Journal of Alloys and Compounds 619 (2015) 16–19

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Letter

Ab initio study on the electronic origin of glass-forming ability in the binary Cu–Zr and the ternary Cu–Zr–Al(Ag) metallic glasses

Z.D. Sha [a,*], Q.X. Pei [b]

[a] International Center for Applied Mechanics, State Key Laboratory for Strength and Vibration of Mechanical Structures, Xi'an Jiaotong University, Xi'an 710049, China
[b] Institute of High Performance Computing, A*Star, Singapore 138632, Singapore

ARTICLE INFO

Article history:
Received 1 June 2014
Received in revised form 28 August 2014
Accepted 1 September 2014
Available online 16 September 2014

Keywords:
Ab initio simulations
Atomic scale structure
Metallic glasses
The glass-forming ability

ABSTRACT

It is believed that the basic local cluster in metallic glasses (MGs) is the key to understand the origin of glass-forming ability (GFA) of MGs. Our *ab initio* simulations on the basic cluster in the binary Cu–Zr MGs as well as in the ternary Cu–Zr–Al(Ag) MGs provide the most straightforward evidence that the electronic stability of the basic cluster in MGs is the origin of the GFA. Our calculations reveal that the stability of the basic cluster is determined by its electronic states near the Fermi level. For the basic clusters in the best glass formers of Cu–Zr MGs, a gap near Fermi level is observed, indicating the stability of the basic clusters. With substitution of one Al(Ag) atom into the basic cluster in $Cu_{50}Zr_{50}$ MGs, a strong *sp-d* coupling of Al(Ag) with Cu and Zr is observed, which results in a stronger bonding and thus more stability of the basic cluster. Our findings provide a check for the atomic structural models proposed over the years for MGs, and have implications for understanding the formation and properties of MGs.

1. Introduction

Metallic glasses (MGs) are very promising engineering materials owing to their superior mechanical properties such as high strength and large elastic strain [1–6]. However, one of the main drawbacks for making the best use of MGs is their low glass-forming ability (GFA), which restricts not only the shape but also the size of MGs and significantly undercuts their practical engineering applications. An in-depth understanding of the origin of GFA is the key in developing the large-sized bulk metallic glasses (BMGs).

It is believed that the basic local cluster in MGs is the key to understand the origin of GFA of MGs [7–9]. Efficient atomic packing with the scheme of solute-centered atomic clusters has been suggested as the basic structure of MGs, which has been verified by a number of binary MGs [7,10,11]. And it has been found that atomic size ratio R^* (ratio of the average size of the surrounding solvent atoms over the size of the solute atom) is the most important factor governing GFA, such as R^* of 0.902 for the ideal icosahedral dense packing [7,8,11]. However, the atomic structures for MGs composed of three or more elements are poorly known and, as a result, the atomic origins of the GFA of MGs have not been well understood so far [12].

Electronic structure and atomic structure interrelations are expected to give more fundamental insights into the stability of the metastable glassy materials. Therefore, the electronic structure perspective on GFA has attracted a lot of interest and is the focus of intense studies [13–17]. In this work, we addresses the electronic origin of GFA based on the understanding of the basic clusters not only in the binary Cu–Zr MGs but also in the ternary Cu–Zr–Al(Ag) MGs. Firstly, for binary Cu–Zr MGs, it is known that the two best glass formers are $Cu_{50}Zr_{50}$ and $Cu_{64.5}Zr_{35.5}$ [10,16,18–22]. And both the experimental measurements and molecular dynamics (MD) simulations have determined that the Cu-centered Cu_6Zr_7 and Cu_8Zr_5 full icosahedra clusters are the basic local clusters in these two best glass formers of $Cu_{50}Zr_{50}$ and $Cu_{64.5}Zr_{35.5}$ MGs, respectively [22–24]. Then we have to ask one question: why the basic clusters are Cu-centered Cu_6Zr_7 and Cu_8Zr_5 icosahedral clusters and others not? What is the correlation between these basic clusters and the origin of the GFA? Secondly, for ternary Cu–Zr–Al(Ag) MGs, minor Al(Ag) alloying in $Cu_{50}Zr_{50}$ MGs can markedly improve GFA [12,25–29]. Then we have to ask another question: what is the change in the atomic-level structure by the minor Al(Ag) alloying? And what is the intrinsic correlation between the obvious improvement of GFA and the minor Al(Ag) alloying? In the present work, we stress satisfactory answers to these questions based on understanding the electronic properties of the basic local clusters. We find out that the origin of the GFA is the electronic stability of the basic cluster in MGs instead of

