Annealing study of amorphous bulk and nanoparticle iron using molecular dynamics simulation

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Annealing study of amorphous bulk and nanoparticle iron at temperatures from 500 K to 1000 K has been carried out using molecular dynamics (MD) simulations. The simulation is performed for models containing $10^4$ particles Fe at both crystalline and amorphous states. We determine changes of the potential energy, pair radial distribution function (PRDF) and distribution of coordination number (DCN) as a function of annealing time. The calculation shows that the aging slightly reduces the potential energy of system. This result evidences that the amorphous sample undergoes different quasi-equilibrated states during annealing. Similar trend is observed for nanoparticles sample. When the samples are annealed at high temperatures we observe the crystallization in both bulk and nanoparticle. In particular, the system undergoes three stages. At first stage the relaxation proceeds slowly so that the energy of system slightly decreases and the samples structure remains amorphous. Within second stage a structural transformation occurs which significantly changes PRDF and DCN for the relatively short time. The energy of the system is dropped considerably and the amorphous structure transforms into the crystalline. Finally, the crystalline sample undergoes the slow relaxation which reduces the energy of system and eliminates structural defects in crystal lattices.

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1. Introduction

A liquid usually crystallizes at a melting point unless cooling is performed so rapidly that it avoids the crystallization and the liquid transforms to a glass phase. When

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amorphous materials obtained by rapid quenching are annealed at temperatures below the melting point, they could undergo structural transformations among different solid states. There are two types of these transitions: (1) the relaxation where the material remains amorphous solid, but some of its properties slightly vary with time; (2) the crystallization where the material transits to the equilibrated state. Understanding of microscopic mechanisms governing those transitions is one of the very important problems in the glass science. Aging (annealing) effect of different materials has been intensively studied by both simulation and experiments for long time.\textsuperscript{1–9} As shown from Refs. 10–15 the diffusion rate in certain amorphous alloys is quite different depending on the way of their production. Moreover, the diffusion constant remarkably decreases upon annealing. Some researchers found a change in the density of amorphous alloys by few percent upon annealing although the crystallization did not occur. This effect is interpreted as a result of the elimination of exceeding vacancies.

Computer simulation could give more detailed information about both relaxation and crystallization. Historically, it perhaps has largest impacts on the fundamentals of materials science in the study of amorphous systems. We can find numerous works concerning aging effects in amorphous systems.\textsuperscript{1,2,4,5} Molecular dynamics (MD) simulations on aging effects in the supercooled liquid show a slight change of statistics properties. However, the dynamical properties exhibit a remarkable aging effect as well as the sample-dependent behavior, meaning that the quenched glass cannot attain the equilibrium for the time scale of simulations due to slow dynamics phenomena.\textsuperscript{1} Other researchers measured the changes in pair radial distribution functions (PRDFs) and non-Gauss parameters with time. They found that the dynamics are spatially heterogeneous which increases during the annealing process.\textsuperscript{1,5} The crystallization may occur in the simulated amorphous sample and it is interesting to see how the amorphous structure transforms into crystalline during the annealing process. The viewing of particle trajectory with time allows deeper understanding of the mechanism of crystallization as well as the relaxation. However, we found only few works concerning this problem.\textsuperscript{16–18} Probably, it is caused by that the crystallization is difficult to realize in simulated models for the time scale of simulation. This motivated us to carry out a systematic study for both relaxation and crystallization of amorphous iron based on MD models.

Nanoparticles have attracted a great interest in recent years due to their enormous importance in science and technology.\textsuperscript{19–22} The nanoparticle can be made either in crystalline or in amorphous states by using reasonable synthesis methods. Crystalline nanoparticles have a well-defined crystal structure with large fraction of surface atoms which provide them unique properties different from bulk counterparts. Whereas, amorphous nanoparticles (ANP) have a disordered structure and it also can be divided into the core whose structural characteristics are close to those of bulk counterparts, and surface which have more porous structure.\textsuperscript{19} Similar to bulk samples, the ANP may undergo the relaxation and crystallization. Hence, the aging effect of ANPs affects its working ability in practice. For instance, in cataly-
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The amorphous Fe$_2$O$_3$ ANPs are more active than the nanocrystalline polymorphs at the same diameter; however, these ANPs can undergo the amorphous-crystalline transformation at temperature about 300°C.\textsuperscript{23} Up to now, the aging effect of ANPs is studied poorly and the information about structural transformation at atomic level in ANP is very limited. Therefore, a simulation of ANP has also been carried out and we focus on the aging effect of ANP.

