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Design of Cu₈Zr₅-based bulk metallic glasses

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Basic polyhedral clusters have been derived from intermetallic compounds at near-eutectic composition by considering a dense packing and random arrangement of atoms at shell sites. Using such building units, bulk metallic glasses can be formed. This strategy was verified in the Cu–Zr binary system, where we have demonstrated the existence of Cu₈Zr₅icosahedral clusters in Cu₆₃.₇Zr₃₈.₃, Cu₆₄Zr₃₅.₅, and Cu₆₄.₄Zr₃₅.₅ amorphous alloys. Furthermore, ternary bulk metallic glasses can be developed by doping the basic Cu–Zr alloy with a minority element. This hypothesis was confirmed in systems (Cu₀.₆₁₈Zr₀.₃₈₂)(₁₋ₓ)NBₓ, where x = 1.₅ and ₂.₅ at. %, and (Cu₀.₆₁₈Zr₀.₃₈₂)₀₈Sn₂. The present results may open a route to prepare amorphous alloys with improved glass forming ability. © 2006 American Institute of Physics. [DOI: 10.1063/1.2213020]

Since the discovery of glassy systems, based on multicomponent systems,35 and recently, complex compositions have been considered necessary in order to inhibit crystallization of the liquid phase during cooling of the melt. However, simpler systems should be of great interest, fundamentally as well as technologically, since they would facilitate the atomic-structure determination for a given BMG, which has been a long-standing problem.1,2,4,12–24 Until now, complex compositions have been considered necessary in order to inhibit crystallization of the liquid phase during cooling of the melt. However, simpler systems should be of great interest, fundamentally as well as technologically, since they would facilitate the atomic-structure determination for a given BMG, which has been a long-standing problem.1,2,4,12–24 Originally, the dense-random-packed model was used to describe metallic glasses.25 This model is based on the assumption that the glass consists of a random arrangement of spherical atoms (hard spheres) of each element. However, it has also been pointed out that localized, directional chemical bonding and the formation of groups of atoms are relevant factors to theories of glass formation and stability.26 The local structure is well defined and similar to that of the crystalline form of the material. Recently, a topological model for metallic glass formation was proposed.27,28 According to that model, a solute occupying either substitutional or interstitial sites in the host lattice can destabilize the lattice by producing a critical internal strain. Besides the structural models mentioned above, several criteria for structural stability of a BMG have been suggested: (1) large value of the reduced glass transition temperature Tₛ/Tₓ, where Tₓ is the glass transition temperature and Tₛ is the liquidus temperature;29 (2) three empirical rules for a large supercooled liquid region: (a) multicomponent system, (b) significant differences in atomic size, and (c) negative heats of mixing among the main constituent atoms;1,3 (3) high gamma value, γ = T₄/(Tₓ + T₄), where T₄ is crystallization temperature;30 (4) interaction between the Fermi surface and the Brillouin zone in a nearly-free-electron model;31 (5) the critical concentration of a solute element required for amorphization decreases, reaches a minimum, and then increases with increasing ratio between the size of the solute and the solvent atoms;27,32,33 (6) there is an optimum ratio R” between the size of the solute atom and the average size of the surrounding solvent atoms for dense packing.27,34 In spite of the criteria mentioned above, the design of alloys with a high glass forming ability (GFA) remains to a large extent unpredictable due to lack of understanding of the local atomic structure. Although polyhedral clusters have been revealed in some metallic glasses,2,12–20 more efforts are still needed to uncover the atomic structure of a given BMG and to predict compositions with high GFA. In this letter, we report a method of designing appropriate polyhedral units to simulate the local atomic structure of binary Cu–Zr amorphous alloys. Our method predicts the formation of Cu₈Zr₅-based BMGs, in which the polyhedral units are indeed experimentally detected.

We have chosen the Cu–Zr binary system as a prototype because of three reasons: (1) it has a wide composition range forming metallic glasses, (2) BMGs can be formed in this system,35 and (3) its phase diagram is known. There are several intermetallic compounds, Cu₅Zr, Cu₅Zr₄, Cu₆Zr₃, Cu₁₀Zr₇, CuZr, and CuZr₂. The Wyckoff sites of Cu and Zr in these compounds are listed in Pearson’s handbook.36 Taking
that the average radius of the shell atoms is Cu27.6Zr72.4. As it turns out, three of our selected clusters, Cu61.8Zr38.2, Cu56Zr44, Cu45.7Zr54.3, and Cu45Zr55, are very close to eutectic compositions. BMG rods have recently been synthesized with compositions Cu61.8Zr38.2, Cu64Zr36, and Cu64.5Zr35.5, as shown below, extended x-ray absorption fine structure (EXAFS) measurements at photon energies corresponding to the Cu and Zr K absorption edges were performed at the HASYLAB synchrotron radiation source (beamline X1) in transmission. Standard data evaluation was carried out using the VIPER and WINXAS programs. In the fitting process, the FEFF-8 code was used to calculate scattering amplitudes and phases.

