Atomic packing in $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ bulk metallic glass

X. D. Wang,^{1,a)} H. B. Lou,¹ S. G. Wang,² J. Xu,² and J. Z. Jiang^{1,b)}

¹International Center for New-Structured Materials (ICNSM) and Laboratory of New-Structured Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

²Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China

(Received 5 November 2010; accepted 27 December 2010; published online 19 January 2011)

Atomic configurations of an $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ bulk metallic glass and its molten state have been investigated. The supercooled liquid and melt have a volume expansion coefficient only two times as large as that below glass transition temperature. Although the dominant polyhedra are 12- and 13-coordinated, the melt has slightly more polyhedra of low coordinated and less of high coordinated than in the as-cast. By Gd addition, half-octahedra with more volume accommodated are likely formed in the polyhedra, causing the local atomic environments of Mg in the melt quite different from the competing crystalline phase, thereby suppressing crystallization upon quenching. © 2011 American Institute of Physics. [doi:10.1063/1.3544049]

Magnesium (Mg)-based alloys have recently drawn more attention due to their low cost, low specific weight, and high strength. The first Mg-based bulk metallic glass (BMG) is $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ discovered in 1991 with the critical size of 4 mm in diameter.¹ From structural simulation,² the glass forming in this alloy was ascribed to the strong interaction between Cu and Y. Zheng *et al.*³ later reported a Mg-based BMG former with the nominal composition $\text{Mg}_{59.5}\text{Cu}_{22.9}\text{Ag}_{6.6}\text{Gd}_{11}$, which could be cast into glassy rods of 27 mm diameter. The compositions of such high glass formers were optimized by using the three-dimensional (3D) pinpointing approach.⁴ However, origins of such high glass-forming ability (GFA) in Mg alloys from structural perspective have not been well understood. Since the metallic glasses are frozen from the liquids bypassing the crystallization, the GFA of the alloy correlates with atomic structure at the liquid state. Due to easy oxidation at high temperature and difficulties in structural measurement, little experimental data of liquid structure for multicomponent alloys have ever been reported.^{5,6}

As a simple system, $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG is selected as a prototype, which is a currently available ternary Mg alloy with the strongest GFA, to form the as-cast glassy rod of 12 mm diameter.⁷ Understanding the structure of $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG could provide insight into the characteristics of atomic packing in the Mg-TM-RE (TM=transition metals and RE=rare earth) BMG family. By combining the synchrotron radiation-based x-ray diffraction (XRD) and x-ray absorption fine structure (XAFS) techniques with reverse Monte Carlo⁸ (RMC) computational method, 3D atomic configuration of the $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG is established, and the particular structural feature of $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG is discussed.

Rod-shaped $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ samples of 6 mm diameter were fabricated by copper mold casting.⁷ The amorphous nature was ascertained by an x-ray diffractometer (Philips X'Pert) with Cu K α radiation and a differential scanning calorimeter (DSC, Netzsch DSC 404c). The high energy

x-ray diffraction was measured on the BW5 station by using synchrotron radiation with wavelength $\lambda=0.124$ Å at HASYLAB/DESY, Hamburg. The samples were smashed and ground into fine powders and then transferred into a capillary of 2 mm diameter. After being pumped, the vacuum in the capillary could reach about 0.01 Pa. Upon heating, the diffraction patterns were automatically collected from 323 K, each with 5 s exposure time and 20 K increment in between. The scattering intensity $I(q)$ (versus scattering vector) was extracted by using the software package FIT2D.⁹ From $I(q)$, the structure factor $S(q)$ and pair distribution function (PDF) $G(r)$ could be obtained by using PDFGETX2.¹⁰ XAFS spectra at Cu K-edge (8979 eV) and Gd L3-edge (7243 eV) were collected in a transmission mode at the beam line C1 of HASYLAB. Standard data analysis was carried out by VIPER program.¹¹

Figure 1 shows the DSC trace of $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG at a heating rate of 20 K/min. The inset of Fig. 1 illustrates the peak shift to the low q values and intensity decreases in $I(q)$ curves with increasing the temperature. Since the first maximum in $I(q)$ has been confirmed to be inversely proportional to the average of the nearest distance between atoms in the real space,^{5,6,12} the thermal volume expansion coefficient α_v could be evaluated by using XRD data in terms of Eq. (1),

FIG. 1. (Color online) Volume expansion of $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG from the as-cast to the supercooled liquid and the melt evaluated by using the first maximum shift in $I(q)$. DSC trace shows the temperature change. Inset gives the first maximum shift in $I(q)$ upon temperature rising.

^{a)} Author to whom the correspondence should be addressed. Electronic mail: wangxd@zju.edu.cn.

^{b)} Electronic mail: jiangjz@zju.edu.cn.