2. Calculation Procedure

We carry out MD simulations of iron using a Pak-Doyama potential\textsuperscript{24} given as

\[
U(r) = -0.188917(1.82709 - r)^4 + 1.70192(r - 2.50849)^2 - 0.198294; \quad r < 3.44 \ \text{Å}.
\] (1)

Here $r$ is the inter-atomic distance in Å and $U(r)$ in eV. The simulation for bulk samples is performed in a cube containing $10^4$ particles under periodic boundary conditions. The equations of motion were solved numerically using the Verlet algorithm with MD step equal to 0.46 fs. Initial random configuration was equilibrated at constant density of 7.0 g/cm$^3$ by relaxation for $10^6$ MD steps at 5000 K in the NVT ensemble (the constant volume and temperature). This melt has been cooled down to a temperature of 300 K. Then it has relaxed by $10^7$ steps to obtain an amorphous model which is called 300 b-sample. From the 300 b-sample we construct four samples by heating to temperatures 500, 700, 900, 1000 K and then relaxing by $10^7$ steps. We denoted these samples to 500b-, 700b-, 900b- and 1000b-sample, respectively. In order to study the aging effect the obtained samples are additionally relaxed over $2 - 3 \times 10^7$ steps in the NVE ensemble (the constant volume and energy). To calculate the coordination number we use the cutoff distance $R_O = 3.35$ Å chosen as a minimum after first peak of PRDF. In order to improve the statistics the structural quantities of interest are obtained by averaging through 100 configurations separated by 500 steps.

The nanoparticle sample is constructed as follows. We first randomly place $10^4$ particles inside a sphere with radii of 33.5 Å. This configuration has been relaxed to reach the minimum of potential energy by using a statistic relaxation method. Namely, for each atom we determine the force acting on it from remaining atoms. Then the atoms move on the direction of determined force by the distance proportional to the force. This procedure is performed many times until the system reaches the minimum of potential energy. After that we perform the relaxation of the obtained sample by using MD simulation under free boundary conditions.\textsuperscript{25} We prepare a nanoparticle sample at 300 K by heating and relaxing within $3 \times 10^7$ steps. This well-equilibrated sample denoting 300 n-sample is used for preparing three samples at temperatures of 500, 700 and 900 K (500n-, 700n- and 900n-samples) by similar way. In the case of 900n-sample few particles at the surface region sometimes have much kinetic energy so that they break out of the nanoparticle. To prevent this we monitor the distance between each particle and center of
nanoparticle $R_i$. If the distance $R_i$ is bigger, a fix value of 34 Å, then the kinetic energy of $i$th particle is set to zero. This procedure forces the particle return to the surface region if it moves far from the nanoparticle.

3. Results and Discussion

First quantity we would like to discuss is PRDF. As shown in Fig. 1, PRDF for a 300b-sample is in good agreement with experimental data in Ref. 26. Therefore, the Pak–Doyama potential realistically represents the structure of amorphous iron. For 500b- and 700b-sample no aging effect on PRDF was found. The PRDFs are almost unchanged over whole time. Hence the structure of considered samples remains amorphous for the time scale of simulation. It seems that the aging effect is difficult to detect by the averaged quantities like PRDF. However, unlike two above samples, a significant change in PRDFs is observed for 900b- and 1000b-samples. In particular, as shown in Fig. 2, the intensities of second peak and several other ones noticeably increase with the annealing time. Moreover, new peaks located at large

![Fig. 1. The PRDF for 300b-, 500b- and 700b-samples.](image-url)
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Fig. 2. The PRDF for 900b- and 1000b-samples.

