The thermal evolution of Cu nanoparticles condensed from the gas phase: MD simulations

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1. Introduction

Studying individual nanoparticles and the nanostructured state is currently one of the most intensively developing fields of research in physics, chemistry, and engineering. Great scientific and practical interest in such research results from the unique properties of nanoparticles that are already or will be widely used in the immediate future for the fabrication of miniature electronic devices, and production of new materials.

Copper clusters hold a most unique position among the whole range of currently used metal nanoparticles. These particles have many unique properties and are relatively inexpensive for manufacturing. Relating to conducting properties copper nanosized particles may compete with silver. Also the range of their usage is wide in the form of catalysts [1]. However the formation of nanoparticles of copper with implementation of application area dependent properties specifies very strict requirements to their producing and processing. One of the promising techniques of nanodispersed particles synthesis process is metals evaporation and condensation in the inert gas atmosphere. Theoretically, this technique makes it possible to synthesize nanoparticles with controlled
chemical composition [2], defect density, structure, and size distribution. Moreover, it is relatively easy to control the parameters of gas-phase synthesis under experimental conditions [3-5].

However one of the main characteristics of vapor phase synthesis method is the substantial inner structure and external shape discontinuity of resulting nanoparticles. Therefore, depending on process parameters up to 90% of particles non-spherical shape and different inner structure may be formed. Production of nanoparticles of desired shape, and structure can be another important step toward their more versatile use. However, the preparation of clusters of certain morphology is a formidable technical task. To solve this problem the method of heat treatment of obtainable metallic particles can be used as a final stage of synthesis from gaseous phase

2. Simulation technique
This section gives a description of the basic principles of the MD procedure used in this study. Any simulation method must first choose some potential of interaction between atoms in the system under consideration. The interatomic potentials used in computer simulations range from ab-initio to simple Lennard-Jones type empirical ones.

The choice of a particular potential depends on the problem formulation, the properties to be examined, the available computing resources, and the desired accuracy of results. Upon analysis of various representations of the potential energy of interatomic interaction, we decided to simulate the formation of Cu nanoclusters from the high-temperature gas phase in terms of the well-established modified tight-binding TB-SMA potentials as introduced by Cleri and Rosato [6].

The starting point of the condensation process was a spatial configuration consisting of 85000 Cu atoms, which were uniformly distributed in a region of space with a volume of \( V = 42600 \text{ nm}^3 \) and periodic boundary conditions. The atomic velocities were set according to the Maxwell–Boltzmann distribution at an initial temperature of \( T_i = 1000 \text{ K} \), which is quite typical of the gas phase synthesis processes [7]. In the inert-gas–metal-vapor mixture used to produce Cu nanoclusters by gas-phase condensation, the inert gas is mainly required to cool the metal vapor and control its temperature. In our approach, external influences are reduced to heat removal from the simulated system. At the start of the simulation, a supersaturated metal vapor fills the condensation region.

The main idea of the proposed gas-phase condensation model is to minimize the rate of formation of primary nuclei from a supersaturated metal vapor. Otherwise, single atoms or small clusters will be captured on the collection surface. This effect is avoided by using an inert gas in the condensation region to reduce the diffusion rate of atoms outside the supersaturated vapor source via an increase in collision frequency.

3. Results and discussion
The formation of a cluster in a metastable gas phase starts with homogeneous nucleation. After termination of this process, the subsequent growth of clusters can proceed according to various mechanisms. The most important of these are agglomeration and coalescence. In the case of agglomeration, clusters combine without changing their shape, whereas during coalescence, clusters fuse and merge together with the formation of a common particle with a shape differing from that of the initial clusters prior to their collision.

To study particles shape and structural properties depending on temperature the gradual heating of copper nanoclusters available from condensation from 100 K to 1200 K with temperature steps of 100 K was modeled. For each temperature particles were held from 3 to 4 ns depending on the cluster size. Clusters under study were chosen in such a way that to fully reflect differences in size, original shape and structure of particles available from condensation. In this simulation, we revealed two typical tendencies:
1) if a particle has a regular internal structure, when heating a cluster to temperature 300-500 K further structure ordering takes place and the number of atoms with coordination number \( z = 12 \) (CP) increases to 55 - 60%. Long-range order destruction begins at \( T = 600 \) K, the complete particle melting occurs at \( T = 1100 \) K (Figure 1);

2) in the absence of the strongly marked closely-packed core of cluster due to intensive kinetic processes under heating, the formation of such core occurs in the temperature range from \( T = 300 \) K to \( T = 700 \) K. With further temperature rise long-range order destruction occurs with the process termination to 1100 K (Figure 1).

