



Research Article

Structural evolution and energy landscape of the clusters in $Zr_{55}Cu_{35}Al_{10}$ metallic liquid and glassJingfeng Zhao^a, A. Inoue^{d,e}, C.T. Liu^b, P.K. Liaw^c, Xiaoping Shen^a, Shiyan Pan^a, Guang Chen^a, Cang Fan^{a,*}^a School of Mater. Sci. & Eng., Eng. Res. Cent. of Mater. Behav. & Des., MOE, Eng. Train. Cent., Nanjing University of Science & Technology, Nanjing 210094, PR China^b Cent. for Adv. Struc. Mater., MBE, College of Sci. & Eng., City University of Hong Kong, Hong Kong, PR China^c Dept. of Mater. Sci. & Eng., University of Tennessee, Knoxville 37996, USA^d International Institute of Green Materials, Josai International University, Togane 283-8555, Japan^e Department of Physics, King Abdulaziz University, Jeddah 22254, Saudi Arabia

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ABSTRACT

Based on pair distribution function studies, a structural parameter, derived from the number of cluster connecting bonds and the coordination number, and energy analysis have been introduced to describe different kinds of local clusters in the liquids and glasses. By applying these analyses to a widely studied Zr–Cu–Al base alloy system, we found that Zr-, Cu- and Al-centered first shell clusters showed different structural evolution and energy distributions during cooling. In terms of their structure and energy states, it is confirmed that the Al-centered first shell clusters play dominant role in the appearance of glass transition prior to the crystallization.

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Understanding the glass transition (GT) is a vital issue and a great challenge in the research of metallic glasses [1]. The study of the structural evolution of metallic liquid and glass is crucial to understand glass forming ability (GFA) and GT [2]. Deep researches have been carried out in the Zr–Cu binary alloy system due to its superior GFA and its simplicity [3]. The addition of the alloying element can lead to the improvement of the GFA and other properties [4–7]. The property changes are essentially from differences of their structures, which include geometric arrangements of the local atoms and their energy distributions. Surely, the structural evolution and energy landscape of the clusters are believed to be the origin of the metallic glass transition [8,9]. It has been reported that short-range order clusters, especially the icosahedron, can be used to characterize the liquid and glassy structure [10–14]. Cheng et al. have proposed that Cu- and Al-centered icosahedral clusters are the basic local structures. The addition of Al to the Zr–Cu binary alloy system not only leads to the increase of the fraction of icosahedral clusters but also enhances spatial connection [10]. Zhang et al. have analyzed the energy distribution of ten types of Voronoi clusters at temperatures above and below the glass transition temperature (T_g). The icosahedral cluster shows the lowest energy in both supercooled liquid and glassy samples [11]. Therefore, it is meaningful to study the structural evolution and energy landscape of the clusters in metallic liquid and glass.

Clusters with different atom arrangements formed in the liquid and glass should have different energy landscapes and structural features in the multicomponent alloy system. In order to further characterize the structural evolution and the cluster energy distributions for identifying the local orders for GT and expecting to gain general insight into the mechanism of the GT, a different approach – a new structural parameter with the combination of the atomic connecting bonds and coordination number (CN) based on a series of studies on pair distribution functions (PDFs) has been proposed. In this letter, we report some results by applying the new approach to a typical Zr–Cu–Al ternary alloy.

The Zr–Cu–Al ternary alloy system is the most fundamental one in a number of stable bulk glassy alloys and has been researched extensively. The selection of the most basic alloy system allows us to apply the derived interpretation to glassy alloys in metal–metal multicomponent alloy systems, which generally follow the three component rules [24]. The investigation we conducted is carried out using classic molecular dynamics simulations with embedded atom method (EAM) potentials proposed by Sheng et al. [10], and the reliability of the potential has been identified by many reports [15–18]. In our work, the unit cell is made up of 16,000 atoms, in which 8768 Zr atoms, 5632 Cu atoms and 1600 Al atoms are randomly arranged. Periodic boundary conditions are imposed on the cubic supercell and time step is set to be 1 fs. The initial structure is heated up to 2000 K, which is about 800 K higher than the melting temperature of $Zr_{55}Cu_{35}Al_{10}$, and then the temperature is hold at 2000 K for 10 ns to break the initial configuration and obtain

