Coalescence between Cu_{57} and Cu_{58} clusters at a room temperature: molecular dynamics simulations*

Zhang Lin(张 林)[a)†], Li Wei(李 蔚)[a)], and Wang Shao-Qing(王绍青)[b)]

[a)] *Institute of Materials Physics and Chemistry, College of Science, Northeastern University, Shenyang* 110004, *China*

[b)] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang* 110016, *China*

(Received 8 July 2009; revised manuscript received 22 September 2009)

Three coalescence processes of Cu_{57}–Cu_{57}, Cu_{57}–Cu_{58}, and Cu_{58}–Cu_{58} clusters at 300 K are investigated by employing molecular dynamics simulations. According to the evolutions of mean square displacement and local atom packing, the coalescence process can be separated into three stages including an approaching stage, a coalescing stage, and a coalesced stage. The simulations show that the coalescence processes and the formed products are sensitive to the respective initial structures of, and the relative configuration between, the two coalescing icosahedron–based clusters.

Keywords: cluster, molecular dynamics, computer simulation, surface

PACC: 3640B, 6120J, 6185, 6800

1. Introduction

Recently, considerable attention has been devoted to nanosize coinage metal clusters which are of great importance in fabricating nanoelectronic devices and novel nano-catalysis.[1−7] For these metallic clusters, their most important chemical and physical properties are greatly dependent on their structures. Therefore, the buildup of these desired clusters must be well controlled and reproducible to make use of their unique properties. To achieve this, it is important to understand structural changes in cluster coalescence. However, until today the structural change accompanied with the cluster coalescence has still been poorly understood due to a lack of sensitive experimental methods to observe local atom rearrangements in the coalescence process. For studying microscopic details of these systems, molecular dynamics (MD) is a common option, owing to prohibitive computational expense from sophisticated *ab initio* approaches.[8−15] In MD simulations, empirical potentials based on the embedded-atom method (EAM) are adequate to characterize these face-centred cubic (FCC) metallic systems, and some EAM versions have been employed to describe the properties of free clusters and clusters supported on surfaces of the same kind of material for FCC metals, such as Cu systems due to their potential applications including catalysis, data storage, medical diagnosis, and biosensing.[16−22] The previous studies employing MD methods show that metal nanoparticles do coalesce, and temperature and size of these nanoparticles have great influence on their coalescences.[23−28] Despite those findings, to the best of our knowledge, the coalescence processes of the clusters are limited for small size clusters containing tens of atoms with icosahedron-based geometries. Because the small clusters have very high surface/volume ratios, their structural changes are extremely sensitive to the number of atoms with the addition or removal of one or a few atoms from these small species as illustrated in the previous work of the author.[16,20,29]

This paper aims to explore the differences in structural change among small Cu_N (N = 57–58) clusters, on coalescing at a room temperature of 300 K, by using molecular-dynamics computer simulations. In the simulations, the whole coalescence process is traced from a time-dependent function. How the structural change is accompanied with the atom packing is demonstrated according to the local environment of EAM atom pairs.

2. Computational details

All the atoms in the simulation are assumed to interact with each other via an EAM potential of

*Project Supported by Special Foundation for State Major Basic Research Program of China (Grant No. G2006CB605103), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, China and the Fundamental Research Funds for the Central University (Grant No. 90405001).

†Corresponding author. E-mail: gsj-cn@tom.com

© 2010 Chinese Physical Society and IOP Publishing Ltd

Cu constructed by Mei *et al.*,[30] and this potential has been used to simulate small copper clusters many times.[16,20−22,29] In the frame of this EAM, the total energy of an N-atom system takes the following form:

$$E_{\rm tot} = \sum_i F_i(\rho_{\rm e}) + \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} \phi_{ij}(r_{ij}) \ , \qquad (1)$$

