THE CRYSTALLIZATION PROCESS IN THE NANO-IRON PARTICLES MODEL

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ABSTRACT

This paper studies the microstructure and the crystallization process in the nano-iron particles model with 10,000 particles at temperatures 300K, 500K, 700K, 900K, 1000K and 1,100K. The model was studied by Molecular Dynamics method (MD) with the Pak-Doyama pair-interaction potential and aperiodic boundary conditions. The microstructure characteristics was analyzed by the radial distribution function (RDF), the size, the energy and the coordination number. The crystallization process was studied through the relationships between the energy and the number of thermal annealing steps, between the number of crystal nucleation and the coordination number, between the number of crystal nucleation with the radius and showed that temperature of crystallization process from 907K to 998K.

Keywords: crystallization process, nano-iron model, molecular dynamics model.

TÓM TẮT

Quá trình tinh thể hóa trong mô hình hạt nano sắt

Bài báo này nghiên cứu vi cấu trúc và quá trình tinh thể hóa trong mô hình hạt nano sắt 10.000 hạt ở các nhiệt độ 300K, 500K, 700K, 900K, 1000K và 1100K. Mô hình được nghiên cứu bằng phương pháp động lực học phân tử (MD) với thế tương tác cặp Pak-Doyama và điều kiện biên không tuần hoàn. Các đặc trưng vi cấu trúc được phân tích qua hàm phân bố xuyên tâm (RDF), kích thước, năng lượng, số phối trí. Quá trình tinh thể hóa được nghiên cứu thông qua các mối quan hệ giữa năng lượng với số bước ủ nhiệt, giữa số mầm tinh thể với số phối trí, giữa số mầm tinh thể với bán kính và xác định được nhiệt độ của quá trình tinh thể hóa trong khoảng từ 907K đến 998K.

Từ khóa: quá trình tinh thể hóa, mô hình nano sắt, mô hình động lực học phân tử.

1. Introduction

Today, the studies on the microstructure and the crystallization process of materials such as Al, Ni, Mg, Fe etc have become popular. Among these materials, the nano-iron particles have received great attention because of their popular applications in science, technology, environment and biomedicine such as the manufacture of electronic components and sensors in information technology, the industrial waste water treatment, the cell separation and the drug transmission in biomedicine ect [1-5]. The above studies have majorily been done by theoretical and experimental methods.

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In recent years, the simulation method has been used to study the influence of temperature and annealing time on the microstructure and the formation of crystal nucleation [6] of nano-iron particles models in the amorphous state as well as the liquid state. Some remarkable results have been obtained.

Studying the crystallization process in the nano-iron particles model by Molecular Dynamics method (MD) has been the latest breakthrough in scientific research. This has contributed to the new understanding of nano-materials with different properties compared to bulk-materials [6-8]. The cause for these differences come from the fact that nano-materials are affected by the quantum effect, the size effect (meaning that when the size of particles becomes decreased, their total surface area becomes increased) and the critical effect (meaning that when the size of the nano-particles reaches to the critical size of some properties). It is the significant difference in properties of the nano-materials, which has led to the attentions and studies of scientists.

The results show that the increase in the thermal annealing time made the atoms (molecules) clotted into masses, leading to the formation of crystals or called the crystallization process (an equilibrated and stable state of materials). We also found that the formation of crystals occurred completely.

In this paper, we studied in detail the crystallization process in the nano-iron particles samples by Molecular Dynamics method.

2. The simulation method

The nano-iron particles model was established by Molecular Dynamics method with the Pak-Doyama pair-interaction potential [9-12] and aperiodic boundary conditions

$$\varphi(r) = a(r+b)^4 + c(r+d)^2 + e$$

with a = - 0.18892, b = - 1.82709, c = 1.70192, d = -2.50849, e = -0.19829

Initially, the nano-iron particles model was scattered randomly 10,000 particles in a spherical block. It was then run with statistical recovery 10^5 steps so that the atoms (molecules) could not be sticked to each other. The model was run thermal stability NVT (the number of particles, the volume and the temperature unchanged) 2.10^5 steps. After that, the temperature was increased to 5,000K with moving steps dT = 1.0K to break the original equilibrated state and turned to the liquid state. in the liquid state, the model was decreased in temperature to 300K with moving step dT = 1.0K. At 300K, the model was run energy stability NVE (the number of particles, the volume and the energy unchanged) 2.10^5 steps. Finally, the temperature was increased to 500K, 700k, 900K, 1,000K and 1,100K with moving steps dT = 0.1K to obtain 05 samples. All obtained samples was run thermal stability NVT 5.10^5 steps, then run energy stability NVE 10^6 steps.

