Molecular dynamics simulation of microstructure and atom-level mechanism of crystallization pathway in iron nanoparticle

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Abstract.
We use the molecular dynamics simulation to study iron nanoparticles (NP) which consist of 5000 atoms at temperatures of 450 and 850 K. The crystallization and structure evolution was analyzed through pair radial distribution function, transition to different x-types, with x is the bcc, fcc and hcp, ico, 14, 12, and dynamical structure parameters. Simulation results that at 450 K, NP contains a large number of ico-type atoms which play a role in preventing of crystallization. The crystallization happened when NP was annealed at 850 K for 40 ns. Transitions to bcc-type do not happen arbitrarily at any location in NP, but instead they are focused in a non-equilibrium region. We showed that the crystallization pathway includes intermediate states between amorphous and crystalline phases. Firstly, a large cluster of cryst-atom is formed in a middle layer of NP. Next, this cluster grows up and the parameter for this cluster increases rapidly. Finally, the cluster of cryst-atom is located in a well-equilibrium region covered a major part of NP. The structure of crystalline NP is strongly heterogeneous and consists of separate local structure regions.

1. Introduction
The interest in NP continues to grow in recent years, because this type material has many attractive properties and important applications in different areas of industry [1-4]. Especially, the crystallization process in nanometer-sized particles has been investigated by both experiment and simulation [5-7]. The transition to crystalline phase is difficult to directly observing in experiments because such events occur rarely and proceed rapidly when they take place. Computational simulation has advance on probing those transitions since it allows to calculating the trajectory of individual atoms. Due to this reason many simulations have been successfully conducted to study the liquid-crystal, amorphous solid-crystal transitions at atomic levels [8-10]. Using molecular dynamics (MD) simulation, Pan et al. in ref. [11] reported that the crystallization contained of enlargement of coordination number and transformation of local symmetry from five-fold to four-fold. Also, Jungblut et al. in ref. [12], the crystallization proceeds through formation of small cluster with bcc structure of which the core transforms into the fcc structure, but the surface remains bcc-structured. However, Polak in ref. [13] reported the evidence for the formation of defective and icosahedra structures, as well as for
the transition of these structures to fcc phase. However, the crystallization as well as the microstructure of Fe NP has been investigated very little. Hence, many aspects about Fe NP remain poorly understood. Thus, in this paper we investigated the micro-structural evolution by terms of common neighbor analysis (CNA), transition of different x-types and angle distribution. We also make a systematic analysis of crystalline-like clusters in order to identify intermediate states.

2. Calculation procedure
MD simulation is carried out for NP models containing 5000 iron atoms under free boundary conditions. The interactions between atoms are calculated by using potential of Pak-Doyma [1,14]. We have constructed two models at 450 and 850 K in a sphere with radius of 28 Å. The 450-model was annealed under constant temperature by using NVT ensemble (constant temperature and volume). The annealing time is about 40 ns. The 850-model is prepared as follows. Initially we heat up the 450-model to 850 K. Then the obtained model was annealed under constant temperature by using NVT ensemble for 40 ns. The pair radial distribution function (PRDF) is calculated using the procedure reported in ref. [15]. To identify the crystalline and amorphous structure, we determine the number of coordination atom with the cutoff distance $r_{cut} = 3.35$ Å. We denote the atoms having 14 and 12 neighbors as 14-type and 12-type atom, respectively. Also, the crystalline atoms are identified by using CNA method [16]. Where, the bcc-type also belongs to 14-type, while 12-type includes the fcc-hcp-type and ico-type. Clearly, the atomic rearrangement the identity of every atom can change from one to another x-type during annealing process. The parameter $F_x$ for particular atom during the observation time $t_{obs}$ is defined as the ratio $n_x(t_{obs})/n(t_{obs})$ where $n(t_{obs})$ is the total number of MD steps during the time $t_{obs}$; $n_x(t_{obs})$ is the number of steps when the identity of given atom is the x-type. For instance, $F_{bcc} = 0.7$ means that the given atom possesses the bcc-type at about 70 % of MD steps within the time $t_{obs}$. The cluster analysis is carried out for specified atoms. Two atoms form a connection if the distance between them is less than $r_{cut}$.

3. Results and discussion
Fig.1 displays the potential energy per atom $E_{pot}$ as a function of time steps. For 450-model, the curve is nearly straight line and $E_{pot}$ slightly fluctuates around -1.31 eV. Unlike 450-model, the 850-model undergoes various structural transformations under annealing. Here the process can be divided into separate stages. Within stages A1 and A3, the energy $E_{pot}$ as well as the number of x-type atoms slightly varies with time steps (see Fig.2). It means that the system exists in two different metastable states.

