Alloy compositions of metallic glasses and eutectics from an idealized structural model

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Abstract

Using an idealized atomic packing model for metallic glasses (MGs), we predict the binary alloy compositions structurally favorable for the stability of MGs. Such compositions are proposed to be the likely candidates to obtain MGs. The predicted compositions coincide very well with the experimental glass-forming range for a large number of systems. The relationship between these compositions and the eutectic compositions in the equilibrium phase diagrams is established. Direct correlations are found for symmetric eutectic systems, especially for deep eutectics, whereas off-eutectic MGs are suggested for asymmetric eutectic systems. Rationales from the structural standpoint are also presented to explain the increased frequency of appearance of eutectics at certain composition ratios (the Stockdale/Hume-Rothery puzzle).

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1. Introduction

Ever since the discovery of metallic glasses (MGs) [1], there have been continuous efforts to understand why certain alloy compositions appear to be more favorable for MG formation [2]. Ultimately, one would hope to be able to predict the locations of glass formers a priori, but so far attempts directed at this goal have met with only limited success [2]. One realization is that MG formation is more likely near eutectic compositions [3–5]. This has often been rationalized by the argument that, compared with other compositions, the eutectic one is where the liquid is stable at a temperature closest to the glass transition temperature, $T_g$ [3–6]. However, glass formation is a non-equilibrium, polymorphous process that happens during fast cooling of the melt, while the eutectic reaction occurs when the liquid and crystalline phases reach full equilibrium. So the connection between the experimentally observed MG formation range and the eutectic compositions in equilibrium phase diagrams requires more involved thermodynamic and kinetic justifications [6,7]. Regarding the eutectics, there is also another long-standing unresolved issue, called the Stockdale/Hume-Rothery puzzle: in the equilibrium phase diagrams of A–B binary systems, eutectics appear frequently at whole number A/B composition ratios of 8/1, 5/1, 3/1, 2/1 and 3/2 [8,9]. It has been proposed that there may be common or similar reasons for the preferred compositions for the formation of MGs and eutectics [9]. The purpose of this paper is to explore these issues from a structural perspective, i.e., by assessing the stability of the amorphous state from their internal structure.

Of course, a prediction of alloy compositions for MG or eutectics formation cannot be fully accomplished by looking at the stability of the amorphous state alone. The properties of the competing crystalline compounds must be taken into account as well. However, it is known that good
glass formers tend to crystallize with unusually small enthalpy release and volume change, suggesting that the amorphous structure itself may be preferentially stabilized at these compositions, to a level close to that of equilibrium compounds. We surmise that such stability is due to the high degrees of short-range order (SRO) in the internal structure, which render the amorphous phase more competitive. Similar ordering, in long range, to form a crystalline phase is assumed to be not possible at the same composition (in addition, some of the SRO types, such as icosahedral, would not be compatible with any crystal order).

The contents of this paper are arranged as follows. In Section 2, we connect the typical thermodynamic and kinetic arguments for MG formation with the internal structures of the supercooled liquid. A simple structural model, and its justifications, is then presented to predict the compositions where MGs are comparatively stable. In Section 3, the predictions are compared with available experimental data in a large number of MG-forming systems. Section 4 discusses the relationship between the favorable MG compositions and the liquid eutectics in equilibrium phase diagrams of different types. Insight into the Stockdale/Hume-Rothery puzzle is provided in Section 5. Limitations of our approach are discussed in Section 6. The paper ends with a summary of conclusions in Section 7.

2. The structural model

2.1. The structural origin of the stability of supercooled liquid and MG

The existence of internal local structures in the seemingly structure-less (amorphous) liquids and supercooled liquids, and in MGs which inherit the structure of the latter, has been recognized for many years [10,11]. Following the early hypothesis of Frank [12], Hume-Rothery and Anderson [8], for example, proposed that there may be Frank icosahedral units in the liquid structure that stabilize the eutectic liquid. Later work revealed the continuous rise of excess specific heat prior to glass transition, which was attributed to the significant SRO developed in the supercooled liquid [11–16]. The eventual MG formed therefore can not be treated as a direct extrapolation of the high-temperature liquid [16]. Structural understanding for MGs and their parent liquids, involving various types of SRO, has improved continuously over the years [17–21]. Recently, some progress has been made in establishing insightful and yet easily tractable descriptions of MG structures, especially for A–B binary MGs with relatively low solute (B) concentrations [10]. This sets the stage for treating MGs and eutectics from a structural standpoint, at least in these relatively simple alloy systems.

