Relation of Structure, Composition and Glass Forming Ability in Zr-Cu Binary Amorphous Alloys

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Abstract. Molecular dynamics simulation was used to simulate Zr-Cu binary system, in which the relationship between structure, composition and glass forming ability was study. Atomic local structures were analyzed from view of chemical and topological short range order. Reduction fraction of full icosahedra(B_c) was developed to establish the relation of structure-composition and glass forming ability(GFA) in Zr-Cu binary system. Obviously peaks were observed at some certain compositions which own the good GFA. As a structure factor, B_c could be a indicator of GFA of Zr-Cu alloys. Our works contributed to further understanding the effect of atomic structures on glass forming.

1 Introduction

Bulk metallic glasses (MGs) was paid much attention due to their unique properties, such as high strength, high elastic strain limit, and high corrosion resistance[1,2,3]. It was a throughout central issues to build the relationship between structure and properties in material science field, because properties of materials were determined by atomic structure [4,5]. However, up to now, detailed micro-structural information was very lack for metallic glasses. It was still a mystery that a small change in composition could lead to sharply change of glass-forming ability (GFA). So, building composition-structure-GFA relationship was very important to study GFA.

Recently, many owning good glasses-forming composition in Zr-Cu binary system were found[6,7]. As a binary alloy system, it was a simple and ideal model system for studying the correlation between atomic structure, composition and GFA. Full Icosahedra(F-ICO) as a short-range order had been found in a lot of amorphous alloys. F-ICO clusters were observed not only in Zr-Cu binary amorphous alloy, but also in high temperature melt by ab initio molecular dynamics(MD)[8,9,10]. In previous works, F-ICO increased the viscosity of the liquids and contributed to an enhance GFA[11,12], whereas other types of polyhedral could not show the property. In present work, topologic and chemical structure change with composition were study extensively. A parameter based on the relative change is introduced

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to build the relationship between structure and GFA.

2 Simulation Method

In the letter, authors performed MD simulations with Tight bonding (TB)potential to explore the effect of the short range ordering structure on GFA for Zr-Cu binary system. The simulation process was in the NTP(constant number of particles-pressure-temperature) ensemble using the Material Explorers software. The MD simulation was carried out in a super cell including 20000 atoms under the periodic boundary conditions. To build different composition alloy models, the appropriate amount of copper atom and zirconium atom were randomly distributed in the initial B2 structure. These alloy models were first equilibrated at T=2000K. After equilibrating the structure in the liquid phase, these models were quenched to rooming temperature (300K) using the conjugated gradient method. The cooling rate was $2K.ps^{-1}$ at zero external pressure. A time step of 2ps was used. The resulting atomic structures were further optimized using the conjugated gradient method.

3 Result and Discussion

Voronoi tessellation technique analyses were used to investigate the atoms' nearest-neighbor environment evolution with composition. The different coordination polyhedral surrounding a central atom could be characterized by the Voronoi index $<n_3,n_4,n_5,n_6,\ldots>$, where n_i denoted the number of i-edged faces of the polyhedron. Based on this, Voronoi tessellation technique was usually applied to analyze topological short range order(TSRO) structure of amorphous state. F-ICO clusters (Voronoi index *<0,0,12,0>*) was the most stable and dense structure in various types of TSRO structures. F-ICO clusters made dynamic of metallic glasses slowed down and increased stability of alloy melt, which benefited GFA in Zr-Cu system[11]. So, the F-ICO cluster was usually used as the key indicator of stability of the glass structure. Moreover, it was worth notice that F-ICO clusters were almost Cu centered in Zr-Cu binary system in our works. It was consistent with the experimental measurement and MD simulations.

The evolution of the fraction of F-ICO clusters($f_{\text{F-ICO}}$) in Zr-Cu alloy as function of temperature (during the quenching process) was obtained, as shown in Fig.1. It was observed that the $f_{\text{F-ICO}}$ value sharply increased as the temperature drop in over composition alloys. The results were in agreement with previous works. Authors evaluated the correlation between Cu content and $f_{\text{F-ICO}}$ at rooming temperature. It was found that the Cu-rich (Cu content more than equal to 50%)systems contained more F-ICO clusters.