From the obtained samples, we analyzed the microstructure by the radial distribution function (PRF), the coordination number and the energy to examine the temperature at which the crystallization process occurred. After the temperature was identified, the appropriate sample was chosen and it was thermal annealled with 4.10^6 steps to study its crystallization process.

3. Results and discussions

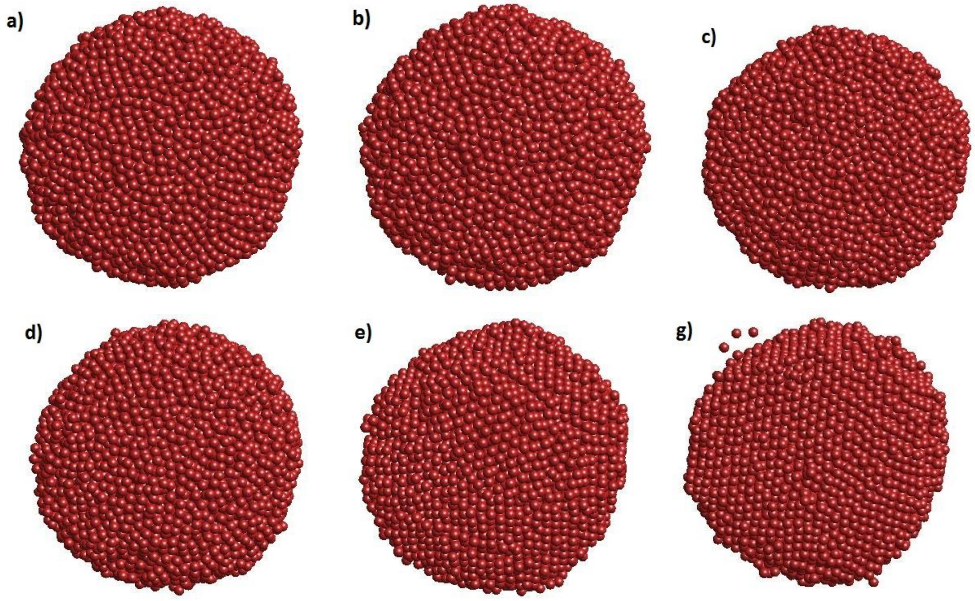

Figure 1. *The shapes of nano-iron samples at temperatures 300K (Figure 1a), 500K (Figure 1b), 700k (Figure 1c), 900 K (Figure 1d), 1,000K (Figure 1e) and 1,100K (Figure 1g).*

The nano-iron particles model with 10,000 particles at temperatures 300K, 500K, 700K, 900K, 1,000K and 1,100K was simulated by Molecular Dynamics (MD) method with the Pak-Doyama pair-interaction potential [9-12] and aperiodic boundary conditions. Its shapes are shown in Figure 1 and its sizes are shown in Table 1.

Table 1. *The size of nano-iron particles at different temperatures*

Temperature (K)	*300*	*500*	*700*	*900*	*1000*	*1100*
Particle size (nm)	*3.337*	*3.358*	*3.385*	*3.362*	*3.424*	*3.450*

The results in Figure 1 and Table 1 show that the shape of the nano-iron particles samples was spherical. The size of sample increased when the temperature was increased from 300K to 1,100K (corresponding to the temperature 300K and the size 3.337nm (Figure 1a); the temperature 500K and the size 3.358nm (Figure 1b); the temperature 700K and the size 3.385nm (Figure 1c)). The size of the sample decreased dramatically at temperature 900 K. From 900 K to 1,100K, the size increased (corresponding to the temperature 900 K and the size 3.362nm (Figure 1d), the

temperature 1,000K and the size 3.424nm (Figure 1e), the temperature 1,100K and the size 3.450nm (Figure 1g)). This result proves that the size of the model increased when the temperature was increased from 300K to 1,100K. It also proves that the crystallization process occurred at the temperature range from 900K to 1,000K and the sample started to be broken and turned to the liquid state at 1,100K.

The microstructure of the samples was studied and the obtained results are shown in Figure 2 and Table 2.

