

# A large-scale molecular dynamics simulation study on the microstructure evolutions of $\text{Ca}_7\text{Mg}_3$ alloy during rapid solidification

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**Abstract:** A large-scale molecular dynamics simulation was performed on the microstructure evolutions of  $\text{Ca}_7\text{Mg}_3$  alloy during rapid cooling process. The structural evolution was analyzed by using the HA bond-type index method and the largest standard cluster analysis method. The validity of the simulation was confirmed by comparing the simulated structure factor  $S(q)$  with the experimental one. Results indicate that the simulated  $S(q)$  is well agreed with the experimental one. Results also demonstrate that the glass transition temperature is at about 580 K at the cooling rate of  $1 \times 10^{13}$  K/s; and the LSCs of [12/555] and [2/433 2/544 8/555] play an important role in the glass transition. These findings can improve the understanding of glass transition of liquid alloy under rapid cooling.

## 1. Introduction

Ca-Mg and Ca-Mg based alloys are desirable candidates for medical implants due to their excellent biodegradable, resorbable and biocompatible properties[1]. In addition, as Ca is a main composition in human bone, and the release of Ca and Mg ions could well improve the bone healing process. Therefore, Ca-Mg and Ca-Mg based alloys are extremely promising materials for application in bone replacement [2]. As we all know, the macroscopical property of material is largely determined by its microstructure fetures formed during the solidification. Therefore, it is important to investigate the microstructure evolutions during the rapid solidification processes of liquid alloys at atomic level. In addition, a large-scale simulation will largely reduce the amount of boundary atoms, which promise the simulation results come more close to the facts. Accordingly, in this work, a large-scale molecular dynamics simulation study on the  $\text{Ca}_7\text{Mg}_3$  system consisting of 1000,000 atoms has been performed to eliminate the finite size effect. The recently developed largest standard cluster analysis (LSCA) [3,4] is adopted to quantify the microstructure evolution in the glass transition.

## 2. Simulation conditions and methods

The classical molecular dynamics simulations were performed for  $\text{Ca}_7\text{Mg}_3$  (700,000 Ca atoms and 300,000 Mg atoms). The MD simulation system was firstly placed in a cubic box under the periodic boundary condition. The interaction potential among atoms was computed by the generalized nonlocal model pseudopotential (GNMP) , which was derived by the first-principle interaction force in the second order perturbation theory [5,6], and the function is



$$V(r) = (Z_{\text{eff}}^2 / r) \left[ 1 - \left( \frac{2}{\pi} \right) \int_0^\infty dq F(q) \sin(rq) / q \right] \quad (1),$$

where,  $Z_{\text{eff}}$  and  $F(q)$ , are, respectively, the effective ionic valence and the normalized energy wave number characteristic, the details of the function can be found in Refs [5] and [6].

We started the calculation at 1173 K (the melting point of  $\text{Ca}_7\text{Mg}_3$  is around 720 K). In order to obtain equilibrium liquid state (it was determined by the energy change of the system), we first let the system running 100,000 steps. And then, the system temperature decreased to 323 K at the cooling rate of  $1 \times 10^{13}$  K/s by using the damped force method [7,8]. At every 50 K, the structural configurations of the system were recorded timely. At last, the characteristic microstructure evolutions of liquid  $\text{Ca}_7\text{Mg}_3$  alloy during rapid solidification were detected and described by the largest standard cluster analysis method.

### 3. Results and discussions

#### 3.1 Structure factor $S(q)$ and pair distribution function $g(r)$

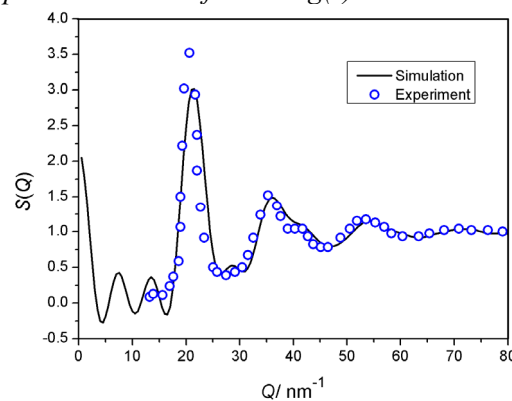


Figure 1. Comparison of  $S(q)$  for  $\text{Ca}_7\text{Mg}_3$  at 323 K between the simulation and experiment result [9,10].

