Irregular phenomenon induced by Ag atomic segregation during the heating process of Ag–Pd cluster*

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This paper studies the melting of icosahedral Ag–Pd bimetallic clusters by using molecular dynamics with the embedded atom method. It finds that the mixed Ag–Pd cluster shows an irregular phenomenon before melting, i.e., the atomic energy decreases with the increase of temperature. It indicates that the segregation of Ag atoms results in this phenomenon by analysing atomic radius distribution. Since the surface energy of Ag is lower than that of Pd, this leads to the result that the decreased energy by the Ag atomic segregation is larger than the increased energy by the heating. This provides a new method to obtain irregular thermodynamic properties.

Keywords: bimetallic cluster, heating, Ag–Pd, molecular dynamics

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1. Introduction

The chemical and physical properties of bimetallic clusters may be tuned by varying the composition, atomic distribution and the size of the clusters.[1] This makes these bimetallic clusters suitable for applications in heterogeneous catalysis and sensors as well as microelectronic and optoelectronic devices.[2] The composition-dependent melting properties of the bimetallic clusters would have a bearing on the method of their synthesis and performance in various areas of application. This leads to the fact that the study of the melting of bimetallic clusters has become a very active field of research.

It was found that the melting temperature of bimetallic clusters has been tuned by selectively doping single impurity.[3] The melting of bimetallic cluster was dependent on the size, concentration and shape.[4,5] Sometimes, the phenomena as structural transformation and solid-liquid coexistence can be induced by the existence of hetero atoms.[6−8] Furthermore, it was also found that the melting can be influenced by the segregation of Cu atom in the onion-like cuboctahedral Cu–Co cluster.[9] Therefore, the hetero element plays a key role in the melting of bimetallic cluster. Upon the Ag–Pd bimetallic cluster, the special melting may be induced by atomic segregation and can be easily explored due to the big difference of surface energy between Ag (1065 mJ/m^2) and Pd (1808 mJ/m^2),[10] however, little attention has been paid to this up to now.

In this paper, molecular dynamics (MD) by a general embedded atom method (EAM) was used to study the segregation-dependent melting of Ag–Pd bimetallic cluster. The temperature-dependent energy curve and atomic radius distribution were used to define the influence of Ag atomic segregation on the melting.

2. Computational details

The present MD simulation employed a fifth-order Gear predictor-corrector algorithm to integrate the equations of Newton. The time step was 1.0 fs. The scaling method was adopted during the simulation to control the system temperature. The canonical ensemble MD simulations were performed with periodic boundary conditions. The EAM potential developed by Zhou *et al.* was used as the atomic interaction.[11,12] The accuracy of the EAM potential on the study of bimetallic clusters was tested by Ref. [4]. The heating processes were divided into three stages: (1) the constructed clusters were relaxed for 1.5 ns at 200 K, then, the clusters were heated up to 300 K with 100 K temperature step and 0.5 ns time step; (2) the clusters were heated up to 900 K from 300 K with 20 K temperature step and 0.5 ns time step; (3) the clusters were heated up to 1300 K from 900 K with 50 K temperature step and 0.5 ns time step.

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Since structural transformation may occur during the heating process,[13] the Ag–Pd cluster with low-energy icosahedral initial structure was used as the objectives. In addition, in order to easily explore the influence of Ag segregation on the melting, two configurations with different Ag distribution in the cluster were considered. Figure 1 shows the Ag and Pd atomic numbers along the radius direction (atomic radius distribution) in the clusters and their corresponding initial morphologies. The cluster was divided into three shells (1st-shell, 2nd-shell, and 3rd-shell) according to the distance between the atom and centre of mass. As shown in Fig. 1, one configuration is the mixed $Ag_{44}Pd_{103}$ cluster. The cluster includes 44 Ag and 103 Pd atoms and they distribute uniformly in the three shells of the cluster. The Ag atoms would segregate to the surface layer (1st-shell) of the cluster due to the lower surface energy during the heating process. The other configuration is the core–shell $Ag_{44}Pd_{103}$ cluster. The 44 Ag atoms distribute on the surface layer (1st-shell) of the cluster, so there is no segregation occurred during the heating process. Therefore, the influence of Ag segregation on the melting can be studied by comparing their melting difference.

