Atomic Simulation of Vitrification Transformation in Mg-Cu Thin Film

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In this study, the effective medium theory (EMT) inter-atomic potential is employed in the molecular dynamics (MD) simulation of the Mg-Cu thin films. The transition of local structures of Mg-Cu thin films is traced at annealing temperatures of 300, 413, and 500 K. Furthermore, the simulation results are compared with the experimental results obtained from the transmission electron microscopy and X-ray diffraction. The gradual evolution of the local atomic pairing and cluster structure is discussed in light of the Mg and Cu atomic characteristics.

Keywords: Molecular Dynamics Simulation, Metallic Glasses, Thin Film, Mg-Cu.

1. INTRODUCTION

It is known that amorphous metallic alloys are disordered materials which lack the periodicity of long range ordering in the atom packing, but the atomic arrangement in amorphous alloys is not completely random as liquid. In fact, many scholars believe that amorphous structures are composed of short range ordering, such as icosahedra clusters or other packing forms related to the intermetallic compounds that would form in the corresponding equilibrium phase diagram.1,2 The short range order is identified as a structure consisting of an atom and its nearest neighbors perhaps two or three atom distance. Recently, it also has been focused more attention on the study of medium range order, which is viewed as a new ordering range between the short range order and long range order in the amorphous structure.3 Mg-Cu based metallic glasses in bulk or thin film forms have their potentials in industry application due to their high strength/hardness and low specific weight, accompanied with the shining surface and high corrosion resistance. The bulk metallic rods/plates and thin film coating can be made by injection casting and sputtering, respectively. For the multi-layer sputtered Mg-Cu thin film, it is meaningful and interesting to explore the structure transition from the pure Mg and pure Cu crystalline thin layers to the mixed amorphous phase during post-sputtering annealing. In this study, the molecular dynamics simulation is applied to study the material properties in the binary metallic glasses. A composite multi-layer consisting of hexagonal closed-packed (HCP) structure (Mg atoms), face-centered cubic (FCC) structure (Cu atoms), and amorphous structure (mixed with Mg and Cu) is examined during thermal annealing at a suitable temperature.4,5

2. MOLECULAR DYNAMICS SIMULATION

In this section, the effective-medium theory (EMT) potential6 is employed in this work to study the Mg-Cu system. The EMT model used in this simulation corresponds to a parameterization of the EMT barriers calculated by Jacobsen et al.7,8 The basic idea of his method is straightforward as that the total energy of a given atom in the system can be determined by the effect of their surrounding atoms. The energy of an atom in an arbitrary environment should be calculated by first estimating it in a well chosen reference system, namely the effective medium, and then by evaluating the energy difference between the real and reference systems. The total energy of the system is written as

\[ E = \sum_i E_{c,i} + \left( E - \sum_i E_{r,i} \right) \]  

where \( E_{r,i} \) is the energy of atom \( i \) in the reference system. The perfect FCC crystal is taken as the reference system in

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The present model. How to derive the form of the correction term \( E - \sum E_{ij} \) in Eq. (1) from the density function theory has been presented in the reference papers.\(^7\)\(^9\) The total energy of the system can be written as
\[
E = \sum_i \left\{ E_i(n_i) + \frac{1}{2} \left[ \sum_{j \neq i} V_{ij}(r_{ij}) - \sum_{j} V_0(r_{ij}) \right] \right\} \tag{2}
\]

The embedding density \( n_i \) describes the superimposing contributions to the electronic density at the site of the atom \( i \) from all atoms \( j \), and is expressed the function of intermolecular distance \( r_{ij} \) and Wigner-Seitz sphere radius \( s_i \) (the same as neutral sphere radius). The formulas of \( E_i \) and \( V_{ij} \) can be found in the Ref. \[8\]. This EMT potential form has previously been shown to give a reasonable overall description of the FCC metals including transition and noble metals as well as their alloys. They have been great used in the study of mechanical properties of crystalline metals.\(^10\)\(^11\) For the Mg-Cu system, Bailey et al.\(^12\) refit the parameters, as listed in Table I, of both elements not only from basic properties of the pure elements but also considering the formation energies of two intermetallic compounds, Mg\(_2\)Cu and MgCu\(_2\).