Here we make a comment on the role of the internal amorphous structure in controlling the behavior of supercooled liquid that forms MG. In a free energy ($G$) vs. composition diagram, the glass-forming range (GFR) in a polymorphous (partition-less) cooling process [16] (such as melt spinning) is determined by the cross-over points of the $G$ curves of the supercooled liquid with those of the crystalline phases. As illustrated in the schematic phase diagrams in Fig. 1, to predict the GFR we will be looking for the composition range when the two $T_0$ lines (dashed lines) cross the glass transition temperature, $T_g$ (the solid line). The $G$ curve of the liquid would dip lower if SRO develops inside the liquid [10,17], as the enthalpy becomes the increasingly dominant term in $G$ with decreasing temperature, such that the $T_0$ lines would plunge with high slopes.

In the supercooled liquid, the compositions favorable for the development of chemical and topological SRO would be where the $G$ curve dips low and moves up with...
decreasing temperature at a slower pace than for other compositions. This low-lying G segment, lagging behind, leads to a range of compositions that possess relatively stable amorphous structures and likely form MGs.

This structural perspective is in fact consistent with the thermodynamic and kinetic arguments commonly used to rationalize MG formation [2,22]. The significant topological and chemical SRO puts the atoms in relatively comfortable positions, energetically reducing their motivation to reach for crystalline states. The atomic arrangements leading to SRO also result in efficient and dense packing, as reflected by the small volume change upon crystallization [23]. Indeed, the calorimetrically measured heat of crystallization of typical MGs is small [22], usually 30–40% of the heat of fusion of the crystalline counterpart, indicating a relatively low driving force for crystallization. The efficient filling of space would also retard atomic mobility and kinetically suppress the formation of the competing compounds.

2.2. Model description

The question is then to locate the composition, around which the amorphous structure tends to reach optimized chemical and topological SRO and efficient filling of space. To this end we take advantage of the insight gained in recent studies of MG structures [10,20]. As shown in Fig. 2 as an example, at relatively low solute compositions (depending on system, but typically <20 at.%) each solute atom tends to be at the center of a cluster, surrounded by solvent atoms only. This preferred “solute-solute avoidance” is a consequence of the chemical SRO to increase the number of direct bonds between unlike species to reduce energy (there is a large negative heat of mixing for the MG-forming systems). The coordination number (CN) of the center solute, and the topology of its coordination polyhedron, tends to maximize the number of A–B bonds for the given space available at the particular atomic size ratio. The single-solute centered clusters are quasi-equivalent [10]. Also, to efficiently fill space these clusters interpenetrate and tend to have 12 neighboring clusters with icosahedral-like five-fold arrangement.

Combining these features, one way to look at the desirable MG structures is to consider them as having maximal binding of solvent atoms by a minimal number of solutes through a maximal solute dispersion [21]. Hence, certain compositions are structurally favorable, because these features cannot be preserved as well at excessive or deficient solute concentrations. Our model configuration described below adopts these principles [10], and attempts to simplify the structural description so that it can be used to calculate the structurally favorable compositions when the key packing requirements are satisfied. Because this work is based on the structural understanding achieved in Ref. [10], the A–B alloys we deal with will all have a clearly dominant solvent (A) and a solute (B) concentration below ~30 at.%, and the eutectics would be the first one on the A side. Simple descriptions for amorphous alloys in the central concentration range are yet to be established (to be reported elsewhere by Y.Q. Cheng, E. Ma and H.W. Sheng).