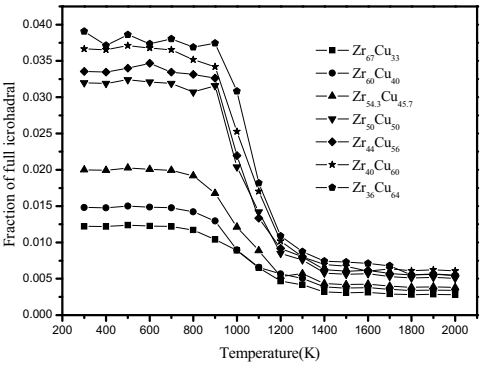

Fig.1 Temperature evolution of the fraction of F-ICO clusters during quenching process in Zr-Cu alloys.

The $f_{F\text{-}ICO}$ Values over the seven compositional ranges, from $Zr_{67}Cu_{33}$ to $Zr_{64}Cu_{36}$, from $Zr_{61}Cu_{39}$ to $Zr_{59}Cu_{41}$, from $Zr_{56}Cu_{44}$ to $Zr_{54}Cu_{46}$, from $Zr_{51.5}Cu_{48.5}$ to $Zr_{48.5}Cu_{51.5}$, from $Zr_{45}Cu_{55}$ to $Zr_{43}Cu_{57}$, from $Zr_{41.5}Cu_{58.5}$ to $Zr_{39}Cu_{61}$, from $Zr_{37}Cu_{63}$ to $Zr_{35}Cu_{65}$, were shown in Fig.2, in which the trend exhibited increase with Cu content. As Cu content increased, the $f_{F\text{-}ICO}$ Value increased quickly and connected with each other. These configurations slowed down the dynamics in Zr-Cu system. Based on the above description, Cu content was the more higher and the more stronger of GFA . In fact, Cu content did not forming direct ratio to GFA in Zr-Cu system. For example, it was well know that the tow best glass formers were $Zr_{50}Cu_{50}$[10,13] and $Zr_{35.5}Cu_{64.5}$[9], at which 2mm rods could be cast completely metallic glasses, in Zr-Cu systems, according to previously reported experimental and simulations result. However, the $f_{F\text{-}ICO}$ values for $Zr_{50}Cu_{50}$ and $Zr_{35.5}Cu_{64.5}$ were not the highest. The $f_{F\text{-}ICO}$ value of $Zr_{50}Cu_{50}$ was particularly far lower than the other Cu-rich alloys. So, the $f_{F\text{-}ICO}$ value could not comprehensively characterize the GFA of Zr-Cu alloys. However, increasing trend was not linear. The average gradient in every compositional range was obviously different. Meanwhile, it was suggested that Cu content was not the unique factor on the forming F-ICO cluster. The promoting effect of Cu content on F-ICO nucleation was different over compositional range.

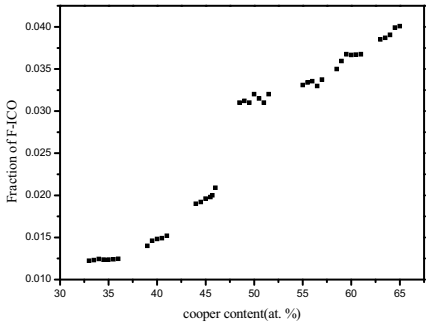

Fig.2 The fraction of F-ICO over the entire range.

In the above composition ranges, the average ratio of Cu to Zr in the nearest shell of every atom was calculated. The curve of coordination number(CN) with Cu content was shown in Fig.3. One might note from Fig.3 that the average CN of Cu-centered and Zr-centered clusters were from $Cu_{5.8}Zr_{7.5}$ to $Cu_{8.34}Zr_{5.46}$ and from $Cu_{6.8}Zr_{8.5}$ to $Cu_{10.59}Zr_{4.9}$, respectively, with Cu-content increased in Cu-rich alloys. The major crystalline phase was $Cu_{10}Zr_7$ for Cu-rich composition in former works[14]. It was shown that the average local chemical environment of atoms closed to $Cu_{10}Zr_7$. It was also implied that more and more atomic clusters having similar structure with $Cu_{10}Zr_7$ would be observed in Cu-rich alloys. The major crystalline phase was Zr_2Cu in Zr-rich composition(Zr content less than 50%)[14]. It was known from Fig.3 that the average CN of Cu-centered and Zr-centered clusters were from $Cu_{5.8}Zr_{7.5}$ to $Cu_{3.69}Zr_{9.38}$ and from $Cu_{6.8}Zr_{8.5}$ to $Cu_{4.6}Zr_{10.337}$, respectively, with Zr-content increase in Zr-rich alloys. It was also known that the local chemical environment of atoms closed to Zr_2Cu with Zr content increase. This was also promoted crystal nucleation rate. To sum up the above arguments, the chemical short range ordering(CSRO) was very sensitive to chemical composition. The evolution of CSRO shortened the atoms' crystallization diffusion distance, and restrained nucleation of F-ICO.

