Size and Composition Dependence of the Frozen Structures in Co-Based Bimetallic Clusters

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Abstract: This paper studies the size-dependent freezing of Co, Co-Ni, and Co-Cu clusters by using molecular dynamics with a general embedded atom method. There is size effect occurs in these three types of clusters. The clusters with large sizes always freeze to form their bulk-like structures. However, the frozen structures for small sizes are generally related to their compositions. The icosahedral clusters are formed for Co clusters (for ≤3.2 nm diameter) and also for Co-Ni clusters but at a larger size range (for ≤4.08 nm). Upon Co-Cu clusters, decohedral structure is obtained for small size (for 2.47 nm). The released energy induced the structural transformation plays a key role in the frozen structures. These results indicate that the preformed clusters with special structures can be tuned by controlling their compositions and sizes.

Keywords: Bimetallic cluster, freezing, molecular dynamics

1 Introduction

New film materials with exceptional structure and functionality have attracted much more attentions due to their wide application in the microelectronic, optoelectronic devices, and high density storage. They can be fabricated by depositing preformed clusters in the size range 1-10 nm [1]. Furthermore, the freezing, nucleation, and growth processes of these clusters occur prior to the formation of a continuous film and may be used to form special structures. Especially for alloy films, their physical and chemical properties can be tuned by varying the compositions and sizes of the preformed clusters [2]. Therefore, the experimental and theoretical investigations on the freezing of bimetallic clusters have become a very active field during the last two decades.

Recently, the size-dependent structural transitions in the Fe-Pt clusters (multiply twinned for 5.9 nm diameter, FCC for 7.6 nm, icosahedron for 4 nm, mixture of

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marks decahedron and truncated tetrahedron for 5-15 nm) were produced by the gas-phase condensation on the amorphous carbon [3, 4]. However, in the research of Pauwels *et al*, the Cu-Au clusters were also condensed on the amorphous carbon, but they found that the clusters formed different shapes (cuboctahedral and decahedral cluster for 1-4 nm diameter) [5]. Therefore, it is reasonable to conclude that their structures can be changed with varying their sizes and compositions. This is very important in exploring the structure-property relationships and finding a controllable method of fabricating film materials. However, understanding and predicting these processes by using experimental studies are very difficult. Since molecular dynamics (MD) is based on deterministic methods and can be used to simulate the evolutions toward equilibrium states. Furthermore, various controllable conditions can be easily induced in the MD simulation. It has become a powerful means of investigating the structural evolutions.

Now, much more attention has been paid to the frozen structures of free pure metal clusters [6, 7]. However, the difference of surface energies between various elements will result in different surface segregations in bimetallic clusters. Therefore, this can make their frozen structures exhibit some new features which are different from the pure clusters. The cooling of $(CoAg)_{864}$ cluster with 30% Ag from 1300 K down to 100 K was simulated by Dorfbauer *et al* [8]. They found that a structure with an Ag shell and HCP-like Co core was formed due to the Ag atoms segregating to the surface layer. In our previous study, we also found that the different segregations of Cu atoms at various temperatures can make Cu-Co clusters form different structures [9]. Fromen *et al* [10] studied the structures of Co-Rh clusters with Co-rich compositions and found that a Co-Rh-Co three-shell structure was still formed in spite of the Co atoms segregating to the surface. Since the segregations are different for Au atoms in Au-Pd clusters at different temperatures, Liu *et al* obtained three-layer icosahedral nanorod, fcc nanorod, or fcc clusters by freezing the Au-Pd clusters from different starting temperatures [11]. Chushak and Bartell studied the freezing structures of Ni-Al bimetallic clusters with different compositions [12]. They found that for the Al-rich and equiatomic compositions the surface segregation of Al atoms inhibited nucleation to an ordered structure. In the case of the Ni-rich composition, the clusters with different sizes froze to different final structures (icosahedron, decahedron, and truncated octahedron). Therefore, it is possible to create new structures with fascinating potential applications by controlling the size- and composition-dependent freezing processes of bimetallic clusters. In fact, in order to expore the relationship of their frozen structrues with the sizes and compositions, it is necessary to study the freezing of pure clusters and compare their results with bimetallic clusters constructed with various physical parameters.

