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Structural Evolutions of the Clusters During the Melting and Coalescence Processes

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Abstract: Study on the behaviors of the melting and coalescence of clusters in atomic scale may create new structure at nanoscale, which is a very important research field. The structural evolutions of clusters Cu_{321}, Co_{321}, and Ni_{321} during their melting and coalescence processes were studied using molecular dynamics simulation with a general embedded atom method in this paper. It was found that the geometries of Cu_{321} and Co_{321} transformed to icosahedron from fcc near their melting points, which leads to the increase of their melting points. Concerning the coalescence, it was found that Cu atoms easily formed a coating layer on the surface of Co_{321} which inhibited the formation of icosahedron in the coalesced complex. The icosahedron was formed during the coalescence of $Ni_{321}Co_{321}$. These results indicated that the structures were tuned by changing the thermodynamic or coalescence processes.

Keywords: Cluster, coalescence, melting, molecular dynamics simulation.

1 Introduction

Thin films produced by depositing preformed atomic clusters have become a very active research field recently [Binns (2001); Lee et al. (2001); Jimenez-Saez, Perez-Martin and Jimenez-Rodriguez (2008)]. Since the cluster coalescence occurs prior to the formation of a continuous thin film, the ability to manipulate behaviors of the clusters at atomic scale is important and may create new structures for broad potential applications such as magnetic memories, microelectronic, and optoelectronic devices [Wang (2003)]. However, understanding and predicting these processes only by experimental study are very difficult, especially for bimetallic clusters. Computer simulation methods, in particular molecular dynamics, have become a

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powerful method to describe the processes.

For the interaction of clusters, much more attention has been paid to the collision under a constant-energy molecular dynamics simulation. The results show that some new features which have been distinguished from one-component systems. For example, there was a solid-liquid transition region during the collision of Ag_{201} and Pd_{201} [Kim et al. (2008)]. Both Ni and Al clusters were fused at a low colliding energy and the collided complex was fragmented at a high colliding energy [Palacios and Iniguez (2002)]. The structures of the collided complexes were different under different collision conditions [Mariscal, Dassie and Leiva (2005)]. These results show that structural evolutions were influenced by tuning the composition, size, and collided condition. However, the collided results are not appropriate to compare with the experimental results because most experiments were carried out under the constant-temperature and constant-pressure conditions. Little attention was paid to the coalescence of alloy clusters under a constant-temperature condition. Main studies were limited to the coalescence of homo cluster [Lewis, Jensen and Barrat (1997); Zachariah and Carrier (1999); Hawa and Zachariah (2006); Ding, Rosen and Bolton (2004); Tian and Guo (2005)]. However, our previous research on the coalescence of alloy clusters Au-Ag, Cu-Ni and Cu-Co under a constant-temperature molecular dynamics showed some new phenomena. An order-disorder transition existed during the coalescence of a solid Au_{767} with a liquid Ag_{767} [Li et al. (2008)]. The coalescence temperature forming a liquid complex is higher than the melting temperature of the cluster with the same size [Li et al. (2010)]. The structure of hcp, fcc or twinned hcp and fcc was fabricated by controlling the coalescence of Cu-Co [Li et al. (2008)]. In spite of these investigations, an understanding of the coalescence of alloy clusters under various states is still lacking and should be further addressed.

In this study, molecular dynamic simulation with a general embedded atom method was selected as the simulation method. The melting of spherical clusters Cu_{321}, Co_{321}, and Ni_{321} was first studied. Since the structural evolutions of these three clusters are different at different temperatures. Various coalesceence temperatures were selected according to the cluster phase (liquid or solid) and structure (fcc or icosahedron) at the corresponding temperature. Then, the coalescence of the clusters was studied to explore the influence of the coalescence on the structural evolutions.

