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Interpenetrating networks in Zr–Cu–Al and Zr–Cu metallic glasses

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ABSTRACT

The short-range order and medium-range order of ternary Zr–Cu–Al and binary Zr–Cu metallic glasses (MGs) have been investigated. When substituting a few percent of Al for Zr in the Zr–Cu alloy, the resultant ternary alloy exhibits more full icosahedra. Furthermore, the number of Zr icosahedral atoms increases significantly since Al-centred full icosahedra favours Zr as neighbour atoms. Additionally, the interconnecting networks in Zr–Cu–Al MG are enhanced significantly through intensive sharing frequencies between the full icosahedra. The reduction of isolated icosahedra in the ternary system lowers the atomic mobility and slows down the dynamics in the supercooled liquid region, which reduces theoretical cooling rate for the preparation of bulk MG.

1. Introduction

Since the first bulk metallic glass (BMG) was reported in 1980s [1], these novel materials have attracted a huge amount of interest around the world due to their outstanding strength, elastic strain, and elastic energy storage ability [2]. Many models have since been proposed to correlate these excellent properties with its atomic structure [3–6]. More notably, the recently proposed quasi-equivalent clusters based on icosahedral ordering [6] have revealed short-to-medium range order in a series of binary and ternary metallic glasses (MGs).

Among all BMGs, the ETM (early transition metals)–LTM (late transition metals)-based amorphous alloys have received the most attention, since they possess good glass-forming ability (GFA) [7]. Specifically, Zr–Cu binary system and its based ternary or quaternary system are usually investigated as representatives of ETM–LTM BMGs. For example, Li et al showed a clear correlation between density change and GFA and also reported three good glass-formers, i.e., $Cu_{50}Zr_{50}$, $Cu_{56}Zr_{44}$ and $Cu_{64}Zr_{36}$, in Zr–Cu system [8]. Fujita et al. made use of both experiment and simulation to investigate ternary $Cu_{45}Zr_{45}Ag_{10}$ alloy. They found that interpenetrating clusters centred by paired and stringed Ag atoms and Cu-rich icosahedra are widely observed in this system [9]. Yang et al. used synchrotron radiation techniques combined with simulations to study structural role of doped atoms in the Zr–Cu–Al MGs. It is found that minor element can affect the glass-forming ability by changing the atomic packing efficiency [10,11].

Moreover, when a small percentage of Al is added to the Zr–Cu binary system, the required cooling rate decreases significantly and the resultant ternary BMG exhibits a unique mechanical behaviour [12–14]. This has sparked worldwide effort to determine the causes of the change in the properties. For example, Wang et al made use of both experiments and simulations to investigate the amorphous $Zr_{46}Cu_{46}Al_8$ alloy. They discovered that Al atoms are homogeneously distributed around Cu and Zr atoms in the $Zr_{46}Cu_{46}Al_8$ system [15]. Cheng et al performed classical molecular dynamics (MD) simulations on $Zr_{47}Cu_{46}Al_7$ MG to study the effect of Al content. It was reported that Zr–Cu–Al ternary system has a larger fraction of full icosahedra than that of Zr–Cu binary system [16]. Yang and co-workers performed the reverse Monte-Carlo simulation upon the synchrotron radiation-based experiments to study atomic structure of $Zr_{48}Cu_{45}Al_7$BMG. They concluded that the addition of Al perturbs the atoms and clusters arrangement due to the strong bonding and dense cluster packing [17].