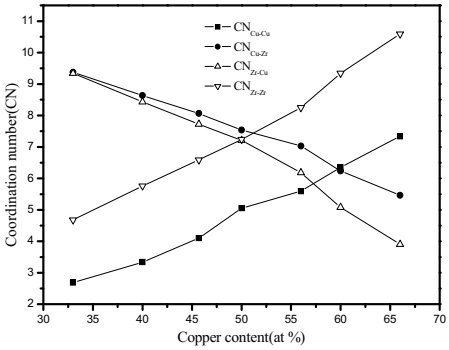

Fig.3 Total and partial CN for the molten Cu-Zr alloys as a function of concentration at rooming temperature.

On the basis of the above statistical analysis and discussion, a new parameter, B_c, was developed to establish the relationship between the atomic structure and GFA for Zr-Cu binary alloys. B_c could be expressed as $B_c=f_{\text{F-ICO}}/1\text{-}f_{\text{Zr}}= f_{\text{F-ICO}}/f_{\text{Cu}}$, where $f_{\text{F-ICO}}$ was the fraction of F-ICO clusters and f_{Cu} , f_{Zr} were Cu and Zr mol content, respectively. B_c was named as "reduction fraction of F-ICO" by authors. The higher B_c value represented that the composition contributed more to form F-ICO clusters and restrained more crystal nucleation as well as stronger GFA.

The curve of B_c of Zr-Cu binary alloy was as shown in Fig.4. B_c was still lower in Zr-rich alloy. It was indicated that the alloy composition not only inhibit the F-ICO cluster forming but benefit the crystal nucleation with Zr increase in Zr-rich content alloy. On the contrary, B_c value in Cu-rich alloy was larger than that in Zr-rich alloy. It was implied that the copper atom in Cu-rich alloy was more easily form F-ICO cluster than that in Zr-rich alloy. Meanwhile, tow peaks at $Zr_{50}Cu_{50}$ and $Zr_{36}Cu_{64}$ were observed as shown in Fig.4(marked by arrows). Furthermore, the good GFA was also reported in $Zr_{40}Cu_{60}$. 1.5mm rods could be cast completely amorphous[11] in $Zr_{40}Cu_{60}$. It was also reflected by B_c value as shown in Fig.4. So, the good match between peak of B_c and GFA indicated that B_c was a fundamental structure factor in determining the ease of glass forming.

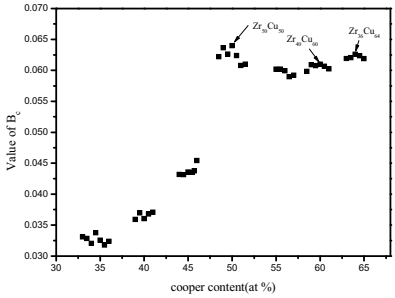

Fig.4 B_c over the entire range.

4 Conclusion

In conclusion, to study the compositional dependence of the GFA for Zr-Cu binary alloys by molecular dynamics. A large number of specimens with vary initial structure were simulated. Voronoi tessellation method was applied to analyze atomic local topological structures. It could be assumed that the composition acted positive and negative roles to glass forming of Zr-Cu alloys. The nucleation rate of F-ICO clusters was increased with Cu

content. It contributed to increasing stability of undercooling melt and GFA of Zr-Cu alloy; On the other hand, the chemical composition leaded to the evolution of chemical short range ordering. The change of chemical short range ordering provided crystal nucleation driving force. Base on above two pointes, reduced fraction of F-ICO, B_c, was proposed to establish the relation of structure-composition-GFA for Zr-Cu binary alloys. Peaks in B_c over broad compositional ranges were clearly observed. These peaks were in good agreement with GFA. In summary, B_c could correctly indicate GFA over a broad compositional rang in the Zr-Cu binary alloy system.

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