

Atomic packing density and its influence on the properties of Cu–Zr amorphous alloys

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This study examined the structural factors that determine the properties of amorphous alloys. The properties of amorphous alloys were found to be intimately related to the atomic packing density, characterized by short-range ordered (SRO) atomic clusters and free volume. With increasing packing density, the modulus and strength increased, while the plasticity decreased. We discuss the fundamental microstructural aspects that influence several representative properties of amorphous alloys in terms of the packing state characterized by fractions of SRO atomic clusters.

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The physical and mechanical properties of crystalline metals are explained by their inherent crystal structures and defects. However, the inherent structures and defects of amorphous alloys are not clearly defined, making it difficult to understand the origin of their properties.

Recently, several pioneering works have attempted to define the atomic-scale structures and defects of amorphous alloys. Spaepen [1] and Argon and Kuo [2], in their free volume model, suggested that the free volume can be regarded as a structural defect in amorphous alloys and the origin of the local plastic deformation. Miracle [3], in his dense cluster-packing model, elucidated for the first time that amorphous alloys consist of various types of short-range ordered (SRO) atomic clusters. Sheng et al. [4] reported that these SRO atomic clusters affect the atomic packing state, which in turn may influence the properties. Although the values of these findings are significant in revealing the existence of various types of SRO structures that comprise amorphous alloys, there is little understanding of the connection between the macroscopic properties of amorphous alloys and their quantifiable structural characteristics.

Many earlier studies implicitly suggested that the properties of amorphous alloys are intimately related

to the free volume fraction, i.e. the packing density [5–8]. Fundamental questions arise as to what determines the packing density and why the properties are affected by it. In order to explore the origin of the properties of amorphous alloys from this perspective, it is essential to define the SRO atomic structures and correlate them with the atomic packing density and the properties of the alloys. The present article addresses some fundamental issues on the origin of the properties of amorphous alloys by correlating several macroscopic properties, atomic packing density and SRO structures of amorphous alloys using the combined techniques of comprehensive experiments and three-dimensional molecular dynamics (3-D MD) simulations.

Considering that most amorphous alloys consist of more than three elements, identification of the atomic packing state characterized by the SRO structures is not feasible. Fortunately, amorphous alloys, which can be synthesized in a bulk form, have recently been reported in some binary systems [9,10]. The Cu–Zr binary system, in particular, can be synthesized in a 1 mm diameter bulk form over a wide compositional range (50–66 at.% Cu) [11]. The most important advantage of this binary system is probably the facility to model the packing state and to quantify the packing density. This is because the alloys are binary and classified as a metal–metal type with a topological short-range order [12].

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the earlier reported data [18,19] superimposed in Figure 2, this general tendency not only confirms that the current data is reliable and reproducible, but also validates that the maximum structural stability is attained at $\text{Cu}_{65}\text{Zr}_{35}$. Therefore, the fact that the properties of the Cu–Zr alloys fluctuate from their maximum or minimum levels at $\text{Cu}_{65}\text{Zr}_{35}$ is considered to be due to their relative degree of the structural stability. As such, in order to understand the physics underlying the composition dependence of the properties of amorphous alloys, it is necessary to identify the structural factors determining their structural stability.

Recent studies showed that the structural stability of amorphous alloys is closely related to the characteristics of the SRO atomic clusters [20], which in turn determine their packing state. In this regard, the atomic packing density is considered to be an important factor affecting the properties of amorphous alloys. Therefore, the atomic packing density was experimentally measured using steel balls of two different sizes to examine the role it plays in the properties of amorphous alloys. Figure 3a shows the variation of atomic packing density with composition, which can be treated as variation in the global packing density of the Cu–Zr binary alloys. With increasing Cu content, the atomic packing density increased up to a maximum level at $\text{Cu}_{65}\text{Zr}_{35}$ and then decreased thereafter. Interestingly, the tendency observed from the packing density vs. composition relationship was very similar to that of the properties vs. composition relationship.