In Fig. 2 we show Cu and Zr K-edge EXAFS spectra for as-spun Cu61.8Zr38.2, Cu64Zr36, and Cu64.5Zr35.5 metallic glasses. A Cu4Zr4icosahedral cluster with a Cu atom at the center position and a CuZr5icosahedral cluster with a Zr atom at the center (Fig. 3) were designed as models for the fits to the experimental Cu and Zr K-edge spectra, respectively. Cu–Zr and Zr–Cu bond distances were forced to be equal during the fitting. As shown in Fig. 2, the observed Cu and Zr K-edge spectra in k and r spaces are well described by the fitting curves. The EXAFS fitting parameters are given in Table I. It is clear that the Cu center atom is indeed surrounded by about five Zr and seven Cu atoms, forming a Cu4Zr5icosahedral cluster, although the Cu4Zr4 model was used as the initial input. Slight differences between the Cu–Cu and Cu–Zr bond lengths indicate a distorted icosahedral cluster with a Cu atom at the center site. On the other hand, the Zr atom is found to have only about four Cu atoms.

In order to select appropriate clusters as basic units for the formulation of BMGs, three factors have been considered: (1) dense packing, (2) random arrangement of atoms at shell sites, and (3) near-eutectic composition. Dense packing is an essential criterion for the atomic structure of BMGs. Suppose that the radius of the center atom in a cluster is \( r_0 \) and that the average radius of the shell atoms is \( r_1 \), according to Miracle and Sanders, the ratio \( R = r_0/r_1 \) should be within 10% from the optimum value \( R^* \) for close packing. Clusters with less than ten atoms were not considered in the present work since \( r_{euc}/r_{Zr} = 0.79 \), which is 10% larger than the optimum value \( R^* = 0.71 \) for a solute atom surrounded by nine solvent atoms. Based on a random arrangement of atoms, the concentration of atoms of the same kind on shell sites might lead to instability of the cluster.

Finally, 11 clusters out of a total of 35 were selected for further study. There are four eutectic points of interest in the present work: Cu61Zr38, Cu56Zr44, Cu45Zr54, and Cu27.6Zr72.4. As it turns out, three of our selected clusters, namely, Cu6Zr5, Cu5Zr5, Cu4Zr5, Cu3Zr5, and Cu2Zr5, are very close to eutectic compositions. BMG rods have recently been synthesized with compositions Cu64Zr35.5 and Cu64Zr36, which have a thickness of 2 mm, Cu9Zr45 (with a diameter of 2 mm), Cu8Zr45 (with a diameter of 1 mm), and Cu7Zr45 (with a diameter of 1.5 mm). This fact strongly suggests that polyhedral clusters are the main building units of Cu–Zr BMGs with near-eutectic compositions. Two key questions will be addressed in the present work: (1) Do polyhedral clusters exist in BMGs based on the Cu–Zr system? (2) If yes, will it be possible to predict other cluster-based BMGs, in which the value of \( R \) is made close to \( R^* \) by alloying with a minority element? To answer these questions, three compositions, Cu61Zr38, Cu64Zr36, and Cu64.5Zr35.5, were selected. As will be shown below, extended x-ray absorption fine structure (EXAFS) measurements at the Cu and Zr K absorption edges indicate that the metallic glasses indeed contain Cu4Zr5icosahedral clusters. Moreover, BMG rods with a diameter of 3 mm could be produced with a minor addition of Nb and Sn, making \( R \) closer to \( R^* \). Cu–Zr ingots with compositions Cu61Zr38, Cu64Zr36, and Cu64.5Zr35.5 were prepared by arc melting of high-purity metals (99.8%–99.9%).

FIG. 1. X-ray diffraction patterns for the as-spun Cu–Zr metallic glasses and as-cast 3 mm (Cu61.8Zr38.2)97.5Nb2.5 and (Cu64.5Zr35.5)98Sn2 BMG rods.
as nearest neighbors, while the Zr–Zr coordination number is about 8. The results above imply that Cu atoms are situated at the center sites of Cu\(_{8}\)Zr\(_{5}\) icosahedral clusters, while the Zr atoms are located at the shell sites. This is understandable, since the radius of the Cu atom (1.28 Å) is less than the radius of the Zr atom (1.61 Å). Various ways of combining Cu-centered Cu\(_{8}\)Zr\(_{5}\) icosahedral clusters may result in slight differences in the composition of the alloy. Thus, our results strongly support the hypothesis above that the atomic structure of Cu\(_{61.8}\)Zr\(_{38.2}\), Cu\(_{64}\)Zr\(_{36}\), and Cu\(_{64}\)Zr\(_{35.5}\) amorphous alloys is mainly made up of Cu\(_{8}\)Zr\(_{5}\) icosahedral clusters.