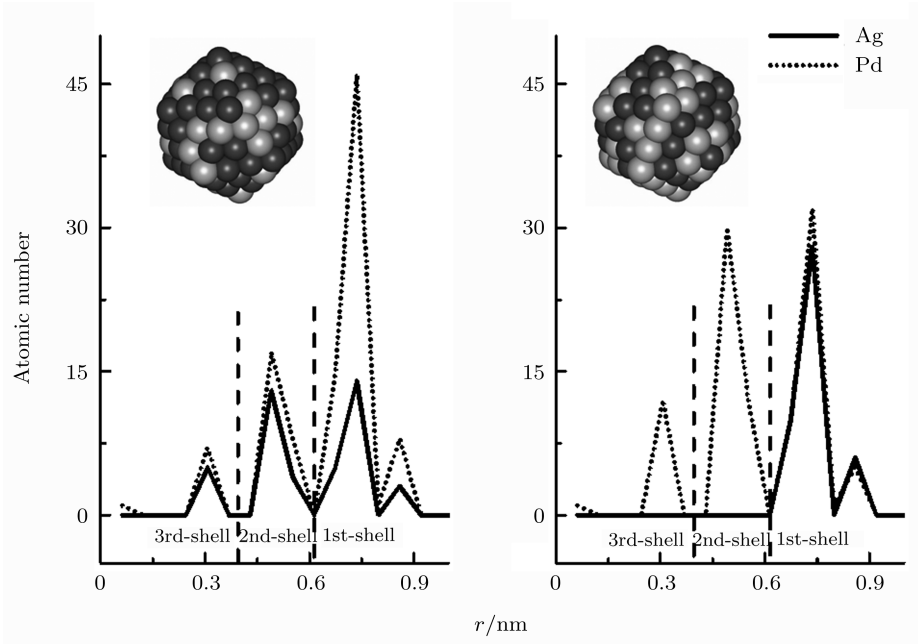


Fig. 1. Atomic radius distributions of mixed $Ag_{44}Pd_{103}$ and core–shell $Ag_{44}Pd_{103}$ clusters, also their corresponding initial morphologies.

3. Results and discussion

Figure 2 gives the variation of energy with temperature for mixed $Ag_{44}Pd_{103}$ and core–shell $Ag_{44}Pd_{103}$ clusters. The method of obtaining the atomic energy is similar to Ref. [14]. For the core–shell $Ag_{44}Pd_{103}$, the atomic energy increases with the increase of temperature before 560 K. An abrupt increase in atomic energy appears at 580 K and indicates that the cluster is melted. After being melted, the atomic energy still increases with the increase of temperature. For the mixed $Ag_{44}Pd_{103}$, the melting process is different from that of the core–shell $Ag_{44}Pd_{103}$. first, the atomic energy in the mixed $Ag_{44}Pd_{103}$ before point A (520 K) is higher than that of the core–shell $Ag_{44}Pd_{103}$. This is because the surface energy of Ag is lower than that of Pd. All the Ag atoms distributed on the surface for the core–shell $Ag_{44}Pd_{103}$ can make the cluster have a lower energy state. Secondly, the atomic energy decreases with the increase of temperature at the range between A and C. This is an irregular phenomenon. After point D, the variation of atomic energy with temperature is similar to the case of core–shell $Ag_{44}Pd_{103}$. This indicates that both clusters have similar atomic distribution and structure in this stage. In addition, there is no sharp increase in atomic energy during the heating of mixed $Ag_{44}Pd_{103}$. It is reasonable to conclude that Ag atomic distribution in the mixed $Ag_{44}Pd_{103}$ leads to this irregular phenomenon since both clusters have same Ag content and heating process.