2 Simulation details

In this study, the initial isolated clusters were first truncated from a $30a_0 \times 30a_0 \times 30a_0$ large bulk. a_0 is the lattice constant of the corresponding bulk. All the clusters include 321 atoms. The initial structures of Cu_{321} and Ni_{321} are fcc, that of Co_{321}

is hcp. The reasons of selecting Cu, Co, and Ni as the subjects were discussed in details in our previous study [Li et al. (2012a, 2012b)]. The initial coalescence clusters were constructed by placing Cu_{321}, Co_{321} and Ni_{321} in the center of a large simulation box ($30a_0 \times 30a_0 \times 30a_0$, the value of a_0 is 0.3615 nm) with the center of mass of the cluster along the X axis. Figure 1 gives the schematic view of the initial setup of the coalescence clusters of $Cu_{321}Co_{321}$ and $Cu_{321}Ni_{321}$.

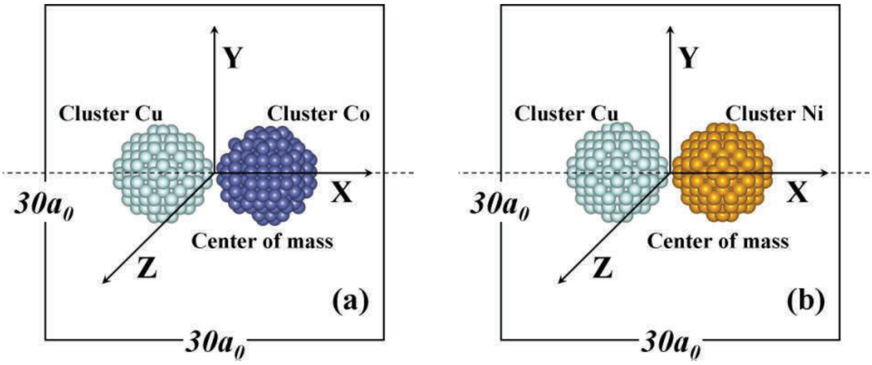

Figure 1: Schematic view of the initial setup of the coalescence clusters. (a) $Cu_{321}Co_{321}$, (b) $Cu_{321}Ni_{321}$.

The simulation method used in this study and its accuracy in simulating bimetallic cluster have been described in our previous studies [Li et al. (2008); Li et al. (2009a)]. The time step was 1 fs. Since the thermodynamic parameters could influence the coalescence temperature of forming a sphere or liquid complex, same heating process was selected for the isolated clusters and coalescence clusters. The isolated clusters (Cu_{321}, Co_{321} and Ni_{321}) and coalescence clusters ($Cu_{321}Cu_{321}$, $Co_{321}Co_{321}$, $Ni_{321}Ni_{321}$, $Cu_{321}Co_{321}$, $Cu_{321}Ni_{321}$ and $Ni_{321}Co_{321}$) were heated up to 1500 K from 200 K with 0.1 ns equilibrated simulation time for each temperature step (20 K). The coalesced complex was obtained by coalescing the coalescence clusters for 5 ns at various temperatures.

3 Results and discussion

In order to define the coalescence temperatures of the hetero clusters, the temperature ranges for the clusters forming different phases (solid or liquid) and structures (fcc, hcp or icosahedron) were first confirmed by simulating the melting. Firstly, the melting point was identified by using the sharp increase of energy with the increase of temperature. Table 1 gives the melting points of the isolated and coalescence clusters.

Table 1: Melting points of the isolated and coalescence clusters.

	Cu_{321}	Co_{321}	Ni_{321}	Cu_{321} Cu_{321}	Co_{321} Co_{321}	Ni_{321} Ni_{321}	Cu_{321} Co_{321}	Cu_{321} Ni_{321}	Ni_{321} Co_{321}
Melting point (K)	800	1280	1080	880	1360	1240	1160	1060	1300

It can be seen from Table 1 that the melting points of the isolated clusters Cu_{321}, Co_{321} and Ni_{321} are 800, 1280 and 1080 K, respectively. The results were compared with the results of others [Lewis, Jensen and Barrat (1997); Nanda, Sahu and Behera (2002)]. It is found that the melting point of Cu_{321} is much higher than the result of others (700 K) and that of Co_{321} is also higher than the result of others (1060 K). However, the melting point of Ni_{321} is similar with the result of others (1030 K). Structural evolutions during the heating processes were observed to confirm the reason. It is found that the structures of Cu_{321} and Co_{321} transformed to icosahedron at the temperature near the melting point, as shown in Figure 2. The transformation temperatures for Cu_{321} and Co_{321} are 780 and 1160 K, respectively. Generally, icosahedron is more stable than the spherical cluster. Therefore, higher temperature is needed to make it melt. This leads to the increase of the melting points of Cu_{321} and Co_{321}. However, there is no similar structural transformation occurs for Ni_{321} even if it melted.

