



Study of Structure Properties of Iron Nanoparticle by Simulation Method

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Abstract Iron nanoparticles (NPs) are investigated by means of molecular dynamics simulation. The crystallization mechanism is studied through the temporal evolution of crystal cluster and potential energies of constituent atoms. The simulation shows that with enough long annealing at 900 K the NP is crystallized into bcc structure. Analyzing the energies of different type atoms, we find that the crystal growth is originated from specific atomic arrangement in the boundary region of crystal clusters. Further study highlights the morphologies of NP. It shows that different morphologies differ strongly not only in the core, but also in the surface of NP.

Keywords nanoparticle, crystallization, molecular dynamics, amorphous and iron

1. Introduction

Like their bulk counterparts, NPs have multiple morphologies, which are also of great interest for the physics community [1-3]. Basically, NPs can be produced in either amorphous or crystalline state. Generally, the amorphous NP has two parts: the core, which has the amorphous structure similar to its bulk counterpart, and the surface, which has more porous structure. Clarifying in details the local structure of NPs is important, because it is related to certain specific properties found for these materials. On other hands, amorphous NP is thermodynamically unstable and the crystallization can be induced by various impacting factors. The stability of amorphous NPs against crystallization plays an important role because it relates to their working capabilities. The crystallization of amorphous NPs is studied mainly by experiments [4-8]. It was shown that the crystallization is realized via the nucleation mechanism. However, not all features of crystallization mechanism at the atomic level in NPs are properly understood. Recently, investigation of crystallization in NPs, either of amorphous or crystalline state, draws more attention from researchers because it may provide more controllable way to reach the desired final characteristics of the materials. Many researchers successfully studied morphology and crystallization of materials using molecular dynamics (MD) simulation [9-12]. An undeniable advantage of this method is its capability to trace the behavior of atoms, both spatially and temporally, what is impossible yet by experiments. In the present work we conduct the MD simulation using Pak-Doyama potentials to study the structure transition of iron NPs [13-15].

2. Calculation procedure

The MD simulation is performed for the NPs containing 5,000 and 10,000 iron atoms with free boundary conditions. The interactions among atoms are calculated with the Pak-Doyma potentials. Initially, all atoms are randomly placed in a sphere with radius of 28 and 34 Å. Then the statistical relaxation is carried out until the system reached the equilibrium. This sample is heated to temperature of 300 K. The obtained sample then is relaxed isothermally (annealing) by 2×10^7 steps to prepare the amorphous NP. The well-equilibrated sample of amorphous NP is names as 300-sample. In order to study the crystallization we have prepared the second sample by heating the 300-sample to 900 K and then relaxing isothermally over 2×10^7 steps. This sample is named as



900-sample. To analyze the structure of NP we determine the pair radial distribution function (PRDF) using the procedure previously reported in [13].

To determine whether a particular atom is Cr-atom or Am-atom, following criteria are applied. That is, the atom is identified as being in the *bcc* configuration if it satisfies two conditions [16]: (i) it has 14 adjacent neighbors; (ii) six among these neighbors have 4 neighbors and remaining ones have 6 neighbors in common with the given atom. The cutoff radius to determine the neighboring atom is equal to 3.35 Å. Such atom and its 14 neighbors belong to Cr-atoms and form a basic nucleus. A basic nucleus locating alone in the amorphous matrix comprises a CC-atom and 14 CB-atoms. Two basic nuclei are linked if they share at least one common Cr-atom. A crystal cluster contains a number of basic nuclei that each nucleus is linked at least to one another nucleus.

3. Results and Discussion

3.1. The structure transformation of NP iron

In Fig.1 we show the number of Cr-atoms, N_{Cr} , as a function of MD steps. As displayed for two cases of NP containing 5,000 and 10,000 atoms, the crystallization process can be divided into three periods. In the first period we do not find any stable crystal cluster. There are only fewer nuclei which form and dissolve for short times. In the second period N_{Cr} significantly increases indicating the substantial growth of crystal clusters. In the third period, as expected, N_{Cr} fluctuates around a fix value indicating that the crystal growth completes. Compared to NP containing 5,000 atoms, a fraction of Cr-atoms in the third period of the NP containing 10,000 atoms are significantly larger. This result indicates that the crystallization strongly depends on the size of NP. As a result, if the size of NP is not enough big, it will not be crystallized.