* Corresponding author. Tel.: +86 29 82666238; fax: +86 29 82664354.
E-mail address: zhendongsha@mail.xjtu.edu.cn (Z.D. Sha).

http://dx.doi.org/10.1016/j.jallcom.2014.09.010
0925-8388/

the topological stability of the basic cluster in MGs. In addition, the electronic stability of the basic cluster is determined by its electronic states at the Fermi level. For the basic clusters in the best glass formers of Cu–Zr MGs, a gap in the density of states (DOSs) at Fermi level is observed, indicating the electronic stability of the basic clusters. With substitution of one Al(Ag) atom into the basic cluster in $Cu_{50}Zr_{50}$ MGs, a strong *sp-d* coupling of Al(Ag) with Cu and Zr is observed at the Fermi level, making a strong bonding and the more electronic stability of the basic cluster accordingly. Our work establishes a direct connection between the electronic structure of the basic cluster and the GFA of MGs, providing a new avenue to examine the GFA of MGs.

2. Computational methods

The first-principles calculation was carried out based on the density function theory and the Perdew–Burke–Eznerhof generalized gradient approximation (PBE-GGA) [30,31]. The projector augmented wave (PAW) scheme as incorporated in the Vienna *ab initio* simulation package (VASP) [32,33]. The Monkhorst and Pack scheme of *k* point sampling was used for integration over the first Brillouin zone [34]. A $1 \times 1 \times 1$ grid for *k*-point sampling and an energy cutoff of 400 eV were used for geometry optimization. Excellent convergence was obtained using these parameters, and the total energy was converged to 2.0×10^{-5} eV/atom. A large supercell dimension with a wall-wall distance of 20 Å between neighboring clusters was used to avoid any interaction between the cluster and its images in neighboring cells. A $11 \times 11 \times 11$ grid for *k*-point sampling was used for the calculations of DOSs.

3. Results and discussion

It should be emphasized that the specific atomic structure for the Cu-centered full icosahedra clusters (ICOs) Cu_xZr_{13-x} is difficult to pin down and rarely reported in the literature, because of the complicated combinations of Cu and Zr atoms in the shell, as illustrated in Fig. 1(a). According to our previous work [16], we fixed this problem via identifying the atomic structure with the lowest binding energy by examining all the possible atomic configurations for each ICO. Our calculations showed that when the Cu and Zr atoms at the shell prefer to bond together, ICO has the lowest binding energy (see the motifs in Fig. 1(b) and (c)). Then their DOSs are calculated. It is noted that only these five icosahedral clusters (Cu_5Zr_8, Cu_6Zr_7, Cu_7Zr_6, Cu_8Zr_5, and Cu_9Zr_4) are taken into account in terms of the composition range for Cu–Zr MGs formation [22]. Gaps between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are observable only for Cu-centered Cu_6Zr_7 and Cu_8Zr_5 icosahedral clusters, as shown in Fig. 1(b). For other Cu_xZr_{13-x} ICOs (Cu-centered Cu_5Zr_8, Cu_7Zr_6, and Cu_9Zr_4 icosahedral clusters) shown in Fig. 1(c), the Fermi levels are at the peak positions of DOSs, indicating the absence of HOMO–LUMO gap in these ICOs. The formation of HOMO–LUMO gap [35,36] reveals that only Cu-centered Cu_6Zr_7 and Cu_8Zr_5 icosahedral clusters are stable among these Cu-centered full icosahedra clusters Cu_xZr_{13-x}. The previous experimental work and MD simulation results have confirmed that only the Cu-centered Cu_6Zr_7 and Cu_8Zr_5 icosahedral clusters are the basic polyhedral clusters in the two best glass formers $Cu_{50}Zr_{50}$ and $Cu_{64.5}Zr_{35.5}$ MGs, respectively [22–24]. Hence, our finding suggest that there is a correlation between the DOSs of the basic polyhedral clusters in MGs and the GFA of MGs, and highlights the significant role of electronic structure in the formation of MGs.