where $\phi_{ij}(r_{ij})$ is a two-body central potential between atoms i and j with a separation of r_{ij} in between, and $F_i(\rho_{\rm e})$ is the embedding energy of the atom i with the electron density $\rho_{\rm e}$. Atomic trajectories are generated in the canonical ensemble MD, and a time step of 1.6×10^{-15} second is used in calculation. The lattice constant a_0 of bulk Cu in the simulation is 3.615 Å (1 Å = 0.1 nm). Initially, we construct a $20\ a_0 \times 20a_0 \times 20a_0$ bulk Cu crystal, then two crystal fragments respectively containing 57 and 58 atoms are extracted from this constructed FCC crystal and kept in MD simulation cells, where the $20a_0 \times 20a_0 \times 20a_0$ is the size of the MD simulation cell. Here the MD simulation cell is large enough to ensure that there does not exist any influence from clusters in its neighbour simulation cells on the studied clusters, owing to periodic boundary conditions used in the simulation. After the extraction, the two clusters have the FCC structures. Then runs take 50×10^4 time steps for the relaxation of the two clusters. In these time steps, the initial 48×10^4 time steps are used to reach equilibration of the two clusters, and subsequently 2×10^4 time steps to record atomic trajectories, which are used to obtain atom average positions. Here, the equilibration means that the atoms in the clusters only have thermal movements around their equilibrium positions. Figure 1 shows atom configurations of the two clusters at 300 K, where atom coordinates generating the atom configurations average over the last 20000 time steps.[29]

A time-dependent function used in the calculations is determined as the following,

$$D_{\rm SD} = \frac{1}{N}\left\langle \sum_{i=1}^{N} \left[\boldsymbol{r}_i(t) - \boldsymbol{r}_i(t-\Delta t)\right]^2 \right\rangle , \qquad (2)$$

where $\langle\rangle$ denotes the average over the entire trajectory; N is the total atom number in the simulated clusters; $D_{\rm SD}$ is the mean square displacement; $\boldsymbol{r}_i(t)$ and $\boldsymbol{r}_i(t-\Delta t)$ are respectively the positions of the ith atom at times t and $t-\Delta t$. When the atoms in the clusters find their equilibrium positions, $D_{\rm SD}$ will keep a value.

In this study, four integers are used to perform local structure analyses or pair analysis(PA).[31,32] The first integer indicates whether the atom pairs are referred to as near-neighbours or, equivalently, are considered to form a bond in a given cutoff distance, where the cutoff distance is chosen to be $0.8a_0$ corresponding to the first peak of radial distribution function.[29] If they are bonded, the integer is 1. The second integer is the number of neighbours common to a bonded atom pair, and the third is the neighbour relationships among the shared neighbours. The fourth integer is arbitrarily added to provide a unique arrangement of the pairs. For example, 1551 pairs correspond to two bonded atoms with five common neighbours that form a pentagon of near-neighbour contacts, and this type of the pair is characteristic of icosahedral ordering. 1421 and 1422 pairs can be found in FCC-like and hexagonal close packed (HCP)-like local structures. Figure 2 depicts schematic diagrams of the three pairs

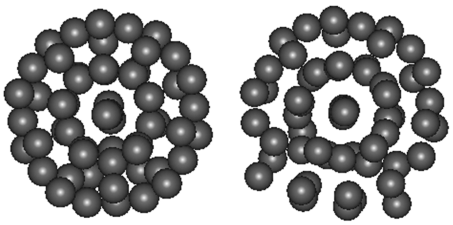


Fig. 1. Structures of Cu_{57} and Cu_{58} clusters at 300 K.