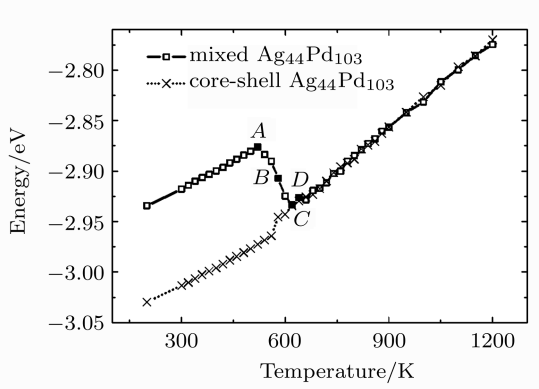


Fig. 2. Variation of energy with temperature for mixed $Ag_{44}Pd_{103}$ and core–shell $Ag_{44}Pd_{103}$ clusters.

In this study, the Ag atomic radius distribution was used to define the influence of Ag segregation on the melting. Figure 3 gives Ag atomic distributions in three shells at different temperatures. At 520 K, the Ag atomic numbers in three shells are the same as its initial case. That is to say, there is no Ag atomic segregation at this temperature. In addition, it is also found that the same case occurs when the temperature is lower than 520 K. Therefore, the atomic energy increases with the increase of temperature in this stage. As shown in Fig. 3(b), the variations of the Ag atomic numbers in three shells are different: an obvious increase in the 1st-shell, an obvious decrease in the 2nd-shell and no change in the 3rd-shell. At point C, there is no Ag atom in the 2nd-shell and only several Ag atoms in the 3rd-shell. All the Ag atoms segregated to the 1st-shell at point D. By comparing the variations of Ag atomic number in the cluster, it can be found that the energy decrease at points A, B, and C is strongly related to the Ag atomic segregation. While for point D, in spite of the Ag atomic segregation, the atomic energy increases in comparison with that at point C. Thus, there should be a sharp increase in atomic energy that makes the energy increase larger than the energy decrease due to Ag atomic segregation. It is reasonable to conclude that the cluster is melted at 640 K. In other words, the melting point of mixed $Ag_{44}Pd_{103}$ is much higher than that of core–shell $Ag_{44}Pd_{103}$. Segregation induced the increase in the melting point of cluster. This result is similar to that of Li *et al.*[4] In their study, they found that the Cu atomic segregation nearby surface layer can make the melting point of Cu–Ni cluster higher than that in the cluster without segregation. In Ag–Pd clusters, since there is a big difference in surface energy between Ag and Pd. Furthermore, the segregated Ag atomic number is also big. These make the melting point of Ag–Pd cluster have a large increase. This also indicates that the melting point of nanoparticle can be controlled by doping element with different physical parameters and controlling their distributions in the cluster.

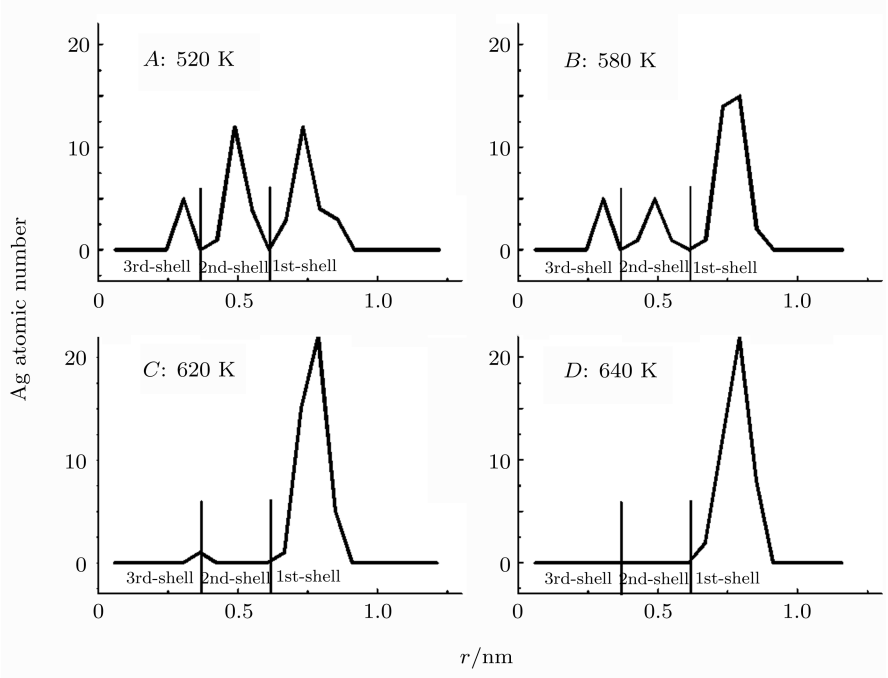


Fig. 3. Atomic radius distributions of mixed $Ag_{44}Pd_{103}$ cluster at different temperatures.

