Crystallization study of iron nanoparticles using molecular dynamics simulation

Pham Huu Kien, Nguyen Thi Thu Ha

Abstract— **The growth and nucleation of iron nanoparticles in amorphous solid have been investigated by molecular dynamics method. It was found that when the sample is heated at 921 K and relaxed over long time, the sample is crystallized into bcc crystal structure. The first nuclei formed most frequently in the area nearby to the surface of the nanoparticle. Then the crystal cluster grows in the direction to the center of nanoparticle. The final crystallized sample has two parts: the core with bcc crystal structure and surface with amorphous structure. When the sample was relaxed at 310 or 550 K we observe a small cluster with size less than 50 atoms. However, this cluster does not grow to larger size. The observed crystallization agrees with the classical theory of nucleation.**

Index Terms— **nanoparticle, crystallization, molecular dynamics, amorphous iron.**

I. INTRODUCTION

Nanoparticles can be produced either in crystalline or amorphous state by means of reasonable synthesis methods [1-4]. The amorphous nanoparticles (ANP) have a disordered structure which can be divided into two parts: the core with structural characteristics closed to those of corresponding amorphous bulks and surface which exhibits a more porous amorphous structure. Due to such specific structure ANPs can have advanced applications in various areas of science and technology [5-9]. For instance, in catalysis Fe_2O_3 ANPs are more active than the nanocrystalline polymorphs at the same diameter [5]. In general, the amorphous state of nanoparticle is thermally unstable and ANP can be crystallized under appropriate annealing schedules. Stability of ANPs against the crystallization is of great interest, since it is related to their working ability in practice. Up to now the crystallization of ANPs is mainly studied experimentally. The phase transition in Co ANPs has been investigated by DSC curves. The glass transition temperature and crystallization temperature of ANPs has been found to be size dependent [9]. A number of studies [10-15] have been done on the crystallization of TiO_2 ANPs. This nanoparticle transforms into the anatase and then into rutile depending on the annealing temperature or preparation conditions. It was revealed that the transformation in TiO_2 ANPs comprises of following stages: i) Interface nucleation of anatase on the contact area of ANP; ii) Crystal growth of anatase by redistributions of atoms either

from amorphous particles or small anatase crystals; iii) Oriented attachment of adjacent anatase particles. We also found few experimental works concerning the amorphous-crystallization transition of Al_2O_3 and CdSe nanoparticles [16-18]. The crystallization mechanism can be studied by simulation methods since it is difficult to trace the motion of atoms directly by experiments. However, presently most simulations focus on crystallization in the liquid and bulk samples [19-23], only few works on crystallization in amorphous matrix and ANPs were found [20, 24]. In the previous work [25] we found that when ANP is annealed at high temperature, it is transformed into crystalline structure. However, the mechanism of crystallization is still not well understood. Therefore it is worth to conduct simulations on crystallization of ANPs at different annealing temperatures in order to clarify the nucleation and growth of crystal cluster in amorphous matrix. In addition, the validity of classical theory of nucleation for ANP was also considered and presented.

II. SIMULATION METHODOLOGY

A classical molecular dynamics (MD) method was used to study the growth and nucleation in an iron nanoparticle. Here we use the Pak-Doyama because it can well describe structural and thermodynamic properties of both liquid and amorphous Fe [22, 25]. Initially, 5500 atoms are randomly replaced in a sphere with radius of 27 Å under free boundary conditions. Then the statistic relaxation is carried out until the system reaches the equilibrium. After that the obtained sample is heated to 310 K and relaxed isothermally by 2.5×10^7 MD steps. We call this well-equilibrated sample 310-sample. For bulk sample the radial distribution function (RDF) for nanoparticle is defined as shown in ref. [25]. To study the crystallization mechanism we also prepare two samples called 550- and 921-sample. These samples were prepared by heating the 310-sample to desired temperature and then relaxing isothermally over 2.5×10^7 MD steps. The crystallization is analyzed via the number of crystallized atoms in obtained 921-sample.

III. RESULTS AND DISCUSSION

Fig.1 shows RDF for core-nanoparticles of 310- and 550-sample, and the evolution of RDF during the relaxation for 921-sample. As the previous work [25], it can be seen that the RDF of 310- and 550-sample is very similar to one of bulk sample. The core of nanoparticle has the same structure as the amorphous iron. In the case of 921-sample the RDF strongly changes during relaxation. For short relaxation time the curve is similar to the one of bulk sample. The structure remained amorphous, and no crystal cluster formed during this period. For longer times, a number of new acute peaks appear showing distinct crystal characteristics. This evidences the transformation from amorphous to crystalline bcc structure.

