# Effect of local structures and atomic packing on glass forming ability in $Cu_xZr_{100-x}$ metallic glasses

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(Received 16 September 2009; accepted 10 December 2009; published online 11 January 2010)

Molecular dynamics simulations are performed for CuZr metallic alloys to study the structural and dynamical features for glass forming ability (GFA). Our analysis shows that in CuZr metallic system, although $\langle 0,0,12,0\rangle$ icosahedral clusters are important, some Zr-centered clusters such as $\langle 0,1,10,4\rangle$ and $\langle 0,1,10,5\rangle$ play a key role in slowing down the dynamics. It is found that these Zr-centered clusters are intrinsically slow and fundamentally determine the stability and slow dynamics. Due to the strong spatial correlation between $\langle 0,0,12,0\rangle$ and Zr-centered clusters, their relative population influences the dense packing and dynamics in metallic glasses, and further the GFA. © *2010 American Institute of Physics*. [doi:10.1063/1.3282800]

Bulk metallic glasses (BMGs) have attracted much attention because of their unique mechanical properties.[1–3] It has been shown that glass forming ability (GFA) of BMGs is crucial for developing new BMGs for engineering applications.[4] Several empirical rules have been proposed to evaluate the GFA of metallic alloys.[5,6] However, due to the lack of detailed structural information of BMGs, it is still an unraveled mystery that a small change in composition or a minor addition of alloying elements can drastically change GFA.[1,7] On the other hand, GFA of an alloy also depends on kinetics of evolution and thermodynamically viable phases in its undercooled melt.[8,9] Therefore, understanding of correlation of local structures and kinetics with GFA is crucial for predicting BMGs with large GFA.

While icosahedral short range order (ISRO) was proposed as local structural unit in metallic liquids and glasses long time ago and has been studied extensively,[10–18] it is still not clear how ISRO arranges in three-dimensional space. Due to the intrinsic non-space-filling character, ISRO cannot achieve global dense packing. Therefore, it is important to understand what roles other local structural units play in the structural and dynamical properties of metallic glasses, what the relationship is between ISRO and other local structures, and how they interact with each other to obtain dense atomic packing and good GFA? So far, however, few studies have be devoted to these important issues.

CuZr binary metallic system has been illustrated to have good GFA and wide glass-forming composition range.[19–21] It is a simple but ideal model system for investigating the relation between local structure and GFA. Several studies have been done for the correlation between local structures, atomic diffusivity, and their GFA in CuZr alloys.[22–28] However, how the local structures change with composition and the influence on GFA are still remain elusive.

In this letter, we performed molecular dynamics (MD) simulations with embedded-atom method (EAM) potential to study the effect of the local structure and dynamical behavior on GFA for $Cu_xZr_{100-x}$ ($x$=20,30,40,50,64.5,80,90) amorphous alloys. Voronoi tessellation was used to characterize the local structures. The dynamics analysis shows that some Zr-centered clusters such as $\langle 0,2,8,6\rangle$, $\langle 0,1,10,4\rangle$, and $\langle 0,1,10,5\rangle$ are always slow and do not change much with compositions, fundamentally determining the stability of metallic glasses. The dynamics of $\langle 0,0,12,0\rangle$ clusters is slowing down as its population increases with Cu content increase. It is also found that there exists strong spatial correlations between $\langle 0,0,12,0\rangle$ and these Zr-centered clusters. The strong spatial correlation and the relative population of these clusters make dynamics slow down and dense atomic packing, which benefits the GFA in CuZr system.

In our simulations for CuZr systems EAM potential developed in Ref. 29 was employed which has been proved to be consistent with experimental measured structure factors.[29,30] The structure models consist of 5000 atoms in the simulation cells with periodic boundary conditions. They were first equilibrated at T=2000 K, then cooled down to 300 K with cooling rate of $4.9\times10^{11}$ K/s. The cell size was chosen to give zero pressure in NVT ensemble for each composition at various temperatures. The details of the generation of the structural models can be found in Ref. 30. In our work, atomic coordinates were collected over 200 000 MD steps (2 fs per step) for structural and dynamical analyses. The structural models for each composition at T=600 K were analyzed.