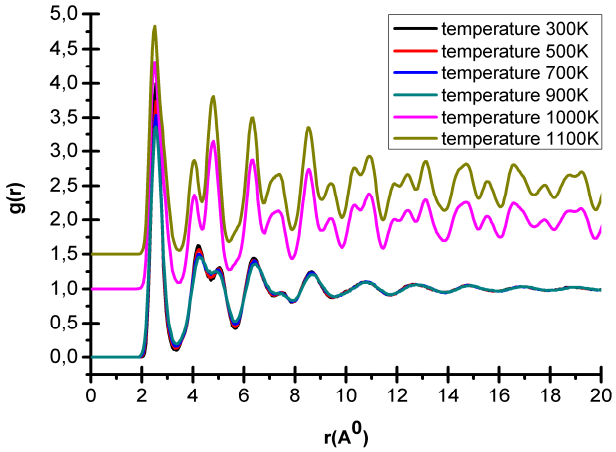

Figure 2. *The radial distribution function of nano-iron particles samples at different temperatures.*

Table 2. *The first peak position and the first peak height of the radial distribution function at different temperatures*

Temperature (K)	300K	500K	700K	900K	*1000*	*1100*
r (A^0)	2.55	2.55	2.55	2.55	*2.5*	*2.5*
g(r)	3.9993	3.7369	3.5376	3.3714	*3.3106*	*3.3279*

The results in Figure 2 and Table 2 show that the first peak position of the radial distribution function was predominant in the nano-iron particles samples with 10,000 particles at temperatures 300K, 500K, 700K, 900K, 1,000K and 1,100K. When the temperature was increased, the value of the first peak position of the radial distribution function was unchanged at the temperature range from 300K to 900 K and from 1,000K to 1,100K. This result proves that the nano-iron particles samples were in the amorphous state at the temperature range from 300K to 900K and they were in the crystalline state in the temperature range from 1,000K to 1,100 K. We also found that the first peak heigh of the radial distribution function decreased when the temperature was increased. This proved the intermolecular distance did not depend on the temperature but it depent heavily on the structural state. The density of atoms (molecules) of the nano-iron particles samples decreased gradually when temperature

was increased. Particularly, the first peak heigh of the radial distribution function increased sharply in the sample at 1,100K. That proved there always existed a far order in the nano- iron particles samples. The first peak heigh of the radial distribution function of the nano-iron particles sample at temperature 300K had the highest value. We found that when the temperature was increased, the first peak heigh of the radial distribution function tended to decrease gradually.

Furthermore, we found that the Pick separation occurred at temperatures 1,000K and 1,100K (this is the basis of the crystallization process) at the second peak of the radial distribution function. Thus, there was an influence of the temperature on the microstructure and the crystallization process of the model.

To clarify this, we investigated the coordination number of the samples at different temperatures, results are shown in Table 3.

Table 3. *The coordination number at different temperatures*

Coordination Number	Coordination number density					
	300	500	700	900	1000	1100
8	0	0	0	0	0	0
9	0	0	0	0	0	0
10	0.0001	0.0001	0.0001	0.0010	0.0002	0
11	0.0085	0.0084	0.0129	0.0207	0.0026	0.0002
12	0.2547	0.2543	0.2547	0.2590	0.0394	0.0062
13	0.408	0.4101	0.4066	0.4151	0.1581	0.1118
14	0.2572	0.2614	0.2686	0.2548	0.7918	0.8805
15	0.0664	0.0623	0.0533	0.0466	0.0073	0.0012
16	0.0051	0.0033	0.0038	0.0028	0.0006	0

Table 3 shows that the coordination number density of the nano-iron particles samples at temperatures 300K, 500K, 700K and 900K reached its maximum value at the coordination number 13. For the samples at 1,000K and 1,100K, the coordination number density reached its maximum value at the coordination number 14. This proves the nano-iron particles samples at temperatures 300K, 500K, 700K and 900K existed in the amorphous state and samples at temperatures 1,000K and 1,100K existed in the crystalline state.

To study the crystallization process, we studied the samples at 300K, 500K, 700K and 900K from the time when the crystallization process had not occurred (by determining the relationship between the energy and the number of thermal annealing steps) then examining the crystallization process of the models, the results are shown in Figure 3.

