Journal of Alloys and Compounds 509 (2011) 8319–8322

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Molecular dynamics studies of short to medium range order in $Cu_{64}Zr_{36}$ metallic glass

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ARTICLE INFO

Article history:
Received 15 February 2011
Received in revised form 16 May 2011
Accepted 18 May 2011
Available online 13 June 2011

Keywords:
Metallic glasses
Atomic scale structure
Molecular dynamics simulation

ABSTRACT

For metallic glasses, the cluster packing scheme addresses mainly the low solute concentration regime and it breaks down beyond a length scale of a few clusters. In the present work, from the viewpoint of core–shell structure rather than cluster packing, short- and medium-range orders in $Cu_{64}Zr_{36}$ metallic glass were investigated using the large-scale atomic/molecular massively parallel simulator. In the first three coordination shells, the total number of atoms within the nth coordination shell is 13, 61, and 169. And the number of atoms on the nth coordination shell is $12n^2$. Besides, the basic atomic structure could be obtained from a central icosahedron surrounded by a shell of $12n^2$ atoms. From the fourth coordination shell on, the total number of atoms is 307, 561, and 924, respectively, consistent with that in an icosahedral shell structure. Our finding suggests that for the optimum glass former in the Cu–Zr binary system, the basic atomic structures over both short- and medium-range length scales have the characteristics of an icosahedral shell structure.

1. Introduction

Previous studies have revealed that solute-centered clusters, rather than individual atoms, can be viewed as the basic local structural motif or short-range order in metallic glasses (MGs) [1–7]. Idealized cluster packing schemes, such as efficient cluster packing on a cubic lattice [8] and icosahedral packing [6] as in a quasicrystal, have been proposed and provided first insights on the medium-range order in MGs. However, these cluster packing schemes addressed mainly the low solute concentration regime [9]. Moreover, these packing schemes break down beyond a length scale of a few clusters [10].

In the present work, we elucidated the short-range order as well as the nature of the medium-range order in $Cu_{64}Z_{r36}$ metallic glass from the viewpoint of core–shell structure rather than cluster-packing. And the length scale is up to 15.3 Å from the first to the sixth coordination shell. In the first three coordination shells, the total number of atoms within the nth coordination shell N is, in fact, 13, 61, and 169. And the number of atoms on the nth coordination shell is $12n^2$. Besides, we recognized that the basic atomic structure within the medium range could be obtained from a central icosahedron surrounded by a shell of $12n^2$ atoms. From the fourth coordination shell on, the total number of atoms is consistent with that in an icosahedral shell structure. Our study indicates that the basic atomic structures in the good glass former over both short- and medium-range length scales have the characteristics of an icosahedral shell structure.

2. Model systems

Molecular dynamics (MD) simulations were performed based on the embedded atom method (EAM) potential in the canonical ensemble (NVT) using the large-scale atomic/molecular massively parallel simulator (LAMMPS) code [11,12]. A super cell containing 16,000 atoms under the periodic boundary conditions (PBC) was used to model the system. The volume of the super cell was fixed in order to reproduce the experimental density. To simulate a random alloy with a given composition, we randomly substituted appropriate amount of copper (zirconium) atoms with the same number of zirconium (copper) atoms in the initial B2 structure ($Cu_{50}Zr_{50}$). The NVT MD simulations were performed, in a temperature range from 0 to 3200 K, in steps of 100 K. A time step of 1 fs was used. At each temperature the MD simulation time for determining the properties was 20 ps. We then cooled the system with a quenching rate of 10 K/ps from 3200 K down to 300 K in steps of 100 K in the NVT ensemble. Finally the supercell volume was adjusted corresponding to zero external pressure and the resulting structure was further optimized using the conjugated gradient method to

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doi:10.1016/j.jallcom.2011.05.071