The Voronoi index $\langle n_3,n_4,n_5,n_6\rangle$, where $n_i$ denotes the number of $i$-edged faces of the Voronoi polyhedron, is used to designate the character of the atomic cluster surrounding an atom. A cutoff of 5 Å is used in our Voronoi analysis. The population variation in the major populated Voronoi polyhedra with Cu content is investigated as shown in Fig. 1. With Cu concentration increasing, the population of $\langle 0,0,12,0\rangle$ and $\langle 0,1,10,2\rangle$ increases, even beyond 64.5% of Cu content. For some other polyhedra such as $\langle 0,2,8,2\rangle$, $\langle 0,2,8,6\rangle$, $\langle 0,1,10,4\rangle$, and $\langle 0,1,10,5\rangle$, the population increases first, then decreases. In addition, the population variation in these clusters is consistent with that of GFA in CuZr system.[20,23,28] Although both $\langle 0,2,8,2\rangle$ and $\langle 0,1,10,2\rangle$ are icosahedral-like clusters,[7,27,32] the population of $\langle 0,2,8,2\rangle$ decreases as Cu content increases beyond 64.5%. This indicates that Cu atoms tend to form the polyhedra which have more five-edged faces. The above analysis suggests that not only icosa-

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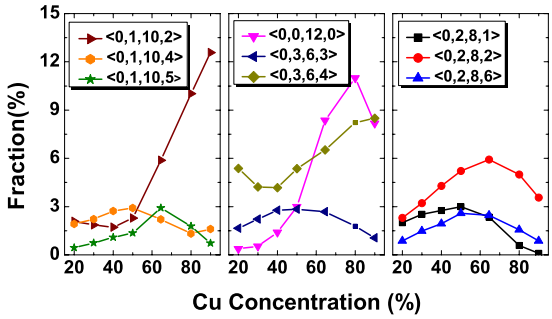


FIG. 1. (Color online) The variation in the population of some Voronoi polyhedra with Cu concentration at T=600 K.

hedral polyhedra of ⟨0,0,12,0⟩ but also some others may be responsible for the GFA in metallic glasses.

To get deep insight into the role of these major atomic clusters in the GFA in this system, we analyze the mean-square displacements (MSD). Figure 2 shows the MSD versus simulation time for various clusters in different compositions. It is found that some Zr-centered clusters such as ⟨0,2,8,6⟩, ⟨0,1,10,4⟩, and ⟨0,1,10,5⟩ are always slow in all compositions, even the slowest as Cu content is less than 50%, and their MSDs are almost independent of the compositions. This implies that these clusters are intrinsically slow in CuZr system. Interestingly, the total fraction of these Zr-centered clusters does not decrease but increases quickly from about 1.7% to 7.5% as Zr content decreases from 80% to 35.5%. Then it decreases quickly to 1.6% at 90% of Cu content. For ⟨0,0,12,0⟩ clusters, it's not slow at lower Cu concentrations. As Cu content increases, its MSD is getting smaller. This indicates that the dynamics of ⟨0,0,12,0⟩ strongly depends on Cu content in this system and correlates with its population. Therefore, it is expected that the population of these Zr-centered clusters may fundamentally determine the dynamics in CuZr system, while the population of ⟨0,0,12,0⟩ clusters further enhances the stability and slow dynamics. Similar dynamical features were also found in high temperature liquids of CuZr metallic system by *ab initio* MD simulations.[31]

To obtain insight into the correlation between structure and dynamics, the spatial correlation between central atoms of polyhedra $i$ and $j$ is analyzed by calculating a nearest-neighbor correlation index $C_{ij}=p_{ij}/p_{ij}^{0}-1$ (Ref. 32) where $p_{ij}$

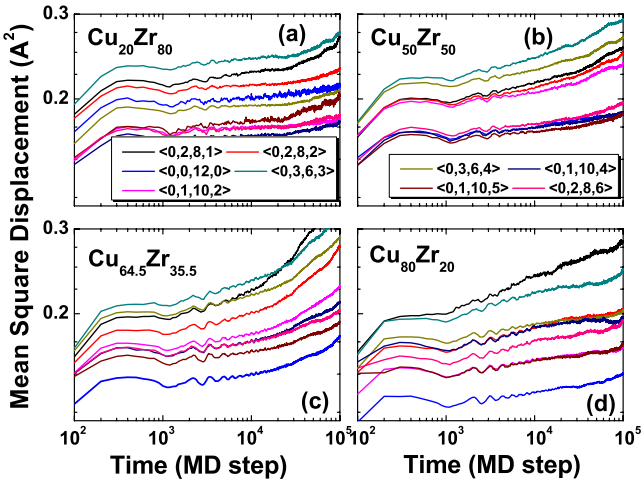


FIG. 2. (Color online) The MSDs of various clusters vs simulation time at T=600 K in four compositions.

