

Atomic Size Distribution Plots for the Structure of Amorphous Metals

Daniel B. Miracle and Oleg N. Senkov¹

Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright Patterson AFB, OH 45433-7817;
¹UES, Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432-1894

The topology of metallic glasses is illustrated by plotting atomic concentration vs. atomic size for each element in an alloy. Two characteristic shapes of the resulting plots are found. Metallic glasses with marginal glass forming ability (critical cooling rate >1000 K/s), including those based on Al, Fe, Mg, and Co, possess a common profile characterized by a single concave-downward peak. The maximum elemental concentration exists at an intermediate atom radius, and most alloys possess both smaller and larger elements. By contrast, bulk metallic glasses, including those based on Zr, Pd, and several rare earth elements, typically display a single concave upward peak. The largest element is the most abundant, and the smallest element is typically the next most concentrated. Solutes of intermediate sizes typically exist at the lowest concentrations. It is suggested that these two profiles represent different underlying topologies, so that marginal glass forming alloys share a common structural model, which is distinct from the structure of bulk metallic glasses. A new model, which reproduces the observed topology, is outlined here. This model considers local elastic strains from both interstitial and substitutional atoms in the competing crystalline solid solution phase. The method developed here provides a prescriptive approach for the exploration of new metallic glass alloys.

Keywords: *amorphous metals, structure, atomic radius distribution plots, bulk metallic glass*

1. Introduction

While a number of features have been proposed to characterize the limited composition range of metallic glass formation, topology is generally considered to be the most important. However, topology-based rules tend to be rather general. For example, an 'inverse Hume-Rothery' criterion suggests that the size of atoms present must differ by at least 12-15%¹. A 'confusion principle' is often cited², which states that good glass formability is favored in systems with a diversity of atom types and sizes. While some success in predicting glass formability is offered by these concepts, neither is sufficiently specific to provide a prescriptive capability to identify new metallic glasses. A more quantitative model has been offered which defines a minimum solute concentration for amorphization as a function of the volume strain introduced by solutes³. This model provides good agreement for many alloys, but does not properly predict the behavior of complex alloys.

The objective of this paper is to present a new technique for illustrating the topology of amorphous metal alloys. This technique provides an efficient visual method for representing the underlying topology, and for discriminating between bulk amorphous metal systems and metallic glasses with marginal glass forming ability. A specific predictive capability is provided by this approach.

2. Atomic Size Distribution Plots

The first step in describing the topology is to consider the number and sizes of the atoms present. Given the large number of known glass formers, the principal challenge is to establish a convenient technique which provides adequate discrimination between different systems. A useful approach must be simple to apply, and should provide insight into the underlying topology of both simple and complex systems. A recent approach has been developed which satisfies these criteria⁴. The atom radius of a given element is plotted along the x-axis, and the concentration of that same atom is plotted along the y-axis in atomic percent. Each element in an alloy thus forms a single point, and all of the points for a given alloy provide a distribution of the atomic sizes and concentrations which characterizes the system. It has been shown that the distributions thus obtained clearly distinguish between bulk metallic glasses and alloys with marginal glass forming

ability (critical cooling rate ≥ 1000 K/s)⁴. To better illustrate the relative sizes, the atomic radii are normalized with respect to the alloy solvent atom.

In the following sections, normalized atom size distribution plots (ASDPs) for a number of metallic glasses will be presented. Metallic glass compositions were obtained from the literature⁵⁻⁸. The metallic radii are based on a recent critical analysis of values in the literature⁴. The values are not expected to be precise, since the actual atomic size will depend upon the local chemical and topological features. Nonetheless, a reasonable basis for comparison is expected.

3. Metal Glasses with Marginal Glass Forming Ability

3.1 Al alloys

Figure 1(a) shows ASDPs for amorphous Al alloys with rare earth (RE) and transition metal (TM) additions. The error bars indicate the concentration range over which amorphous alloys have been produced. Binary alloys are represented by the dashed line, and ternary alloys are indicated by the solid curve. Figure 1(b) provides ASDPs for amorphous Al alloys with early and late TM's.