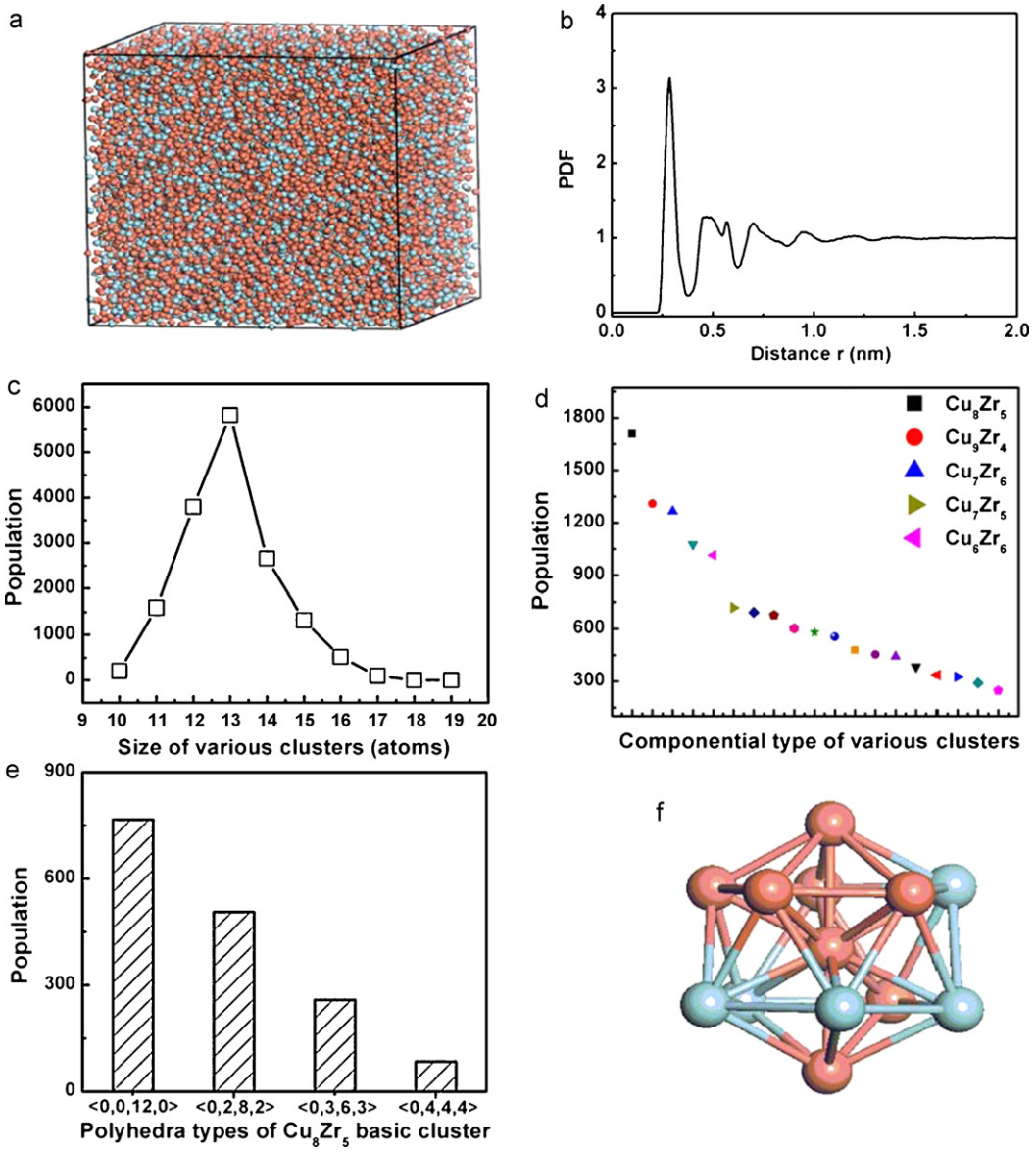

Fig. 1. Short-range order in $Cu_{64}Zr_{36}$ MG within the first coordination shell. (a) Configuration (16,000-atom) of a $Cu_{64}Zr_{36}$ MG obtained by MD simulation. (b) Total PDF of $Cu_{64}Zr_{36}$. (c) and (d) Populations of various clusters in terms of size and component, respectively. (e) Distribution of the polyhedron type of Cu_8Zr_5 basic cluster. (f) A representative motif of Cu_8Zr_5 polyhedra cluster (red: Cu, and gray: Zr). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

obtain the inherent structure. The inherent structure was analyzed by sorting out the nearest-neighbor environment of each atom of all species present, in terms of the Voronoi polyhedra [13]. The density of the final glass structure was checked to be within 1% error of the experimental one.

