit cell of Cu$_8$Zr$_3$, there are eight non-equivalent sites, and centered by each is defined a cluster [12]. In expressing a cluster, the center atom and the nearest-neighbor atoms are separated by a hyphen and all is enclosed within a pair of square brackets, for instance, centered by Cu^4 is defined an icosahedron [Cu–Cu$_7$Zr$_5$], where the superscript denotes the sequence of the non-equivalent site in unit cell and the subscripts the number of atoms.

Since a specified cluster generally overlaps with the same neighboring clusters, the cluster is reduced to a smaller one, called the reduced cluster [7]. The reduced cluster plus certain number of glue atoms constitute the building block [reduced cluster](glue atom)$_x$, which is also the phase formula expressed by this cluster. For instance, the Cu^4-centered cluster [Cu–Cu$_7$Zr$_5$] in Cu$_8$Zr$_3$, after edge-sharing four Zr atoms with other two neighboring clusters (as shown in Fig. 2), becomes the reduced cluster [Cu–Cu$_7$Zr$_3$], which
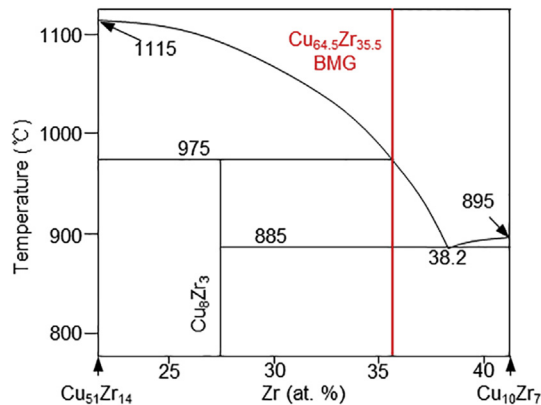
Fig. 1. Part of the Cu–Zr phase diagram covering the $Cu_{61.8}Zr_{38.2}$ eutectic zone, adapted from Ref. [8]. The $Cu_{64.5}Zr_{35.5}$ BMG [9] is marked.

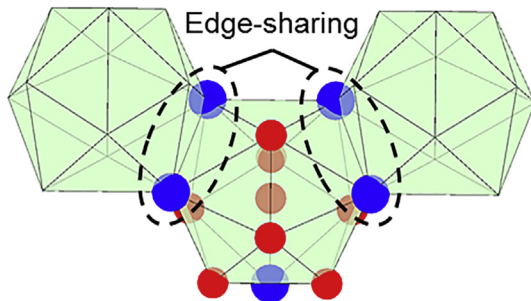**Fig. 2.** One [Cu^4–Cu_7Zr_5] cluster edge-shared with two neighboring ones in Cu_8Zr_3. The four shared Zr atoms are outlined. The larger sphere in blue is Zr, the smaller one in red is Cu. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is exactly the phase formula [Cu–Cu_7Zr_3] (= Cu_8Zr_3).

Among multiple clusters in a given alloy phase, there must be at least one cluster, termed the "principal cluster", which represents the principal short-range-order characteristics of the structure, and serves as the unit of local structure heritage between amorphous state and its crystalline counterpart [7,11,13]. As confirmed by an *ab initio* calculation [14], it is the most strongly bonded part in the structure and consequently should exhibit high cluster isolation degree [7,11]. Therefore, the principal cluster can be usually selected employing the "phase formula rule": the principal cluster should be selected from a large phase formula containing the minimum number of glue atoms [7]. For Cu_8Zr_3, the Cu^4-centered icosahedral cluster [Cu–Cu_7Zr_5] generates the largest phase formula [Cu–Cu_7Zr_3] of eleven atoms and zero glue atom, so that it should be taken as the principal cluster (see Supplementary material [15]).

In a similar manner, the clusters in the other eutectic phase $Cu_{10}Zr_7$ of the $Cu_{61.8}Zr_{38.2}$ eutectic can also be defined, and the Zr^2-centered cluster [Zr–$Cu_{10}Zr_6$] is selected as the principal cluster for the largest phase formula [Zr–$Cu_{10}Zr_4$]Zr_2. Now that the principal clusters [Cu–Cu_7Zr_5] and [Zr–$Cu_{10}Zr_6$] of the two relevant eutectic phases Cu_8Zr_3 and $Cu_{10}Zr_7$ have been determined, these two clusters are then combined with 2, 4 or 6 Cu and Zr glue atoms, and after examining all the combinations, the scheme the closest to an integer form generates a dual-cluster formula [Cu–Cu_7Zr_5 + Zr–$Cu_{10}Zr_6$]$Cu_3Zr = Cu_{21}Zr_{13} \approx Cu_{61.8}Zr_{38.2}$ (at. %),

reproducing quite accurately the experimental eutectic composition $Cu_{61.8}Zr_{38.2}$.