Although a significant number of RE solutes can produce amorphous alloys, and although a range of concentrations have been successfully used, the ASDP shows that the RE additions represent a single component from a topological perspective. These elements have radii that are between 122–132% of Al. Similarly, TM solutes represent a single topological component, with atom radii 10–14% smaller than Al. Several of these atoms interact strongly with Al, and evidence for bond shortening exists⁹. Thus, the actual relative atomic size may be smaller than is represented in Figure 1(a).

ASDPs for amorphous Al alloys with early and late TM solutes display general features similar to Al-RE-TM glasses. Both larger and smaller atoms are present at significantly lower concentrations relative to Al. Nb and Ti atoms are nearly the same size as Al, and so the concentrations of these solutes have been added to Al. The inverse Hume-Rothery criterion is only barely satisfied. Al-(Ni or Cu)-(V or Mo) alloys are an exception, forming a concave upward ASDP with a single shallow minimum at an intermediate atom size.

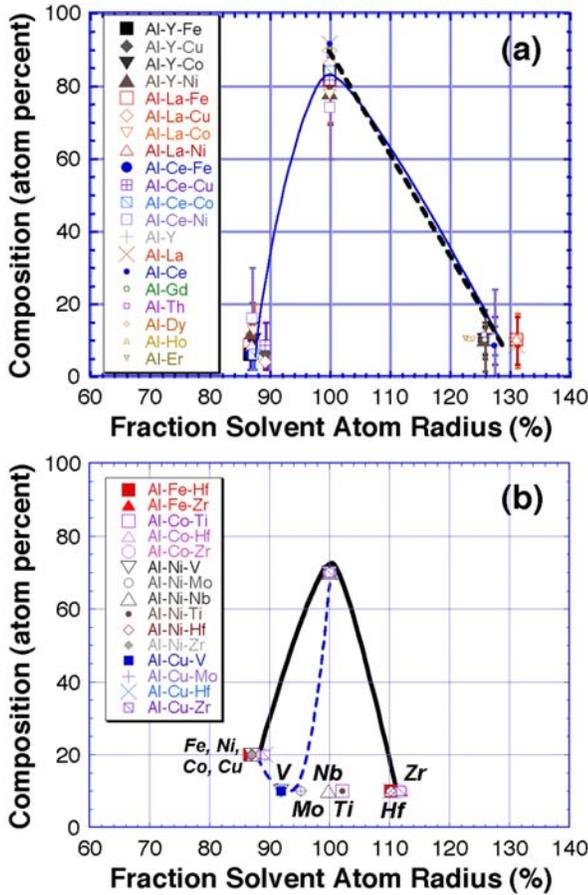


Figure 1 Normalized atom size distribution plots for amorphous Al with (a) rare earth and transition metal solutes, and (b) early and late transition metals. All radii have been normalized with respect to the radius of Al.

3.2 Mg alloys

Binary amorphous Mg alloys possess solutes either larger or smaller than Mg (Figure 2). The general features of ASDPs for ternary alloys are similar to those for amorphous Al. However, the larger solute atoms are generally not as large in a relative sense as for amorphous Al, while the smaller solutes tend to be significantly smaller than for Al.

3.3 Fe alloys

Amorphous Fe alloys display an ASDP (Figure 3) that is similar to those of amorphous Al and Mg alloys. Large atoms of 115–130% of the radius of Fe and smaller atoms of 88–93% of the radius of Fe define the main peak. Amorphous Fe alloys often contain one or more metalloid, such as B, C, or P. These solutes are much smaller than Fe, and so extend the ASDP asymmetrically. Metalloids are sometimes present at levels slightly higher than for solutes at about 90% of the radius of Fe, producing a shallow minimum at this value. Some amorphous Fe alloys contain only solute atoms that are smaller than Fe, as shown by the solid line in Figure 3.