3. Results and discussion

A typical view of three-dimensional atomic configuration (16,000-atom) for a $Cu_{64}Zr_{36}$ MG is shown in Fig. 1(a). The resulting total pair distribution function (PDF) is shown in Fig. 1(b). As one can see, the second peak exhibits pronounced split, indicating the development of short-range order in the glassy structure [14]. The cut-off distance of the *n*th coordination shell is shown in Table 1 [10]. Fig. 1(c) displays population of the size of the various clusters within the first coordination shell. It is clear that the basic cluster with atom = 13 is dominant. In order to further examine the local structure, population of the various clusters within the first coordination shell is shown in Fig. 1(d). The five most populous clusters are listed. It is found that Cu_8Zr_5 basic cluster prevails within the first coordination shell. Then distribution of the polyhedron type of Cu_8Zr_5 basic cluster is shown in Fig. 1(e). Most of Cu_8Zr_5 basic clusters are in the form of full icosahedra with index of $\langle 0,0,12,0 \rangle$. A representative motif of Cu_8Zr_5 polyhedra cluster is shown in Fig. 1(f).

Table 1
The cut-off distance of the *n*th coordination shell.

The *n*th coordination shell	Cut-off distance (nm)
1	0.34
2	0.62
3	0.87
4	1.06
5	1.295
6	1.53