In this study, MD with a general embedded atom method (EAM) was used to study

the size and composition dependence of the frozen structures. Here, upon pure metal clusters, Co was selected as the objective because the structural transformation between FCC and HCP in Co bulk may result in different frozen structures with the change in cluster sizes. Then, Cu and Ni were doped to form different bimetallic clusters for the following reasons: (1) The difference in surface energy. Cu (1592 mJ m^{-2}) is much lower than Co (2197 mJ m^{-2}) while Ni (2104 mJ m^{-2}) is similar to Co. This will lead to different segregations for Cu and Ni atoms in Co-based clusters during their freezing processes. This is helpful to study the influences of compositions on the frozen structures. (2) The small differences in atomic radii of Co (0.1385 nm), Cu (0.1412 nm), and Ni (0.1378 nm) can avoid the formation of amorphous structure in the clusters due to the large lattice mismatch [13]. Then, the freezing processes of Co, Co-Ni, and Co-Cu clusters with different sizes were simulated. Finally, the size and composition dependence of frozen structures was described by using the bond order parameters [14] and the snapshots.

2   Simulation details

Generally, the validity of a MD model is strongly related to the accuracy of interatomic potential. However, since the cutoff distances are different for different metals, the potential functions of pure metals are not suitable to simulate alloys. Zhou *et al* [15] developed a general EAM and can force the potentials of 16 metals to go smoothly to zero at the same cutoff distance. Therefore, it was used as the interatomic interactions in this study. The details of simulation method were described in our previous paper [9]. Its accuracy in simulating the thermodynamics of bimetallic clusters with a broad range of the compositions and sizes has also been assessed [16]. In addition, this model has also been used to study the structural evolutions of bimetallic clusters by our group [17, 18].

The clusters with cuboctahedral shape were trucated from a $30a_0 \times 30a_0 \times 30a_0$ large FCC bulk, where a_0 is the lattice constant of bulk. The atomic numbers in the clusters are 561 (2.47 nm), 923 (2.93 nm), 1289 (3.2 nm), 2057 (4.08 nm), and 3871 (4.85 nm), respectively. The bimetallic clusters were constructed by randomly substituting Co atoms with 50% Ni (Cu). Then, these clusters were subsequently heated up to 1700 K from 200 K and then cooled down to 200 K. The time step was 1.6 fs. The equilibration time for each temperature cycle (20 K) was 0.1 ns. Since the clusters were frozen from the liquid states, the influence of initial structures on the frozen structures can almost be neglected. At the same time, the temperature and time dependence of the frozen structures can also be excluded due to the same thermodynamic process. Therefore, the variations of frozen structures were mainly contributed from their sizes and compositions. The global Wigner value W_6 of the bond order parameters, which is less sensitive to the definition of the nearest

neighbors [19], was used to define the structural evolutions in this study.

3   Results and discussion

Figure 1 presents the snapshot overviews frozen to 200 K for Co, Co-Ni, and Co-Cu clusters with different sizes. Clearly, the frozen morphologies of Co clusters are different for different sizes. The frozen structures for Co_{561} and Co_{923} clusters are icosahedral and formed by six 5-fold symmetry axes and a quasispherical shape with 20 (111)-like facets. The clusters with other sizes were constructed by packing of (111) planes. In addition, the frozen morphologies of Co clusters are obviously different from the clusters with doping Ni or Cu. As the previous studies pointed out, the atoms with low surface energy will segregate to form a shell on the cluster surface and inhibit the formation of some structures [9, 12]. Therefore, the difference of surface energies for Cu, Ni, and Co will result in different segregation and make the clusters form various structures. In the Co-Cu clusters, the Cu atoms segregate to the surface layer and make the cluster keep low energy state, while no similar case occurs for the Ni-Co clusters. This leads to that the surface layer is almost composed by Cu atoms for the Co-Cu clusters. While the surface layer of the Co-Ni clusters consists with almost equiatomic Co and Ni. This difference in segregation leads to the Co-Cu and Co-Ni clusters form different structures with the variation of cluster sizes. For the Co-Ni clusters, except for Co_{3871} cluster, the clusters with other sizes formed icosahedral shape. For the Co-Cu clusters, the influence of segregation on the frozen structures was obvious. No icosahedron formed for all the sizes, only $(CoCu)_{561}$ formed a decahedral shape. In addition, for bimetallic clusters with other sizes, the twinned case as shown by elliptical zone in figure 1 occurs due to different atomic diffusion in bimetallic clusters. It is reasonable to conclude that the frozen morphologies are strongly related to the cluster sizes and can be affected by the atomic segregation after doping with different alloys.