3. BMG composition interpretation

As assumed, a dual-cluster formula contains two subunits issued from the eutectic phases. Then, this formula can be dissociated into two individual cluster formulas both of the ideal cluster formula form [cluster](glue atom)$_{1 or 3}$. In this case, there are four possible dissociation schemes: [Cu–Cu_7Zr_5]Cu_3 + [Zr–$Cu_{10}Zr_6$]Zr, [Cu–Cu_7Zr_5]Cu_2Zr + [Zr–$Cu_{10}Zr_7$]Cu, [Cu–Cu_7Zr_5]Zr + [Zr–$Cu_{10}Zr_6$]Cu_3, and [Cu–Cu_7Zr_5]Cu + [Zr–$Cu_{10}Zr_6$]Cu_2Zr. Among them, the last one is the only scheme that contains the ideal cluster formula [Cu–Cu_7Zr_5]Cu $\approx Cu_{64.3}Zr_{35.7}$ (e/u = 23.7) [6] that could explain the optimum glass former $Cu_{64.5}Zr_{35.5}$ [9] in this eutectic zone as shown in Fig. 1. The e/u of this ideal cluster formula is calculated by $e/u = 1.25^3 \pi Z/(3\rho_a r_1^3)$, where Z is the number of atoms in unit cluster formula, ρ_a the atomic density (number of atoms per unit volume), and r_1 the cluster radius calculated by arithmetic mean of all the radial distances [6].

Following the same process, the dual-cluster formulas for other BMG-forming eutectics in Cu-(Zr, Hf), Ni-(Nb, Ta) and Al-Ca systems are also accurately expressed and are each dissociated into two individual cluster formulas, where one of them corresponds to a BMG former, as listed in Table 1 (see Supplementary material [15]). Most of the BMG formulas obtained by dissociating dual-cluster formulas are identical to the previously solved ones [6], except [Zr–Cu_8Zr_6]$CuZr_2$ being different from the initially proposed [Zr–Cu_8Zr_6]Zr. Though both formulas explain the $Cu_{50}Zr_{50}$ BMG [16], the present one gives an e/u = 23.7 which is the closest to the ideal 24, using the averaged radial distance of the two-shelled nearest neighbors as r_1, in sharp contrast to e/u = 21.0 of the previously proposed formula [Zr–Cu_8Zr_6]Zr.

4. Discussion

In order to unveil the unique characteristics of the BMG formulas, the dual-cluster formulas for non-BMG-forming eutectics in Cu-(Hf, Ti) binary systems are also compared, as shown in Table 1. It is noticed that the eutectics dealt with here are bounded by two intermetallic compounds, which are supposed to favor glass formation [17].

By scrutinizing and comparing the cluster formulas in Table 1, the characteristics of BMG formulas can be unveiled as summarized below:

1) The BMG formula complies to the general requirement for an ideal cluster formula, i.e., [cluster](glue atom)$_{1 or 3}$ and $e/u \approx 24$;
2) The center and the glue sites are occupied by the same atomic species, making the formula a "balance" shape;
3) The composition of the BMG formula is located within the eutectic zone between the two eutectic phases.

As can be seen from Table 1, the dual-cluster formula for a BMG-forming eutectic can always be dissociated into two cluster formulas, one of which being a BMG-type formula (satisfying the three characteristics). In contrast, the non-BMG-forming eutectic formula [Hf–$Cu_{10}Hf_6$ + Cu–Cu_4Hf_8]Cu_4 can cover an ideal cluster formula [Hf–$Cu_{10}Hf_6$]Cu_3 with e/u = 24.4, close to the ideal value of 24. However, its three glue atom sites are entirely occupied by Cu, while the center atom site is occupied by Hf, thus violating the 'balance' shape of the ideal cluster formula for BMGs. The composition [Hf–$Cu_{10}Hf_6$]$Cu_3 \approx Cu_{65}Hf_{35}$ also exceeds the eutectic zone (41.2–66.7 at. % Hf).

The non-BMG-forming Cu–Ti system, presents two eutectic