Unlike crystals with long-range ordered lattice, the atoms in MGs will not sit on regularly arranged sites and the local structure is not identical throughout the material. There will be a structural fluctuation with different degrees of SRO from location to location, and the inter-cluster connection can be through face-sharing, edge-sharing, vertex-sharing and no-sharing schemes, as shown in Fig. 2 [10]. To arrive at a simple model that allows easy calculation of compositions, an “average” or equivalent configuration of atom arrangement would need to be assumed as an approximation. In our simple model, a 2-D schematic of which is depicted in Fig. 3, this structure is composed of single-solute (B) centered clusters, connected with 12 neighboring clusters of equal size in a five-fold (icosahedral-like) arrangement, via sharing of a corner solvent (A) atom. We take the vertex sharing as the representative, because the atomic (or mass) density calculated in this scheme is consistent with experimental measurements for a number of MGs [24–30]; see Fig. 4 and its caption.

This idealized configuration is, of course, not meant for accurate description of the exact structural features (and their distributions) in real MGs. Rather, it is intended to represent an average and basic configuration. The merit of such simplified model constructs lies in its convenience for easy computations of alloy compositions, while capturing the main packing principles (see above) or producing macroscopically equivalent properties [20,21].

The composition of a glassy alloy with such idealized local order in the short-to-medium range can then be calcu-
lated. The CN of solute B atom at center for the given atomic size (radius) ratio $R$, where $R = r_B/r_A$ as tabulated in [31–34], can be easily calculated using the equations in Refs. [31,32], for efficient intra-cluster packing as stipulated in our model:

$$
CN = \begin{cases} 
4\pi/ \left( 6 \arccos \left( \sin(\pi/3) \left[ 1 - 1/(R+1)^2 \right]^{1/2} \right) - \pi \right) 
\text{for } 0.225 \leq R < 0.414, \\
4\pi/ \left( 8 \arccos \left( \sin(\pi/4) \left[ 1 - 1/(R+1)^2 \right]^{1/2} \right) - 2\pi \right) 
\text{for } 0.414 \leq R < 0.902, \\
4\pi/ \left( 10 \arccos \left( \sin(\pi/5) \left[ 1 - 1/(R+1)^2 \right]^{1/2} \right) - 3\pi \right) 
\text{for } 0.902 \leq R,
\end{cases}
$$

Each B-centered cluster has one B atom and CN A atoms. But since each A solvent in this particular cluster is shared by this cluster itself and 12/CN times by the neighboring clusters, only $1/(1 + 12/CN)$ of this solvent atom belongs solely to this cluster. The total number of solvent A per solute B is thus

$$
S = \frac{CN}{1 + \frac{12}{CN}}
$$

Then the predicted solute concentration, $X_P^B$ in at.% is simply

$$
X_P^B = \frac{1}{1 + S} = \frac{CN + 12}{CN^2 + CN + 12} \times 100
$$

Note that this simple calculation is for an amorphous structure modeled in Fig. 3, and contains no requirement or assumption that the clusters pack with a crystal-like pattern (such as face-centered cubic (fcc) or body-centered cubic (bcc) [20,21]). As discussed above, $X_P^B$ will be the predicted composition for the structurally-favored MG. The GFR, if the MGs actually form in lieu of crystalline competitors, is expected to be around this composition. Note that for a relatively narrow GFR, $X_P^B$ is an approximate estimate of $X_T^B$, where the most stable supercooled liquid resides when the two $T_0$ lines cross (see Fig. 1).

The predicted $X_P^B$ results are shown (red square) in Fig. 5 for 33 binary systems, and Fig. 6 for another 12 binary systems. The separation of these 45 systems into two groups is based on the type of eutectic systems and will be discussed in Section 4. Because our structural picture is only applicable when solute B is the clear minority species, no predictions will be offered in Figs. 5 and 6 for high at.% B situations.

3. Relationship with the experimental glass-forming range

Figs. 5 and 6 also display the glass-forming composition range (GFR) observed in experiments (mostly melt spinning experiments) [14,21,24,25,31,35–50]. The 45 binary systems included here involve different chemical and atomic size ratios. Other than these systems, there are a number of others in which MG formation was observed in experiments, but the GFR studied was only in the cen-
tral composition range (B > ~30 at.%) These systems are not included in the comparison and will not be discussed here, as our structural model and predictions are not adequate for compositions in the middle section of the phase diagram (see Section 6).