FIG. 2. (Color online) Comparison in (a) $S(q)$ and (b) $g(r)$ of experimental data (solid line) with RMC simulated data (open circle) for $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG at 298 and 723 K, respectively. Inset of (a) is a cubic box containing 20 000 atoms of Mg, Cu, and Gd atoms obtained after simulation convergence. Inset of (b) shows the changes in partial $g(r)$ of different atomic pairs at 298 and 723 K.

$$\alpha_v = \frac{(1/q)^3 - (1/q_0)^3}{(1/q_0)^3} = (q_0/q)^3 - 1, \quad (1)$$

in which q_0 and q are the peak positions for the first scattering maxima in $I(q)$ at 298 K and a studied temperature. We found that the thermal volume expansion coefficient for this glass below glass transition temperature T_g is about $7.63 \times 10^{-5} \text{ K}^{-1}$; however, in the supercooled liquid region and above liquidus temperature it is about $1.41 \times 10^{-4} \text{ K}^{-1}$, showing a nearly twice relationship between them. Unlike La-based BMG,⁵ the expansion coefficient of the melt is nearly five times as large as that below T_g . Thus, it is most likely that the atomic packing in the melt is somewhat similar to in the as-cast $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG.

The density of the as-cast sample measured at 298 K is about 4.03 g/cm^3 by Archimedeian method. For the liquid melt at 723 K, it was evaluated to be about 3.87 g/cm^3 by using the first maximum shift in $I(q)$ to estimate the volume change. Figures 2(a) and 2(b) show good agreement between the experimental structure factor $S(q)$, pair correlation function $g(r)$, and RMC calculated ones. Such agreement makes it possible to construct the 3D atomic packing of $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG. The inset of Fig. 2(a) displays the final atomic configuration at 298 K in a cubic box with an edge length of 74.33 Å , containing 20 000 atoms of Mg, Cu, and Gd. On the $S(q)$ curve for the as-cast sample at 298 K, a prepeak could be observed before the first maximum, which was also reported in most Al-based metallic glasses.^{13,14} However, the intensity of this prepeak becomes weak after

FIG. 3. (a) Total fraction changes of major polyhedra and (b) fraction changes for those centered by Mg, Cu, and Gd atoms, in $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG at 298 and 723 K.

melting at 723 K. From the partial $S(q)$ of simulation, it is found that the contribution to this prepeak is mainly from the related scattering of Gd-Gd pairs. On the pair correlation function $g(r)$ as shown in Fig. 2(b), the shoulders on the first and the second peaks at 298 K become undistinguishable when the temperature was heated to 723 K. The inset of Fig. 2(b) shows the distribution of partial atomic pairs in the as-cast (298 K) and the molten (723 K) states. Compared with the as-cast sample, the number of Cu-Cu pairs has a trend to increase in the melt. Also, the expansion becomes more distinctive between big atoms, like Mg-Mg, Mg-Gd, and Gd-Gd, leading to the first peak in $g(r)$ to be broad.

Using Voronoi tessellation method,¹⁵ the coordination number (CN) and polyhedron type around each atom can be analyzed. The cutoff distance of 4.0 Å was selected according to the range of the first peak on the total $g(r)$ curve. Figure 3(a) shows the distribution of major CNs in the nearest neighbor of $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG at 298 and 723 K. 12- and 13-coordinated polyhedra are dominant in both states, being nearly 60% of the total, and those lower than 2.0% are not shown. In the 723 K liquid melt, the numbers of 13-, 14-, and 15-coordinated polyhedra decrease, while the numbers of 10-, 11-, and 12-coordinated ones increase compared to the 298 K as-cast sample. Figure 3(b) demonstrates the distribution of CNs around atoms of each component. Note that around Mg atoms are mainly 11, 12, 13, and 14 coordinates. Dominant polyhedra are 12- and 13-coordinated. Around Cu atoms, 11- and 12-coordinated polyhedra are dominant. Due to big atomic radius of Gd atom, the polyhedra centered by Gd are highly coordinated with CN=13 and 14. On the average, the CNs have similar values in both states of about 12.5, 11.5, and 13.5 around Mg, Cu, and Gd atoms in the 298 K as-cast sample and of about 12.4, 11.2, and 13.3 in the 723 K molten sample. This similarity explains that the strong glass could be regarded as the “frozen” liquid. Moreover, from the position of the first maximum in the partial $g(r)$, the bond lengths except for Cu-Cu (2.55 Å), others like Mg-Mg (3.0 Å), Mg-Cu (2.71 Å), Cu-Gd (2.86 Å), Mg-Gd (3.15 Å), and Gd-Gd (3.45 Å), are obviously shortened compared with the radii of two hard spheres, which can realize the dense packing around Mg and Gd big atoms.