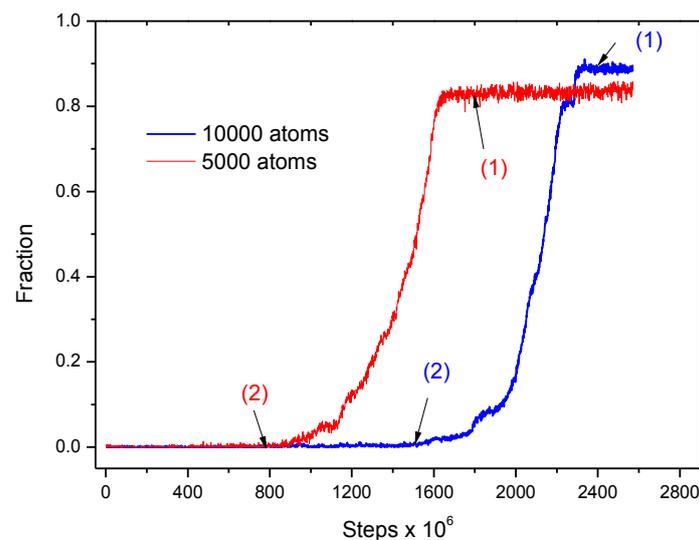


Figure 1: The dependence of number of Cr-atoms as a function of steps for 900-sample; index 2, 1 correspond with the first and third period for 5000- and 10000-atoms nanoparticles.

The PRDFs determined at points in the first, the third periods, *bcc* iron crystal are shown in Fig.2. In both of the cases, the PRDFs found in the third period have many peaks which demonstrate the crystalline structure. Another PRDFs determined in the first period is similar to PRDF of the bulk sample indicating that the structure of NP is still amorphous [16]. The position of peaks of the PRDF in the third period is close with ones in the *bcc* iron crystal. It is also powerful evidence that with enough long annealing at 900 K, the NP is crystallized into *bcc* structure. Moreover, as can be seen in Fig.2, the PRDFs do not depend on the size of NP. It means that the size effect of NPs for the crystallization cannot be explained through the PRDF.



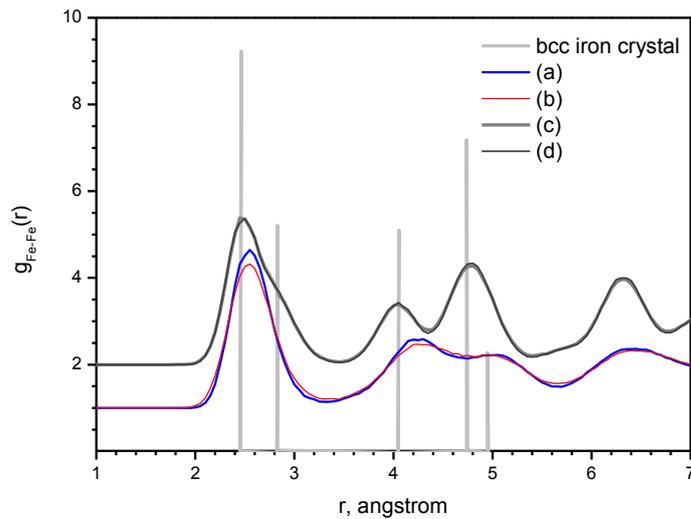


Figure 2: The PRDFs determined at the moment in the first period (1), in the third period (2); (a), (c) for NP containing 5000; (b), (d) 10000 atoms; and bcc iron perfect crystal.

3.2. The crystallization mechanism of nanoparticle iron

Fig.3A shows the number N_{Cr} during 3×10^6 steps in the first period. One can see that N_{Cr} varies in the interval from 0 to 30 atoms. This means that the nuclei form and dissolve for short times. To identify what atoms are Cr-atoms during the considered time interval, at every MD steps we find Cr-atoms and record them. The number of Cr-atoms recorded is shown in Fig.3B. It can be seen that about 300 atoms take part in the formation of nuclei. It means that the amorphous NP contains a number of small groups of Am-atoms which gather nearby and locate at different places in NP. The Am-atoms of these groups arrange like the strongly distorted crystal lattice. Sometime they rearrange and form nuclei. Further examination shows that the number of recorded Cr-atoms in the core is much larger than in the surface. Obviously this is originated from the porous amorphous structure of the surface.

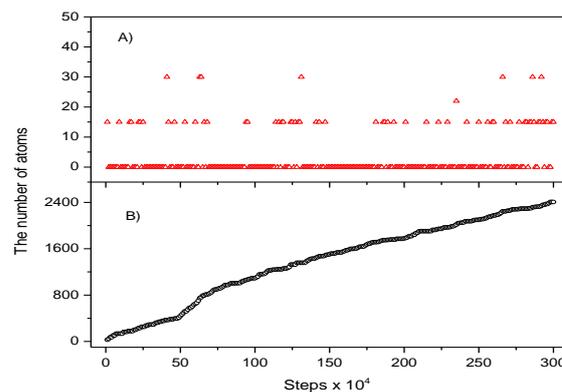


Figure 3: A) The number of Cr-atoms detected during 3×10^6 steps at the first period; B) The number of Cr-atoms recorded within this time interval for NP containing 10,000 atoms.