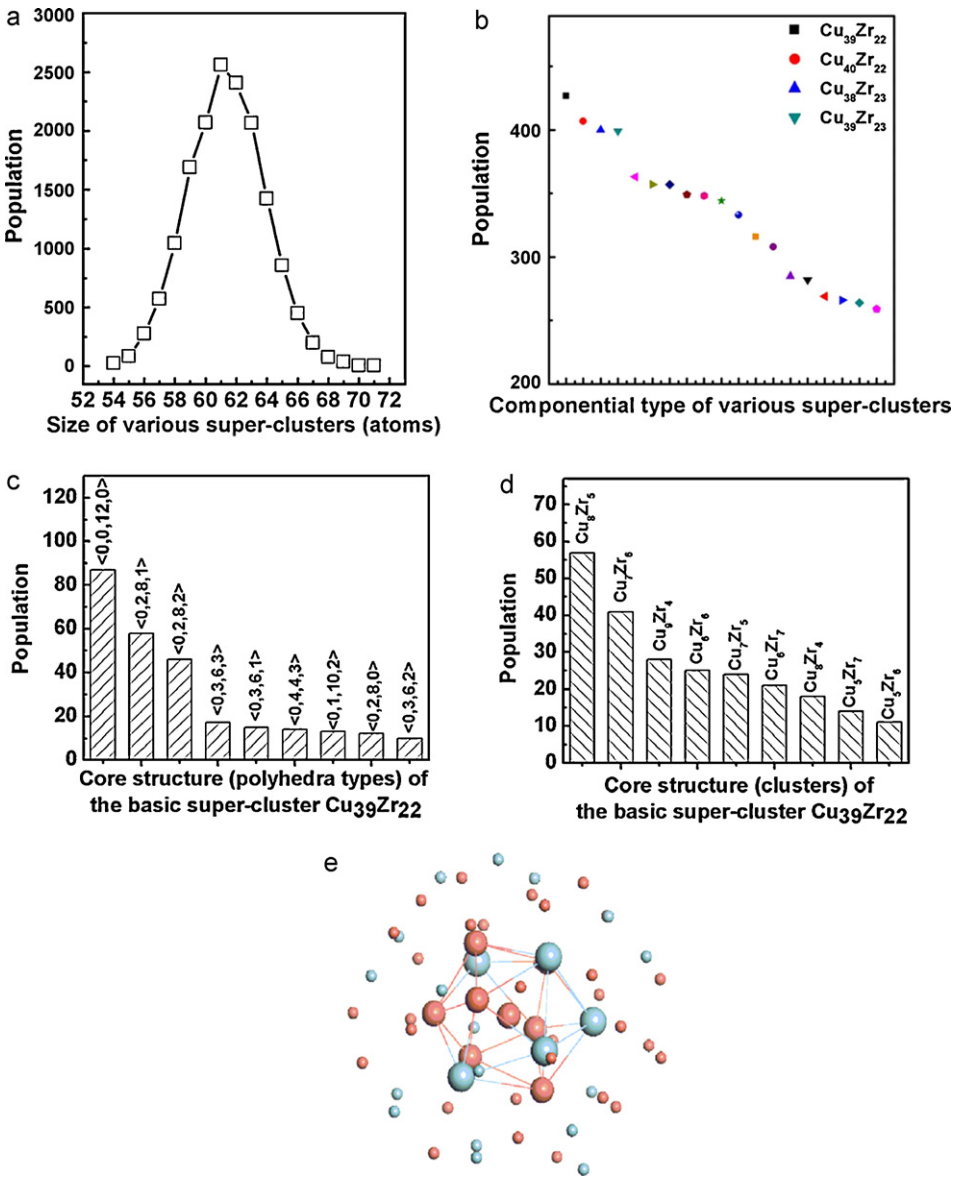

Fig. 2. Medium-range order in $Cu_{64}Zr_{36}$ MG within the second coordination shell. (a) and (b) Populations of the various super-clusters in terms of size and component, respectively. (c) and (d) Distributions of the core structure of the basic super-cluster $Cu_{39}Zr_{22}$ in terms of type of polyhedra and type of clusters, respectively. (e) A representative motif of super-cluster $Cu_{39}Zr_{22}$.

We next address the medium-range order in $Cu_{64}Zr_{36}$. Fig. 2(a) and (b) displays populations of the various super-clusters within the second coordination shell, in terms of size and component, respectively. It is found that the basic super-cluster with atom = 61 is dominant and the most populous super-cluster is $Cu_{39}Zr_{22}$ within the second coordination shell. And this super-cluster's composition can recover the bulk's stoichiometry. Fig. 2(c) and (d) displays distributions of the core structure of the super-cluster $Cu_{39}Zr_{22}$ in terms of type of polyhedra and type of clusters, respectively. The full icosahedral $\langle 0,0,12,0 \rangle$ is the most abundant polyhedron in the core structure, and the most populous cluster in the core structure is Cu_8Zr_5. A representative motif of super-cluster $Cu_{39}Zr_{22}$ is shown in Fig. 2(e), in which the atoms of the external shell are represented with small spheres.

The detailed atomic structure within the third coordination shell is shown in Fig. 3. Fig. 3(a) and (b) displays populations of the various super-clusters in terms of size and component, respectively. Within the third coordination shell, the basic super-cluster with atom = 169 is dominant and the most populous super-cluster is $Cu_{108}Zr_{61}$. A representative motif of super-cluster $Cu_{108}Zr_{61}$ is shown in Fig. 3(c).

Based on the above analyses from the first to the third coordination shell, it is found that atomic packing in MGs follows some rules. The total number of atoms within the nth coordination shell N is, in fact, 13, 61, and 169. And the number of atoms on the nth coordination shell is $12n^2$, namely, 12, 48, and 108. Undoubtedly, the icosahedral short order exits in the short range (see Fig. 1(f)). Moreover, within medium range the basic atomic structure could be obtained from a central icosahedron surrounded by a shell of $12n^2$ atoms (see Figs. 2(e) and 3(c)).