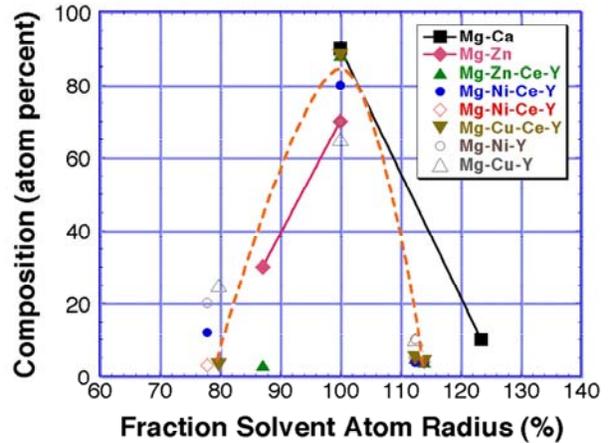


Figure 2 Normalized atom size distribution plots for amorphous Mg alloys. The solid lines represent binary alloys, and the remaining alloys are indicated by the dashed line. All radii have been normalized with respect to the radius of Mg.

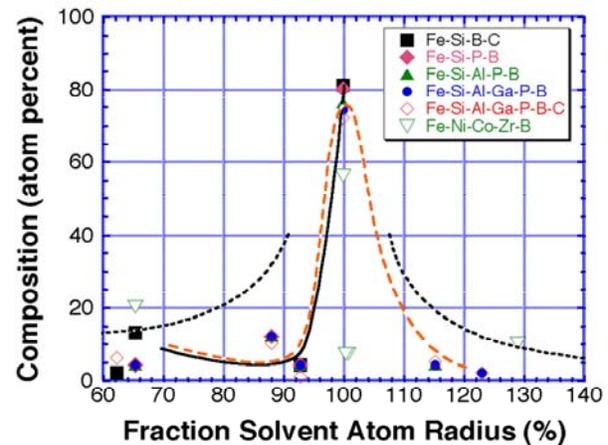


Figure 3 Normalized atom size distribution plots of amorphous Fe alloys. The solid line represents Fe-Si-B-(C,P) alloys, and the remaining alloys are indicated by the dashed line. The dotted lines represent the predicted minimum solute concentration, as discussed in Section 6. All radii have been normalized with respect to the radius of Fe.

3.4 Ni and Co alloys

Although not shown here, the general features of ASDPs for amorphous Ni and Co alloys are similar to those for amorphous Fe alloys. Both larger and smaller solute atoms produce a single concave downward peak centered at an intermediate atom, and metalloid solutes generate an asymmetric distribution at small atom sizes.

4. Bulk Metallic Glass Systems

4.1 Zr alloys

Bulk metallic glasses based on Zr exhibit ASDPs (Figure 4) that are markedly distinct from those discussed above. The solvent atom possesses the largest radius in all cases, and the smallest atom is generally the second most concentrated element. Atoms with radii intermediate to these values are generally at lower concentrations, producing a shallow minimum and a concave upward ASDP. The ASDPs of the Vitreloy alloys possess a notably smooth and consistent set of ASDPs. Be is the smallest element in Vitreloy 1 and 4, and Cu/Ni are the smallest atoms in Be-free Vitreloy alloys. Other Zr-based glasses

clearly follow the same trends, but show small deviations from this model.

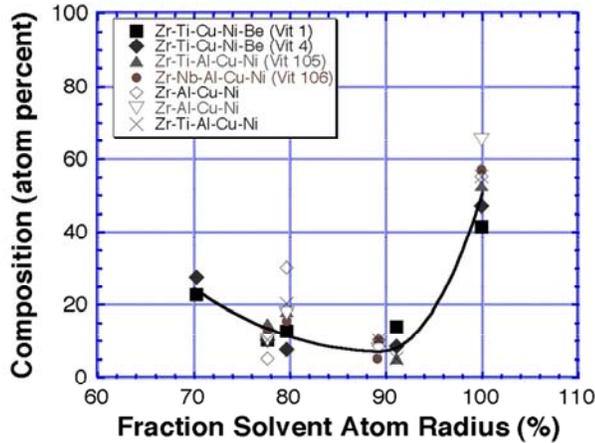


Figure 4 Normalized atom size distribution plot of amorphous Zr alloys. All radii have been normalized with respect to the radius of Zr.

4.2 Pd alloys

Most ASDPs of Pd alloys (Figure 5) are similar to those for Zr glasses. The solvent is always the largest atom, and a single concave upward ASDP is observed. Pd-Ni-P displays an ASDP that is essentially a straight line, where the element concentration decreases linearly with decreasing atom size.