In Fig. 4 we show the snapshots of Cr-atom arrangement of which are generated at different moments in the second period. At early moment two crystal clusters are found in the core. Then these clusters grow and merge into a large cluster. After that the merged cluster expands over the whole NP. It is worth to note that Cr-atoms gather nearby two clusters. From Fig.5 following remarks can be made: (i) Unlike those in the first period, the stable crystal clusters have been created in the core; (ii) New nuclei now are not generated at different places, but only nearby the boundary regions of crystal clusters; and (iii) The crystal growth is inhibited when the boundary region of crystal clusters moves to the surface. As such, the frequency of nuclei formation in the boundary regions is much bigger than one in the amorphous phase. The crystal cluster grows in the direction to cover the core and then to spread outward to the surface. The fully crystallized NP consists of the core, which has the crystalline bcc structure, and the surface, which has the porous structure.

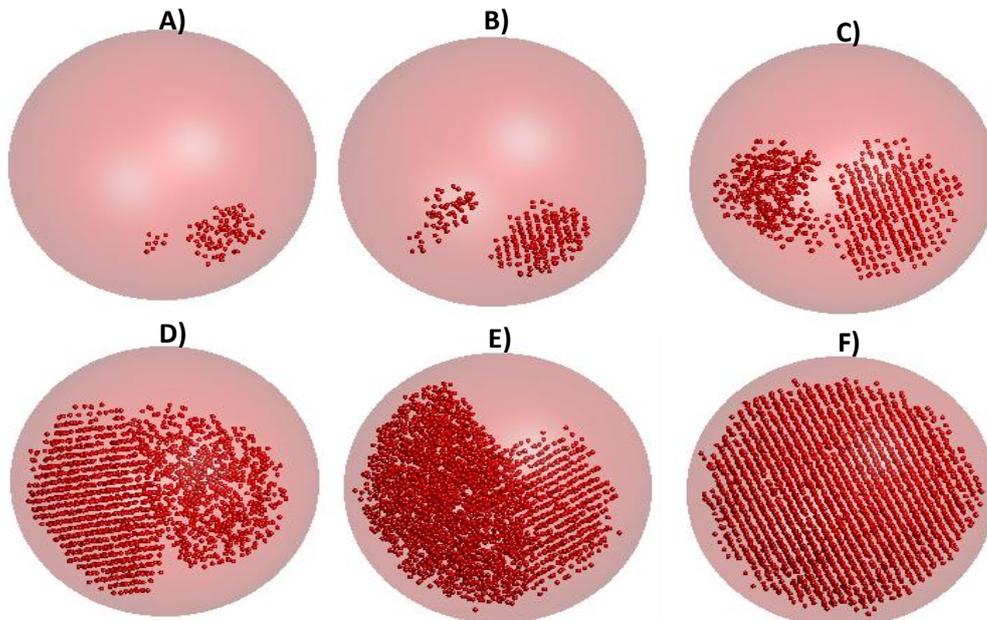


Figure 4: Snapshot of Cr-atom arrangement for NP containing 10,000 atoms: A) $N_{Cr}=188$; B) $N_{Cr}=568$; C) $N_{Cr}=1651$; D) $N_{Cr}=4440$; E) $N_{Cr}=6162$; F) $N_{Cr}=8907$;

The the mean potential energy per atom (MEPA) of different type atoms as a function of number of Cr-atoms in the cluster is shown in Fig.5. There is a location of 120 atoms where the MEPA of CC-atoms and CB-atoms is smaller than that one of AB-atoms. This location corresponds to the so called critical size. The clusters with the size bigger than critical value are stable and tend to grow; otherwise they are unstable and having higher probability of disappearing.

In summary it is shown that at the early stage of annealing the small nuclei are formed in different places of NP. Due to porous structure of the surface, the frequency of nucleus formation in the core is much higher than that one in the surface. MEPA of CB-atoms and CC-atoms of small clusters is close to the MEPA of AB-atoms. The nuclei are unstable and dissolve for short times. After enough long annealing a number of nuclei are formed nearby creating a stable crystal cluster in the core of NP.