In addition, it can also be seen from Table 1 that the melting point of the homo coalescence cluster is higher than that of the corresponding isolated cluster. This is because these clusters coalesced to form a large one. The melting point increases with the increase of the cluster size. For the coalescence of hetero clusters, the melting points of $Cu_{321}Co_{321}$ and $Cu_{321}Ni_{321}$ are between the melting points of the corresponding isolated clusters. While the melting point of $Ni_{321}Co_{321}$ is higher than those of Ni_{321} and Co_{321}.

According to the melting points and structures of the isolated clusters at various temperatures, several coalescence temperatures were selected. The temperatures of the solid-solid and the liquid-liquid hetero coalescences ($Cu_{321}Co_{321}$, $Cu_{321}Ni_{321}$ and $Ni_{321}Co_{321}$) are 500 and 1500 K, respectively. Two temperatures of the liquid-solid coalescence were selected. The temperature of the liquid-solid $Cu_{321}Ni_{321}$ at a low temperature is 800 K, that at a high temperature is 900 K. For $Cu_{321}Co_{321}$, these two temperatures are 800 and 1100 K, respectively. For $Ni_{321}Co_{321}$, they are 1080 and 1200 K, respectively. Then, the clusters coalesced for 5 ns at above-mentioned temperatures. The snapshots and pair distribution functions were selected to study the coalesced structures. Figure 3 gives the configurations of the coalesced com-