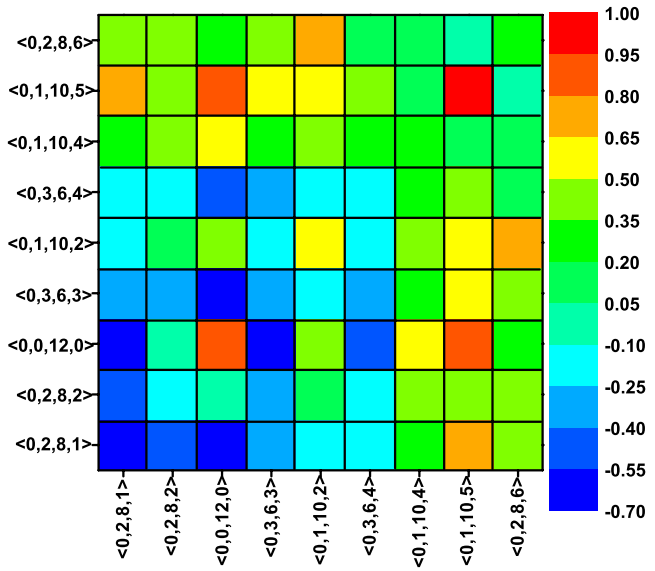


FIG. 3. (Color online) The matrix of spatial correlation index $C_{ij}$ of some clusters in $Cu_{50}Zr_{50}$.

and $p_{ij}^{0}$ are the probability of polyhedra types $i$ and $j$ being the nearest neighbors in a structure model and a structure in which the distributions of indices are spatially uncorrelated, respectively. Therefore, the positive and negative values indicate a preference and an avoiding of polyhedra $i$ and $j$ being nearest neighbors, respectively.

Figure 3 shows the correlation matrix of $C_{ij}$ for those atomic clusters in the structure of $Cu_{50}Zr_{50}$. For other structure models at different compositions and temperatures, the correlation matrix shows the similar features. Generally Cu-centered clusters tend to avoid other Cu atoms except for ⟨0,0,12,0⟩, but tend to be the nearest neighbors with Zr-centered clusters. However, Zr-centered clusters can be the nearest neighbors with either Cu or Zr atoms. Such a general preference of clustering of small- and big-sized clusters may lead to dense packing in metallic glasses. In specific, both ⟨0,0,12,0⟩ and ⟨0,1,10,5⟩ have strong tendency of being nearest neighbors with themselves and each other. ⟨0,0,12,0⟩ also has tendency of being nearest neighbors with ⟨0,1,10,2⟩ and ⟨0,1,10,4⟩. This indicates that ⟨0,0,12,0⟩ prefers to be the nearest neighbors with the pentagon-rich polyhedra, leading to dense packing in metallic glasses.

As shown in Fig. 1, as Cu content increases, more and more ⟨0,0,12,0⟩ clusters are formed. Due to the strong spatial correlation, they tend to connect with themselves, which may slow down the dynamics of ⟨0,0,12,0⟩ significantly.[7,32] On the other hand, due to the increase of the population of slow Zr-centered clusters, the strong spatial correlation and dense packing between them can further slow down the dynamics of the systems. Figure 4 shows the distribution of ⟨0,0,12,0⟩, ⟨0,1,10,4⟩, and ⟨0,1,10,5⟩ in four different compositions. It is clear that in $Cu_{20}Zr_{80}$ the fraction of these three types of clusters is very small, and most of ⟨0,0,12,0⟩ are isolated. As shown in Fig. 2, the dynamics of isolated ⟨0,0,12,0⟩ is not slow compared to ⟨0,2,8,6⟩, ⟨0,1,10,4⟩, and ⟨0,1,10,5⟩. As Cu content increases, the fraction of all these clusters increases quickly and connect with each other. The formation of such configurations makes the dynamics of

