Molecular Dynamics Study of Iron Cluster Coalescence at Sub-Melting Point Temperatures

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The coalescence of two iron clusters (Fe300+Fe300 → Fe600) at temperatures below the cluster melting points has been studied by molecular dynamics (MD). At temperatures ≈200°C below the melting point phase change from the icosahedral Fe300 structure to the face centered cubic (fcc) Fe600 structure occurs even though the clusters are not molten. Moreover, surface melting is not required for the coalescence or the phase change. At lower temperatures elongated Fe600 clusters that are not fcc, and that may be metastable, are formed.

1. Introduction

Nano-clusters and nanowires are of great interest due to their potential applications in designing new materials, novel sensors and other nanodevices. Properties of these nanodevices at elevated temperatures will depend, among other things, on their thermal characteristics. Although there have been many studies of the thermal properties of nanoclusters and nanowires[1-3], most of them have focused on the liquid-solid phase transition. These studies include, for example, the cluster size and structure dependence of the melting point and the importance of surface melting on the phase transition[1, 3]. Far less attention has been paid to the coalescence of clusters at temperatures below the cluster melting point, even though it is known that this process may have important ramifications in growth and design of nanodevices. For example, it is not clear whether the coalescing clusters will keep their original (crystalline) structures and form grains in the larger cluster, or whether a new (crystalline) phase can be formed at these low temperatures. Hence, studies of the mechanism of sub-melting point coalescence is of both fundamental scientific and technological interest.

In this paper we present molecular dynamics (MD) simulation results of the coalescence of two Fe300 clusters, Fe300+Fe300 → Fe600, at temperatures below their melting points. At temperatures ≈200°C below the melting points there is a phase change from the icosahedral Fe300 to the face centered cubic (fcc) Fe600 structure, whereas at lower temperatures the Fe600 cluster is elongated. The mechanism of the sub-melting point phase transition is also investigated.
2. Potential energy surface and simulation methods

Previous investigations have shown that the many-body interaction potential, which is based on the second moment approximation of the tight binding model [4], is good for studying the thermal properties of the pure [5] and alloy [6] transition metal systems. The parameters for the iron cluster studied here are obtained by fitting the cohesive energy, lattice parameter and elastic constants of γ-Fe (fcc structure) to experimental data[7].

Annealed Fe_{300} and Fe_{600} structures were obtained from MD simulations where the initial geometries of the clusters were selected by randomly placing the iron atoms in a sphere and then annealing to 0 K[8]. These structures were used to obtain the cluster melting points by ramping the temperature of the clusters (initially in their annealed geometries) from 600 to 1300 K in steps of 50 K. At each temperature a 500 ps canonical simulation was run to obtain the Lindemann index at that temperature, and the temperature where there is a sudden increase in the Lindemann index is the melting point [9,10].

Simulations of the coalescence of two Fe_{300} clusters were initialized by placing them, in their annealed geometries, 2.2 nm apart. Constant temperature coalescence was studied by canonical MD simulations using the Berendsen velocity scaling method[11]. To investigate the effect of a bath gas, constant energy trajectories – which simulate coalescence in vacuum – were run under similar conditions. In both types of simulations a 1fs integration step size was used. Simulations were terminated when a (meta)stable Fe_{600} cluster was obtained.

3. Results and Discussion

Figure 1 shows the annealed Fe_{300} and Fe_{600} structures. The annealed Fe_{300} structure is icosahedral, which is the same as the known structure for the magic number Fe_{309} cluster of similar size [12]. The difference between the annealed Fe_{300} and known Fe_{309} structures is that the high energy Fe atoms at the icosahedral vortices are missing in the Fe_{300} structure. The annealed Fe_{600} structure is fcc with a twin boundary. Although it is not known if this is the global minimum energy structure (which may be single crystal fcc), it is expected that this annealed structure is very similar in geometry and energy to the global minimum energy structure (several annealing simulations with significantly different initial conditions yielded similar fcc structures with twin boundaries).

Figure 2 shows the Lindemann index obtained for Fe_{300} and Fe_{600} clusters at temperatures between 600 and 1300 K. The melting points are 1100 K for Fe_{300} and 1150-1200 K for the Fe_{600} cluster.
Figure 1. Annealed structures of the Fe_{300} (a) and Fe_{600} (b) clusters. Fe_{300} is icosahedral and Fe_{600} is fcc with a twin boundary.

Figure 2. Melting process of Fe_{300} and Fe_{600} clusters. The sharp increase in the Lindemann index is due to melting of the clusters.

Figure 3 shows the energy relaxation and final structures during the coalescence of two Fe_{300} clusters at 900, 700, 500, 200 and 2 K. It is evident that the shape of the final (meta)stable Fe_{600} cluster depends on the temperature. At 900 K the stable Fe_{600} cluster is essentially spherical and has an fcc structure, which is similar to its annealed structure shown in Figure 1. At lower temperatures the Fe_{600} cluster is elongated, having a rod-like shape with an aspect ratio of about 1.5 at 700 K and a peanut shape at temperatures lower than 500 K.