Since the properties of amorphous alloys are very susceptible to the amount of free volume [1,2,5–8], the composition dependence of the atomic packing density and the properties was again tested by correlating free volume evaluated based on MD simulations. Parameters such as the Rosato–Guillope–Legrand (RGL)-type potential [21] were recently developed to realistically model

Cu–Zr amorphous alloys. However, for simplicity and convenience, we used a simple pair potential based on the Lennard-Jones 4–8 potential as an attempt to probe a possible composition dependence of free volume and to depict the packing state characterized by the SRO structures of the hypothetical model alloys.

There are various methods by which one can define free volume. The definition of free volume sometimes refers to the fraction of matter having a lower atomic coordination than that of a reference material that has dense packing. This study, however, assessed the relative free volume by calculating the volume difference (ΔV), which is obtained by the ratio of the volume increment with respect to the corresponding crystalline structures as defined by

$$\Delta V = (V_{\text{amo}} - V_{\text{cry}})/V_{\text{cry}}, \quad (1)$$

where V_{amo} and V_{cry} represent the volume of the amorphous and crystalline phases determined from MD, respectively. V_{cry} was estimated based on the atomic volumes of one-component single-crystalline states of Cu and Zr, by taking the atomic composition into account. Therefore, ΔV is the volume increment associated with the crystalline-to-amorphous transformation of Cu–Zr alloys, suggesting that alloys with large values in ΔV roughly correspond to those with large amount of free volume.

Figure 3b shows the composition dependence of the volume change (ΔV) associated with the crystalline-to-amorphous transformation of Cu–Zr alloys. The value of ΔV in the Cu–Zr binary system was a minimum at $\text{Cu}_{70}\text{Zr}_{30}$, while it increased when the Cu content deviated from 70%. When comparing Figure 3b with Figure 3a, the composition corresponding to the minimum ΔV was close to that corresponding to the maximum atomic packing density. Despite the slight difference between the two data, the results strongly support the existence of inverse proportionality between atomic packing density and free volume.

A comparison of the properties (Figs. 1 and 2) and the packing density (Fig. 3a) seems to suggest that there may be a correlation between the properties and the packing density and SRO structures. This finding reflects the fact that densely packed alloys have higher strength and lower plastic strain, and vice versa. Therefore, the packing density, which determines the structural stability, is believed to be a dominant factor influencing the properties of amorphous alloys. Accordingly, this study identifies the atomic-scale structures of amorphous alloys characterized by SRO atomic clusters which determine both the packing density and structural stability.

The variations in the microstructures as characterized by the SRO atomic clusters were investigated as a function of the composition, in order to examine the atomic-scale interpretation of the packing density and its role in several representative properties of Cu–Zr amorphous alloys. Identifications of the SRO atomic clusters and their effect on the packing state were made based on Voronoi analysis [22]. It was found from 3-D MD simulations that each amorphous alloy consists of more than 100 different types of Voronoi polyhedra (data not shown). Among these polyhedra found in $\text{Cu}_x\text{Zr}_{100-x}$, five major polyhedra were selected and their

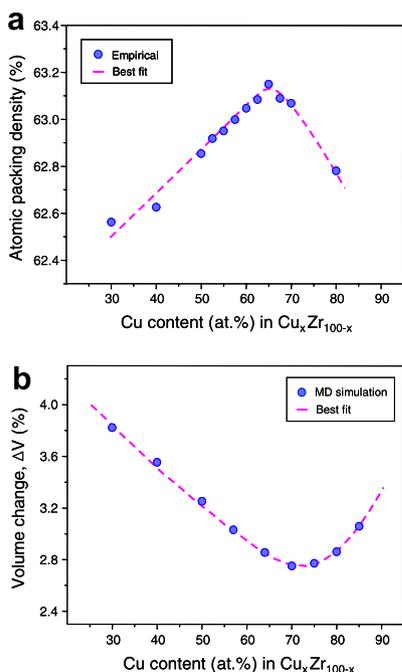


Figure 3. Variations in (a) the packing density and (b) the volume change, i.e. relative free volume measured as a function of the composition in the $\text{Cu}_x\text{Zr}_{100-x}$ alloys.