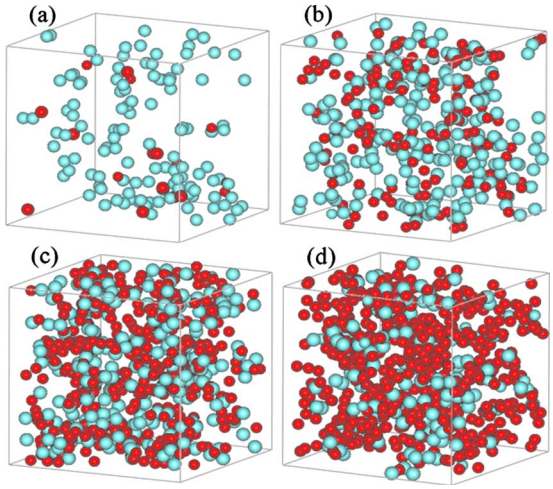


FIG. 4. (Color online) The snapshot of the central atoms of $\langle 0,0,12,0\rangle$ (red or dark), $\langle 0,1,10,4\rangle$ (green or light), and $\langle 0,1,10,5\rangle$ (green) clusters in (a) $Cu_{20}Zr_{80}$, (b) $Cu_{50}Zr_{50}$, (c) $Cu_{64.5}Zr_{35.5}$, and (d) $Cu_{80}Zr_{20}$.

$\langle 0,0,12,0\rangle$ slower with Cu content increase, enhancing the slow dynamics in CuZr system.

Although the population of $\langle 0,0,12,0\rangle$ increases and the dynamics become slower, the GFA becomes weaker as Cu content is more than 64.5%. This is because the fraction of $\langle 0,1,10,4\rangle$, $\langle 0,1,10,5\rangle$, and $\langle 0,2,8,6\rangle$ clusters, which play fundamental role in the structure stability in CuZr system, starts to decrease. This affects the atomic packing as well as dynamics in this system. It is known that the icosahedral $\langle 0,0,12,0\rangle$ clusters cannot extend in three-dimensional space, and $\langle 0,0,12,0\rangle$ themselves tend to form stringlike network as its fraction increases.[17,32,33] These Zr-centered clusters are responsible for connecting $\langle 0,0,12,0\rangle$ strings with other polyhedra to densely fill the remaining space, because they can be the nearest neighbors of $\langle 0,0,12,0\rangle$ as well as other clusters as shown in Fig. 3, and are able to connect them together to achieve dense atomic packing in space. The decrease in the fraction of these Zr-centered clusters will weaken the dense packing and GFA.

On the other hand, the atomic radius ratio $R$ of icosahedral clusters at different compositions also indicates the important role of the population of Zr-centered large clusters in the efficient atomic packing. Our analysis shows that $R \approx 0.897$, 0.934, and 0.962 at Cu content of 64.5%, 80%, and 90%, respectively. For an unstrained icosahedron $R=0.902$.[34] Therefore, the icosahedral packing is quite efficient in $Cu_{64.5}Zr_{35.5}$ metallic glass. For $Cu_{80}Zr_{20}$, the icosahedral clusters are strained, but 20% Zr atoms are sufficient to minimize the distortion and icosahedral packing is still efficient.[12,13,34] As Cu content increases to 90%, icosahedral clusters have been highly strained and 10% Zr atoms are not enough to minimize the distortion. The icosahedral packing is not efficient anymore, so that the population of icosahedral clusters decreases. Therefore, the population of Zr-centered clusters is also responsible for the slow dynamics and dense packing in CuZr system, and these clusters play a fundamental role in achieving good GFA.

Note that the cooling rate used in our MD simulations is much faster than that in experiments. However, our previous studies have shown that such structure correlations and icosahedral stringlike packing will become even more evident with a much lower cooling rate.[32]

In summary, both $\langle 0,0,12,0\rangle$ icosahedral clusters and some Zr-centered clusters such as $\langle 0,2,8,6\rangle$, $\langle 0,1,10,4\rangle$, and $\langle 0,1,10,5\rangle$ have significant effects on the dynamic behavior, dense atomic packing and GFA in CuZr system. The population of these Zr-centered clusters fundamentally determine the stability and slow dynamics of CuZr metallic glasses, while the population of $\langle 0,0,12,0\rangle$ will further enhance the slow dynamics and GFA.

W.H.W. acknowledges the financial support of the NSF of China (Grant Nos. 50731008 and 50621061) and MOST 973 (Grant No. 2007CB613904). Work at Ames Laboratory was supported by the U.S. Department of Energy, basic Energy Sciences under Contract No. DE-AC02-07CH11358.

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