In each of these 45 systems, the best glass-forming composition has not been pinpointed exactly. But, as shown in Figs. 5 and 6, there are systems for which the GFR is rather narrow, on the solvent A side. These are the cases where our predictions should work the best, and where GFR should coincide with $X_{eu}$ (blue triangle) seen in the phase diagram. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Relationship with equilibrium eutectic compositions

As discussed earlier, the composition $X_B^P$ is a prediction for the structurally favorable supercooled liquid and MG. We have argued that it would fall in the experimental GFR, and can be an approximation of $X_T^0$ (Fig. 1). Then how would it correlate with the eutectic composition seen in the phase diagram, $X_{eu}$ in Fig. 1, representing the most stable equilibrium liquid? We note that for symmetric eutectic systems, where the slopes of the liquidus and of the $T_0$ lines are similar on either side of the eutectic, $X_B^P$ and $X_{eu}$ would be rather close and both near the center of the GFR, as depicted in Fig. 1a. As such, our $X_B^P$ naturally also predicts $X_{eu}$ very well, as demonstrated in Fig. 5 (compare the red square with blue triangle). For 90% of the systems in Fig. 5, the absolute error, $|X_{eu} - X_B^P|$, is less than 4.5 at.% B.

For asymmetric eutectics (see Fig. 1b), where the liquidus (and the $T_0$ lines) have significantly different slopes on each side, $X_B^P$ remains to be good predictions of GFR ($X_T^0$), Fig. 6. But as illustrated in Fig. 1b, $X_B^P$ deviates significantly from $X_{eu}$ in such asymmetric eutectic diagrams, so our predictions would not directly provide $X_{eu}$. Indeed, for all these systems shown in Fig. 6, $X_B^P$ and GFR ($X_T^0$) are clearly off-eutectic, as expected. Previously, the experimental off-eutectic GFR was explained by invoking growth
and T
cept [6,7,51]. Our prediction based on structural concepts and kinetics arguments based on the eutectic coupled zone concept [6,7,51]. Our prediction based on structural concepts and eutectic lines yields an off-eutectic GFR as well, and as such offers an explanation from the thermodynamic stability standpoint. Our prediction is simple to use, quantitative and does not require growth kinetics parameters that are usually not available [6,7].

Note that so far the high degree of local order (Fig. 3) is for MGs and deeply undercooled liquids. Such ordering would be less in equilibrium liquids at/above the eutectic temperature. However, some eutectics are rather “deep”, with plunging liquidus. In these deep eutectic systems, the liquid can be also stabilized to a rather low temperature, compared with the temperature expected for a truly random liquid solution. Therefore, the ordering features we have discussed would exist to some extent, serving as a structural origin of the stabilization of the equilibrium liquid at the eutectic composition. The deep eutectics are relatively symmetric, so our predictions work well for both the nonequilibrium glass/liquid and X
eu.

However, for the symmetric eutectics that are not deep, the SRO developed inside the liquid at and above the eutectic temperature would be no longer comparable to the level inside MGs. As discussed before, we are correctly predicting GFR and X
B
eu, and the X
eu would be nearby due to the symmetric nature of the eutectic (Fig. 1a). But the eutectic liquid does not necessarily have the extraordinary SRO in Fig. 3 for stabilization. The symmetric eutectic feature comes from the shapes of the G curves of the three involved phases and their behavior upon temperature changes. The eutectic temperature and composition are determined by the well-known common tangent construction in the three-phase equilibrium.

For asymmetric eutectic systems, the eutectics are usually not deep. Our predictions are only meant to estimate the locations of GFR and X
B
eu, which can no longer be automatically linked to X
eu. The eutectic composition is determined by the well-known common tangent construction in the three-phase equilibrium.

5. The Stockdale puzzle

Fig. 7 reproduces the frequency plot used to arrive at the conclusion that eutectics appear frequently at whole number A/B composition ratios of 8/1, 5/1, 3/1, 2/1 and 3/2 [8,9]. We first note that although these ratios do appear more favorable for eutectics, the peaks are not sharp and around each of these ratios there is a broad distribution. One can only say that near these ratios the probability to form eutectics is somewhat higher. Our data collection can shed light on this issue.