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the equilibrium liquid state. The cooling process is conducted according to the following method. The system is cooled from 2000 K to 300 K with a total time of 34 ns and suspended for 1 ns to obtain the configuration for the corresponding temperature with a temperature interval of 100 K. The effective average cooling rate is 5×10^{10} K/s. The whole process is carried out in the NPT ensemble with a Nose–Hoover thermostat for temperature control and a Nose–Hoover barostat for pressure control. The external pressure is set as zero.

The tight-bond cluster model not only explains the phenomenon that there is much difference in the strength and plasticity between the metallic glasses and their corresponding supercooled liquid well but also enables us to quantitatively characterize local atomic structures in amorphous alloys. The tight-bond cluster model mainly contains three components, clusters, interconnecting zones (i-zones) and free volume. The connection between the nearest atoms is classified into cluster, i-zone and free volume connecting bonds. For different alloy systems, according to the radii of different elements in the specific system, the quantification of the cluster, i-zone and free volume connecting bond length can be defined by comparing the metallic glass structure with the corresponding crystallized structure obtained from the experiments. According to the quantitative definition, the number of cluster connecting bonds can be calculated [19–21]. By integrating the whole first shell of PDFs, we can gain the CNs at different temperatures for different alloy systems. As a result, in the structure analysis of the local clusters in the liquid and glass systems, the CN in conjunction with the tight-bond cluster model is employed. Cluster connecting bonds are formed between atoms with the strongest bonding among the above three kinds of connecting bonds. The proposed structural parameter, denotes the ratio of the number of the cluster connecting bonds of a given atom to the CN for the given atom in the first shell can be used to further characterize the packing density of the local clusters. The data of the PDFs and radial distribution functions (RDFs) for the nearest atom pairs from the neutron scattering experiments on the as-cast bulk metallic $Zr_{55}Cu_{35}Al_{10}$ glass and its completely crystallized counterpart measured at a cryogenic temperature of 15 K, which can minimize the thermal induced atomic vibration effect, is sufficient for the calculation of the proposed structural parameter. The radii of Zr, Al and Cu are 1.62 Å, 1.43 Å and 1.28 Å, respectively. Beyond 3.33 Å, which is 2.8% larger than Zr–Zr characteristic value 3.24 Å, there are almost no Zr–Zr nearest atom pairs existing within the PDF for the crystallized counterpart. As a result, the initial bond length for the i-zone atom pairs, also the ending bond length for the cluster atom pairs is set at least 2.8% greater than their characteristic atomic radii. The initial bond length for the free volume atom pairs is set at 9.6% larger than their characteristic atomic radii because the free volume regions do not exist in the crystallized counterpart and the terminal of the RDF for the crystallized counterpart is 9.6% greater than the Zr–Zr characteristic atomic radius [20,21].

The potential energy (PE) for every atom can be obtained from the classic molecular dynamics simulations. The cluster formation energy

$E_{p,c}$ for an N-atom cluster is defined as $E_{p,c} = (1/N \sum_{i=1}^N (E_{p,i} - E_{ref,\alpha}))$, where $E_{p,i}$ is the PE for the *i*th atom in the cluster and $E_{ref,\alpha}$ is the reference energy for the type α atom [4]. The crystal chemical PE (hcp Zr, fcc Cu and fcc Al) is used as the reference energy. We use $E_{p,c}$ to analyze the energy distribution of the local clusters in the liquid and glass. We define the effective radius for an N-atom cluster as $r_{eff} = (1/(N-1) \sum_{i=1}^{N-1} d_{c,i})$, where $d_{c,i}$ is the distance between the central atom and the shell atom.