Then, the detailed structural evolutions of above-mentioned clusters during the freezing processes were investigated by using the W_6 parameter, as shown in Figure 2. As displayed in the figure, when the clusters are liquid, their W_6 values fluctuate near the zero value at a large range due to two reasons. One is the frequently changes in atomic positions in the liquid clusters due to atomic convection; the other is that the structure used to calculate the W_6 value is not an average of many structures but an instantaneous structure. But after the clusters freezing, the W_6 values almost keeps unchanged with the decrease in temperature. This indicates that the frozen structure was formed at the freezing point and not at the cooling process. Figure 2(a) illustrates the W_6 parameters of the Co clusters. It can be seen that the W_6 values of Co_{561} and Co_{923} clusters during the freezing processes are almost
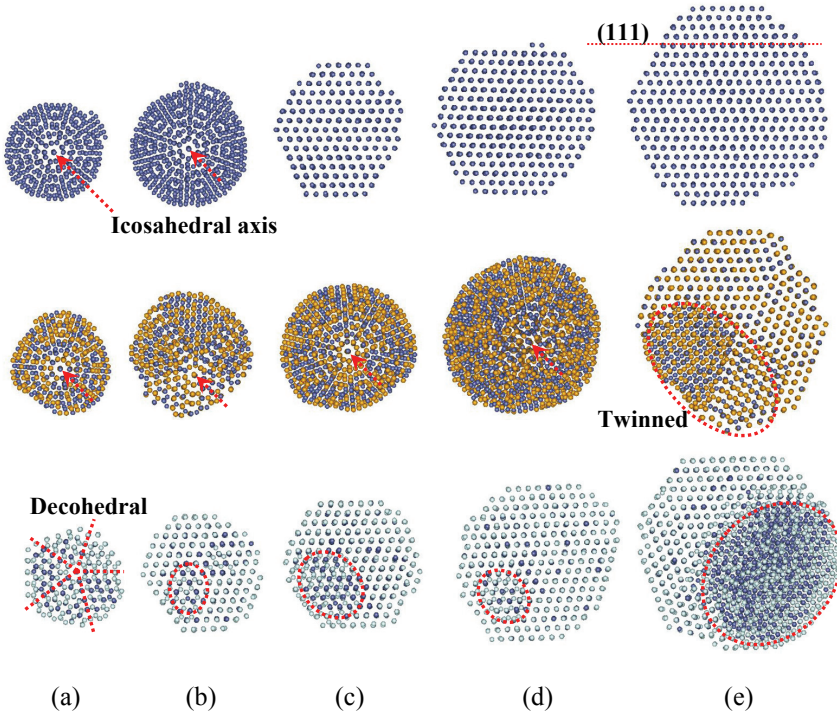
Figure 1: Snapshot overviews at 200 K of the frozen clusters. The atomic numbers in the clusters are 561 (a), 923 (b), 1289 (c), 2057 (d), and 3871 (e), respectively. The top row shows the Co clusters, middle row shows the Co-Cu clusters, and below row shows the Co-Cu clusters

identical and same to the standard values of icosahedron (-0.169754) [19], namely, the Co clusters with small sizes ($\leq$2.93 nm) froze to form icosahedron. While for Co_{1289}, Co_{2057}, and Co_{3871} clusters, all of their W_6 values are same to that of HCP structure (-0.012442), which is same to the Co bulk. This indicates that the clusters with large size ($\geq$3.2 nm) froze to form a Co bulk-like structure. The results agree well with the experimental results that the Co-Rh nanoparticles with larger sizes (4-6 nm) exhibit a greater stability of bulk-like structures [20]. For the Co-Ni clusters, displayed in figure 2(b), except for that $(CoNi)_{3871}$ cluster formed an FCC bulk-like structure, the Co-Ni clusters with other sizes froze to form icosahedral structures. Therefore, the size-dependent frozen structures also existed for the Co-Ni clusters. But the size froze to form an icosahedron is much larger than that of the Co clusters. Since the structural evolution is strongly related to the release of energy [13,

18], the variation of energy in the clusters, frozing from the disorder structure at 1700 K to the icosahedral structure at 200 K, was calculated. It is found that the released energy of $(CoNi)_{561}$ is larger than that of Co_{561}. Thus, the Co-Ni clusters can form icosahedral shape at a large size range. As the Co-Cu clusters concerned, only the W_6 value of $(Co-Cu)_{561}$ exhibits the features of decahedron and is different from others which froze to form FCC clusters. These frozen structures are different from both the clusters Co and Co-Ni. As discussed above, this is because the segregated Cu atoms formed a shell on the surface layer and inhibit the transformation of icosahedron. But for the small size, the released energy can drive Co-Cu cluster to form decahedron.