It is also evident from Figure 3 that there is a large, approximately 20 eV, energy decrease when the two Fe_{300} clusters impact with each other (between ≈10-40 ps) and that there is a rapid restructuring of the Fe atoms at the cluster-cluster interface. This is observed at all temperatures, including the lowest temperature of 2 K. Considering the fact that scaling to this temperature was done at each time step during the simulation, which means that increased kinetic energy due to cluster-cluster attraction and impact does not facilitate this structural reorganization, it appears that the rapid reorganization of the Fe atoms at the cluster-cluster interface is due to a local change in the potential energy felt by the interfacial atoms. That is, due to the contact between the two clusters, the cohesive energy of the atoms at the interface decreases and the cluster restructures.

As shown in Fig. 3, coalescence at 900 K occurs over two distinct stages. During the first stage, 0-20 ps, the Fe_{300} clusters impact and coalesce into a spherical, non-crystalline (glass-like) structure (see the line graph in Fig. 3). As discussed above, the energy decreases by about 20 eV during this stage. This non-crystalline Fe_{600} cluster is metastable, and requires ≈60-80 ps to relax to the lower energy crystalline fcc structure (similar to its annealed structure in Figure 1). Additional evidence that there is no melting during coalescence is that the Fe atoms that originate from the different Fe_{300} clusters do not mix and are still well
separated in the final Fe₆₀₀ structure. This is in contrast to previous studies of the coalescence of clusters and nanorods that indicate that diffusion of surface atoms is the dominant driving force in the solid state coalescence process [13-15]. Extensive surface diffusion, which requires high thermal activation energies and long time, is not observed during the coalescence in our simulations.

As discussed above, elongated Fe₆₀₀ clusters are found at the lower temperatures (2 – 700 K). These structures do not have the fcc structure of the annealed Fe₆₀₀ cluster and, even though they are stable on our several ns simulation timescale and on an experimental timescale, they may be metastable (i.e., kinetically stable). However, it is important to note that the fcc Fe₆₀₀ structure formed at 900 K was formed from a disordered, non-crystalline intermediate at an energy of ≈-2240 eV (see Figure 3). The metastable intermediates at the lower temperatures are crystalline (essentially having the
isicosahedral structures of the Fe\textsubscript{300} clusters) and their energies are much less than -2240 eV (see Figure 3). Hence, if these elongated, low temperature Fe\textsubscript{600} clusters are indeed metastable intermediates for the fcc structure, the mechanism for the transition to the fcc geometry may be different from that at 900 K.

The constant temperature trajectories discussed above simulate coalescence in a high pressure gas environment. To investigate the effect of the bath gas, the velocity scaling was omitted, i.e., constant energy trajectories were propagated. This simulates cluster coalescence in vacuum. Figure 4 shows the results when the initial temperature of the separated clusters was 700 K (i.e., it corresponds to the 700 K trajectory shown in Figure 3). The total energy is -2245 eV. Since the total energy is held constant, the reduction in potential energy during coalescence leads to an increase in the kinetic energy and hence the temperature. This is shown in Figure 4. However, it is important to note that, even though there is an increase in temperature, it never exceeds the clusters’ melting points.

Figure 5 shows four snapshots of the cluster geometries during coalescence. These snapshots are taken from the times marked A-D in Figure 4. Panel A shows the icosahedral structures of the two Fe\textsubscript{300} clusters shortly after impact. Since there is no temperature scaling, the kinetic energy increases by about 20 eV and can accelerate coalescence. This leads to a disordered intermediate (B), which undergoes a phase transition to the fcc structure shown in panel C. This is very similar to the dynamics observed for coalescence at 900 K (see Figure 3). Thus, the presence of an ambient gas may have a large effect on the (meta)stable cluster that is formed and/or the time that is required to form a stable structure.

Panels C and D in Figure 5 show the Fe\textsubscript{600} structure at 60 ps and 2.2 ns. The balls in panel C clarify the atoms that form two small islands on the surface of the cluster. These islands are not stable and are substantially reduced in size or disappear at 2.2 ns (see panel D). Hence, small islands on the cluster surface are less stable than the larger ones or, alternatively, the surface atoms at high curvature positions are not stable. The aspect ratio of the Fe\textsubscript{600} cluster decreases from 1.4 (panel C) to 1.2 (panel D) and the structure in panel D is thus more ‘spherical’ than that in panel C. Although diffusion of the atoms in the islands reduces the aspect ratio of the Fe\textsubscript{600} cluster, the atoms that originate from the two Fe\textsubscript{300} clusters are well separated in the final structure, supporting the fact that surface melting is not extensive and is not required for cluster coalescence.

3. Conclusion

The coalescence of two Fe\textsubscript{300} clusters below their melting point is studied by molecular dynamics (MD). In contrast to grains found in bulk materials, two clusters can coalesce into a stable structure at temperatures lower than their
melting points. The simulations show that the cluster shape depends on the temperature. When two or more clusters come into contact there is a change in the local environment for the atoms in the cluster-cluster interface region. This can be seen as a change in their local potential energy environment, and this leads to a structuring of these atoms in the coalesced cluster. At higher temperatures (which are still below the melting point) this can lead to a disordered phase that is intermediate to a stable crystalline phase. Hence, phase change can occur below the melting point. At low temperatures elongated structures, that may be metastable, are formed. It is also clear from the simulations that extensive surface melting is not required to explain the fabrication of larger devices from nanoclusters.

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References

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