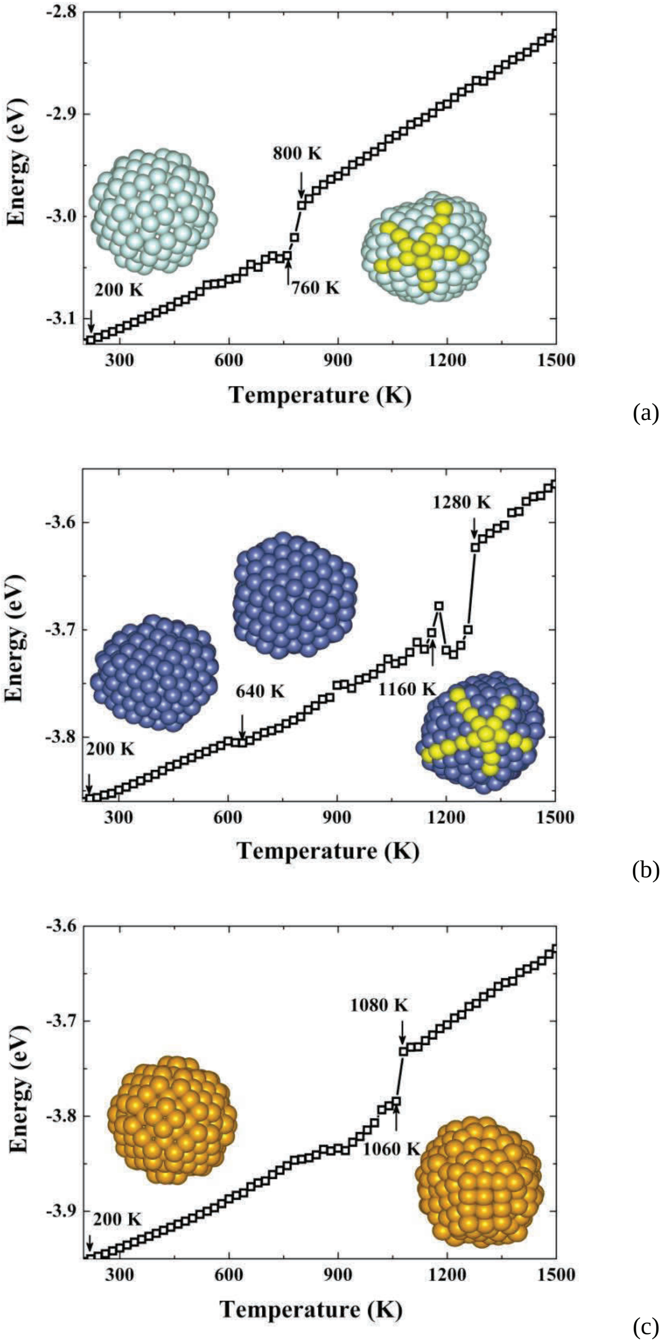

Figure 2: Energy-temperature melting curves of the clusters Cu_{321} (a), Co_{321} (b) and Ni_{321} (c) and their snapshots at various temperatures.

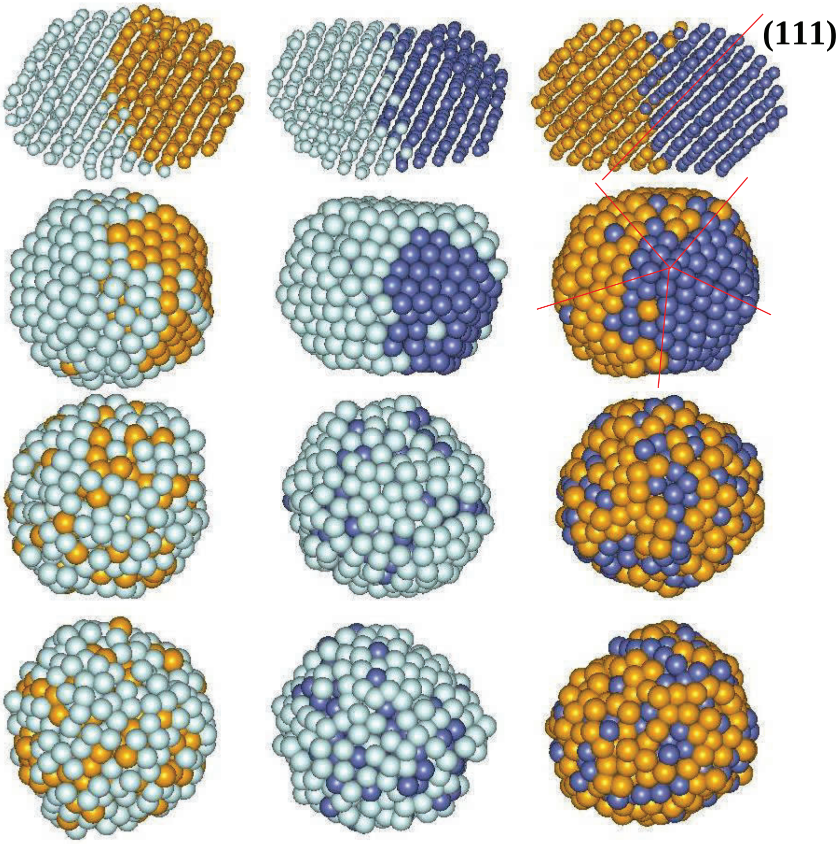

Figure 3: Snapshots of the coalesced complexes for the coalescence clusters at different temperatures. All the snapshots from top to bottom are sequential the coalescences of solid-solid, liquid-solid at a low temperature, liquid-solid at a high temperature, and liquid-liquid coalescences.

plexes.

For all the three kinds of the coalesced complexes, the shapes transform to a sphere from a rod-like with the increase of the temperature. The alignment of (111) planes only occurs for the solid-solid coalescence at 500 K. This is because the stacking of (111) planes can make the cluster remain at a low energy state. Since the melting points and surface energies of Cu, Co and Ni are different, the energy obtained by the atoms is also different at the same temperature. This leads to the atomic diffusion abilities are different during the coalescence processes.