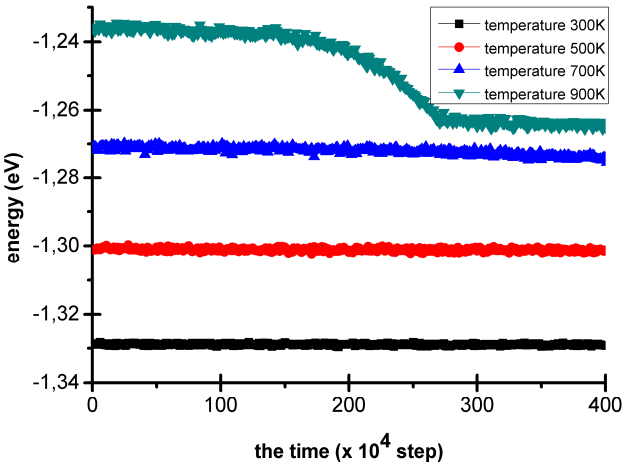

Figure 3. *The influence of the thermal annealing time on the energy of samples*

We can see from Figure 3 that there were two stages here. At the first stage with step numbers smaller than $1.5.10^6$, we see that the energy of all samples at 300K, 500K, 700K and 900K changed insignificantly in their values. This was the stage of the crystal nucleation formation. The latter stage with step numbers from $1.5.10^6$ steps to 4.10^6 steps showed that the energy of samples at 300K, 500K, 700K changed insignificantly in their values. This proved these samples were in the amorphous state. The sample at 900K started to changed in its energy at the steps number range from $1.5.10^6$ to $2.7.10^6$ steps. When the step numbers were greater than $2.7.10^6$ steps, the energy value started to be stable. This is called the crystal growth stage.

The above results proves that the crystallization process was significantly influenced by the thermal annealing steps. To study this in detail, we investigated the influence of the radius and the coordination number on the process of crystal growth, results are shown in Figure 4.

The results from Figure 4a and Figure 4b correspond to the sample at 700K. With the number of thermal annealing steps smaller than 2.10^6 steps, the crystal nucleation mainly occurred at the core area of the nano-particles with the radius smaller than 2,3nm (Figure 4b). The production and the annihilation processes of the crystal nucleation were almost balanced in the coordination number range from 6 to 14 (Figure 4a). The formation of crystal nucleation had the direction from the core area to the surface layer and occurred intensively in the radius 1,38nm. When the number of thermal annealing steps was increased to 2.10^6, we found that the formation of crystal nucleation had the direction from the core area to the surface layer of the nano-iron particles corresponding to the radius greater than 2.3nm (Figure 4b). However, the crystallization process occurred slowly after 3.10^6 thermal annealing steps.