As we all know, the simulated pair distribution function can be transformed to structure factor  $S(q)$  by Fourier transformation. Usually, the validation of simulation result is confirmed by contrasting the calculated  $S(q)$  with the one obtained by experiment. In this work, the total  $S(q)$  is got to compare with the experimental one [9,10], as shown in figure 1. As we can see, the calculated  $S(q)$  is well fitted with the one get by experiment. Therefore, the GNMP is accurate for describing the  $\text{Ca}_7\text{Mg}_3$  alloy system. In addition, the Wendt-Abraham parameter [11] is adopted to determine the glass transition temperature  $T_g$  of the  $\text{Ca}_7\text{Mg}_3$  system in the rapid cooling process. It is defined as below:

$$R = g(r)_{\text{min}} / g(r)_{\text{max}}, \quad (2),$$

in which  $g(r)_{\text{min}}$  and  $g(r)_{\text{max}}$  are, respectively, the magnitudes of the first shell maximum and the first minimum in the pair distribution functions. Then, the glass transition temperature  $T_g$  is the turning point in the slope of the curve. As shown in figure 2, it can be clearly seen that the intersection of the two straight lines indicates that the glass transition of  $\text{Ca}_7\text{Mg}_3$  is at about 580 K. This result is very close to that of Barnett et al [12], in which the liquid  $\text{Ca}_{67}\text{Mg}_{33}$  was cooled at the rate of  $3.2 \times 10^{13}$  K/s, and the glass transition occurred at about 570 K. The difference can be considered derived from the small difference in component and cooling rate.

The glass transition temperature is higher than that of our previous simulation result of 540 K cooling at the rate of  $1 \times 10^{12}$  K/s [13], and 530 K cooling at the rate of  $5 \times 10^{11}$  K/s [14]. Considering the well known fact that the faster cooling rate will result in higher glass transition temperature, so, our calculations are pretty consistent with each other in simulating the rapid quenching process of  $\text{Ca}_7\text{Mg}_3$  alloy.

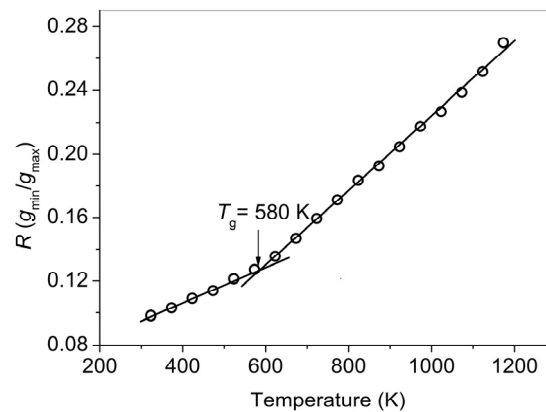


Figure 2. Temperature dependence of the  $R(g_{\min}/g_{\max})$  for  $\text{Ca}_7\text{Mg}_3$  alloy during the rapid solidifications.

### 3.2 Bond-type index analysis

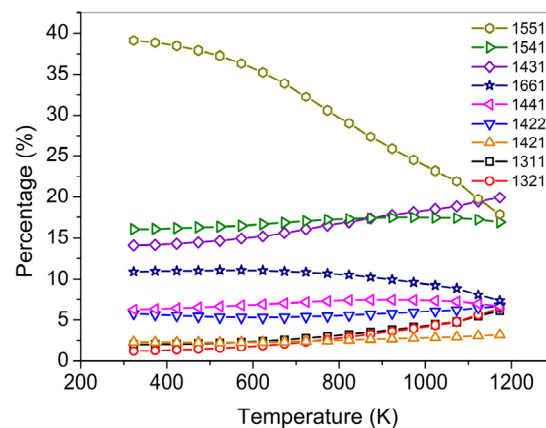


Figure. 3. The percentage of the main bond-types as a function of temperature during the rapid cooling process.