Fig.2 also shows that during stages A2 and A4 the energy $E_{pot}$ decreases fast and the numbers of bcc-type and 14-type atom fast increase in the expense of 12-type atoms. Clearly, this demonstrated that unlike stages A1 and A3, the system exists in unstable states and tend to transform to bcc-crystalline phase. Thus, the crystallization proceeds with increasing 14-type atoms, i.e. the system is more compact. On the other hand, the number of ico-type atoms in contrast decreases to zero. This is clarified that the ico-atoms prevent the transformation from amorphous to crystalline phase. Moreover, the crystallization is accompanied with transformation of local symmetry from five-fold to four-fold [11,12]. At stage A5, the energy $E_{pot}$ and number of x-type atoms are slightly fluctuated around fix values (~1.29 eV). It means that the crystallization is completed and the system is in a more stable state.

The change of PRDFs during annealing process is shown in the fig.3. We can see many peaks appear at large distance $r$ as the 850-model has annealed within 40 ns. It shows the formation of crystal structure.

Next, we investigate the cluster formation for three sets of atoms and $t_{obs} = 0.5$ ns. First set consists of atoms with $F_{14} = F_{bcc} = 0$. Most of atoms of this set are located in a surface
area of NP because of the coordination number of surface atoms is smaller than 14. The second set comprises atoms with \( (F_{14} > 0) \). In contrast, majority of atoms of second set are located in the core of NP. Third set comprises atoms with \( (F_{bcc} > 0) \) and \( (F_{14} > 0) \). These specified atoms are denoted respectively as \( S_{atoms} \), \( C_{atoms} \) and \( Cr_{atoms} \) for advantage. Table 1 and 2, we display characteristics of clusters at different moments, \( t=2, 20 \) and \( 40 \) ns. With \( < F_{bcc} > \) is obtained by averaging \( F_{bcc} \) over all atoms of clusters and characterizes about the degree of bcc-crystallization. It can be seen that \( C_{atoms} \) form a large cluster covering a major part of NP, while \( S_{atoms} \) form a number of clusters. With increasing time \( t \), the number of \( S_{atoms} \) and \( C_{atoms} \) is slightly changed, while the number of \( Cr_{atoms} \) largely increases.

At early moment, \( Cr_{atoms} \) form a number of clusters. Most of them are small, but more than 50 % of \( Cr_{atoms} \) belong to a main cluster. As the time proceeds, small clusters disappear

**Figure 1.** Potential energy per atom as a function of time steps.

**Figure 2.** Number of type atoms as a function of time steps for NP annealed at 850 K.
Figure 3. PRDF for NPs: A) at 450 K, t = 40 ns; B) 850 K, t = 1 ns; C) 800 K, t = 40 ns.

Figure 4. Schematics of separate regions for crystallized NP: where (1) and (2) regions located in the surface area have the amorphous structure, while other ones (3 and 4 region) possess the bcc-crystalline structure. The degree of bcc-crystallization for (4) region is larger than that for (3) region.

and the main cluster grows fast (see Table 2). It means that the transitions to bcc-type do not happen arbitrarily at any location of NP, but instead those transitions are concentrated in a non-equilibrium region where the atoms strongly rearrange. Moreover, the size of this region grows under time t. Namely, behavior of $C_{\text{r}_{\text{atoms}}}$ resembles the process of nucleation and growth where the cluster of $C_{\text{r}_{\text{atoms}}}$ plays a role of the nucleus and main cluster represents the critical nucleus. On the other hands, Table 2 also shows that parameter $F_{\text{bcc}}$ for main cluster increases rapidly. For example, $<F_{\text{bcc}}>$ is equal to 0.0473 at $t = 2$ ns, while it approaches to 0.75 at $t > 16$ ns. It notes that other parameters such as $<F_{14}>$ and $<F_{12}>$ also largely change.
Figure 5. Snapshot of distribution of atoms in different region of crystallized NP: where, red ball is crys-atom, blue ball is amorphous-atoms.

with time t. This shows that although the structure of main cluster is similar to bcc-crystalline one, its microstructure at early moment strongly differs from that at late moment, i.e. the microstructure of main cluster strongly changes under annealing process. The main cluster of $Cr_{atoms}$ at early stage represents a pre-crystalline phase of which the structure differs from the one of amorphous and bcc phase. Next, at $t > 20$ ns the parameter $<F_{bcc}>$ as well as the size of main cluster are slightly fluctuated around fix values. It means that the crystallization is completed and the $Cr_{atoms}$ are located in a well-equilibrium region of NP. Therefore, we can conclude that the crystallization pathway comprises of different intermediate states between amorphous and crystalline ones.