In Figs. 5 and 6, there are different groups of A–B alloys. For late transition metal (A)–early transition metal (B) systems, such as Co–Hf (X
eu = 11 at.% Hf) in Fig. 5, the eutectic composition tends to be in the range of 8–13 at% B. Such compositions can be attributed to the R ratio of these pairs (and corresponding CN and X
B
, see equations above). These systems would thus enhance the frequency around 8/1 (~11 at.% B).

For metal (A)–metalloid (B) systems, for example Fe–B, (X
eu = 17 at.%), the eutectic compositions (15–20 at.%) in the phase diagrams cluster around a ratio of 5/1 (17 at.%). A number of examples of our predictions for such systems can be seen in Fig. 5. These contribute to the 5/1 peak in Fig. 7. Again, it is the particular R ratio, which is rather common for many metal–metalloid systems, that makes such eutectic compositions more frequent.

On the other hand, simple metal (A)–transition metal (B) systems like Ca–Cu (X
eu = 24 at.%), early transition metal (A)–late transition metal (B) systems like Zr–Fe, and rare earth (A)–simple metal (B) systems like La–Al, consist of large solvent atoms and as such require relatively low CN and high concentrations of the smaller B to pack efficiently. The resulting X
eu would be close to the peak at 3/1 (25 at.% B).

In other words, different types of elements have different positions in the periodic table, and hence different atomic sizes and bonding types. Combining elements from these groups to form binary alloys hence leads to certain frequently occurring atomic size ratios. The latter, as we showed above (also see equations), in turn lead to certain CN values and correspondingly preferred eutectic compositions. These, when added on top of the other eutectic systems, contribute to the apparent peaks in Fig. 7.

Therefore, our analysis from the structural perspective does help explain the Stockdale puzzle. The higher-than-average likelihood for eutectics (especially symmetric and deep eutectics) at certain compositions indeed has a structural origin. Our finding is a step forward from the work of Hume-Rothery and Anderson [8], who hypothesized that there may be Frank icoshedral units, and/or 1–5–1–5–1 pentagonal atomic chains in the liquid structure. They speculated that such ordered structures in the liquid can be decorated in such a way that at certain compositions B–B nearest neighbors are avoided/reduced, lowering the
free energy. Similar arguments were proposed by Yavari very recently [9] using the hard sphere cluster packing model of Miracle [20]. Our analysis above, in comparison, is based on more concrete structural information from recently obtained direct evidence in unraveling the amorphous structures [10]. In particular, as reflected in our model, the B–B avoidance is indeed relevant, but the intra-cluster (nearest-neighbor) packing may not be always icosahedral [11,52] and can be of various types [10,53] with different CN (Eq. (1)) for different R. For inter-cluster packing, some icosahedral-like medium-range dense arrangement of overlapping clusters is present. Direct measurement of these features in high-temperature liquids is difficult, but our discussions above suggest they are likely to be present to some extent at least for deep eutectic liquids.

6. Limitations of the model predictions

To arrive at the predictions we have assumed a single CN for a MG (given A–B pair), but a real MG can have a moderate local CN variation from solute to solute (i.e. cluster to cluster) [10]. In fact, strain relaxation does not allow a fixed CN throughout the glassy material [20]. The bulk averaged CN actually does not have to be an integer. As a matter of fact, the atoms in MGs are not hard spheres that keep their radius as in the unary system, but “soft” ones via many-body interactions [10]. Evidently, the efficient packing achieved in a MG under the particular chemical interactions and kinetic constraints is not going to follow the picture as that simplified in Fig. 3. Therefore, our model and its prediction are only for a trend estimate. To guard against the use of our model in Fig. 3 (or any similar model [20,53]) as accurate structure inside MGs, we reiterate that the main purpose of such an idealized construct representing the average configuration is to allow for easy calculations.

Our predictions are meant to suggest the composition around which the MG amorphous structure may be more preferable with respect to other compositions in the neighborhood in a given system, from the structural viewpoint. They do not, however, guarantee a high GFA (also see discussion in Section 1). For example, from our equations, paring similarly sized A–B would lead to a CN around 12, and $X_B^{\text{P}}$ around 14 at.% B. Experimentally, no such MGs can be found, as observed in Figs. 5 and 6. In other words, even at these structurally favorable compositions these systems do not yield MG at all, for melt spinning. It is known that such elements, which would tend to be from the same group in the periodic table and chemically similar as well, usually lead to very low GFA. Following the spirit of Hume-Rothery, and that of Egami for MGs [31], Inoue [54], for example, suggested that >12% atomic size difference is needed for glass formation to win over the formation of crystalline solutions.

