Computational Materials Science 44 (2008) 802–806

Contents lists available at ScienceDirect

Computational Materials Science

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

Structural characterization of $Mg_{65}Cu_{25}Y_{10}$ metallic glass from *ab initio* molecular dynamics

R. Gao [a], X. Hui [a,*], H.Z. Fang [a], X.J. Liu [a], G.L. Chen [a], Z.K. Liu [b]

[a] State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, PR China
[b] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, United States

ARTICLE INFO

Article history:
Received 9 September 2007
Received in revised form 24 May 2008
Accepted 28 May 2008
Available online 7 July 2008

PACS:
31.15.Ar
31.15.Ew
61.43.Bn
61.43.Dq

Keywords:
Ab initio molecular dynamics
Mg-based BMG
Pair correlation function
Coordination number
Structure factor

ABSTRACT

Ab initio molecular dynamics simulation (AIMD) was performed on the structural evolution of $Mg_{65}Cu_{25}Y_{10}$ alloy from 2000 K to 300 K. Pair correlation functions (PCFs), coordination numbers (CNs) and structure factors (SFs) of this glassy alloy were characterized. With the temperature decreased, the first peaks of both PCF and SF become narrower and higher, and shift to higher displacement or higher scattering vector. At the room temperature, the second peaks of both PCF and SF curves occur splitting, and the height of first peak of partial PCF for heterogenic atomic pairs is larger than that for homogenic atomic pairs. The generalized coordination numbers in this alloy are in good agreement with the results calculated by using efficient atomic packing model, which approves the atomic configuration of this alloy is in terms of dense packing. It was also found that the shape of both PCF and SF, and the CNs occur distinct change around 750 K.

1. Introduction

Mg-based bulk metallic glasses (BMGs) have being attracted great interest due to the increasing demand for light-weight and low-cost structural material. Among all the discovered Mg-based BMG alloys, Mg–TM–Y (TM: transition metal) alloy system is one of the most popular investigated BMG alloys, which has been known to exhibit a large supercooled liquid region and high glass forming ability (GFA) with critical cooling rates below 100 K/s. Up to now, a variety of Mg–TM–Y BMG alloys, e.g. Mg–Cu–Ag–Y [1], Mg–Cu–Zn–Y [2], Mg–Cu–Y–Nd [3], and Mg–Cu–Ni–Zn–Ag–Y [4] have been successfully prepared by using conventional copper mold casting method with the critical diameter of 6–16 mm. Especially, this alloy system has exhibited excellent physical, chemical and mechanical properties such as high specific strength, good corrosion, and low elastic modulus compared with the corresponding crystalline alloys [5,6]. The fracture strength of these Mg-based BMGs has been reported to be from 760 to about 1200 MPa, which is about 2–4 times as that of currently engineering magnesium crystalline materials [1–4]. The large GFA and the excellent performance of this kind of Mg-based BMGs, together with their relative low-cost, abundant deposit and easy recycling ability, make them promising for engineering application.

Compared with the other BMG alloys, however, the structural characterization of the Mg–TM–Y BMG alloys is less understood. For this kind of BMG alloys, the previous works were mainly focused on the composition design and various properties. Although some works on the GFA have been conducted by investigating the phase diagram characterization [7] and crystalline phases [8], detailed atomic configuration of this kind of Mg-based glassy alloys has not been known. No information of the atomic position and short to medium range order in the atomic packing of this kind of alloys has been reported. Consequently, the understanding of glass transition, GFA and composition design of Mg-based BMG alloys have been severely restricted.

In this paper, we perform *ab initio* molecular dynamics (AIMD) simulation [9] of the structural evolution of $Mg_{65}Cu_{25}Y_{10}$ alloy from liquid to glass state. This alloy is one of most early discovered Mg base BMG alloys. Most of the yttrium bearing Mg-based quarternary and quinary BMG alloys have been developed based on this ternary alloy, such as $Mg_{65}Cu_{15}Ag_{10}Y_{10}$ [1], $Mg_{65}Cu_{20}Zn_5Y_{10}$ [2] and

* Corresponding author. Tel.: +86 10 62333066; fax: +86 10 62333474.
E-mail address: huixd01@hotmail.com (X. Hui).