fractions plotted as a function of the alloy composition (see Fig. 4a). Although an icosahedron, i.e. (0, 0, 12, 0), is the dominant SRO structure, it is not feasible to discretely describe the general microstructures of amorphous alloys in terms of polyhedra, due to the abundance of the polyhedron types and their structural complexity. It is noted, however, that every polyhedron is constructed from five different elemental forms of 2-D atomic clusters, namely the so-called Voronoi polygons, i.e. triangle, tetragon, pentagon, hexagon and heptagon. Therefore, for the analyses of the SRO structures and their role in determining the properties of amorphous alloys it would be convenient if the structural features of amorphous alloys were described in terms of the Voronoi polygons. Figure 4b shows the variations in the fractions of the Voronoi polygons with composition. With increasing Cu content, the fraction of pentagons continuously increased up to a maximum level (at $\text{Cu}_{70}\text{Zr}_{30}$) and then decreased thereafter. On the other hand, the fractions of the other non-pentagonal polygons showed the opposite tendency to that of the pentagon. This suggests that alloys with different compositions have different packing states, i.e. different microstructures, which in turn would result in different thermomechanical properties as well as GFA.

It is noted from Figures 3a and 4b that the composition dependence of the pentagon is proportional to the packing density, while the other non-pentagonal polygons have inverse proportionality. This finding provides a clue to the observed relationship between the global packing density and the properties of amorphous alloys. It is known that the pentagon has a fivefold symmetry and often has a quasi-crystalline structure, such as an icosahedron, exhibiting the densest packing together with the highest shear resistance. In contrast, the tetragon and the hexagon have translational symmetry and

often form an ordinary crystalline structure. Therefore, the highest strength, modulus, hardness, GFA, along with the lowest plasticity exhibited by $\text{Cu}_{65}\text{Zr}_{35}$, are believed to originate from the densely packed nature associated with the enrichment of the pentagonal clusters or icosahedron. On the other hand, both the highest plasticity and the lowest strength of $\text{Cu}_{50}\text{Zr}_{50}$ are considered to stem from the loosely packed nature associated with the enrichment of the non-pentagonal polygons or loosely packed polyhedra.

In view of the results obtained so far, we consider that the fundamental structural aspect affecting the properties of amorphous alloys viewed on the atomic-scale is the atomic packing state, which was characterized in the present work by the fractions of the various SRO atomic clusters defined by Voronoi polygons. However, better structural modeling efforts are needed to confirm the structure/packing state vs. property relationship proposed here for Cu–Zr bulk amorphous alloys.

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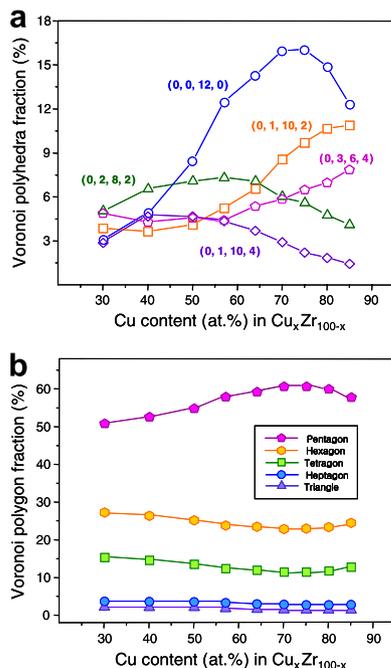


Figure 4. Variations in the fraction of (a) the Voronoi polyhedra and (b) Voronoi polygons measured as a function of the composition in $\text{Cu}_x\text{Zr}_{100-x}$.

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