Nagel and Tauc [37] theoretically predicted that good GFA is closely related to the decrease of DOSs at the Fermi energy, or Mott's pseudogap, within the framework of the nearly-free-electron model. Yu et al. also suggested that the best GFA can be obtained when the Fermi surfaces nearly touch the quasi-Brillouin boundaries based on a systematic study on the specific heat coefficient [17]. In the present work, we show convincingly that there exists a gap in the DOSs at the Fermi level in the basic cluster of the best glass formers $Cu_{50}Zr_{50}$ and $Cu_{64.5}Zr_{35.5}$, providing compelling evidence that the DOSs at the Fermi level indeed is closely correlated with the GFA. Our finding pins down the electronic origin why Cu-centered Cu_6Zr_7 and Cu_8Zr_5 icosahedral clusters are the basic clusters in the best glass formers $Cu_{50}Zr_{50}$ and $Cu_{64.5}Zr_{35.5}$ MGs, respectively.

To find the origin of the gap in the DOSs at the Fermi level, the partial density of states (PDOSs) of the unstable Cu-centered Cu_5Zr_8 and the stable Cu_6Zr_7 icosahedral clusters are plotted in Fig. 2. For the Cu-centered Cu_5Zr_8 icosahedral cluster, the states near the Fermi level are dominated by both Cu and Zr *d* electrons (see Fig. 2(a)). The *d*–*d* interaction leads to less stability because of the symmetry of the *d*-electron wavefunction. In contrast, the states near the Fermi level in the stable Cu-centered Cu_6Zr_7 icosahedral cluster are mainly attributed to the Zr-*d* electrons

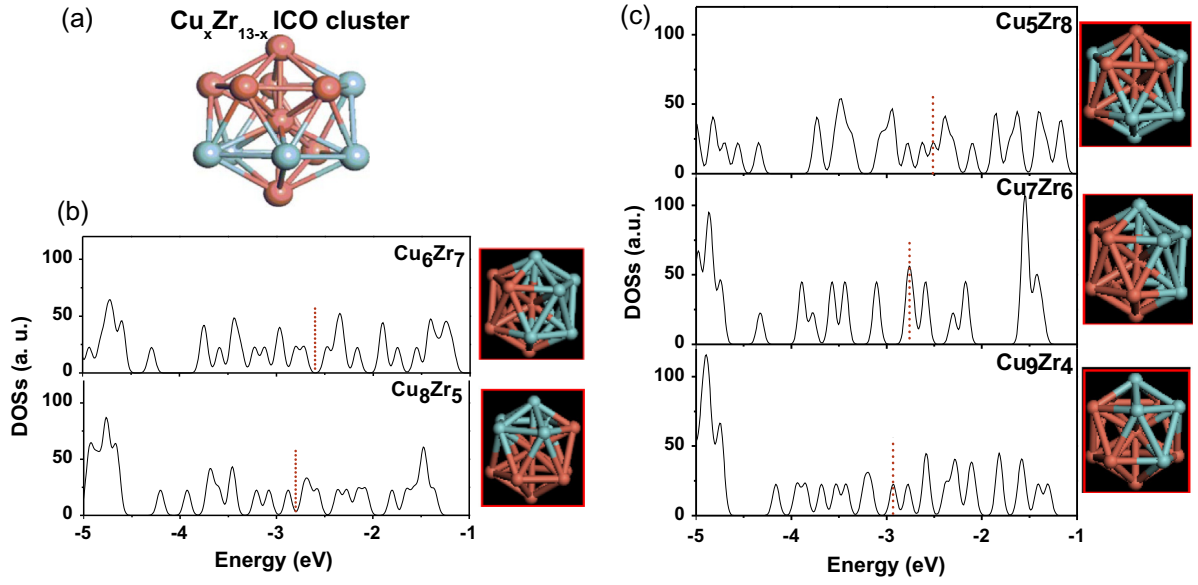

Fig. 1. (a) Illustration of a Cu-centered Cu_xZr_{13-x} ICO cluster. (b) The HOMO–LUMO gaps at the Fermi level are observed for the Cu-centered Cu_6Zr_7 and Cu_8Zr_5 ICO clusters. (c) The Fermi levels are at the peak positions of DOSs for the Cu-centered Cu_5Zr_8, Cu_7Zr_6, and Cu_9Zr_4 ICO clusters. The motifs show the atomic structures of the clusters. Only these five ICO clusters are taken into account in terms of the composition range for Cu–Zr MGs formation.