0927-0256/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.commatsci.2008.05.031

$Mg_{65}Cu_{15}Ag_5Pd_5Y_{10}$ [10]. Based on AIMD calculation, we can obtain the pair correlation functions (PCFs), the coordination numbers (CNs), and the structure factors (SFs) of this alloy. These results are expected to be beneficial to the deep understanding of glass transition, GFA and composition design of whole Mg–TM–Y system BMGs.

2. Methodology

The AIMD calculations were implemented by using Vienna *ab initio* simulation package (VASP) [11–13]. The AIMD simulation presented here are based on density functional theory (DFT) which is generally accurate for metals and semiconductors. Kohn–Sham equations of the DFT were solved using the generalized gradient approximation (GGA). All-electron wave-functions were used to describe the electron–ion interaction obtained from ultrasoft pseudopotentials [14].

In this work, we employed a cubic supercell method to simulate the atomic configurations of $Mg_{65}Cu_{25}Y_{10}$ alloy during the cooling process from liquid to glassy state. The supercell contains 140 atoms which include 35 Cu, 91 Mg and 14 Y atoms. The simulation was performed in a canonical NVT (constant number, volume and temperature) ensemble. Only Gamma point is used for the set-up of K-point file. The time step used in the simulation is equal to 5 fs. The calculations were proceeded as following: firstly, the supercell was assigned to be $14.63 \times 14.63 \times 14.63$ Å^3, which is deduced from the experimentally measured density of the glass at room temperature. The initially random distributed atoms were well equilibrated by running 2000 time steps at 2000 K. Then, the liquid was sequentially quenched to 1200 K, 950 K, 750 K, 600 K, 450 K and 300 K at the cooling rate of 2×10^{14} K/s. At 1200 K temperature step, the new quenched structure is relaxed for 5 ps to reach its intrinsic thermal equilibrium. For the other temperature steps, the quenched structures were relaxed for 2.5 ps. The structure configuration of the system was recorded at every temperature step. The whole simulation process is run for 36 ps, which is schematically illustrated in Fig 1.

During the simulation, the supercell volume was firstly adjusted to make the external pressure close to zero. Then a relax calculation was conducted to reach its inherent structure of the alloy which has minimum energy landscape. Fig. 2 shows the variation of atomic density with the temperature of this alloy. In this figure, we also show our experimentally measured density of the glass alloy at room temperature. It is seen that the difference between the calculated and experimental data is about 5.5%, indicating that our simulation is valid.

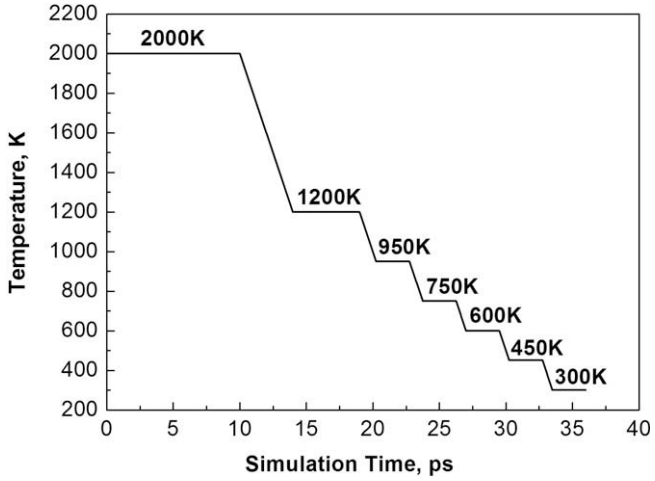

Fig. 1. Schematic of the quenching process for $Mg_{65}Cu_{25}Y_{10}$ alloy.