4.3 Lanthanide alloys

Bulk metallic glasses based on Nd and Y (Figure 5) show an ASDP similar to that for Zr bulk glasses, with a single shallow minimum and a minimum atom radius of 70–75% of the solvent. Metallic glasses based on La and Sm display an ASDP similar to that for Pd-Ni-P, with a nearly linear decrease in concentration for smaller atoms.

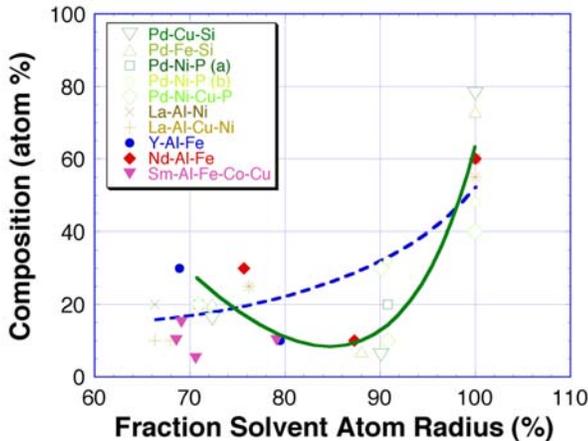


Figure 5 Normalized atom size distribution plots of amorphous alloys based on Pd and several rare earth elements. All radii have been normalized with respect to the radius of the respective base elements. The dashed line represents alloys based on La and the last two Pd alloys. The solid line represents the remaining alloys.

5. Oxide Glasses

ASDPs of several common oxide glasses, based on ionic radii of the constituent atoms, show a strong resemblance to those for bulk metallic glasses (Figure 6). The primary feature is a broad, concave upward profile, and the largest atoms are those with the highest molar

concentration. A smaller second peak, concave downward, is evident at the smallest atom sizes for Vycor, Pyrex, and borosilicate glass, as a result of B additions. Although this feature is not observed in metallic glasses, amorphous Fe alloys may exhibit a tendency toward this topology (Figure 3), and Zr-based bulk metallic glasses without Be exhibit a similar profile. The range in atom sizes is very broad for oxide glasses, and extends to 18% of the anion radius, and to less than 10% in glasses containing B.

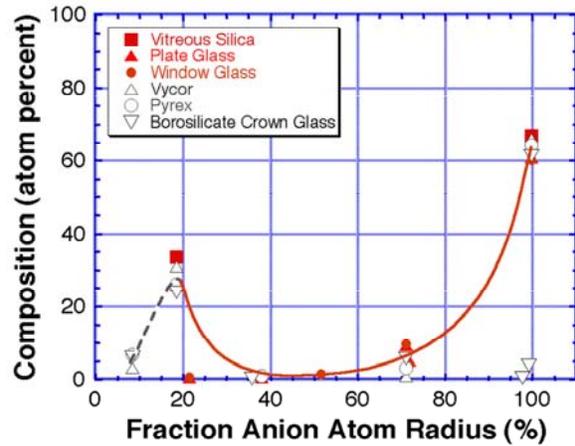


Figure 6 Normalized atom size distribution plot of common oxide glasses. All radii have been normalized with respect to the radius of the oxygen anions.

6. Discussion

Metallic glasses with marginal glass forming ability typically possess both larger and smaller solute elements relative to the solvent. The larger atoms range from 110–130% of the solvent radius and the smaller atoms are often 80–92% of the solvent radius. Thus, metallic glasses typically have at least one solute that is outside a bound of $\pm 12\%$ of the solvent radius. Nearly all amorphous metals with marginal glass forming ability are represented by an ASDP with a single concave downward peak at the intermediate atom radius of the solvent element. A slight asymmetry to this peak is often observed, as for Al–RE–TM, Mg, and Co glasses. The presence of metalloid atoms produces a strong asymmetry of the ASDP to values of normalized atomic radius of about 65%.

The characteristic shape of the ASDP profile for marginal glass forming metals suggests a common underlying topology. It is therefore suggested that a single structural model may represent most metallic glasses with marginal glass forming ability. Further, these observations strengthen the proposal that topology is the dominant factor in the formation of metallic glasses. For example, both very strong chemical interactions (Al–Ni or Al–Fe) and rather weak interactions (Al–Cu) are provided in a single family of alloys, but all form metallic glasses over nearly identical composition ranges with nearly identical topologies, as shown by the ASDPs.