Finally, at time point t, we realized the location of main cluster through $r_{CM}$ (distance from the cluster centre to centre of NP). At early moment $r_{CM}$ is equal to 12.44 Å (see Table 2) which demonstrated that the main cluster is located in a middle layer of NP. As the time proceeds, $r_{CM}$ tend to decreases to 0.63, it means that the mass center of cluster locates near the center of NP. This can be understood that the main cluster rapidly spreads over major part of NP core. Accordingly, we can conclude that the structure of main cluster is strongly heterogeneous. In other words [1], the crystallized NP comprises various regions with different microstructure. Especially, it can be divided into separate regions as schematically described in Fig.4 and 5. It can be seen that the distribution of atoms in the separate regions are not uniform; they tend to form the separate clusters in NP. It means that structure of NP is strongly
Table 1. Size distribution of clusters. Here, $S_{\text{clus.}}$ is number of atoms in cluster; $N_{\text{clus.}}$ is the number of clusters; $S_{\text{atoms}}$ consists of atoms with $F_{14} = F_{\text{bcc}} = 0$; $C_{\text{atoms}}$ comprises atoms with $(F_{14} > 0)$; $Cr_{\text{atoms}}$ comprises atoms with $(F_{\text{bcc}} > 0)$ and $(F_{14} > 0)$.

| $S_{\text{clus.}}$ of $S_{\text{atoms}}$ | $N_{\text{clus.}}$ of $S_{\text{atoms}}$ | $N_{\text{clus.}}$ of $S_{\text{atoms}}$ | $N_{\text{clus.}}$ of $S_{\text{atoms}}$ | $N_{\text{clus.}}$ of $S_{\text{atoms}}$ |
|--------------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
|                                      | $t=2$ ns                      |                                | $t=20$ ns                     |                                | $t=40$ ns                     |
|                                      | 1281 1 3660 1 0.0011 77 1 0.0473 | 1233 1 3767 1 0.7021 3524 1 0.7505 | 1230 1 3770 1 0.7006 3525 1 0.7493 |

Table 2. The characteristics of crys-atom clusters under range of different simulation time. Here $r_{CM}$ is distance from the cluster centre to centre of NP; $N_{\text{clus.}}$ is number of clusters; $S_{\text{clus.}}$ is number of crystal-atoms in main cluster.

| $t$(ns) | $N_{\text{clus.}}$ | $S_{\text{clus.}}$ | $r_{CM}$ | $< F_{\text{bcc}} >$ |
|---------|-------------------|-------------------|----------|-------------------|
| 2       | 25                | 77                | 12.22    | 0.0473            |
| 4       | 24                | 128               | 14.01    | 0.1097            |
| 6       | 15                | 1062              | 10.57    | 0.4133            |
| 16      | 1                 | 3566              | 1.06     | 0.7272            |
| 20      | 1                 | 3524              | 0.93     | 0.7505            |
| 40      | 1                 | 3525              | 0.63     | 0.7493            |

heterogeneous. Namely, the structure organization of NP includes four different phases: porous amorphous phase located nearby the surface of NP, dense amorphous- bcc crystallization- and mix-phases in different layers of NP. Obviously, this phenomena is very interesting because the characteristic of structure heterogeneous may be relate to dynamical heterogeneous which this issue is attracting research attention for NPs [13-16].

Conclusion
In this paper, the structure of iron NP at temperature of 450 and 850 K has been investigated. Several results are shown as follows:

i) The ico-type atoms play a role in the preventing of crystallization in amorphous NP at 450K. The crystallization has occurred undergo annealing at 850 K. We found that the number
of 14-type atoms strongly increases, while the number of 12-type and ico-type atoms decreases. The crystallization is accompanied with transformation of local symmetry from five-fold to four-fold.

ii) The transitions to bcc-type do not happen arbitrarily at any location, but instead they are focused in a non-equilibrium region in NP. We revealed that the crystallization pathway comprises of various intermediate states between amorphous and crystalline ones.

iii) We showed that structure heterogeneous is separate regions in crystalline NP. Nearby the surface of NP are two regions with the porous and amorphous structure. Other regions covered a major part of the core of NP with the bcc-crystalline structure.

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