

# Study of crystallization mechanisms of Fe nanoparticle

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**Abstract.** In this paper, the nanoparticle (NP) Fe was investigated by means of molecular dynamics simulation. The crystallization mechanism was studied through the time evolution of crystal cluster and potential energies of different atom types. The simulation shows that the NP was crystallized into bcc crystal structure when it was annealed at 900 K for long times. At early stage of the annealing, small nuclei form in different places of NP and dissolve for short times. After long times some nuclei form and gather nearby which create the stable clusters in the core of NP. After that the crystal clusters grow in the direction to cover the core and then to spread into the surface of NP. Analyzing the energies of different type atoms, we found that the crystal growth is originated from specific atomic arrangement in the boundary region of crystal clusters.

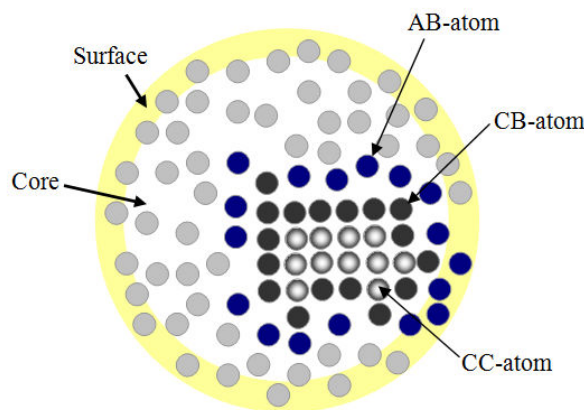
## 1. Introduction

Recently, interest in NPs has increased strongly owing their unique properties [1, 2, 3, 4, 5]. For example, amorphous iron and iron-based NPs exhibits unique magnetic, optical and sorption properties, and this may lead to their advanced application in nanotechnology. Like bulk counterparts, NPs have different morphologies which are also of great interest for the physics community. NPs can be produced either in amorphous or crystalline states. The amorphous NP has two parts: the core which has the amorphous structure similar to the bulk counterpart, and the surface which has more porous structure. Clarifying in detail 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 may be crystallized. The stability of amorphous NPs against crystallization plays an important role because of this related to their working ability in practice. The crystallization of amorphous NPs is studied mainly by experiments [6, 7, 8, 9, 10, 11, 12]. It was shown that the crystallization is realized via the nucleation mechanism. However, the crystallization mechanism at the atomic level is poorly understood. Especially, it is still unclear how the free surface affects on the nucleation and crystal growth. Crystallization mechanisms of materials can be studied by means of molecular dynamics (MD) simulation [13, 14, 15], since it is difficult to trace the behavior of atoms directly by experiments. In present work we conduct the MD simulation with using Pak-Doyama potentials to study the crystallization mechanisms of Fe NPs.



## 2. Calculation procedure

The MD simulation is performed for a system containing  $10^4$  Fe atoms with free boundary conditions and the Pak-Doyma potentials. Initially, all atoms are randomly placed in a sphere with radius of  $34\text{\AA}$ . Then the statistical relaxation is carried out until the system reached the equilibrium. This sample has heated to temperature of 300 K. The obtained sample then has relaxed isothermally (annealing) by  $2 \cdot 10^7$  steps to prepare the amorphous NP. The well-equilibrated sample of amorphous NP is called 300-sample. We additionally have prepared two 300-samples to examine the influence of initial configurations. The result shows that no effect of initial configuration was found for the structural properties. In order to study the crystallization we have prepared second sample by heating the 300-sample to 900 K and then relaxing isothermally over  $2 \cdot 10^7$  steps. This sample is called 900-sample. To analyze the structure of NP we determine the pair radial distribution function (PRDF) using the procedure reported in previous work [16].