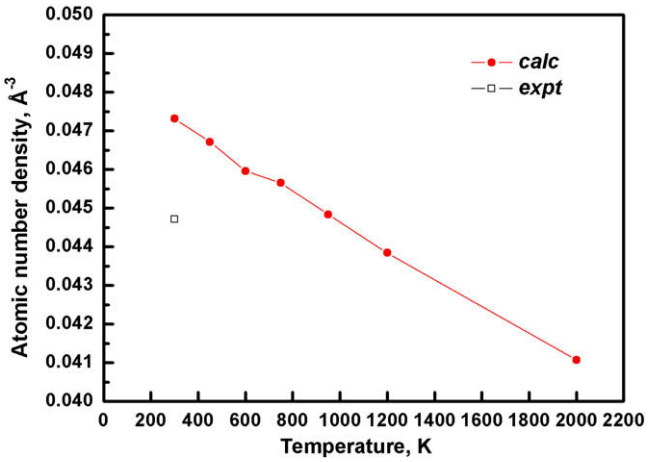

Fig. 2. Variation of atomic number density with the temperature during AIMD simulation for $Mg_{65}Cu_{25}Y_{10}$ alloy.

3. Results and discussion

3.1. Pair correlation functions

Pair correlation function is one of the main parameters which are used to reveal the structure characteristics of local atoms in liquid and amorphous states. The partial pair correlation function $g_{ij}(r)$ is defined by the probability of finding particle i in the spherical shell where particle j is taken as the center. Fig. 3 shows the partial PCFs of heterogenic atomic pairs (a), and homogenic atomic pairs (b) of $Mg_{65}Cu_{25}Y_{10}$ alloy calculated at 300 K. It is shown that the height of first peak follows the order of Y–Cu > Cu–Mg > Mg–Y > Mg–Mg > Cu–Cu > Y–Y. The second peak in all curves occurs splitting evidently, reflecting the formation of amorphous structure.

For the homogenic atomic pairs, the change in the height of first peak may be affected by the concentration of component. However, for the heterogenic atomic pairs, this change is not proportional to the concentration. This may be caused by the ordering of atomic packing. Among the three heterogenic atomic pairs, the Y–Cu pair shows more obvious splitting in second peak and higher value in first peak than the others, which reveals that the short range order (SRO) of Cu–Y seems to be strongest. This phenomenon may be explained based on the thermodynamic properties. It has been reported that Cu–Y has larger value of the heat of mixing ($\Delta H^{mix} = -22$ kJ/mol) than those of Cu–Mg ($\Delta H^{mix} = -3$ kJ/mol) and Mg–Y ($\Delta H^{mix} = -6$ kJ/mol) [15]. In Fig. 3, it is also seen that there are differences between the positions of the first peak of these partial PCFs due to different atomic radius. The different positions of the first peaks in the partial PCFs will affect the shape and position of first peak in the general PCFs of this alloy as shown in the following section.

Fig. 4a shows the PCFs referenced as Y atom obtained by combining $g_{YCu}(r)$, $g_{MgY}(r)$ and $g_{YY}(r)$ with equal weights at different temperatures. In this case, it is seen that the first peak becomes narrower and higher, and the valley deeper when the temperature is lowered. This illustrates that the disordered degree in this alloy descends during quenching, and some kinds of SRO tend to emerge. It is noted that the first diffuse peak of $g_Y(r)$ has a distinct change at low temperature below 750 K, which becomes evidently higher and obviously shifts toward right with decreasing the temperature. The experiment data displays that the onset melting point of $Mg_{65}Cu_{25}Y_{10}$ alloy is 727.9 K [16], closely the 750 K. In our work, it is shown that Y atom in this alloy is rearranged more remarkably at the temperature near the onset melting point. It is also observed that the first peak in $g_Y(r)$ at 300 K is lower than that of corresponding partial PCFs (in Fig. 4) because the first peaks in