The relationship between the average PE of all atoms and the temperature is shown in Fig. 1(a). Crystallization is often accompanied by energy mutation. However, there is no abrupt change in PE here. The PE of the system decreases basically in a linear trend as the temperature drops, and the turning point can be observed between 700 K and 800 K. Through linearly fitting and extrapolating the two parts of the PE curve in the temperature range of 1200 K to 900 K and 300 K to 600 K, the T_g in the simulation is identified at 710 K. It is basically in line with the experiment T_g with the value of 657 K measured by differential scanning calorimetry [20], if the cooling rate difference is taken into consideration. According to the T_g , the PE curve is classified into two stages, 1900 K to 800 K and 700 K to 300 K.

The first stage is from 1900 K to 800 K above the T_g in the liquid. In this stage, the atoms can make a long distance migration. The heat of mixing (ΔH_{mix}) between different atoms is the dominant factor governing the atomic motion. As the temperature decreases, the nearest atoms are rearranged according to the ΔH_{mix} and the first shell coordination number (CN) of the whole system increases. As far as Zr, Cu and Al are concerned respectively, the variation of the CN for their first shell clusters presents different trends, as shown in Fig. 2. The CN for the Zr-centered first shell clusters increases basically in a linear trend with the shell Zr, Cu and Al atoms all increasing as the temperature decreases because the ΔH_{mix} for Zr–Zr, Zr–Cu and Zr–Al are highly negative. The CNs for Cu- and Al-centered clusters increase firstly and then decrease with the shell Zr atoms increasing and the shell Cu and Al atoms decreasing during the cooling in the first stage as the ΔH_{mix} for Cu–Al, Al–Al and Cu–Cu are less negative. The turning point for the CNs for Cu- and Al-centered clusters is at 1500 K and 1200 K, respectively. Compared to Cu atoms, it is easier for Al atoms to bond with Zr atoms in consideration of the values of ΔH_{mix} for Zr–Al (–44 kJ/mol) and Zr–Cu (–23 kJ/mol), resulting in more shell Zr atoms in the Al-centered clusters than that in the Cu-centered clusters (shown in Fig. 2(b)). It explains why the beginning temperature for the decrease of the CN for the Cu-centered clusters is higher than the Al-centered clusters. The second stage is between 700 K and 300 K below the T_g in the glass. Compared with the first stage, the atoms can only make a short migration. As a result, the average CN in the nearest shell of the system remains basically unchanged. As for Zr-, Cu- and Al-centered first shell clusters respectively, there is only a very small change.

By applying the proposed structural parameter to the most basic $Zr_{55}Cu_{35}Al_{10}$ liquid and glass systems, it is found that the variation

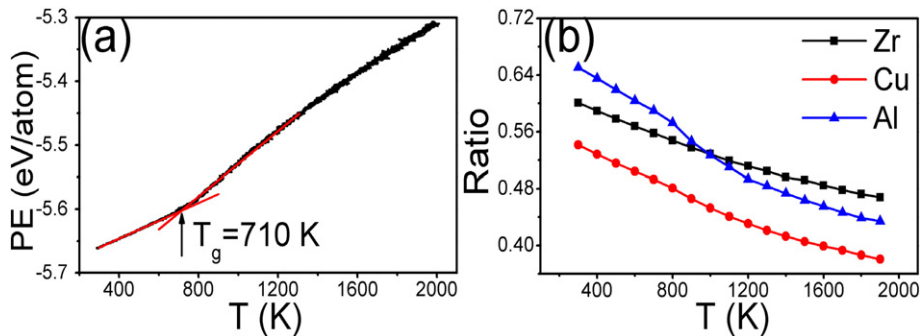


Fig. 1. (a) The variation of the average potential energy (PE) of $Zr_{55}Cu_{35}Al_{10}$ alloy as a function of temperature during the cooling process. (b) The variation of the ratio of the cluster connecting bonds of the central atom to the CN for the central atom in the first shell in the Zr-, Cu- and Al-centered clusters.

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