Also, the predicted compositions in Figs. 5 and 6 do not have a capability to form bulk metallic glasses (BMGs). Binary BMGs occasionally form at compositions in the middle section of the phase diagram such as in the Cu–Zr [51,55–57], Cu–Hf [57,58], Ca–Al [59] and Ni–Nb [60] systems. In such a case of high B contents, B has to have direct contacts with other B atoms, and it is not possible to isolate each B in a cage formed by A atoms only. Of course, our structural picture in Fig. 3 is not applicable for such cases; a different model is required.

Also, we have not yet extended our analysis to ternary and multi-component systems, which are usually needed to further improve bonding, ordering and packing efficiency to elevate GFA to a level sufficient to yield BMGs. However, the simple binaries treated here are the base systems for BMG formation. For example, “binary eutectic clusters” [61] were proposed as basic units for designing BMGs in multi-component systems. Our analysis provides concrete descriptions as to realistically what these clusters and units might be.

In addition, it should be recognized that the “structure” dealt with above in Fig. 3 is not merely topological and does implicitly rely on some chemical effects, since the negative heat of mixing between the solvent–solute pair is the basis for the solute-centered cluster with a solvent in the first coordination shell. However, the structure platform we have adopted here does not involve the details of the chemistry and electronic interactions, which need to be invoked along with the properties of competing compounds to explain, for example, two systems having different MG formation behavior but sharing the same structural features.

Regarding the Stockdale/Hume-Rothery puzzle, our discussions here shed some light on at least the first three peaks in Fig. 7. The next two (2/1 and 3/2) peaks at high B contents are beyond the range of compositions that can be handled with our model, which focuses on the first eutectic point on the A side in binary systems.

7. Conclusions

Taking advantage of the recent advances in understanding the structure of MGs, we have idealized the amorphous structure to predict the compositions where the amorphous structure is relatively stable. From the structural perspective, the stability of an MG (and its parent supercooled liquid from which the structure is inherited) is higher if chemical and topological SRO can be well developed inside its structure. Candidate compositions for MG formation should therefore be nearby. The usefulness of this conjecture seems justified through the agreement with experimental MG formation results, as shown in Figs. 5 and 6. However, beyond the MG stability, a general and rigorous approach to glass-forming ability must consider carefully the behavior of competing crystalline phases.

One major feature of our method is that it is extremely simple. The idealized model structure is assumed to be fully amorphous without the need for crystal-like packing patterns. The intra- and inter-cluster atomic packing follows the same structural building principles and overlapping
schemes [10,62] as those determined for realistic MGs, but with averaging simplifications to allow a uniform structural description for straightforward calculations. The coordination numbers and compositions can be computed easily and quickly with minimal calculations. This approach is remarkably successful, when compared with the MG compositions in experiments. This indicates that a structural consideration is relevant, such that even simple models along this line can be used to rationalize the formation of MGs.

The favorable compositions predicted for the stability of amorphous structure (and indirectly for the potential formation of the thermodynamically metastable MGs) are correlated with equilibrium eutectic compositions in the phase diagrams. Direct one-to-one correspondence is found for symmetric eutectic systems. The structural rationales are relevant especially for some eutectics that are “deep”, where the liquid is structurally stabilized relative to a random solution, the degree of this stabilization varying from system to system. For asymmetric eutectic systems, our predictions offer an additional explanation to the observation of off-eutectic GFR in experiments.

The structural rationales also explain the long-standing Stockdale/Hume-Rothery puzzle. The increased frequency of appearance of eutectics at certain composition ratios is a consequence of some frequently encountered A–B atomic size ratios, as the eutectic-forming pairs come from different groups of elements in the periodic table (also true for MG-forming pairs [63]). The insight gained is useful, because the eutectic reactions are ubiquitous in metallurgical settings, and important in many other applications such as the development of low-melting point alloys (e.g., lead-free solders).

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