It was found that the formation of icosahedral cluster was always accompanied with a sharp decline in the energy curve [18]. In other words, the energy was released to drive the structural transformation. Here, the energy was described as the released energy ΔE and used to define the driving force of icosahedral transformation. The inset in Figure 3 shows the calculated method of ΔE during the heating process. Since these solid phase change of icosahedron only occurs the cluster with initial cuboctaheron, the pure Co clusters including 561, 923, 1404, and 2057 atoms were selected to study the relationship between the released energy and size, as shown in Figure 3. ΔE decreases with the increase in cluster size. This indicates that the released energy decreased during the freezing process and the driving force was also decreased. Therefore, it is difficult to form icosahedral shape for the large clusters. Furthermore, the released energy was also affected by the doping of alloy element and the variation of their physical parameters.

4   Conclusions

The frozen structures of Co-based clusters with different sizes and compositions were studied by using MD with a general EAM potential. It is found that their frozen structures were size-dependent. The Co clusters with small sizes (≤ 3.2 nm) froze to form icosahedron, while the bulk-like HCP structures were formed for large sizes. This is because the released energy induced the structural transformation decrease with the increase in cluster size. In addition, the frozen structures were changed with doping different Ni or Cu. For doping Cu atoms, a shell inhibited the formation of icosahedron was formed by the segregated Cu atoms. Therefore, the Co-Cu clusters formed bulk-like FCC structures, only for the small size (2.47 nm) froze to form a decohedral structure. Upon the Co-Ni clusters, the addition of Ni increases the released energy and the clusters formed icosahedron at large size range (≤ 4.08 nm). Bulk-like FCC structures formed only for the clusters with much larger size. These results indicate that the structure of preformed clusters can be controlled by varying their sizes and compositions.
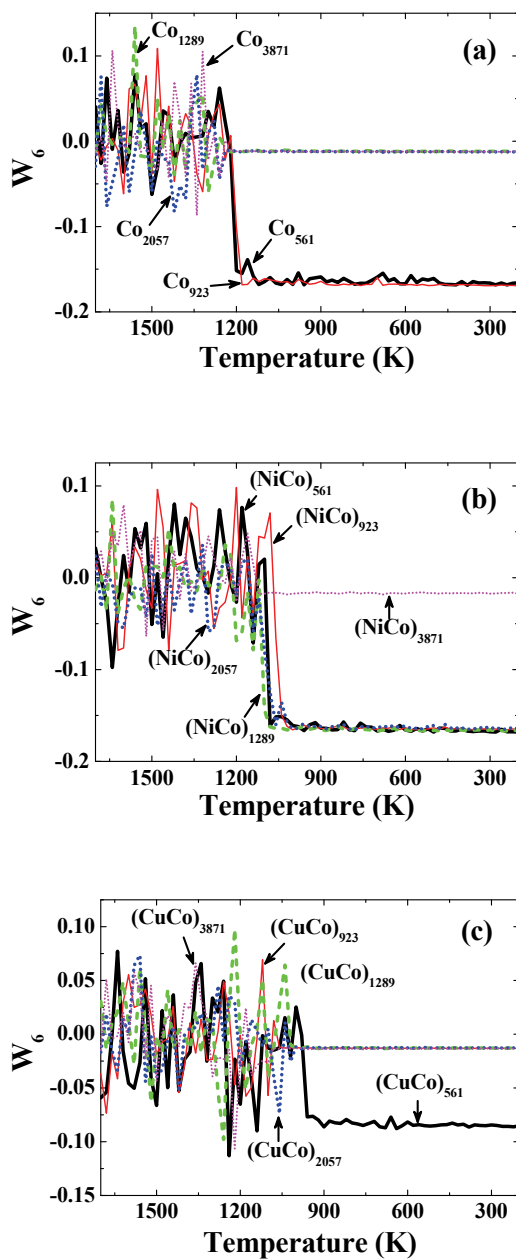
Figure 2: Temperature-dependent bond order parameter W_6 of clusters with different sizes during the freezing processes. (a) Co clusters, (b) Co-Ni clusters, (c) Co-Cu clusters
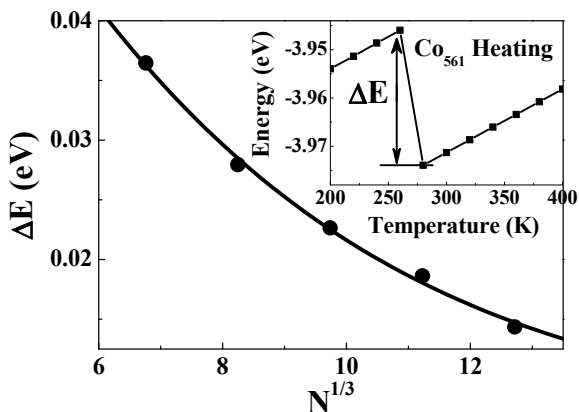
Figure 3: The size-dependent energy ΔE induced the icosahedral transformations during the heating processes. The definition of ΔE was shown in the inset figure

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