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The transformation to the crystalline phase can be observed directly by the number of amorphous and crystal atoms during the relaxation. As shown in Fig.2, the process can be divided into three periods. In the first period the crystal cluster grows slightly, meanwhile for the second period crystal grows up rapidly. This demonstrates that if the size of crystal cluster is bigger than some critical value, then the growth develops rapidly to a maximal size. The critical size is found to be 200-250 atoms. In the third period the number of crystal atoms fluctuates and the size of crystal cluster reached a maximal value. In Fig.3 we plotted two quantities: 1) N_{CrS}/N_{Cr} relates to the fraction of surface-crystal atoms which locate in the boundary area between crystalline and amorphous phases; N_{CrS}/N_{Cr} =0.93 for the basic nucleus (N_{CrS} =14; N_{Cr} =15); 2) The dependence of $N_{CrI}^{1/2}$ on $N_{Cr}^{1/3}$. For first period N_{CrS}/N_{Cr} varies frequently from 0 to 0.93. This indicated that a basic nucleus forms, but it is not stable and disappears after short times. It is well known that if the crystal cluster has a spherical shape, the number of surface-crystal atoms is proportional to $R^{1/2}$ and the number of crystal atoms to $R^{1/3}$. Here R is radius of the spherical cluster. It means that N_{CrS}/N_{Cr} decreases monotonously with increasing the radius R, and the dependence of $N_{CrS}^{1/2}$ on $N_{Cr}^{1/3}$ is linear. As shown in Fig.3, for longer relaxation times the fraction of surface-crystal atoms decreases to a finite value. Moreover, all points fall into a straight line when the number of crystal atoms is bigger than 310 ($N_{Cr}^{1/3} > 6.5$). Therefore, the small cluster formed during initial period has non-spherical shape, but it grows to a sphere after long relaxation time.

During the relaxation, atoms in the coordination cell rearrange leading to formation of different short-order configurations. These configurations can be characterized by the potential energy E_{cell}. In Fig.4 we plotted the mean potential energy of an atom belonging to the amorphous (E_A) and crystal phase (E_{Cr}). In the case when the size of formed crystal cluster is 15 atoms, i.e. a basic nucleus, E_{Cr} varied from -2.2 eV to -2.7 eV; meanwhile E_A was about -2.4 eV (see Fig.4a). This implies that the basic nucleus have different configurations of which the energy E_{cell} is closed to one for amorphous phase. Therefore, during this period the nucleus is not stable, and it can transform into the short-order configuration of amorphous phase. So, in this case the rate of amorphous-cell $\rightarrow$ crystal-cell is close to the one of crystal-cell $\rightarrow$ amorphous-cell. This results in that the crystal cluster does not grow to bigger size. In the case when the forming crystal cluster consists of several basic nuclei (the size of crystal cluster is 50-100 atoms), the energy E_{Cr} for crystal phase is much smaller than E_A. In particular, E_{Cr} varied from -2.57 eV to -2.85 eV; meanwhile E_A was about -2.4 eV (see Fig.4b). This results in that the rate of amorphous-cell $\rightarrow$ crystal-cell is much larger than one of crystal-cell $\rightarrow$ amorphous-cell. Hence, we observe the rapid growth of crystal cluster. Further increasing the crystal cluster shifts the energy E_{Cr} for crystal phase to lower value. Similar picture is observed for small crystal cluster of 310- and 550-sample (see Fig.4c and 4d). Due to low annealing temperature the formation of large crystal cluster is not observed in our simulations. The observed behavior agrees with classical theory of nucleation.

CONCLUSION

In this paper, the nucleation and growth mechanism is studied by tracing the basic nuclei during relaxation process. We found that the crystallization happens when the sample is relaxed for long times at 921 K. The phase change to crystalline state is evidenced through the RDF and the size of crystalline cluster. The result shows that the sample transforms from amorphous to the bcc crystalline structure. Final crystallized sample consists of two parts: a core with crystalline structure and a surface with amorphous structure. The critical size of crystalline cluster is found to be 250-310 atoms. The observed crystallization mechanism agrees with the classical nucleation theory. The nucleation happens not randomly in the sample, but intensively in the area nearby to the surface of nanoparticle. In the case when the sample is relaxed at 310 or 550 K, a small crystal cluster consisting of several basic nuclei has been detected. However, these nuclei do not grow to a large size and the structure of nanoparticle remains amorphous.