Adding a third element, having a larger atomic radius than Cu, at shell sites of the Cu\(_{8}\)Zr\(_{5}\) icosahedral clusters should result in a higher R value and thereby a higher GFA. Consequently, one would expect a whole class of Cu\(_{64}\)Zr\(_{35}\)-based BMGs according to our model. In order to test this hypothesis, we have selected Nb (atomic radius of 1.47 Å) and Sn (atomic radius of 1.51 Å) as the minority elements and prepared amorphous alloys according to the formulas (Cu\(_{61.8}\)Zr\(_{38.2}\)Sn\(_{8}\)Nb\(_{1}\)), (Cu\(_{61.8}\)Zr\(_{38.2}\)Sn\(_{2}\)Nb\(_{2}\)), and (Cu\(_{61.8}\)Zr\(_{38.2}\)Sn\(_{2}\)Nb\(_{3}\)). It is found that BMG rods with a diameter of 3 mm could indeed be produced (Fig. 1) by copper mold.

In conclusion, basic polyhedral clusters have been derived for intermetallic compounds at near-eutectic composition by considering a dense packing and random arrangement of atoms at shell sites. Using such building units, BMGs can be formed. This strategy was verified in the Cu–Zr binary system, where we have demonstrated the existence of Cu\(_{8}\)Zr\(_{5}\) icosahedral clusters in Cu\(_{61.8}\)Zr\(_{38.2}\), Cu\(_{64}\)Zr\(_{36}\), and Cu\(_{64}\)Zr\(_{35.5}\) amorphous alloys. Furthermore, ternary BMGs can be developed by doping the basic Cu–Zr alloy with a minority element. This hypothesis was confirmed in systems (Cu\(_{x}\)Zr\(_{38.2}\)Sn\(_{8}\)Nb\(_{1}\)), where x = 1.5 and 2.5 at. %, and (Cu\(_{x}\)Zr\(_{38.2}\)Sn\(_{2}\)Nb\(_{3}\)). The present results may open a route to prepare amorphous alloys with improved GFA.

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\]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Atom at center</th>
<th>Cu</th>
<th>Zr</th>
<th>Cu</th>
<th>Zr</th>
<th>Cu</th>
<th>Zr</th>
<th>Cu</th>
<th>Zr</th>
<th>Cu</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(<em>{61.8})Zr(</em>{38.2})</td>
<td>Cu</td>
<td>2.53(2)</td>
<td>2.68(7)</td>
<td>5(2)</td>
<td>2(2)</td>
<td>9(2)</td>
<td>2(2)</td>
<td>18(1)</td>
<td>18(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(<em>{64})Zr(</em>{36})</td>
<td>Zr</td>
<td>2.68(7)</td>
<td>3.01(3)</td>
<td>4(2)</td>
<td>8(2)</td>
<td>9(1)</td>
<td>29(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(<em>{64})Zr(</em>{35.5})</td>
<td>Cu</td>
<td>2.53(2)</td>
<td>2.69(7)</td>
<td>5(2)</td>
<td>3(2)</td>
<td>36(2)</td>
<td>12(1)</td>
<td></td>
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<tr>
<td>Cu(<em>{64})Zr(</em>{35.5})</td>
<td>Zr</td>
<td>2.69(7)</td>
<td>3.01(3)</td>
<td>4(2)</td>
<td>8(2)</td>
<td>9(1)</td>
<td>28(2)</td>
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\[ \text{Cu}_{0.618}\text{Zr}_{0.382} \text{ and Cu}_{2.69} \text{ Zr}_{3} \text{ atomic radius of 1.28 Å, and Sn (atomic radius of 1.51 Å) as the minority elements and prepared amorphous alloys according to the formulas (Cu}_{0.618}\text{Zr}_{38.2}\text{Sn}_{8}\text{Nb}_{1}, (Cu}_{0.618}\text{Zr}_{38.2}\text{Sn}_{2}\text{Nb}_{2}, and (Cu}_{0.618}\text{Zr}_{38.2}\text{Sn}_{2}\text{Nb}_{3}. It is found that BMG rods with a diameter of 3 mm could indeed be produced (Fig. 1) by copper mold.}
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