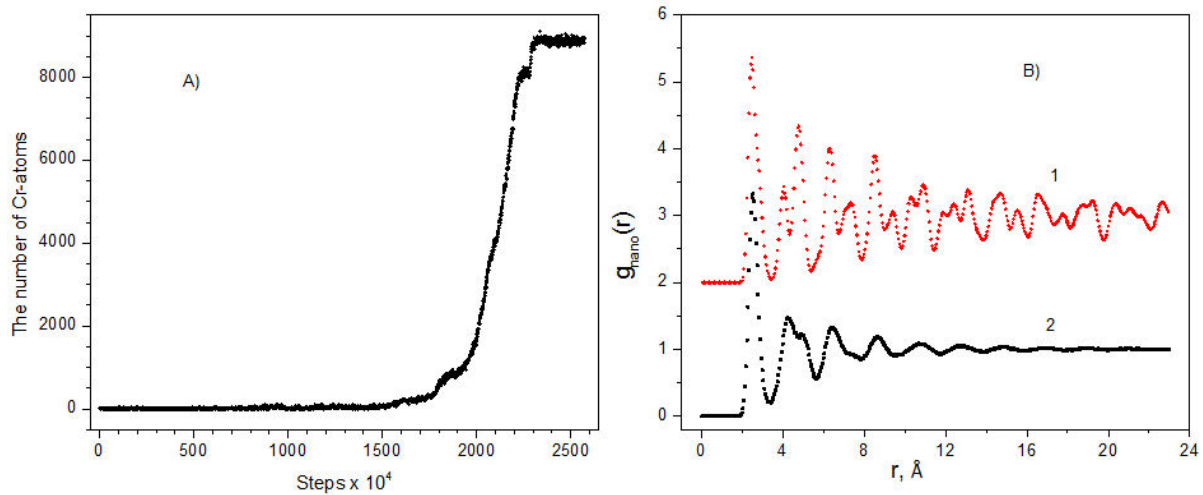
**Figure 1.** Schematic illustration of NP Fe.

In Figure 1 we schematically illustrate the NP. There is a crystal cluster in the sample. For the convenience the atoms belonging to amorphous and crystalline phases are called Am-atom and Cr-atom, respectively. In following we denote  $N_{Am}$  and  $N_{Cr}$  to the number of Am-atoms and Cr-atoms, respectively. There is a boundary region between amorphous and crystalline phases. We call Am-atoms, Cr-atoms in the boundary region AB-atom and CB-atom, respectively. The remaining Cr-atoms is called CC-atom. We denote  $N_{CB}$  and  $N_{CC}$  to the number of CB-atoms and CC-atoms, respectively. Obviously  $N_{Cr} = N_{CB} + N_{CC}$ . To determine a particular atom be Cr-atom or Am-atom, following criteria were applied. That is, the atom was identified as having the bcc configuration if it satisfies two conditions: (i) it has 14 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  $3.35\text{\AA}$ . Such atom and its 14 neighbors belong to Cr-atoms and form a basic nucleus. An basic nucleus locating alone in the amorphous matrix comprises a CC-atom and 14 CB-atoms. Two basic nuclei are linking if they have at least an common Cr-atom. A crystal cluster contains a number of basic nuclei that each nucleus links at least to another nucleus.

## 3. Results and discussion

In Figure 2A we show the number of Cr-atoms,  $N_{Cr}$  as a function of steps. The 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 which indicates that the crystal growth completes. The PRDFs determined at points in first and third periods are shown in Figure 2B. The PRDF found at third period has many peaks which demonstrate the crystalline structure. Another one determined at first period is similar to PRDF of the bulk sample which indicates that the structure of NP is still amorphous.

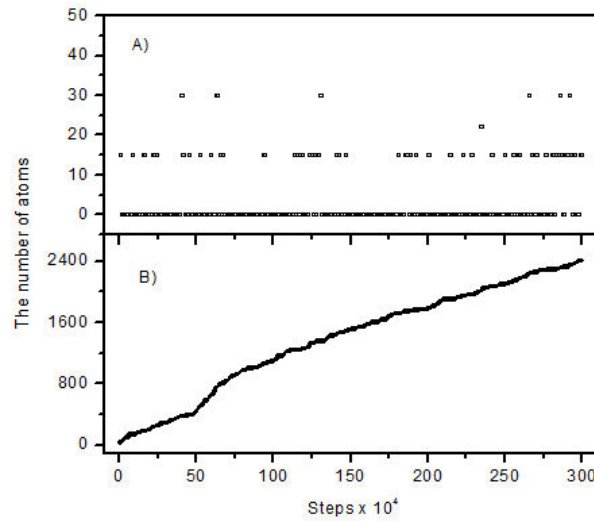


**Figure 2.** A) The dependence of number of Cr-atoms as a function of steps for 900-sample; B) the PRDFs determined at the moment in the first period (2) and in the third period (1).