In this study, an initial sandwich model is constructed by stacking an FCC Cu layer, an HCP Mg layer, and an FCC Cu layer along the \( z \) axis. Two interfaces between the Cu and Mg layers are set in the \( [0001] \) direction of FCC Cu and \( [0002] \) direction of HCP Mg along the \( z \) direction, respectively. The length scale in \( x \), \( y \), and \( z \) dimensions of an FCC Cu layer is 3.5 nm \( \times \) 6 nm \( \times \) 1.5 nm and of an HCP Mg layer is 3.5 nm \( \times \) 6 nm \( \times \) 3.5 nm. The numbers of Cu and Mg atoms in this sandwich model are 5,467 and 3,595, respectively. In addition to the \( z \) direction, the periodic

<table>
<thead>
<tr>
<th>Element</th>
<th>( E_0 ) (eV)</th>
<th>( S_0 ) (Å)</th>
<th>( V_0 ) (eV)</th>
<th>( \eta_i ) (Å)</th>
<th>( k ) (Å(^{-1}))</th>
<th>( \lambda ) (Å(^{-1}))</th>
<th>( n_i ) (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-3.51</td>
<td>1.412964</td>
<td>2.476</td>
<td>3.12170</td>
<td>5.17763</td>
<td>3.60166</td>
<td>0.06140</td>
</tr>
<tr>
<td>Mg</td>
<td>-1.487</td>
<td>1.766399</td>
<td>2.22987</td>
<td>2.541137</td>
<td>4.435425</td>
<td>3.292725</td>
<td>0.035544</td>
</tr>
</tbody>
</table>

Fig. 1. Mg-Cu binary phase diagram.

Fig. 2. The schemes of the projections of atomic positions annealed at (a) 300 K, (b) 413 K, and (c) 500 K. The red circle represents Cu and blue circle represents Mg.

boundary condition is employed on the x–y plane. Due to the lattice difference between Cu and Mg, the dimensions of the periodic boundary along the x and y directions are chosen to be large enough to minimize the mismatch effects at the Mg and Cu interface. In order to speed up the formation of a disordered state in the interface between two metals which are reasonably existing present in reality, an equal number of Cu and Mg atoms are artificially exchanged in the interface. After exchanging the Cu and Mg atoms, the sandwich model is annealed at 300, 413 and 500 K, respectively, for $5 \times 10^6$ time step by employing in the NVT ensemble and the equations of motion are solved by the velocity-Verlet algorithm.

3. RESULTS AND DISCUSSION

As shown in Figure 1, the Mg-Cu equilibrium phase diagram which refers a possibility of interface reactions of the Mg-Cu intermetallic phases formed in the Mg-Cu multilayer. There are two intermetallic compounds can form in the Mg-Cu system. In the Cu-rich side, $\text{Cu}_2\text{Mg}$ is a quite stable phase existing in the Mg-Cu system because the radii of major Cu atoms (1.28 Å), is smaller than surrounding Mg atoms (1.6 Å which results in a greater packing fraction to form a Laves phase. In the Mg-rich side, a complex competing crystalline phase, $\text{Mg}_2\text{Cu}$, can exist in the Mg-Cu system, where the larger atoms is majority. $\text{Mg}_2\text{Cu}$ is an orthorhombic structure but is not as stable as $\text{Cu}_2\text{Mg}$. For glass formation in the Mg-Cu system, the thermodynamic calculations and experiments indicated that the glass favor forming over the composition range of 12–22% Cu, including a lowest eutectic point at 14.5% Cu. Thus, it is expected that the amorphous phase or the $\text{Mg}_2\text{Cu}$ phase have the chance to form in the lower temperature conditions.