HA bond-type index method [15] is popular in describing and analyzing the microstructure evolutions in liquid, amorphous and crystalline systems. In this method, the 1551, 1541 and 1431 bond-types are typical structure element of liquid and amorphous states [16].

In figure 3, the HA bond-type index method is adopted to describe the local configurations in the system. As we can see from figure 3, during the liquid state, 1551, 1541 and 1431 bond-types act as character structures and play a dominate role. As temperature decreases, the relative number of 1551 bond-type increases sharply (from 17.85% at 1173K increases to 39.09% at 323K). Meanwhile, the other bond-types change slightly. It suggests that many local configuration in metallic glass are inherited from liquid, the glass is a freeze of liquid structure in some degree.

### 3.3 The largest standard cluster analysis

The largest standard cluster analysis (LSCA) was recently developed by Tian et al [3,4]. It is good at quantifying microstructures of both ordered and disordered systems. The LSCA do without any pre-set constant cut-off distance to determine neighboring or bonded atoms. That is different from many other structure analysis methods. If a constant cut-off distance is adopted, the results obtained by the analysis method may derive from the facts and miss some important details of microstructure evolutions. The LSCA overcomes the shortcoming by using a topological criterion through determining an upper limit of cut-off distance for the local microstructures around every atom.

In order to detect the key structural characteristics, the evolutions of top 10 LSCs (it is find out from the samples determined by top 10 in number for each sample) with temperature is shown in figure 4. Totally 14 kinds of LSCs are chosen from the 18 samples (one per 50 degree from 1173 K to

323 K). As shown in figure 4. All kinds of LSCs increase slightly until the temperature decreases to 873 K, both [12/555] and [2/433 2/544 8/555] increase remarkably, and play a dominate role in the glass transition. It is different from the result analyzed by another method [14], in which only the icosahedron cluster was detected play a key role in the glass transition. It further confirms the superiority of the new analysis method of LSCA, by which much more details of microstructure evolutions could be detected during the phase transition.

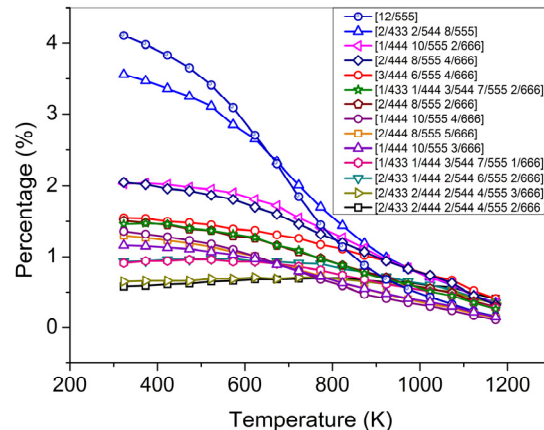


Figure. 4. The number percentage of 14 LSCs as a function of temperature during the cooling process.

#### 4. Conclusions

In this study, a rapid cooling process of a large-scale liquid  $\text{Ca}_7\text{Mg}_3$  system (1000,000 atoms, Ca: 700,000, Mg:300,000) has been performed. The microstructure evolutions during the phase transition have been explored with a recently developed method of LSCA. The main results can be concluded as follows: 1) glass structure is formed mainly with 1551, 1541 and 1431 bond-types at the cooling rate of  $1 \times 10^{13}$  K/s, and the glass transition temperature is at about 580 K; 2) the LSCA provide much more details of microstructure evolutions, and the [12/555] and [2/433 2/544 8/555] play a dominate role in the formation of amorphous structure.

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