The solvent is always the largest atom in bulk metallic glasses. The next highest concentration generally occurs for the smallest atom. Atoms of intermediate size often have the lowest concentrations. Thus, the ASDPs for bulk metallic glasses are typically characterized by a single concave upward peak. As an exception, some Pd–Ni–P and Sm-based glasses display atomic concentrations that

decrease monotonically with decreasing radius. In addition, a small number of metallic glasses with critical cooling rates below 1000 K/s also show a single, broad, concave upward plot⁴⁾. Nevertheless, ASDPs of bulk metallic glasses typically provide a clear distinction from metallic glasses with marginal glass forming ability.

A topological model for the destabilization of binary crystalline alloys has been proposed³⁾. Based on atomic strains introduced by solute atoms, the minimum solute concentration required to form an amorphous product is inversely related to the difference in atomic volume. The minimum solute concentration predicted from this model is illustrated by the dotted line in Figure 3. While good agreement is shown for many marginal glass forming metals, this model predicts a minimum solute concentration that decreases with increasing deviation from the size of the solvent atom. Therefore, this model does not predict the increase in solute concentration observed for small solutes in bulk metallic glasses⁴⁾.

A recent model properly represents ASDPs for bulk metallic glasses⁴⁾. From earlier work^{3,9-11)}, the amorphous state can be produced when the competing crystalline phase becomes destabilized. This earlier work emphasized substitutional solutes in the competing crystalline phase, and lattice strains and minimum concentrations were determined from this point of view. However, interstitial site occupancy becomes preferred in the competing crystalline solid solution as the solute atoms become increasingly smaller relative to the solvent. Solute atoms that are less than 81% of the solvent radius will produce a smaller elastic strain in an interstitial site than in a substitutional site¹²⁾. Further, interstitial atoms smaller than this critical size will produce *smaller* strains per solute atom, so that a larger concentration is required to destabilize the crystalline solid solution. This model thus provides a physical basis for an *increasing* critical solute concentration for atoms which are increasingly smaller than about 81% of the solvent radius. A more complete description of this model has recently been provided¹²⁾.

The ASDPs for oxide glasses exhibit a striking similarity to ASDPs of bulk metallic glasses. While earlier studies have concluded that a dense random packing model may be appropriate for metallic glasses^{13,14)}, these results have emphasized metal-metalloid glasses, which do not represent the topology of many of the alloys considered here. Further, evidence of chemical short- and medium-range order has been found¹⁵⁻¹⁷⁾, so that a cluster model for metallic glasses may be relevant. Such a model has recently been proposed for the atomic structure of marginal glass forming metals¹⁸⁾. However, additional studies will be required to explore the validity of this proposition.

The method illustrated here provides a prescriptive approach for the exploration of new bulk glass alloys. Once the desired solvent atom is selected, the type and composition of solute elements can be selected so as to reproduce a given ASDP. This approach thus provides a powerful tool for the exploration of complex, multicomponent bulk metallic glass alloys.

7. Concluding Remarks

A simple approach for visualizing topology in complex amorphous metals is provided. Amorphous metals

with marginal glass forming ability possess a solvent at an intermediate atomic radius, and both larger and smaller solute atoms are present at significantly lower concentrations. Thus, marginal glass forming metals are represented by an atom size distribution plot with a single concave downward peak. The common topology represented by similar atom size distribution plots suggests that a single structural model may represent most metallic glasses with marginal glass forming ability.

In bulk metallic glasses, the largest atom is the solvent, and the next most concentrated element is typically the smallest. Other elements exist at lower concentrations, so that a single, broad, concave upward atom size distribution plot is obtained. Thus, bulk metallic glasses display a topology that is clearly distinct from marginal glass forming metals. A model which accurately reproduces the observed topology of bulk metallic glasses has been outlined here, which considers both interstitial and substitutional site occupancies for solute atoms in the competing crystalline solid solution phase. The current topological description provides a prescriptive approach for the exploration of new bulk metallic glass alloys.

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