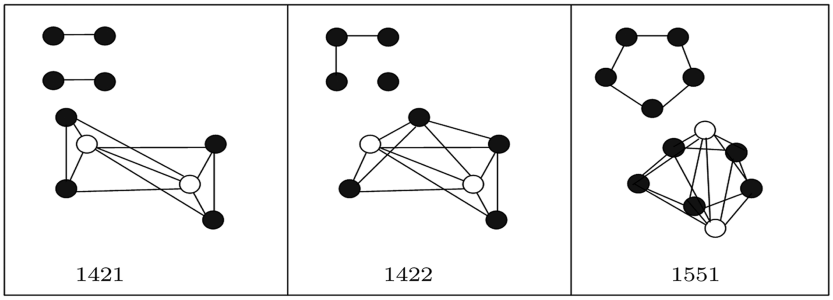


Fig. 2. Schematic diagrammatic configurations of 1421, 1422, and 1551 pairs.

that are prevalent in the system we have studied in this work. In this figure, open circles represent bonded atoms, while solid circles denote neighbour atoms that are shared by the two bonded atoms.

3. Results and discussion

Figure 3 illustrates the $D_{\rm SD}$ variations in three coalescence processes respectively corresponding to Cu_{57}–Cu_{57}, Cu_{57}–Cu_{58}, and Cu_{58}–Cu_{58} clusters as a function of time. As illustrated in this figure, $D_{\rm SD}$ curves exhibit some similarities including those for short time, they increase abruptly as time goes on, owing to the ballistic motion of atoms, and for long time plateaus to appear, which is more pronounced for the coalescence between two Cu_{57} clusters. The occurrence of the plateaus results from atoms that escape from the cages formed by their surrounding neighbour atoms. The more atoms are at their local equilibrium positions, the longer time in plateau regime is required. In the coalescences of the Cu_{57}–Cu_{58} and Cu_{58}–Cu_{58} clusters, the $D_{\rm SD}$ rises linearly as time goes on at intermediate parts of some plateaus in lower slopes than those for short times, implying that the atomic motion becomes diffusive. In the coalescence between two Cu_{58} clusters, it should be also noted that after 1.2 ns, there is an abrupt increase with time increasing, suggesting that large structure changes occur due to the drastical interchanging of positions among atoms. The following MD observations related to the local structural changes will be used to interpret change differences in the coalescences.

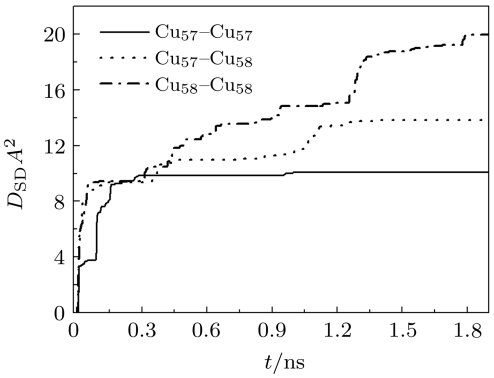
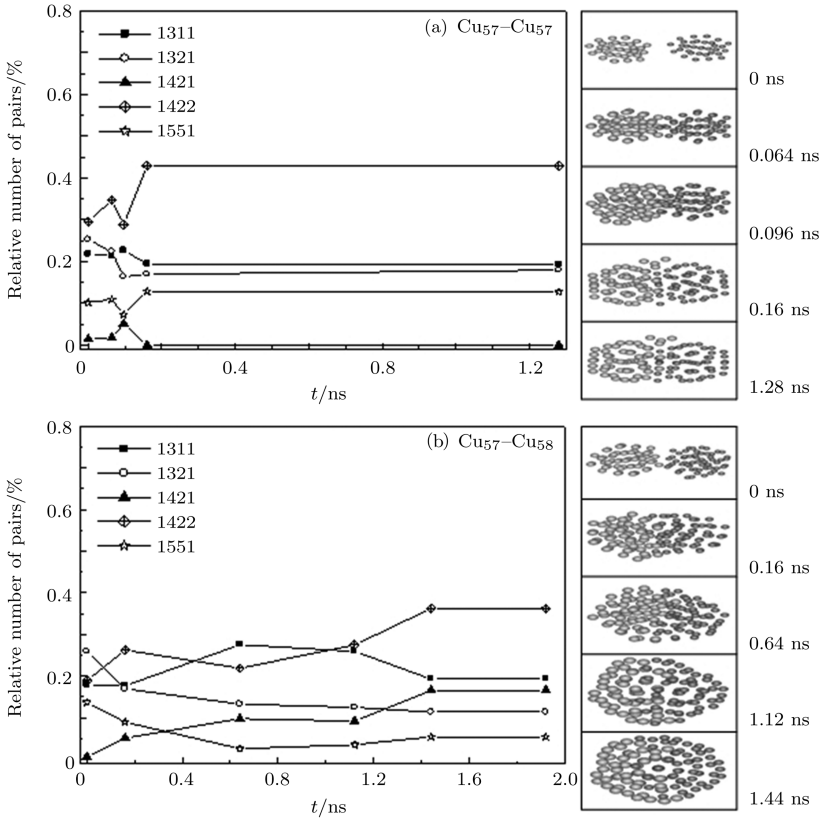


