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"Order" in metallic glass: Maximum uniformity distribution of cluster electrochemical potential

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HIGHLIGHTS

- Geometry configuration: the clusters in metallic glasses are spherical geometry.
- The CECP: the clusters electrochemical potential is equilibrium distribution.
- Physic mechanism: atomic arrangements are dominated by the CECP equilibrium rule.

ABSTRACT

Metallic glass (MG) possesses many superior properties and hence has broad technical application prospect. However, the thermodynamic mechanism of its atomic arrangement has not been well understood to date. To better understand the thermodynamic mechanism of atomic arrangement in MG, a new concept named cluster electrochemical potential (CECP) is proposed in this study. By employing the molecular dynamics simulation, spatial distribution of the CECP has been investigated. Our results reveal that the seemingly disordered atomic arrangement in MG is controlled by the maximum uniformity distribution of CECP rule. These results provide a new viewpoint to better understand the thermodynamic mechanism of atomic arrangement in MG.

1. Introduction

Due to its disordered atomic packing structure, metallic glasses (MG) exhibit many superior properties compared to their crystalline counterparts [1–3]. To better take advantage of MG, a comprehensive understanding of its structure, properties and structure-property correlations is highly desirable. Although considerable efforts have been devoted to studying MG structure during the past decades [4–12], the structural characteristics of MG are still mysterious.

To date, many geometric models for MG have been suggested, such as dense random packing of hard spheres model [4], dense cluster packing model [8], quasi-equivalent clusters model *etc* [9,13]. Although all these proposed models can well describe the MG's atomic arrangement to a certain extent, the thermodynamic mechanism for the atomic arrangement cannot be understood by these models. To this end, the Random first-order transitions (RFOT) theory has been proposed by Lubchenko [14] and Parisi [15] et al. They suggested that there exists non-periodic "ordered structure" in MG, which can decrease system total energy and stabilize MG atomic structure. Recent study have obtained consistent results [16], where Yang et al. proposed that the local structure entropy can be regarded as a structural parameter to reflect the structural order degree of the non-periodic "ordered structure", and can be used to predict the local cluster rearrangement accurately. Owing to extensive property of local structure entropy the relative stability between the clusters with different atomic numbers cannot be compared by local structure entropy. As for MG, its properties are not only related to its local structure, but also related to the spatial distribution of these local clusters' state (including stability and electronic state *etc*), as well as their correlation of each local clusters' state. Electrochemical potential (ECP) is an intensive property that plays an important role in physical and chemical properties [17–19], and it is usually used to describe the escaping tendency of an electron from a chemical system [20,21]. Hence, ECP not only can be used as a parameter to describe the local clusters' state, but also can be used to

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compare the stability of each cluster. A new concept named cluster electrochemical potential (CECP) has been proposed in this work, which can be considered as a parameter to describe the local clusters' state and their correlation in MG.

In this work, classical molecular dynamic (MD) simulations were performed on a series of binary Cu-Zr alloys (including $Cu_{46}Zr_{54}$, $Cu_{50}Zr_{50}$ and $Cu_{64}Zr_{36}$, which have similar excellent glass forming ability) and the spatial distributions of the CECP are investigated. Our computational results uncover that the maximum uniformity distribution for CECP is a crucial order, which dominates the atomic arrangement in MG.

2. Methods

In this work, molecular dynamic (MD) simulations have been performed by using the large-scale atomic/molecular massively parallel simulation (LAMMPS) package [22]. In our computational scheme, all models were investigated with periodic boundary conditions in all three directions. The isothermal-isobaric (NPT) ensemble was used and the metallic bonding interactions have been described by developed embedded-atom method (EAM) potentials [23]. The time step used in all the simulations was 1 fs. The calculation process was carried out in atmospheric pressure.

Three types MG models ($Cu_{46}Zr_{54}$, $Cu_{50}Zr_{50}$ and $Cu_{64}Zr_{36}$) were built and each model contains about 0.1 million atoms. A typical model is shown in Supplementary Fig. S1. To better simulate the structures, the models were initially melted and equilibrated for 2 ns (*ns*) at 2000 K, then cooled them to 300 K at a rate of 10^{12} K/s (computational detail see Method). Finally, optimized MG models were obtained. The corresponding density is 7.23 g/cm^3, 7.31 g/cm^3 and 7.63 g/cm^3 for the three studied models of $Cu_{46}Zr_{54}$, $Cu_{50}Zr_{50}$ and $Cu_{64}Zr_{36}$ MGs, respectively. These values coincide well with previous computational and experimental ones [24,25], confirming the reliability of the potential used in this work.

3. Results and discussion

To investigate the local structural feature of the MG models and study the cluster structure, the coordination number (CN), volumes, and the geometric feature of cluster are studied in this work. The CN and the volumes of atoms have been analyzed by Voronoi tessellation method [26]. The distribution of the CN and volumes of the atoms is shown in Supplementary Fig. S2. One can see that the most favorable CN of Cu and Zr atoms in the $Cu_{46}Zr_{54}$ MGs are 12 and 14, respectively. But for both $Cu_{50}Zr_{50}$ and $Cu_{64}Zr_{36}$ MGs, the most favorable CNs of Cu and Zr atoms are 12 and 15, respectively. These results are consistent with previous MD results [23,27]. For three kinds of MGs models considered, the CN of Cu atom is always smaller than that of Zr atom. This can be contributed to a smaller radius of Cu atom as compared to that of Zr atoms. This is verified by our results for volumes of atoms.