Unlike MEPA of atoms in small clusters, MEPA of different type atoms in stable clusters decreases in following order: AB-atom \rightarrow CB-atom \rightarrow CC-atom. Such order implies that the crystal cluster prefers to grow rather than to shrink. The crystal growth is inhibited when the boundary region of crystal cluster moves onto the surface. Hence, the crystal cluster firstly grows in the direction to fill out the core and then spreads outward to the surface. The fully crystallized sample possesses the crystalline phase in the core and still maintains the amorphous phase in the surface.



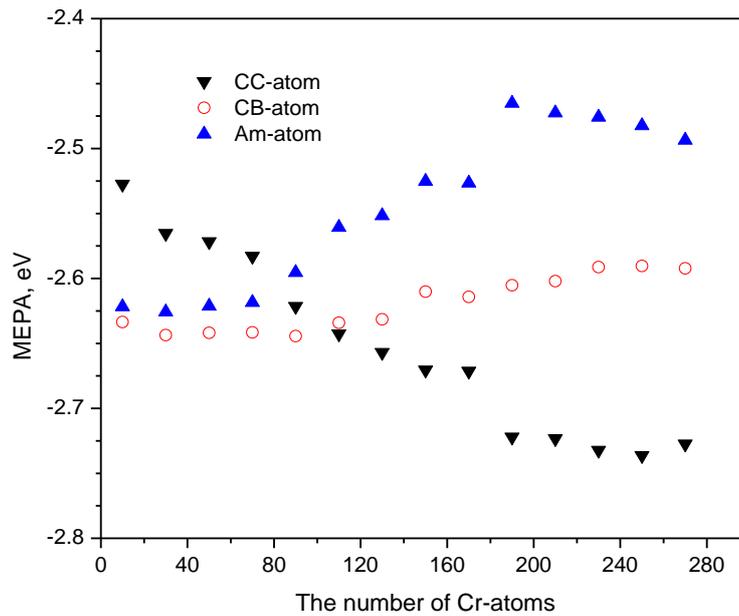


Figure 5: The dependence of MEPA as a function of the number of Cr-atoms in the crystal cluster for NP containing 10,000 atoms.

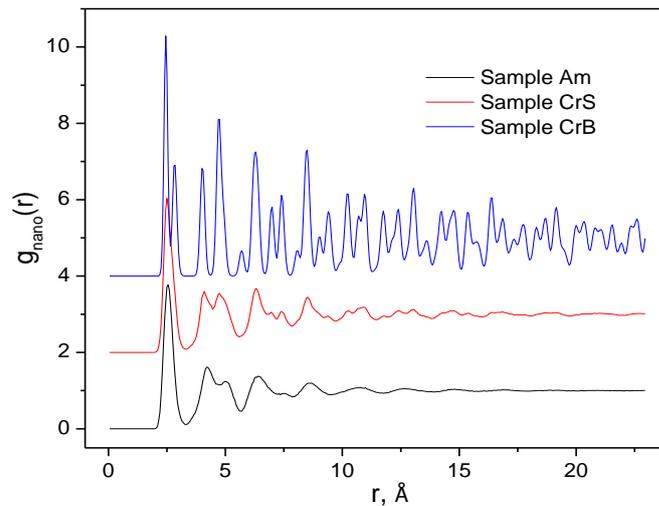


Figure 6: PRDF of three samples annealed at 300 K for NP containing 10,000 atoms.

3.3. The different morphologies of nanoparticle iron

The PRDFs of three samples are shown in Fig.6. The PRDF curves for samples amorphous (Am) and samples crystalline surface (CrS) are similar to those for amorphous bulk sample. Unlike PRDF of the sample Am, at the second coordination sphere PRDF of the samples crystalline surface (CrS) has the right sub-peak higher than the left sub-peak. Therefore, the existence of small amount of crystals changes the height ratio of these two sub-peaks. For the sample CrB PRDF shows many peaks which indicate the crystalline structure. In particular, two first peaks around 2.51 and 2.89 Å corresponds to the shortest distance ($3^{1/2}a/2$) and second shortest distance (a);



here a is the lattice constant. The next peak containing the distance $2^{1/2}a$ is seen around 4.1 Å. The fourth peak around 5 Å corresponds to the distances $3^{1/2}a$.

4. Conclusion

According to our simulation, the crystallization occurred when the amorphous sample was annealed for long times at 900 K. The fully crystallized NP consists of the core with bcc crystal structure and the surface with porous amorphous structure. Analyzing the potential energies of different type atoms, we found that MEPA shown that the crystal growth is originated from specific atomic arrangement in the boundary region between amorphous and crystalline phases. Further study concerns the morphologies of NP. It was shown that different morphologies of NP differ strongly not only in the core but also in the surface. The crystalline sample may contain a small amount of crystals which changes the height ratio of two sub-peaks in the PRDF.

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