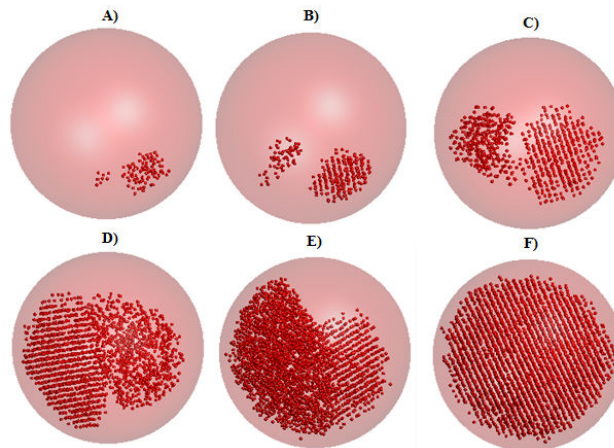
Figure 3A shows the number  $N_{Cr}$  during  $3 \cdot 10^6$  steps in the first period. One can see that  $N_{Cr}$  varies in the interval from 0 to 30 atoms. This means that the nuclei form and dissolve for short times. To identify what atoms are Cr-atoms during the considered time interval, at every MD steps we find Cr-atoms and record them. The number of Cr-atoms recorded is shown in Figure 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.

In Figure 4 we show the snapshots of arrangement of Cr-atoms which are generated at different moments in the second period. At early moment two crystal clusters were found in the core. Then these clusters grow and merge into a large cluster. After that the cluster expands over whole NP. It is worth to note that Cr-atoms gather nearby two clusters. From Figure 4 following remarks can be made. (i) Unlike 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; (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 into the surface. The fully crystallized NP consists of the core which has the crystalline bcc structure and the surface which has the porous structure.

Consider a small crystal cluster. The CC-atoms and CB-atoms can rearrange so that the crystal cluster dissolves. This rearrangement depends on the mean potential energy per atom (MEPA) for CB-atoms, CC-atoms and AB-atoms. In particular, if MEPA of CB-atoms and CC-atoms is close to MEPA of AB-atoms, then such rearrangement is easy realized. In the case when



**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.

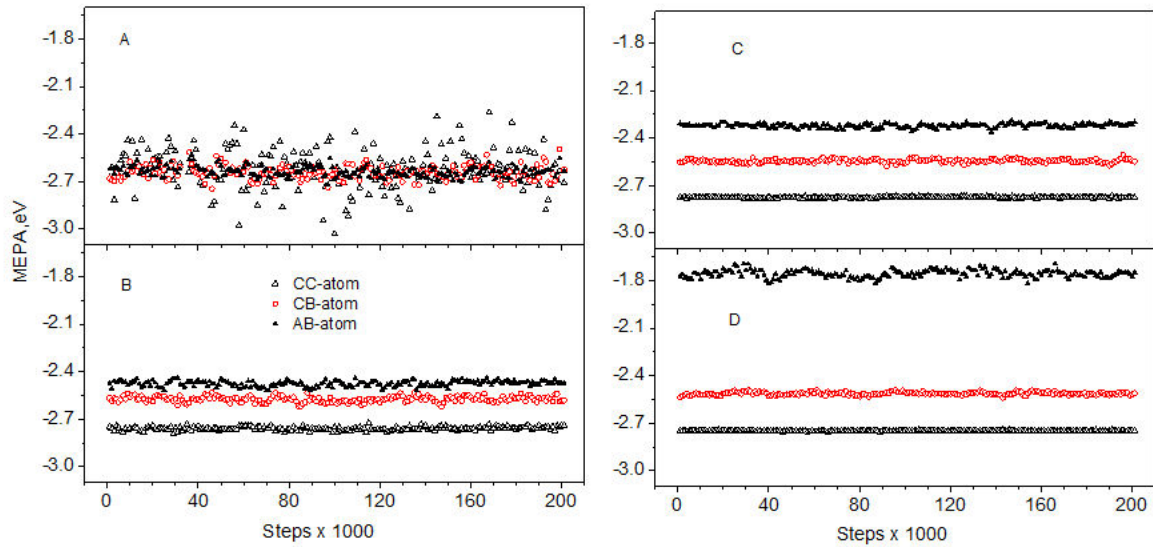


**Figure 4.** Snapshot of Cr-atom arrangement: A)  $N_{Cr} = 188$ ; B)  $N_{Cr} = 568$ ; C)  $N_{Cr} = 1651$ ; D)  $N_{Cr} = 4440$ ; E)  $N_{Cr} = 6162$ ; F)  $N_{Cr} = 8907$ .

the MEPA of those atoms is significantly smaller than one of AB-atoms, such rearrangement in contrast is less probable. Therefore, useful information on how the nuclei form, can be derived from MEPA for CB-atoms, CC-atoms and AB-atoms.