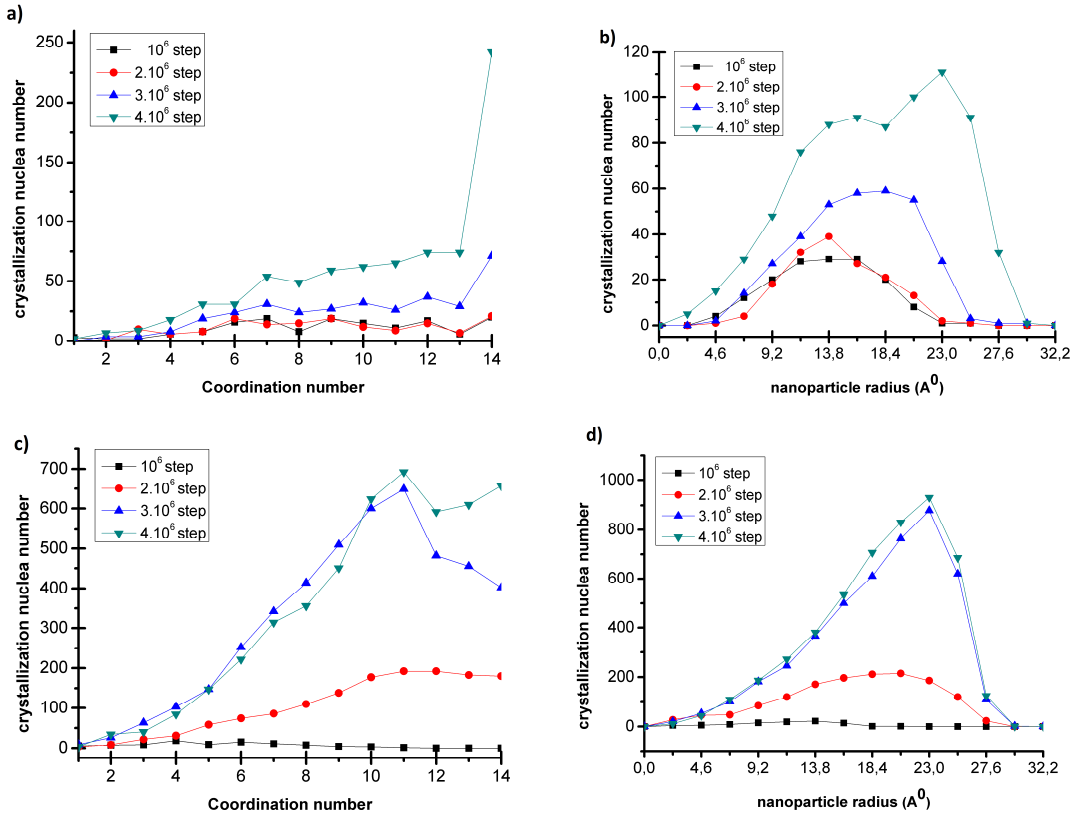

Figure 4. *The coordination number and the crystal formation radius with different running steps at temperature 700K (Figure 4a, 4b) and 900K (Figure 4c, Figure 4d)*

Similarly with the sample at 900K, we found that the formation of crystal nucleation had the direction from the core area to the surface layer of the nano-iron particles corresponding to the radius greater than 2.3nm (Figure 4d). However, the crystallization process occurred quickly after 3.10^6 thermal annealing steps corresponding to the extended coordination number from 4 to 14 (Figure 4c). The crystallization was most easy to occur in the sample at 900K, meaning that the range in which the crystal nucleation occurred tended to extend with the direction from the core area to the surface layer of the nano-iron particles until the formation of crystal nucleation occurred completely.

To examine the temperature in which the crystallization process occurs, we focused on studying the nano-iron sample at temperature 900K (with the energy changed intensively and favorable conditions for the crystallization process to occur), the results are shown in Figure 5.

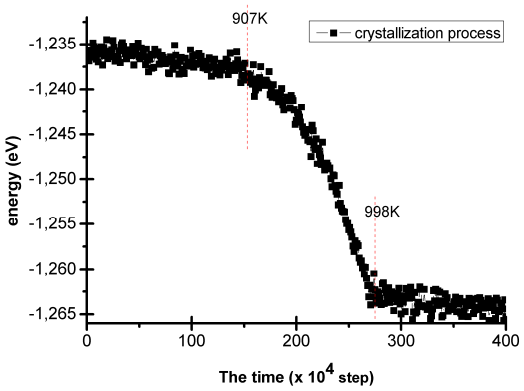

Figure 5. *The crystallization process of the sample at 900K*

The above results show that with the step numbers smaller than $1.5.10^6$ (corresponding to the temperature at 907K), the energy of the crystallization changed slightly (the production and the annihilation processes of the crystal nucleation were almost balanced). When the number of thermal annealing steps was increased to $2.7.10^6$ (corresponding to the temperature at 998K), the energy of the crystallization increased intensively, almost linearly with temperatures from 917K to 998K. Obviously, the crystallization occurred in this temperature range.

The above results show that there was an influence of the temperature and the number of thermal annealing steps on the microstructure and the crystallization processes in the nano-iron particles model. The mechanism of crystallization process is as follows:

*When the number of thermal annealing steps is increased leading to the decrease in the energy of the samples, the crystals concentrates on the low energy area, which causes the formation of crystal nucleations. The formation of crystal nucleations occurs until there is only the interaction between crystal nucleations in the samples, that is also the time the crystallization process occurs completely.

*The formation of crystal nucleation has the direction from the core area to the surface layer, in spherical shapes and occurs slowly at the surface layer. This is caused by the surface effects.

4. Conclusions

The study of the crystallization process of the nano-iron particles model with 10,000 particles at temperatures 300K, 500K, 700k, 900K, 1000K and 1100K by Molecular Dynamics method with the Pak - Doyama pair-interaction potential have obtained the following results:

- The choose of the Pak - Doyama pair-interaction potential for the nano-iron particles model was suitable because it gave consistent results with experiments.

- The shapes of atoms (molecules) of the nano-iron particles model were spherical.

- The main structure in the nano-iron particles model was the BBC structure with atoms (molecules) concentrated mainly at the core layer of the model. This led to the differences in microstructure of the model.

- When the temperature was increased from 300K to 500K, 700K, 900K, 1,000K and 1,100K, we found that the first peak position of the radial distribution function prevailed and it changed when there were changes in the structural status (amorphous, crystalline). The first peak height of the radial distribution function decreased with increasing temperature.

- The crystallization process in the nano-iron particles model had the direction from the core area to the surface layer, in spherical shapes and occurred slowly at the surface layer. This was caused by the surface effects with the crystallization temperatures from 907K to 998K.

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