Fig. 3. $D_{\rm SD}$ variations in three coalescence processes respectively corresponding to Cu_{57}–Cu_{57}, Cu_{57}–Cu_{58}, and Cu_{58}–Cu_{58} clusters as a function of time.

Figure 4(a)–4(c) present changes of relative numbers including 1311, 1321, 1421, 1422 and 1511 pairs in the three coalescence processes of Cu_{57}–Cu_{57}, Cu_{57}–Cu_{58}, and Cu_{58}–Cu_{58} as a function of time, where the



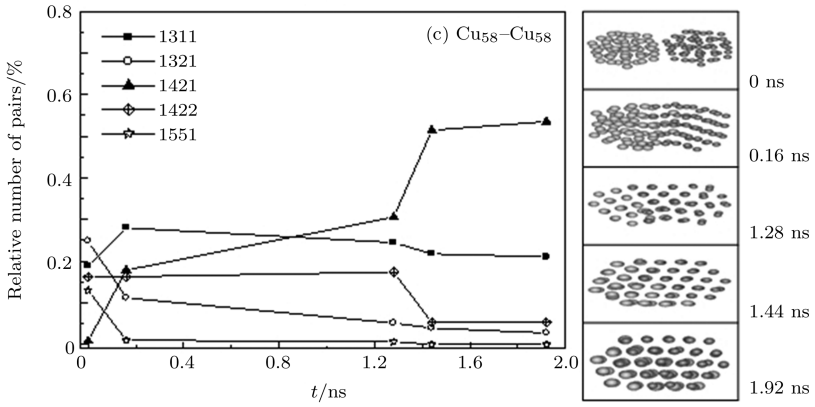


Fig. 4. Pair relative number changes in the three coalescence processes of Cu_{57}–Cu_{57}, Cu_{57}–Cu_{58} and Cu_{58}–Cu_{58} as a function of time.

relative number is the ratio of the number of one kind of the atom pairs to the sum of the atom pairs, and it can be used to determine the local structure changes in the coalescence processes. As presented in these figures, accounting for the high ratios of surface atoms in these clusters contributing to the 1321 and 1311 pairs, initially there are 1551 and 1422 pairs taking up about 40% of the total pairs, which are proven that the Cu_{57} and Cu_{58} clusters have the icosahedron-based geometry structures. There are also a few of other types of pairs, implying that these two clusters are not of perfect icosahedron. The right parts of these figures show the atom packings in the three processes at different times, where the atom packing is a snapshot taken at a given instant during the simulations.

As shown in Fig. 4(a), at 0.064 ns, two Cu_{57} clusters approach each other, and there exist the reductions in numbers of the 1311 and 1321 pairs, suggesting that the number of surface atoms is reducing due to the formation of an interface region between the two clusters. The numbers of 1421, 1422, and 1551 pairs increasing with the numbers of 1311 and 1321 pairs decreasing, suggest that some local FCC, HCP, and icosahedral structures are formed in the interface region. Therefore, the local structure changes in the approaching stage contribute to the abrupt increase of D_{SD} as plotted in Fig. 3. Then, after the three types of pairs including 1422, 1551 and 1321 present decrease behaviours from 0.064 to 0.096 ns, the three types of pairs increase from 0.096 to 0.16 ns, whereas the other two types of pairs have the increases from 0.013 to 0.096 ns followed by the decreases from 0.096 to 0.16 ns. These behaviours suggest that in the coalescing stage after 0.064 ns, the atoms in the two clusters continuously interchange their positions, and more atoms move into the interface region. Hence, an interface region with a more large area is formed as shown by the atomic packing at 0.16 ns. In the following time, only a few of atoms in the coalesced clusters interchange their positions, and these pairs and D_{SD} have not large changes. It should be noted that in the formed bi-icosahedron structure, none of the FCC local structures can be observed.