For these three elements, Cu (1592 mJm^{-2}) has the lowest surface energy and the surface energies of Co (2197 $\mathrm{mJm^{-2}}$) and Ni (2104 $\mathrm{mJm^{-2}}$) are almost identical. Therefore, Cu atoms preferably diffuse along the surface of Ni and Co during the coalescence processes of $Cu_{321}Ni_{321}$ and $Cu_{321}Co_{321}$. However, that the atoms diffuse along the surface of the cluster is difficult to occur for the coalescence of $Ni_{321}Co_{321}$. For the liquid-solid coalescence at a low temperature, the surfaces of the coalesced complexes for $Cu_{321}Ni_{321}$ and $Cu_{321}Co_{321}$ were almost coated by the Cu atoms. This is because Cu_{321} melted and Cu atoms can freely diffuse along the surface of Ni_{321} and Co_{321}. For the coalescence of $Ni_{321}Co_{321}$, since their surface energies are almost identical, the Ni atomic diffusion along the surface of Co_{321} is difficult to occur. The coalesced complex was composed by the hemispheres of Ni and Co. Only a few Ni atoms diffused along the surface of Co_{321}. Furthermore, the coalesced complex exhibits an icosahedral character. All the coalesced complexes form liquid sphere during the liquid-solid coalescence at the high temperature. This is different from the results of the coalescence heating. This is because the coalescence clusters did not experience the structural transformation from fcc or hcp to icosahedron. The temperature of $Ni_{321}Co_{321}$ coalesced to form a liquid sphere at 1200 K. The different coalesced shapes indicate that different configurations can be fabricated by controlling the coalescence processes of the clusters with different physical parameters (such as melting point and surface energy).

Since the crystal structure can not be obtained only by using the configurations, the structures of the coalesced complexes were studied by using pair distribution functions (PDFs). Figure 4 gives the PDFs of the coalesced complexes of $Cu_{321}Ni_{321}$, $Cu_{321}Co_{321}$ and $Ni_{321}Co_{321}$ at different temperatures. For the solid-solid coalescence, the peak positions of PDF of the coalesced complexes coincide with those of the nearest neighbours of fcc calculated by using $\sqrt{2n}a_0$ (where n is the nth nearest neighbour, a_0 is lattice constant). For the liquid-solid coalescence at a low temperature, the PDFs of $Cu_{321}Ni_{321}$ and $Cu_{321}Co_{321}$ also exhibit fcc character and are similar to those of the solid-solid coalescence. The only difference is that the intensity of the peak becomes weak. This is because the increase of the coalescence temperature accelerates the coalescence and leads to a large lattice distortion and weak intensity of the peak. For $Ni_{321}Co_{321}$, the coalesced complex exhibits an icosahedral character. This result is consistent with the result of the snapshot. For the liquid-solid coalescence at a high temperature, the PDFs of the coalesced complexes exhibit liquid character, which is short-range order and long-range disorder.

Overall analysis of above-mentioned results indicates that the structural evolutions during the heating and coalescence processes are different. Icosahedron was formed for Cu_{321} and Co_{321} during the heating processes, while no for Ni_{321}. This is because the formation of icosahedron was induced by the release of excess energy of cluster [Li et al. (2009)]. The released excess energy of Co is larger than