However, the previous work focused on the number of full icosahedra found in the Zr–Cu–Al and Zr–Cu systems that leads to the formation of the short-range order (SRO). Unfortunately, SRO is unable to explain the macroscopic change in properties of the BMGs. Therefore, the interconnection of full icosahedra to form medium-range order (MRO) in the form of vertex, edge, face, or tetrahedral sharing [6], is believed to give rise to different dynamics and mechanical properties in these two BMGs. Following this idea,

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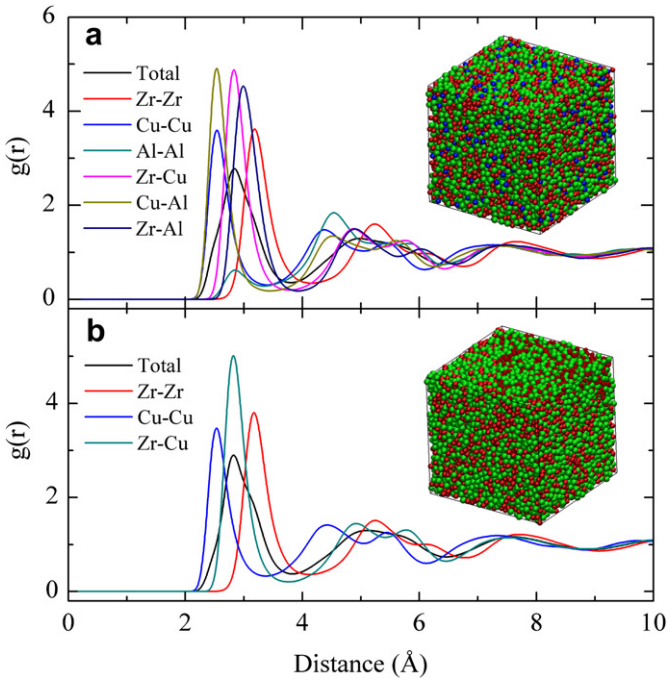

Fig. 1. Total and partial PDFs of (a) $Zr_{46}Cu_{46}Al_8$ and (b) $Zr_{54}Cu_{46}$ MGs. The insets are 3D configurations of these two alloys. The green, red and blue balls represent Zr, Cu, and Al atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

we extend the previous work by exploring the sharing frequencies of full icosahedra and atoms from the viewpoint of MRO, and to address quantitatively the atomic structural change caused by adding Al to the Zr–Cu binary alloy.

2. Simulation methodology

In this work, we made use of classical MD simulations [18] based on embedded atom method potential [16,19] to investigate binary $Zr_{54}Cu_{46}$ and ternary $Zr_{46}Cu_{46}Al_8$MGs. Each simulation model consists of 16,000 atoms and periodic boundary conditions were imposed in all the three axial directions. The system was quenched rapidly under the NPT ensemble (zero pressure) at 5×10^{11} K/s from 2000 K to 300 K to obtain the amorphous state (insets of Fig. 1).

Pair distribution functions (PDFs) were generated to obtain interatomic distance and coordination numbers (CNs). The Voronoi method, which tessellates the space into small regions [20], was then employed to analyse the atomic structure. Here, the Voronoi index, $<n_3, n_4, n_5, n_6>$ is used to describe different clusters, in which n_i denotes the number of i-edged faces in Voronoi cells and the sum of n_i is the coordination number for a specific solute atom. For instance, a perfect icosahedron is labelled as $<0, 0, 12, 0>$. If one fivefold 155-type pair (the centre atom and one neighbour atom have 5 common neighbour atoms that are connected to form 5 bonds [21]) is broken, it will then result in a distorted icosahedron with a Voronoi index of $<0, 2, 8, 2>$. Finally, based on the result of the Voronoi cells, the vertex, edge, face, and tetrahedral sharing frequencies of full icosahedra and atoms were investigated.

Table 1
Interatomic distances (Å) for amorphous $Zr_{46}Cu_{46}Al_8$ and $Zr_{54}Cu_{46}$ alloys.

Alloys	Zr–Zr	Cu–Cu	Al–Al	Zr–Cu	Cu–Al	Zr–Al
$Zr_{46}Cu_{46}Al_8$	3.14	2.56	2.86	2.84	2.56	2.98
$Zr_{54}Cu_{46}$	3.14	2.54	N/A	2.84	N/A	N/A

Table 2
Coordination numbers for amorphous $Zr_{46}Cu_{46}Al_8$ and $Zr_{54}Cu_{46}$ alloys.