In the approach stage of the coalescence between Cu_{57} and Cu_{58} clusters, the two clusters also present large structural changes and interface formation, which is similar to the coalescence between two Cu_{57} clusters as plotted in the pair changes and atomic packing at 0.16 ns. These changes from the drastic moving of the atoms result in the abrupt increase of the D_{SD} curve of the Cu_{57}–Cu_{58} clusters. In the following coalescing stage from 0.16 to 0.64 ns, the adjustment of atom positions mainly depends on atom diffusion, and there are the decreases in numbers of 1422, 1551 and 1321 pairs, as well as the increase in number of 1421 pairs. At 0.64–1.12 ns, atom position interchanges contribute to the increases of 1422 and 1551 pairs, implying that these interchanges are conducive to the formation of an icosahedron-based geometry when the two clusters become one cluster. Accompanied with the decrease of the surface area in the coalescence process, the decrease in number of 1321 pairs occurs. Then at 1.12–1.44 ns, the atoms in the produced cluster continue to interchange their positions, and finally form an icosahedron-based structure.

Although in the initial stage of the coalescence process between two Cu_{58} clusters have similar approaching and deformation behaviours to those of the above two coalescence processes, the two Cu_{58} clus-

ters have different change patterns as shown in the pair changes and the atom packing related to the $D_{\rm SD}$ changes as illustrated in Fig. 3. In the changes of the pairs, the increase in number of 1421 pairs and the decrease in number of 1551 pairs can be apparently observed, suggesting that owing to the coalescence, the structures of the coalescing clusters are transformed from the icosahedron-based geometries into an FCC-based geometry. As the coalescence is processing from 0.16 to 1.28 ns, the other types of pairs are not greatly changed, except for the increase in number of 1421 pairs, where these local structure changes originate from the atom diffusion. Then at 1.28–1.44 ns, there exists an abrupt increase in number of 1421 pairs, whereas the other types of pairs are decreased, especially for the 1551 pairs which are decreased to zero in number. These imply that the cluster in the coalescing process is mainly composed of FCC local structures as well as some HCP local structures, and no icosahedron local packing can be observed. These changes are visually presented in the right part of atomic packing, where at 1.44 ns, the formed cluster presents FCC ordered structures with abc packing order along the $< 1\bar{1}2 >$ direction. After 1.44 ns, a few of atoms in the coalesced cluster interchange their positions, contributing to the small changes in pair number.

4. Conclusions

We perform molecular-dynamics calculations to investigate the differences in structural change among three coalescence processes for Cu_{57}–Cu_{57}, Cu_{57}–Cu_{58}, and Cu_{58}–Cu_{58} clusters at 300 K within the framework of the EAM. In the three processes, the times spent in the approaching and the coalescing stages are shortest for the coalescence between two Cu_{57} clusters. Although the three coalescences present similar approaching behaviours in their initial stages, owing to the ballistic motion of atoms, the structural changes and formed clusters in the following coalescence processes present different patterns. As two Cu_{57} clusters approach each other, they still keep their icosahedron-based structures, but when two Cu_{58} clusters approach each other they are transformed into a cluster with an FCC local structure. In the coalescing stages, the two Cu_{57} clusters form a bi-icosahedron based geometry with an interface, and only a few of atoms in the clusters interchange their positions after coalescing. Concerning the coalescence between the Cu_{57} and Cu_{58} clusters, the atoms in the clusters continuously interchange their positions via the atom diffusion after they have approached each other, thereby forming a stable icosahedron-based geometry. Thus, the three cases present a picture of the structural differences causing the different change patterns and formed products during the coalescence processes for the clusters containing tens of atoms with the icosahedron-based geometries.