The energy decrease can be induced by the segregation of Ag atoms to the surface layer. On the other hand, the atomic energy can also be increased by the movement of Pd atoms to the inner of cluster. Therefore, this will lead to the difference in the atomic energy when one Ag or Pd atom distributes at different positions (the edge, corner in 2nd or 3rd-shell and the edge, corner, (111) plane in 1st-shell). In order to define the influence of atomic segregation on the atomic energy, the atomic energy with one Ag or Pd atom at different positions was calculated by relaxing the cluster 1.0 ns at 0 K. The results were shown in Tables 1 and 2. It can be seen that the decrease in atomic energy when one Ag atom segregates to 1st-shell from 2nd or 3rd-shell is much larger than the case of Pd. However, it is difficult to define the detailed atomic positions at the edge, corner, and plane during the heating process of Ag–Pd cluster. This is because the lattice distortion would appear due to the difference in atomic radius of Ag and Pd when the atomic positions of Ag and Pd were changed. Thus, the averaged segregated energy was used to consider the influence on the melting. Then, this averaged energy was combined with the segregated atomic numbers at different temperatures to fit the variation in atomic energy with the increase of temperature. Figure 4 gives the fitted energy at the irregular melting stage. The results show that the trend of fitted values is agreed well with the simulated results. This also fully proved that the irregular phenomenon was induced by the Ag atomic segregation. In addition, the atomic energy due to atomic segregation at 640 K decreases with the increase of temperature, but that the cluster melted at this point leads to the increase of atomic energy.

Table 1. Variation of the atomic energy at 0 K when one Ag atom in different positions in the 2nd-shell and 3rd-shell segregated to different positions in the 1st-shell. (unit: eV)

1st-shell	2nd-shell		3rd-shell
	corner	edge	corner
edge	–0.00570	–0.00485	–0.00522
corner	–0.00730	–0.00664	–0.00681
(111)	–0.00506	–0.00420	–0.00457

Table 2. Variation of the atomic energy at 0 K when one Pd atom in different positions in the 2nd-shell and 3rd-shell segregated to different positions in the 1st-shell. (unit: eV)

1st-shell	2nd-shell		3rd-shell
	corner	edge	corner
edge	0.00307	0.00265	0.00281
corner	0.00424	0.00382	0.00398
(111)	0.00260	0.00218	0.00281

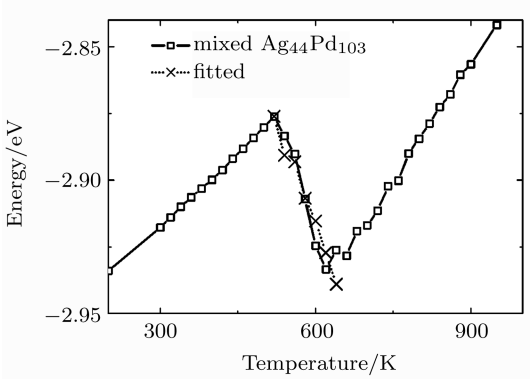


Fig. 4. Temperature-dependent energy for mixed $Ag_{44}Pd_{103}$ cluster and the fitted energy at the irregular melting stage obtained by using the segregated atomic numbers with segregated energy.

4. Conclusions

This paper studied the melting of Ag–Pd bimetallic cluster by using molecular dynamics with the EAM potential. An irregular phenomenon that atomic energy decreases with the increase of temperature during the heating process was founded. This is because the surface energy of Ag is much lower than that of Pd. The decrease of atomic energy can be induced by Ag segregating to the surface layer of cluster. This provides a method to fabricate the nanoparticles with special thermodynamics by controlling the alloy composition and concentration during their formation process.

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