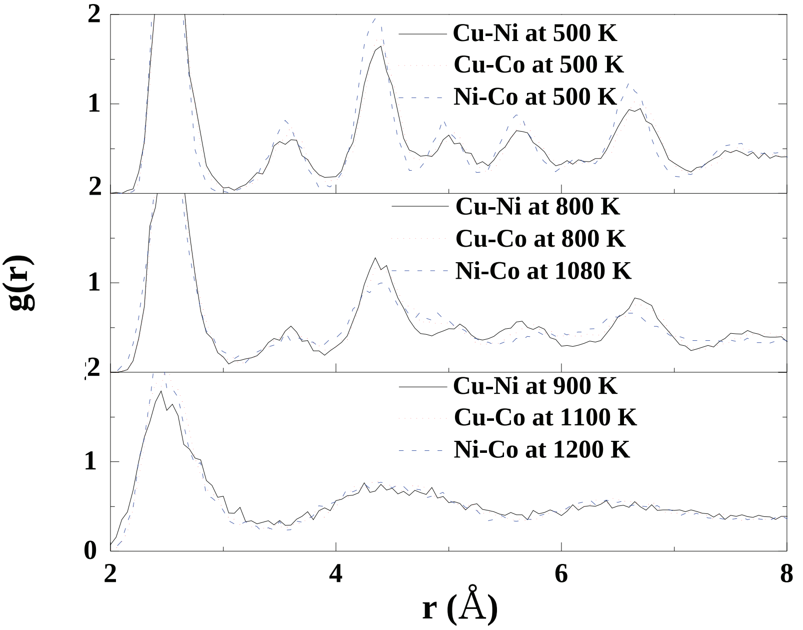

Figure 4: Pair distribution functions of the coalesced complexes of $Cu_{321}Ni_{321}$, $Cu_{321}Co_{321}$ and $Ni_{321}Co_{321}$ at different temperatures.

that of Cu and Cu is larger than that of Ni [Li et al. (2009)]. This leads to the occurrence of above-mentioned phenomenon. For the coalescence, icosahedron was formed only for the liquid-solid coalescence of $Ni_{321}Co_{321}$ at a low temperature. For the solid-solid coalescence, the energy is not large enough to make the clusters transform to icosahedron. For the liquid-solid coalescence at a high temperature and liquid-liquid coalescence, the liquid coalesced complexes were formed due to the high temperature. For the liquid-solid coalescence at a low temperature, the melted Cu atoms can not nuclear to induce a structural transformation. Since the formation of the clusters was generally induced by using surface nucleation or surface reconstruction [Nam et al. (2002); Rodriguez-Lopez et al. (2004)]. The melted Cu atoms formed a coating layer on the surface of the clusters Co and Ni, which inhibited the structural evolution. These results indicate that the structural evolutions were affected by the coalescence.

4 Conclusions

The melting of the clusters Cu_{321}, Co_{321}, and Ni_{321} were studied using molecular dynamics simulation with a general embedded atom method. It was found that the structures of Cu_{321} and Co_{321} transformed to icosahedron near their melting points. The formation of the icosahedron increased their melting points. Several temperatures were selected to make the cluster remain at different phases according to their melting points. The coalescences of the clusters at different phases were studied. The structural evolutions of the coalesced complexes were compared with those of the clusters during the heating processes. The results show that the coating layer on the surface of the cluster Co_{321} formed by Cu atoms inhibited the formation of the icosahedron in the coalesced complex. The icosahedron was induced by the existence of Co_{321} during the coalescence of $Ni_{321}Co_{321}$. All the results indicated that the control of the thermodynamic or coalescence may be used to tune the structure of cluster.

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References

Binns, C. (2001): Nanoclusters deposited on surface. *Surf. Sci. Rep.*, vol. 44, no. 1-2, pp. 1-49.

Ding, F.; Rosen, A.; Bolton, K. (2004): Size dependence of the coalescence and melting of iron clusters: a molecular-dynamics study. *Phys. Rev. B,* vol. 70, no. 7, pp. 075416.

Hawa, T.; Zachariah, M. R. (2006): Coalescence kinetics of unequal sized nanoparticles. *J. Aerosol Sci.,* vol. 37, no. 1, pp. 1-15.

Jimenez-Saez, J. C.; Perez-Martin, A. M. C.; Jimenez-Rodriguez, J. J. (2008): Epitaxy of softly deposited small Co nanoclusters on Cu (001) surfaces. *Phys. Stat. Sol. A,* vol. 205, no.6, pp. 1330-1336.

Kim, D. H.; Kim, H. Y.; Kim, H. G.; Ryu, J. H.; Lee, H. M. (2008): The solid-to-liquid transition region of an Ag-Pd bimetallic nanocluster. *J. Phys.: Conden. Matter,* vol. 20, no. 3, pp. 035208.

Lee, S. C.; Hwang, N. M.; Yu, B. D.; Kim, D. Y. (2001): Molecular dynamics simulation on the deposition behavior of nanometer-sized Au clusters on a Au (001) surface. *J. Cryst. Growth,* vol. 223, no. 1-2, pp. 311-320.