A series of atomic position projections in the interfacial layers during the structural evolution, corresponding to at 300, 413 and 500 K, are illustrated in Figures 2(a), (b), and (c), respectively. An inter-diffusion behavior occurred in the interfacial layers caused by the energy difference between Mg and Cu, resulting in the disorder-like structures in the Mg-Cu interfacial layers. The Mg and Cu atoms far away from their interfaces, which are not presented in the figure, are still retained the crystalline state during the processes. Compared with the Mg atoms which display a relatively uniform distribution in the interfacial layers caused by the energy difference between Mg and Cu, the disorder-like structures in the Mg-Cu interfacial layers. The Mg and Cu atoms far away from their interfaces, which are not presented in the figure, are still retained the crystalline state during the processes. Compared with the Mg atoms which display a relatively uniform distribution in the interfacial layers caused by the energy difference between Mg and Cu, the disorder-like structures in the Mg-Cu interfacial layers. The Mg and Cu atoms far away from their interfaces, which are not presented in the figure, are still retained the crystalline state during the processes. Compared with the Mg atoms which display a relatively uniform distribution in the interfacial layers caused by the energy difference between Mg and Cu, the disorder-like structures in the Mg-Cu interfacial layers. The Mg and Cu atoms far away from their interfaces, which are not presented in the figure, are still retained the crystalline state during the processes. Compared with the Mg atoms which display a relatively uniform distribution in the interfacial layers caused by the energy difference between Mg and Cu, the disorder-like structures in the Mg-Cu interfacial layers. The Mg and Cu atoms far away from their interfaces, which are not presented in the figure, are still retained the crystalline state during the processes.

To define whether the amorphous structures have been formed in the interfacial layer in this sandwich model, the density profile of each species $\alpha$ along the $z$ direction $\rho_{\alpha}(z)$, which can measure the number of $\alpha$ atoms within a certain distance interval along the $z$ axis, is calculated.
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20 25 30 35 40 45 50 55

Intensity

(a)

(b)

Mg2Cu (080)
Mg (0002)
Cu (111)

2 theta

as-deposited
30 min
60 min
90 min
120 min at 473 K

Fig. 4. (a) TEM image and (b) XRD pattern showing the structural transformation of the Mg-Cu multilayer system annealed at 413 K.

to describe and quantify the mixing circumstances at each of interfacial region in this model. The density profiles $\rho_{Mg}(z)$ of the Mg atoms (red line) and $\rho_{Cu}(z)$ of the Cu atoms (green line) are shown in Figure 3 for three different simulation states corresponding to Figure 2. Figure 3 shows that the density profiles of the Mg and Cu atoms merge at the interfacial region, indicating the occurrence of mixing phenomena on the atomic scale. Some different species atoms in the interfacial region diffuse, indeed, in the areas over each other. The intermixing of Mg and Cu atoms at the interfacial region is not accompanied with the obvious local loss of crystalline order, although the thickness of the mixing areas present a well mixed and smooth distribution with increasing temperature.

It must be recognized that the amorphous structures have not been generated in this sandwich layers yet, even though higher temperature had been used to offer more kinetic energies for atoms. This may be caused by the employed NVT ensemble that constrained the space on the X–Y plane, resulting in a lower degree of freedom for atoms to change their positions extensively in all directions. However, the Mg-Cu amorphous alloys are also difficult to produce in our laboratory. A transmission electron microscopy (TEM) image of the Mg-Cu multilayer system produced by sputtering is given in Figure 4. The bright zone is the Mg layer with a thickness of 150 nm, and dark zone is the Cu layer with a thickness of 50 nm. The Mg2Cu compound structure was found in this multilayer system when this specimen was annealed at 413 K, as shown in Figure 4. The structural transformation of the specimen during annealing at 413 K is also shown in the X-ray diffraction (XRD) pattern. The strong peaks at 19.5° and 39.6° imply that the Mg2Cu phase gradually forms along with a decrease of the Cu and Mg peaks.

4. SUMMARY

The structural transition of Mg-Cu multilayer annealing at three temperature conditions had been studied by employing EMT potential in the MD simulation. As increasing temperature, there are more kinetic energy off er interfacial atoms to relax their local structures. However, the NVT ensemble applied the constraint on the lateral sides in the simulation box. That is similar to a high pressure condition which results Cu atoms congregate in the Mg matrix from network to clusters. On the other hand, the experiment results also show that there are not obvious amorphous structures in the similar condition, just Mg2Cu compound forming in the Mg-Cu multilayer. The same simulation work employed in the NPT ensemble, which results in a realistic situation in agreement with the experimental environment, will be presented in the future as soon as possible.

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