As shown in the Cu-Zr BMGs, the icosahedron-based topological packing is a main feature. Introducing a certain

FIG. 4. (Color online) (a) Comparison in XAFS spectra of experimental data (solid line) with RMC simulated ones and (b) polyhedra centered by Mg, Cu, and Gd atoms, showing high probability of half-octahedral and tetrahedral existence.

amount of Al in the binary leads to denser packing, enhancing the GFA.^{16–18} Now a question is raised: are there similar 12- and 13-coordinated polyhedral packings favorable in the $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG and induce its high GFA? Figure 4(a) is the comparison between XAFS results of Cu K-edge, Gd L3-edge, and RMC simulated for the as-cast $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG. It indicates that the nearest neighbors by RMC simulation with 20 000 atoms in principle possess the local features of a real sample. Checking the structures of polyhedra centered by different atoms, a major characteristic of atomic packing in $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG as demonstrated in Fig. 4(b) emerges, that is, two triangles with an edge sharing are inclined to form a quadrangle, transforming two tetrahedra into one half-octahedron. This is similar to the structural relationship between a truncated octahedron (cuboctahedron) and an icosahedron.¹⁹ It was reported that icosahedron is the major configuration existing in monatomic liquids.²⁰ However, for a complex alloy, our results show that although polyhedra consisting of 12 atoms surrounding a central atom are dominant in the $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ glass and melt, they are usually not the perfect icosahedra or cuboctahedra, but often contain the structural features of both, i.e., tetrahedral packing and half-octahedral packing. If we set the edge length of a cuboctahedron or an icosahedron as a , then both clusters can be contained by a cubic box with minimum edge lengths $L = \sqrt{2}a$ and $L = (1 + \sqrt{5})/2a$, respectively. The volume can be calculated to be $V = L^3 - 8 \times 1/3 \times 1/2 \times (L/2)^3 \approx 2.3567a^3$ for a cuboctahedron and $V = 20 \times 1/3 \times 1/2 \times (\sqrt{3}/2)a^2 \times \sqrt{(3L^2 - 1)/12} \approx 2.1816a^3$ for an icosahedron. Thus, with the same 12 coordination numbers, the volume of a cuboctahedron is a little larger than that of an icosahedron. Since the atomic radius of Al (1.43 Å) is between Cu (1.28 Å) and Zr (1.60 Å), minor addition of Al increases the packing density and favors the formation of icosahedral clusters in Cu-Zr-Al BMGs. In contrast, Gd atom has the radius of 1.80 Å, larger than that of Mg (1.60 Å) and Cu (1.28 Å), which can enlarge the cluster volume wherever it locates in the center or on the shell, causing the high probability of occurrence of the half-octahedral packing in the $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ glass. In addition, intermetallic Mg_2Cu is a major crystalline phase competing with glass formation. In this phase, the polyhe-

dron around Cu atom is $\langle 0\ 2\ 8\ 0 \rangle$, and around Mg it is $\langle 0\ 0\ 12\ 3 \rangle$. However, the major atomic environments around Cu atoms in $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG are $\langle 0\ 2\ 8\ 1 \rangle$ and $\langle 0\ 2\ 8\ 2 \rangle$, those around Mg atoms are $\langle 0\ 2\ 8\ 2 \rangle$ and $\langle 0\ 3\ 6\ 4 \rangle$, and those around Gd atoms are $\langle 0\ 3\ 6\ 4 \rangle$ and $\langle 0\ 2\ 8\ 4 \rangle$, respectively. The local structural difference is mainly around Mg atoms, which could suppress the precipitation of Mg_2Cu phase upon rapid quenching, thus leading to the high GFA of this BMG.

In conclusion, the atomic structure of $\text{Mg}_{61}\text{Cu}_{28}\text{Gd}_{11}$ BMG together with its liquid structure has been studied. As indicated, the atomic-packing feature of the alloy melt is quite similar with the as-cast glassy state. Although 12- and 13-coordinated polyhedra are dominant, the melt has slightly more polyhedra of low coordinated and less of high coordinated than in the glass. Incorporation of large Gd atoms is expected to form the half-octahedra with more volume accommodated with respect to the tetrahedron clusters.

The authors are grateful to the HASYLAB staff at Hamburg for the assistance during the measurements at BW5 and C1 stations. Financial support from the National Natural Science Foundation of China (Grant Nos. 51071141, 60776014, 60876002, 10804096, 50890174, 10702062, 50920105101, 10979002, and 51050110136), Zhejiang University-Helmholtz Cooperation Fund, and the Department of Science and Technology of Zhejiang province is gratefully acknowledged. S.G.W. and J.X. were supported by the National Basic Research Program of China (973 Program) under Contract No. 2007CB613906.

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