We then also extend the same analysis from the fourth to the sixth coordination shell. The super-clusters with atom = 307, 561, and 924 are dominant, respectively. Fig. 4 shows the overall trend of the total number of atoms within the nth coordination shell for $Cu_{64}Zr_{36}$ MG. For comparison, trend of the total number of atoms in an icosahedral shell structure is also plotted, in which the total number of atoms within the nth shell N for ($n \geq 1$) is, 13, 55, 147, 309, 561, 923, etc., and the number of atoms on the nth icosahedral

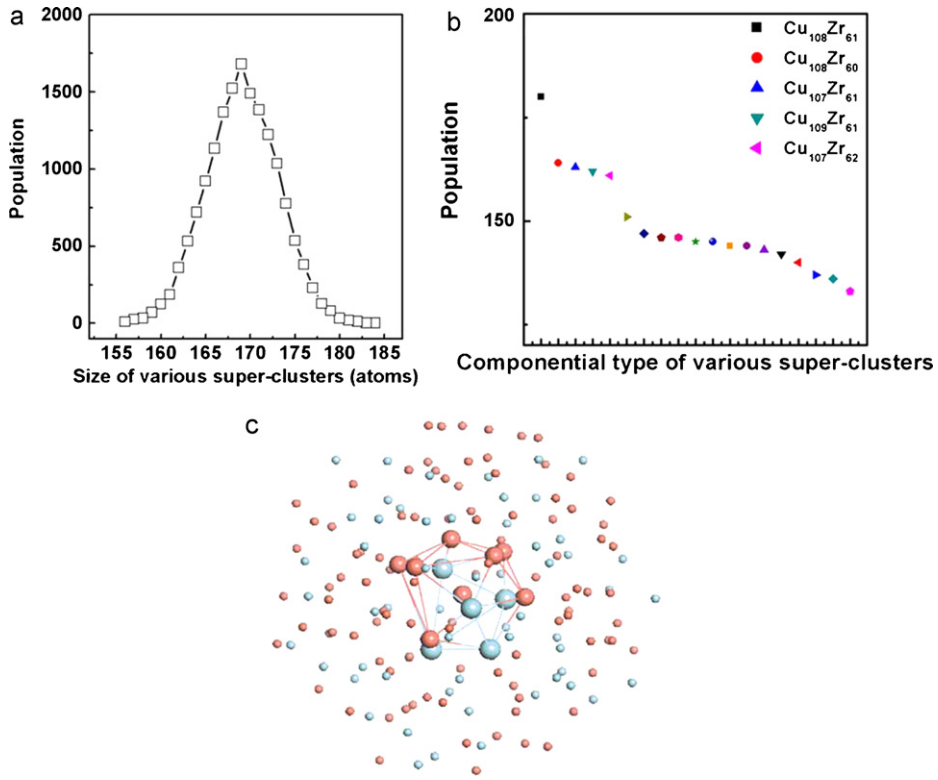

Fig. 3. Medium-range order in $Cu_{64}Zr_{36}$ MG within the third coordination shell. (a) and (b) Populations of the various super-clusters in terms of size and component, respectively. (c) A representative motif of super-cluster $Cu_{108}Zr_{61}$.

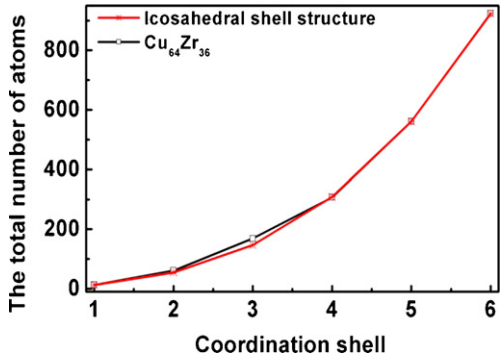

Fig. 4. The overall trend of the total number of atoms within the nth coordination shell for $Cu_{64}Zr_{36}$ MG. Trend of the total number of atoms in an icosahedral shell structure is also plotted for comparison.

shell is $10n^2+2(n\geq 1)$ [15,16]. $Cu_{64}Zr_{36}$ is well known to be the best glass former in the Cu–Zr alloy [17–20]. The trends shown in Fig. 4 indicate that for the optimum glass former in the Cu–Zr binary system, the basic atomic structures over both short- and medium-range length scales have the characteristics of an icosahedral shell structure.