Alloys	CN_{Zr}	CN_{Cu}	CN_{Al}	CN_{all}
$Zr_{46}Cu_{46}Al_8$	15.23	11.10	12.31	13.1
$Zr_{54}Cu_{46}$	14.96	11.14	N/A	13.2

3. Results and discussion

3.1. Short-range order

Fig. 1 shows the total and partial PDFs for amorphous $Zr_{46}Cu_{46}Al_8$ and $Zr_{54}Cu_{46}$ alloys. We observe from the figure that although there is only 8% Al in the ternary system, the SRO of Zr–Al and Cu–Al is dominant as shown by the well-pronounced first peaks in the PDFs. At the same time, the addition of Al to the Zr–Cu binary system did not weaken the SRO of Zr–Cu as exemplified by the nearly unchanged first peaks of Zr–Cu partial PDFs in Fig. 1(a) and (b). Therefore, the additional amount Al has strengthened the SRO of all unlike bonds in the ternary system, which is beneficial for icosahedral formation as shown latter.

From the PDFs, the interatomic distances have also been extracted as listed in Table 1. One can see that the distance of Cu–Al pair in the ternary system has been shortened by approximately 6% when compared with atomic radii, which is a characteristic property in Al-involved MGs [7,22]. Table 2 shows the CNs for these two systems. It is observed that Zr has a CN of about 15, while Cu is centred by around 11 atoms in both binary and ternary system. Moreover, Al has a CN of 12.3 in the ternary system, which is mainly contributed by Zr and Cu neighbour atoms as illustrated in the pronounced first peaks in the PDFs in Fig. 1.

The fraction of full icosahedra and other forms of clusters represented by the Voronoi indices in the $Zr_{54}Cu_{46}$ and $Zr_{46}Cu_{46}Al_8$ systems are depicted in Fig. 2. According to the figure, the fraction of full icosahedra found in the $Zr_{46}Cu_{46}Al_8$ alloy is nearly twice of that in the $Zr_{54}Cu_{46}$ system. This is because there are more Cu-centred full icosahedra in the ternary system and the addition of Al in the ternary system provides for more than 1.5% of Al-centred full icosahedra. We also note that 18.8% of the Al atoms function as

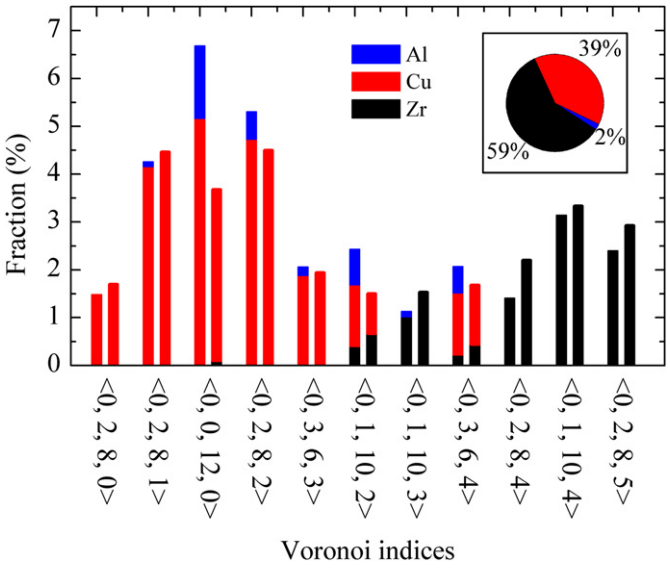

Fig. 2. The distribution of the most frequently found Voronoi indices in $Zr_{46}Cu_{46}Al_8$ (left histograms) and $Zr_{54}Cu_{46}$ (right histograms) MGs. The inset represents the Zr–Cu–Al combinations in the nearest neighbour shell of all Al-centred full icosahedra in $Zr_{46}Cu_{46}Al_8$ alloy.