Distances appeal. This result indicates that the observed PRDFs do not resemble the amorphous structure, but it represents another one which, as shown below, is the crystalline structure.

The aging effect can be detected through the distribution of coordination number (DCN). The simulation result on DCN is shown in Fig. 3. For low-temperature samples (500b- and 700b-samples) one can see a pronounced peak located at the point 13. The height of the peak is about 0.4 and the DCN in general is unchanged with annealing time. Meanwhile, for high-temperature (900b- and 1000b-samples) samples DCN strongly varies. Within a relatively short time the height and location of the peak of DCN are 0.4 and 13, respectively. After annealing of $2 \times 10^7$ steps the height of DCN peak increases up to 0.6 and its location shifts to 14. This result clearly evidences the structural transformation in high-temperature samples.

Further information about the aging effect is inferred from the potential energy of system during annealing process. As shown in Fig. 4 the energy for low-temperature samples oscillated around a defined value. Although the amplitude of these fluctuations is large, but it is clear that the energy has a tendency to slightly decrease with annealing time. This means that the system stays in metastable states over whole time and spontaneously transits to more stable states, i.e., to the state having smaller potential energy. In principle, the system can reach the equilibrium upon infinite long annealing. However, the time requested is too large so that we do not observe it in the simulation.
Fig. 3. The distribution of coordination number.

Fig. 4. The dependence of potential energy as a function of annealing time for bulk samples.
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For high-temperature samples the energy of system initially oscillated around some value like the case of low-temperature sample, but after moderated time it rapidly dropped to a much lower value. The energy decrease is about 0.032 eV for both 900b- and 1000b-samples. The close energy decrease for two samples evidences the transformation from amorphous into the similar crystalline structure. With longer annealing the energy of system again oscillates around a new fix value (see Fig. 4). This result clearly shows that the system undergoes three stages. At first stage although the relaxation proceeds fast, the samples structure remains amorphous and only the energy of system varies. Within the second stage a structural transformation occurs. The energy of system is dropped and the structural characteristics such as PRDF, DCN strongly varies. The amorphous structure now transforms into the crystalline. The last stage is the relaxation of crystalline sample. Like first stage the energy has a tendency to slightly reduce which relates to the elimination of structural defects in crystalline lattices.

The crystalline structure can be seen from the snapshot of particles arrangement in the simulation box which is shown in Fig. 5. Here one can see the amorphous structure for the short-time annealing sample and crystalline for long annealing sample. The crystal in the obtained sample resembles the bcc lattice which has eight nearest neighbors and four others at the next coordination sphere.

The snapshot of particles arrangement in 300n-sample is shown in Fig. 6. One can see that the simulated nanoparticle has a spherical form. Furthermore, it

![Fig. 5. The snapshots of particles arrangement in (a) short-time and (b) long annealing 900b-sample.](image)
Fig. 6. The snapshot of 300n-sample.

Fig. 7. The (a) DCN and (b) $\rho(R)$ for 300n-sample.

consists of the surface and core. The particles at surface have less coordination number comparing to particles in the core. This fact can be seen from the DCN shown in Fig. 7(a). Unlike bulk samples the DCN is spread in much wider range. It varies from 4 to 17, meanwhile the corresponding values for bulk sample are 10
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and 17. Moreover, for the bulk sample a pronounced peak is seen at the point 13. Whereas for nanoparticle there are two peaks located at the coordination number of 9 and 13. Obviously, the appearance of two peaks evidences different contributions of particles in surface and core to DCN. The main peak is originated from particles in the core, and small peak from ones in the surface. Note that the height of main peak for nanoparticle is much lower than one for bulk sample. This result evidences a large fraction of surface particles.