The coordinate atom type and their proportion as a function of given central atom type and CN is listed Supplementary Table S1, as can be seen that the Cu proportion in coordinate atoms for Cu center atom is less than the average Cu proportion in alloy, and the Zr proportion in coordinate atoms for Cu center atom is larger than the average Zr proportion in alloy. It also shows that the Zr proportion in coordinate atoms for Zr central atom is close to alloy average Zr proportion, and the Cu proportion in coordinate atoms for Zr center atom is close to average Cu proportion in alloy. It is noticed that with increasing CN for both Cu and Zr center atoms, the Cu proportion in coordinate atoms increases, while the Zr proportion in coordinate atoms decreases with increasing CN for both Cu and Zr central atoms. This indicates that an atom with higher CN prefers to connect with the atoms with smaller radii. Based on these results, we can conclude that Cu atoms prefer to approach to Zr atoms, and the arrangement of atoms is not random. This result also consistence with the Random first-order transitions and local structure entropy theory. And an ab-initial calculation by Tian [28] has demonstrated the existence of Cu-centered Cu_8Zr_5 icosahedral clusters as the major local structural unit in the $Cu_{64}Zr_{36}$ amorphous alloy by the cluster-plus-glue-atom model. But previous studies on Cu-Zr metallic glasses are more focus on Cu-centered clusters, neglect the Zr-centered clusters. Here we considered the cluster centered on each element to study the cluster electrochemical potential.

To investigate the distribution of coordination atoms, sphericity (S) of each cluster is calculated by the following formula:

$$S = 1 - \frac{1}{\bar{r}}\sqrt{\frac{1}{N}\cdot\sum_{i=1}^{N}(r_i - \bar{r})^2}, \quad (1)$$

where N represents the nearest neighbor atom number of a cluster, r_i represents the distance from the central atom to ith nearest neighbor atom in a cluster, and $\bar{r}$ represents the average value of r_i in a cluster. Thus, the sphericity value should be between 0 and 1, inclusively. The sphericity measures the probability of coordination atom distribution on a same spherical surface. The closer the value of sphericity to 1, the higher the probability of coordination atom distribute on a same spherical surface. As the cluster defined by Voronoi methods are signing by < n1, n2, n3, n4 > , the atom numbers in a cluster are equal to the number of corresponding polyhedral planes, which is the sum of n1, n2, n3 and n4. And the coordinate numbers of all clusters are in range of 8 and 20. In this work, the cluster is defined by Voronoi tessellation method, and the corresponding sphericity of clusters was calculated. The results for the three MGs are given in Fig. 1(a), which shows that the sphericity of a cluster with Zr central atoms is larger than that of a cluster with Cu central atoms, and the average sphericity of the clusters with both Cu and Zr central atoms in the three MGs is all greater than 0.88. This indicates that the coordination atoms around one central atom are almost located at a same spherical surface.

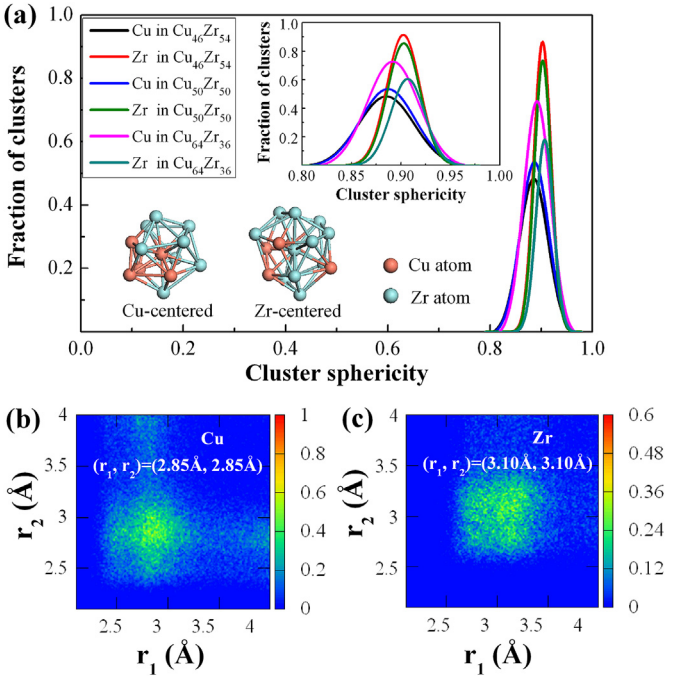

Fig. 1. The sphericity and partial angular-limited three-body correlations (ALTBC) maps of clusters centered by different atoms in three MGs. (a) Sphericity distribution in three MGs. The value of sphericity is more close to 1, the clusters is more close to ideal spherical. The partial ALTBC maps for clusters with central atoms are Cu (b), and Zr (c) in the $Cu_{46}Zr_{54}$ MGs. The ALTBC represents the probability of existing a bond with length r_1 almost aligns with a bond with length r_2. In this work, the angular deviation from 180° is smaller than 10°. Therefore, the neighbor atoms' arrangement state can be reflecting by the ALTBC to a certain extent by counted bonds length around the central atom.