4. Conclusion

In conclusion, short- and medium-range orders in the $Cu_{64}Zr_{36}$ MG have been investigated from the first to the sixth coordination shell up to 15.3 Å length scale. In the first three coordination shells, the total number of atoms within the nth coordination shell N is 13, 61, and 169. And the number of atoms on the nth coordination shell is $12n^2$. Besides, we recognized that the basic atomic structure could be obtained from a central icosahedron surrounded by a shell of $12n^2$ atoms. From the fourth coordination shell on, the total number of atoms within the nth coordination shell N is 307, 561, and 924 with the characteristics of an icosahedral shell structure. Our study indicates that for the good glass former in the Cu–Zr binary system, an icosahedral shell structure prevails in both short and medium ranges.

References

[1] A. Zhang, D. Chen, Z. Chen, J. Alloys Compd. 509 (2011) 648.
[2] T. Egami, J. Non-Cryst. Solids 353 (2007) 3666.
[3] N. Jakse, A. Pasturel, Appl. Phys. Lett. 93 (2008) 113104.
[4] J. Antonowicz, D.V. Louzguine-Luzgin, A.R. Yavari, K. Georgarakis, M. Stoica, G. Vaughan, E. Matsubara, A. Inoue, J. Alloys Compd. 471 (2009) 70.
[5] A. Zhang, D. Chen, Z. Chen, J. Alloys Compd. 477 (2009) 432.
[6] H.W. Sheng, W.K. Luo, F.M. Alamgir, J.M. Bai, E. Ma, Nature (London) 439 (2006) 419.
[7] G.A. Almyras, Ch.E. Lekka, N. Mattern, G.A. Evangelakis, Scr. Mater. 62 (2010) 33.
[8] D.B. Miracle, Nat. Mater. 3 (2004) 697.
[9] M.Z. Li, C.Z. Wang, S.G. Hao, M.J. Kramer, K.M. Ho, Phys. Rev. B 80 (2009) 184201.
[10] D. Ma, A.D. Stoica, X.-L. Wang, Nat. Mater. 8 (2009) 30.
[11] Z.D. Sha, B. Xu, L. Shen, A.H. Zhang, Y.P. Feng, Y. Li, J. Appl. Phys. 107 (2010) 063508.
[12] Z.D. Sha, R.Q. Wu, Y.H. Lu, L. Shen, M. Yang, Y.Q. Cai, Y.P. Feng, Y. Li, J. Appl. Phys. 105 (2009) 043521.
[13] Y.Q. Cheng, E. Ma, Appl. Phys. Lett. 93 (2008) 051910.
[14] H.Z. Fang, X. Hui, G.L. Chen, Z.K. Liu, Appl. Phys. Lett. 94 (2009) 091904.
[15] K.H. Kuo, Struct. Chem. 13 (2002) 221.
[16] A.L. Mackay, Acta Crystallogr. 15 (1962) 916.
[17] D.H. Xu, B. Lohwongwatana, G. Duan, W.L. Johnson, C. Garland, Acta Mater. 52 (2004) 2621.
[18] Z.D. Sha, Y.P. Feng, Y. Li, Mater. Chem. Phys. 127 (2011) 292.
[19] Z.D. Sha, Y.P. Feng, Y. Li, Appl. Phys. Lett. 96 (2010) 061903.
[20] D. Wang, Y. Li, B.B. Sun, M.L. Sui, K. Lu, E. Ma, Appl. Phys. Lett. 84 (2004) 4029.