Lewis, L. J.; Jensen, P.; Barrat, J. L. (1997): Melting, freezing, and coalescence of gold nanoclusters. *Phys. Rev. B,* vol. 56, no. 4, pp. 2248-2257.

Li, G. J.; Wang, Q.; Cao, Y. Z.; Du, J. J.; He, J. C. (2012a): Size and composition dependence of the frozen structures in Co-based bimetallic clusters. *Physics Letters*

A, vol. 376, no. 4, pp. 534-537.

Li, G. J.; Wang, Q.; Cao, Y. Z.; Wang, K.; Du, J. J.; He, J. C. (2012b): Icosahedral-decahedral transformation in the (PdAg)309 cluster induced by Ag atomic segregation. *CMC:Comput. Mater. Con,* vol. 30, no. 3, pp. 195-206.

Li, G. J.; Wang, Q.; Li, D. G.; Lü, X.; He, J. C. (2008): Structure evolution during the cooling and cooling after coalescence processes of Cu-Co bimetallic clusters. *Phys. Lett. A,* vol. 372, no. 45, pp. 6764-6769.

Li, G. J.; Wang, Q.; Li, D. G.; Lü, X.; He, J. C. (2009): Size and composition effects on the melting of bimetallic Cu-Ni clusters studied via molecular dynamics simulation. Mater. *Chem. Phys.,* vol. 114, no. 2-3, pp. 746-750.

Li, G. J.; Wang, Q.; Li, H. T.; Wang, K.; He, J. C. (2008): Coalescence of heteroclusters Au767 and Ag767: a molecular dynamics study. *Chin. Phys. B,* vol. 17, no. 9, pp. 3343-3349.

Li, G. J.; Wang, Q.; Liu, T.; Wang, K.; He, J. C. (2010): Molecular dynamics simulation of the melting and coalescence in the mixed Cu-Ni nanoclusters. *J. Clust. Sci.,* vol. 21, no. 1, pp. 45-55.

Li, G. J.; Wang, Q.; Wang, K.; Liu, T.; Li, D. G.; He, J. C. (2009): Composition, concentration and configuration dependence of the icosahedral transformations in Cu-based bimetallic clusters. *Model. Simul. Mater. Sc.,* vol. 17, no. 5, pp. 055005.

Mariscal, M. M.; Dassie, S. A.; Leiva, E. P. M. (2005): Collision as a way of forming bimetallic nanoclusters of various structures and chemical compositions. *J. Chem. Phys.,* vol. 123, no. 18, pp. 184505.

Nam, H. S.; Hwang, N. M.; Yu, B. D.; Yoon, J. K. (2002): Formation of an icosahedral strueture during the freezing of gold nanoclusters: surface-induced mechanism. *Phys. Rev. Lett.,* vol. 89, no. 27, pp. 275502.

Nanda, K. K.; Sahu, S. N.; Behera, S. N. (2002): Liquid-drop model for the size-dependent melting of low-dimensional systems. *Phys. Rev. A,* vol. 66, no. 1, pp. 013208.

Palacios, F. J.; Iniguez, M. P. (2002): Fusion and fragmentation of colliding metal clusters. *Nucl. Instrum. Meth. Phys. Res. B,* vol. 196, no. 3-4, pp. 253-260.

Rodriguez-Lopez, J. L.; Montejano-Carrizales, J. M.; Pal, U.; Sanchez-Ramirez, J. F.; Troiani, H. E.; Garcia, D.; Miki-Yoshida, M.; Jose-Yacaman, M. (2004): Surface reconstruction and decahedral structure of bimetallic nanoparticles. *Phys. Rev. Lett.,* vol. 92, no. 19, pp. 196102.

Tian, D. X.; Guo, X. Y. (2005): Coalescence kinetics of free and supported metal clusters. *Comput. Mater. Sci.,* vol. 34, no. 1, pp. 14-21.

Wang, G. H. (2003): *Cluster Physics.* Shanghai Science & Technology Press.

Zachariah, M. R.; Carrier, M. J. (1999): Molecular dynamics computation of gas-phase nanoparticle sintering: a comparison with phenomenological model. *J. Aerosol Sci.,* vol. 30, no. 9, pp. 1139-1151.