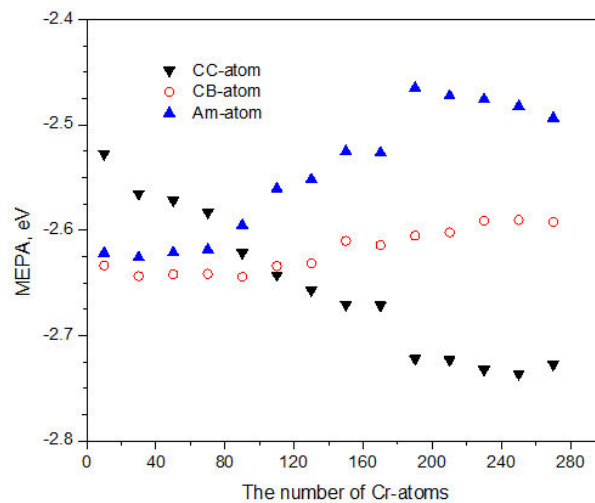
The time dependence of MEPA for different clusters is shown in Figure 5. One can see that for small crystal clusters, MEPA of CB-atoms is close to one of AB-atoms, and MEPA of CC-atoms fluctuates largely. It means that the crystal clusters are unstable and the distortion degree varies largely for different crystal clusters. As the size of the crystal clusters increases, MEPA of AB-atoms increases which is related to that the crystal cluster spreads into the surface where the energy of atoms is bigger than ones in the core. In the case of large crystal clusters, MEPA of different type atoms decreases in following order: AB-atom  $\rightarrow$  CB-atom  $\rightarrow$  CC-atom. It follows that the growing of the cluster leads to decreasing the energy of NP, while the shrinking of the cluster to increasing the energy of NP.

The MEPA of different type atoms as a function of number of Cr-atoms in the cluster is



**Figure 5.** The MEPA of different type atoms as a function of steps for the crystal clusters: A)  $N_{Cr}=15-85$  atoms; B)  $N_{Cr} = 600-700$  atoms; C)  $N_{Cr} = 4100-4400$  atoms; D)  $N_{Cr} = 8900-9100$  atoms.

shown in Figure 6. There is a point of 120 atoms where the MEPA of CC-atoms and CB-atoms is smaller than one of AB-atoms. This point 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.



**Figure 6.** The dependence of MEPA as a function of the number of Cr-atoms in the crystal cluster.

In summary it is shown that at early stage of annealing the small nuclei form in different places of NP. Due to porous structure of the surface, the frequency of nuclei formation in the core is much larger than 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 long annealing a number of nuclei form nearby, which create a stable crystal cluster in the core of

NP. Unlike small cluster, MEPA of different type atoms for stable clusters decreases in following order: AB-atom  $\rightarrow$  CB-atom  $\rightarrow$  CC-atom. Such order leads to that the crystal cluster prefers to growing rather than to shrinking. The crystal growth is inhibited when the boundary region of crystal cluster moves to the surface. Hence, the crystal cluster grows in the direction to cover the core and then to spread into the surface. The fully crystallized sample consists of the crystalline phase in the core and amorphous phase in the surface.

#### 4. Conclusion

In this paper, the crystallization of Fe NPs has been investigated by means of molecular dynamics simulation. The nucleation mechanism is studied through the time evolution of crystal clusters and the potential energy of different type atoms. According to our simulation, the crystallization occurred when the amorphous sample was annealed for long times at 900 K. At early stage of the annealing the small crystal clusters form in different places of NP and dissolve for short times. After long annealing, the stable crystal clusters have been created in the core of NP. After that these clusters grow in the direction to cover the core and then to spread into the surface. 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 unlike small cluster, for large cluster MEPA of CC-atoms, CB-atoms and AB-atoms decreases in following order: AB-atom  $\rightarrow$  CB-atom  $\rightarrow$  CC-atom. It means that the crystal growth is originated from specific atomic arrangement in the boundary region between amorphous and crystalline phases.

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