To give more detail information about the local structure of nanoparticle we have calculated the dependence of particles density $\rho(R)$ on the distance $R$ from the center of nanoparticle. The quantity $\rho(R)$ is determined as follows. We find the number of particles located in a spherical shell formed by two surfaces of two spheres having radius of $R - 0.25$ Å and $R + 0.25$ Å. The center of these spheres coincided with the center of nanoparticle. As shown in Fig. 7(b), for the distance less than 28 Å, $\rho(R)$ fluctuates around the value of 0.0825 particle/Å$^3$. With further increasing $R$ the $\rho(R)$ is dropped to zero. From Fig. 7(b) the thickness of the surface is calculated and it equals to about 4.0 Å. Note that the density of bulk sample is 0.0823 particle/Å$^3$. Combined these result we can conclude that the core of nanoparticle has a radius of 28 Å and the same density as a bulk sample. The surface has a thickness of 4.0 Å and a more porous structure.

The PRDF of bulk sample $g(r)$ is defined as

$$g(r) = \frac{n(r)}{4\pi r^2 dr \rho_0},$$

where $n(r)$ is the number of particles in a spherical shell with thickness $dr$ at a distance $r$ from another particle; $\rho_0$ is the number density in the sample. We have calculated the local number density function given as follows:

$$\eta(r) = \frac{n(r)}{4\pi r^2 dr}.$$  \hspace{1cm} (3)

Unlike $g(r)$ the function $\eta(r)$ approaches to $\rho_0$ in the limit of $r \to \infty$. For nanoparticle we determine the function $\eta_{\text{nano}}(r)$ as follows. Consider a nanoparticle with radius $r_{\text{nano}}$ which is centered at the point O and a particle locating at the point A [see Fig. 8(a)]. To determine $\eta_{\text{nano}}(r)$ we find all particles in a spherical shell with thickness $dr$ at a distance $r$ from the point A. We denote this number of particles to $n_{\text{nano}}(r)$. The considered shell shown in Fig. 8(a) has two parts which is located inside and outside the nanoparticle. Let the volume of these parts be $V_{\text{in}}$ and $V_{\text{out}}$, respectively. Obviously $V_{\text{in}} + V_{\text{out}} = 4\pi r^2 dr$. The function $\eta_{\text{nano}}(r)$ is defined as

$$\eta_{\text{nano}}(r) = \frac{n_{\text{nano}}(r)}{V_{\text{in}}}. $$  \hspace{1cm} (4)

Here the bracket $<>$ means that it is obtained by averaging over different particles in the nanoparticle. Figure 8(b) displays $\eta_{\text{nano}}(r)$ for 300n-sample. This quantity approaches to the number of density of nanoparticle equal to 0.0689 Å$^{-3}$. As mentioned above the 300n-sample has a radii of 32.0 Å and a surface with thickness
of 4.0 Å. If all particles in the surface are removed, then we obtain a nanoparticle with radii of 28.0 Å (core-nanoparticle). In Fig. 8(b) we show the quantity $\eta_{\text{nano}}(r)$ for the core-nanoparticle together with $\eta(r)$ for the bulk sample. One can see that these functions almost coincided. Note that the number density of the core is very close to one of the bulk sample. Combined these results we can conclude that the structure of the core is very similar to the structure of bulk sample.

Similar to bulk sample the aging effect is not found for 500$n$- and 700$n$-samples through $\eta_{\text{nano}}(r)$ and DCN. As shown in Fig. 9 these quantities are almost unchanged upon annealing. The aging effect can be seen only from the potential energy of system which is shown in Fig. 10. Here one can see that the energy of nanoparticle has a tendency to slightly decrease with annealing time. It means that upon annealing the system undergoes among different quasi-equilibrated states, but not reaches the equilibrated state due to the time requested for reaching the equilibrium exceeds the time scale of simulation.