References

[1] Beck T L, Jellinek J and Berry R S 1987 *J. Chem. Phys.* **87** 545

[2] Ercolessi F, Andreoni W and Tosatti E 1991 *Phys. Rev. Lett.* **66** 911

[3] Sebetci A and Guvenc Z B 2004 *Modelling Simul. Mater. Sci. Eng.* **12** 1131

[4] Zhang Z, Hu W Y and Xiao S F 2006 *Phys. Rev.* B **73** 125443

[5] Liu H B, Ascencio J A, Alvarez M P and Yacaman M J 2001 *Surf. Sci.* **491** 88

[6] Chushak Y G and Bartell L S 2001 *J. Phys. Chem.* B **105** 11605

[7] Yildirim E K and Guvenç Z B 2006 *Modelling Simul. Mater. Sci. Eng.* **14** 947

[8] Wen Y H, Zhang Y, Zhu Z Z and Sun S G 2008 *Acta Phys. Sin.* **58** 2585 (in Chinese)

[9] Lei X L, Wang X M, Zhu H J and Luo Y H 2009 *Chin. Phys.* B **18** 2264

[10] Wang H Y, Li X B, Tang Y J, King R B and Schaefer III H F 2007 *Chin. Phys.* **16** 1660

[11] Feng C J, Xue Y H, Zhang X Y and Zhang X C 2009 *Chin. Phys.* B **18** 1436

[12] Li Z J and Li J H 2008 *Chin. Phys.* B **17** 2951

[13] Mao H P, Wang H Y and Sheng Y 2008 *Chin. Phys.* B **17** 2110

[14] Yang P, Ge J H and Jiang Z Y 2007 *Chin. Phys.* **16** 1014

[15] Dai Y, Dai D, Huang B and Yan C 2005 *Eur. Phys. J.* D **34** 105

[16] Zhang L, Zhang C B and Qi Y 2008 *Phys. Lett.* A **372** 2874

[17] Xu S N, Zhang L, Qi Y and Zhang C B 2010 *Physica* B **405** 632

[18] Rosu M F, Pleiter F and Niesen L 2001 *Phys. Rev.* B **63** 165425

[19] Jacob T, Anton J, Sarpe-Tudoran C, Sepp W D, Fricke B and Bastuǵ T 2003 *Surf. Sci.* **536** 45

[20] Zhang L and Sun H X 2009 *Solid State Commun.* **149** 1722

[21] Zhang L, Xu S N, Zhang C B and Qi Y 2009 *Comput. Mater. Sci.* **47** 162
[22] Zhang L, Zhang C B and Qi Y 2009 *Physica* B **404** 205
[23] Boisvert G and Lewis L J 1997 *Phys. Rev.* B **56** 7643
[24] Hawa T and Zachariah M R 2005 *Phys. Rev.* B **71** 165434
[25] Hawa T and Zachariah M R 2006 *J. Aerosol Sci.* **37** 1
[26] Yadha V and Helble J J 2004 *J. Aerosol Sci.* **35** 665
[27] Zhao L Y and Choi P 2004 *J. Chem. Phys.* **120** 1935
[28] Yukna J and Wang L C 2007 *J. Phys. Chem.* C **111** 13337
[29] Zhang L and Sun H X 2009 *Chin. J. Chem. Phys.* **22** 69
[30] Mei J, Davenport J W and Fernado G W 1991 *Phys. Rev.* B **43** 4653
[31] Honeycutt J D and Andersen H C 1987 *J. Phys. Chem.* **91** 4950
[32] Clarke A S and Jonsson H 1993 *Phys. Rev.* E **47** 3975