ACKNOWLEDGEMENT

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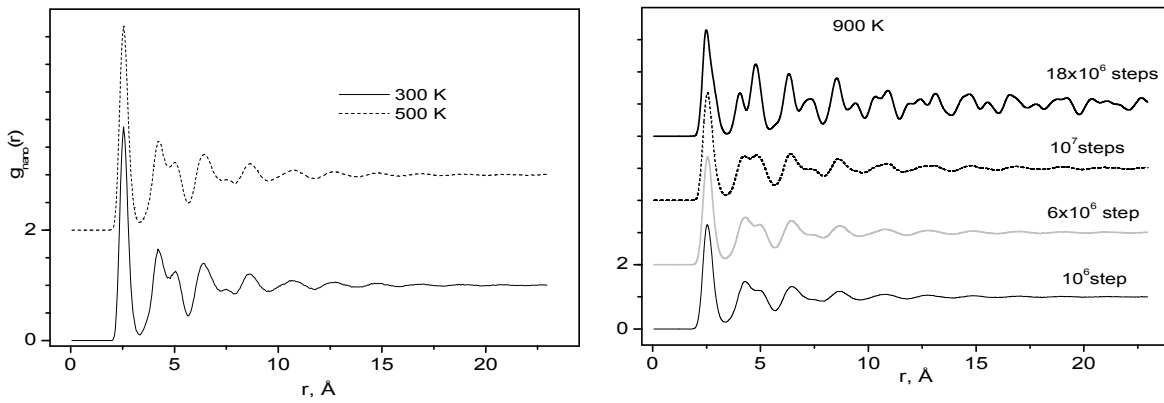[25] P. H. Kien, M. T. Lan, N. T. Dung and P. K. Hung, *Int. J. Mod. Phys.* B 28 (2014) 1450155.

Fig.1 RDF for nanoparticles isothermally relaxing at 310, 550 K (left) and the evolution of RDF of 921-sample during relaxation (right).
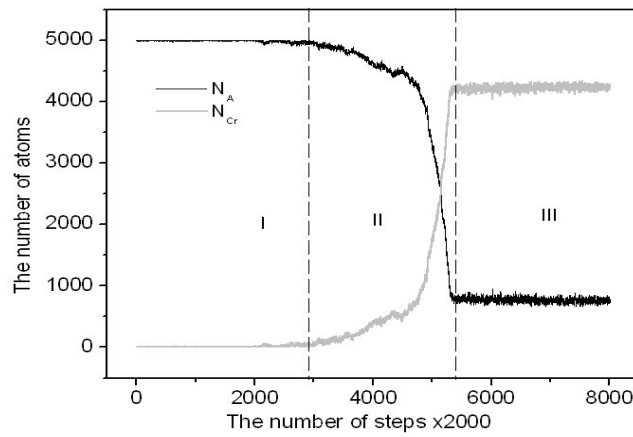