When the nanoparticle is annealed at a temperature of 900 K, we observe a transformation to crystalline state. As shown in Fig. 11 the local density number function as well as DCN exhibits a significant change during annealing process. In particular, the height of second peak of $\eta_{\text{nano}}(r)$ grows from 0.11 to 0.23 and many new peaks located at large $r$ appeal. Moreover, most particles (about 75%) have the coordination number of 14. Meanwhile for short-time annealing sample only 18% particles have a coordination number of 14. This result evidences the transformation from amorphous to the crystalline structure. The snapshot of particles arrangement

Fig. 8. (a) The illustration of determining the local number density function for nanoparticle; (b) the function $\eta_{\text{nano}}(r)$ for 300$n$-sample (top) and $\eta(r)$ for 300b-sample (bottom).
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Fig. 9. The function (a) \( \eta_{\text{nano}}(r) \) (b) DCN for 500n- and 600n-samples.

Fig. 10. The dependence of potential energy as a function of annealing time for nanoparticle samples.
Fig. 11. The (a) function $\eta_{\text{nano}}(r)$ and (b) DCN for 900n-sample.
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Fig. 12. The snapshot of short-time annealing (top) and long-time annealing (bottom) 900nm-sample.

in short-time annealing and long annealing samples is shown in Fig. 12. Here one can see that the long annealing sample has a crystalline structure and its spherical form is stronger distorted comparing to short-time annealing sample. The crystal in long annealing sample resembles a bcc lattice.

According to the classical crystallization theory, the crystallization consists of two events: new nucleuses are generated and then they grow to the crystal. Similar
process is observed in our simulation. In particular, the particles having the coordination number 14 (we denote it to particle A) collect together nearby into clusters. Then the clusters containing particles A grow. The particles with other coordination number are denoted to particle B. After a long annealing the number of particles B becomes independent with time and they represent the structural defect like vacancy or grain boundary. The snapshot of particles B for crystalline bulk sample is shown in Fig. 13. It is interesting to note that the particles B are not uniformly distributed in the simulation box, but grouped into small clusters, i.e., the point defects (vacancy) are not created in our simulation. In Fig. 14 we show the snapshot of particles B in the nanoparticle for three cases. First one is snapshot of all particles B. The two other cases show only the particles B located in the sphere with radius of 28 Å and 26 Å. It is clear that the crystallization leads to most particles B located in the surface region. Moreover, only few particles B locate at a distance less than 26 Å from the center of nanoparticle. These particles are not uniformly distributed in the sphere, but grouped into three clusters.

4. Conclusion

In this paper we have investigated the aging effect for both bulk and nanoparticles iron at temperatures ranging from 500 K to 1000 K. Our main conclusions are the following.

(i) The rapidly-quenched bulk samples are far from the equilibrium for the relatively long annealing time of $10^6 - 3 \times 10^7$ MD steps. When the samples have been
Fig. 14. The snapshot of particles B in a crystal nanoparticle sample: (a) all particles B; (b) the particles B located in a sphere with radii of 28 Å; (c) the particles B located in a sphere with radii of 26 Å.
annealed at low temperatures, their structure remains amorphous for annealing times much longer than the time scale of simulation. The structural characteristics such as PRDF and DCN are almost unchanged during annealing process. The aging causes only small local rearrangement of particles leading to slightly decreasing the potential energy of system. It means that the system spontaneously undergoes among different quasi-equilibrated states. As the sample has been annealed at high temperatures we observe the crystallization of amorphous solid iron. The system undergoes following stages: (1) The relaxation of amorphous sample; (2) The transformation from amorphous into the crystalline state which causes a significant change in PRDF, DCN and the potential energy of system; (3) The relaxation of crystalline sample.

(ii) The rapidly quenched nanoparticle has the amorphous structure and consists of surface and core. The core has the same density and local number density function as the amorphous bulk sample. The aging causes the similar effect like the case of bulk sample. In particular upon annealing at low temperature the nanoparticle stays in quasi-equilibrium states and spontaneously transits to more stable states, i.e., the state with smaller potential energy. In the case of annealing at high temperature we observe a transformation to crystalline structure leading to significant change in DCN and the local number density function.

(iii) The crystalline samples obtained upon annealing contain two types of particles. The particles A have the coordination number of 14 and the particles B represent the structural defect of crystalline lattice. The particles B are not uniformly distributed in the sample, but grouped into clusters. For the nanoparticle most of particles B locate in the surface region.

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