Fig.2 The time dependence of number of atoms N_A and N_{Cr}

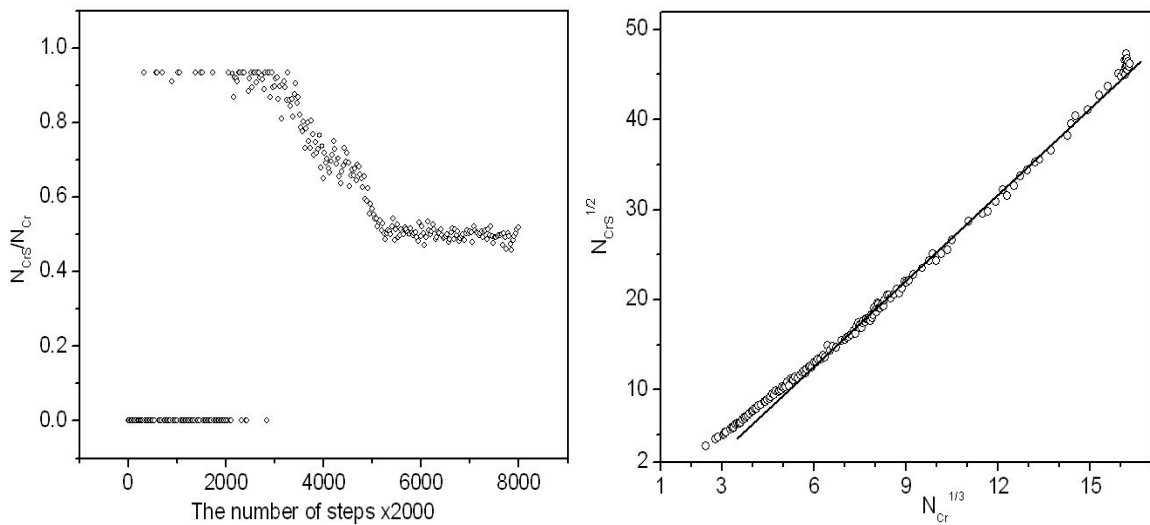**Fig.3** Ratio between numbers of surface-crystal and crystal atoms (left) and the dependence of $N_{CrS}^{1/2}$ as a function of $N_{Cr}^{1/3}$
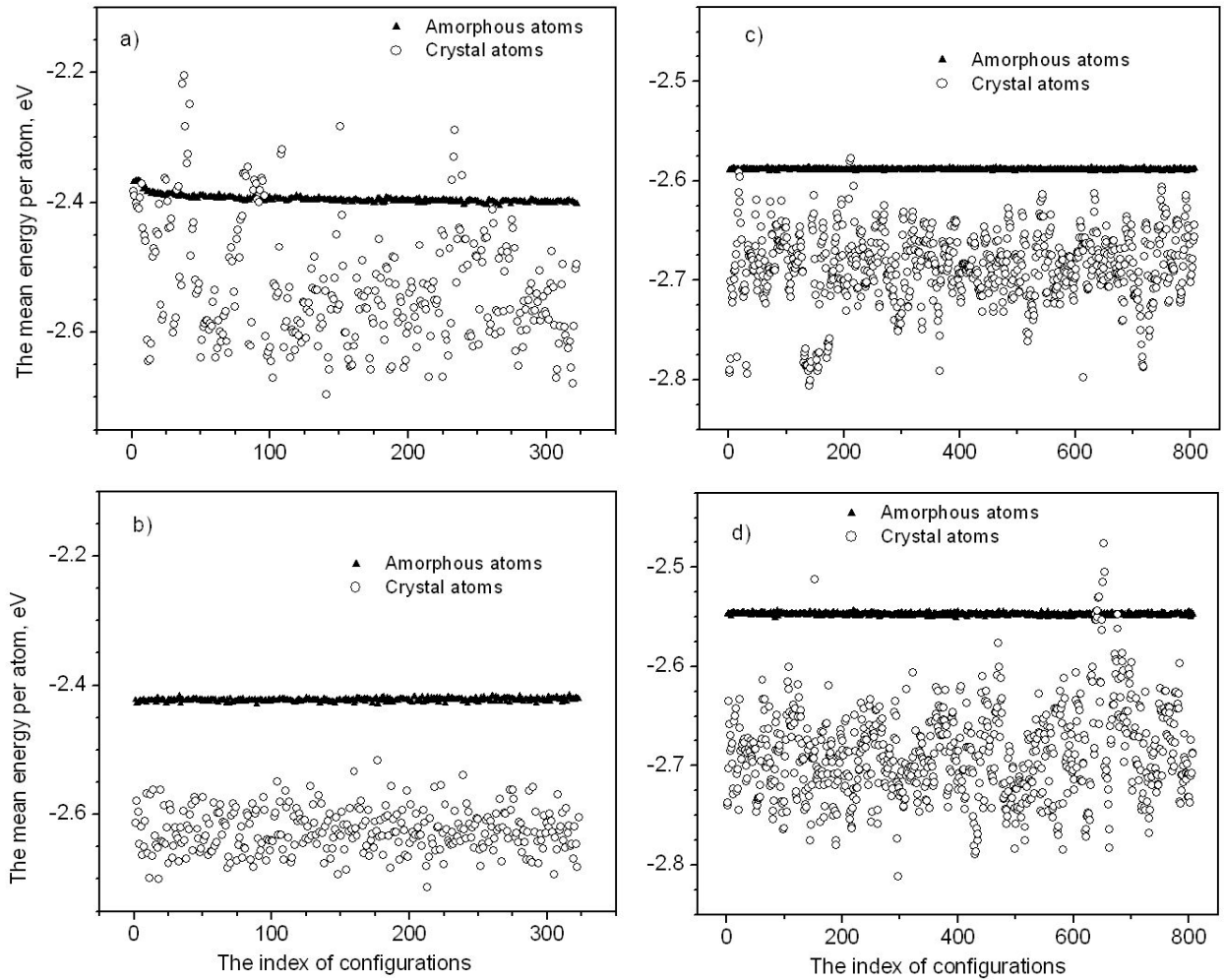
Fig.4 The mean energy of amorphous and crystal atoms for different configurations; a) N_{Cr}= 15 atoms; 921-sample b) N_{Cr} varies from 50 to 100 atoms; 921-sample; c) N_{Cr} of 15 - 50; 310-sample; d) N_{Cr} of 15-50; 550-sample.