Relatively low maximum values of atoms with coordination number \( z = 12 \) in particles under study (not more than 65%) is attributed to the fact that surface atoms were disregarded. The atoms share in a cluster of ideal spherical form is determined from the formula \( \frac{N_s}{N} = 4 \cdot \frac{1}{N^{1/3}} \) (where \( N \) – number of atoms in a particle, \( N_s \) – number of surface atoms) and can reach approximately 40% for a cluster consisting of 1061 atoms and approximately 29% for a cluster, consisting of 2807 atoms. Taking it into consideration we can conclude that in condition of simulated thermal influence there is practically complete ordering of synthesized particles internal structure.

To explain such a behavior (Figure 1) in details the processes of clusters atomic restructuring in condition of thermal influence is analyzed. In Figure 2 there are “snapshots” of \( \text{Cu}_{2686} \) cluster evolution at short-term thermal influence. This cluster pertains to the first group of particles having explicit close-packed core. The colors of the atoms denote the result of a CNA analysis [8] as follows: atoms drawn in blue (green) have a local crystalline fcc (hcp) environment; yellow atoms have no identified structure, however their coordination number is \( z = 12 \). Atoms with coordination numbers \( z \neq 12 \) are drawn in red.

We can see that in the early stages (Figure 2 a) the particle consisted of three combined with each other clusters with various internal organization. However, at \( T = 300 \) K (Figure 2 b) there are distinct processes of transforming internal structure of amorphous area dividing the biggest initial cluster and element with face-centered cubic and hexagonal close-packed structure.

As a result of heating up to \( T = 500 \) K the processes of intensive thermo-activated self-diffusion of surface atoms in the places of connection of two cluster parts begin, and by \( T = 700 \) K this leads to formation of unified oval exterior form for this particle (Figure 2 d). The further increasing of temperature just slightly changes the exterior form and in accordance with the principle of surface energy minimum the particle is aiming to take spherical shape. At \( T = 900 \) K the melting processes begin, in consequence of which the destruction of long-range order with completion of process at \( T = 1200 \) K occurs (Figure 2 f). This behavior was neither very complex nor unusual, since the driving force for the combination of small clusters and formation of a common structure of the initial agglomerated particle was the existence of a large disordered region involving almost the entire \( \text{Cu}_{2686} \) cluster.

For all the six researched particles shown in Figure 1 with temperature increasing the share of atoms with coordination number \( z = 12 \) grows and peaks by the temperature from 400 to 700 K.
depending on particle’s size and ordering of internal structure. Thus, to improve the internal morphology of particle by thermal influence method there is no need in increasing temperature over $T = 700$ K, although the external configuration of cluster in this case does not always take perfect spherical shape and can remain at restructuring intermediate stage presented by ellipsoid.

In such a way several dozens of various clusters were thermally treated, and after analyzing the results we can conclude that the thermal processes influence the formation of the cluster external appearance and structure quite much. Although the observed particles of copper had different form and internal structure there was significant grading of such difference at higher temperatures.

However, not all investigated particles were influenced by the thermal process in cluster form and internal structure. The analysis has shown that thermal treatment in case of about 30% of clusters synthesized from gaseous environment had led neither to the formation of unified structure, nor to the formation of spherical shape. As one of the typical examples in Figure 3 there is a Cu$_{1771}$ cluster that during the whole process of heating constituted two particles with various internal structures divided by an amorphous layer. Being heated from $T = 100$ K up to $T = 800$ K the parts of the cluster have adopted almost spherical shape with simultaneous reduction of contacting area (Figure 3 c). The particle is fully dissolved without packaging of interacting segments at further increasing of temperature (Figure 3 e and f).

It was suggested that such a behavior of particles at thermal treatment can be the result of sintering process at rather low temperatures of perfect spherical clusters with icosahedral structures. Because of the low temperature of kinetic energies environment the collision of particles was insufficient for the activation of surface atoms interdiffusion, and the clusters were just “sticking” to each other due to their interacting forces. As the icosahedral structure corresponds to minimal value of energy, at further heating the initial lightly connected icosahedral clusters saved such a construction of atoms and simultaneously turned into maximal possible sphere. We should also note that clusters gained through direct experiments on

**Figure 2.** Evolution of a Cu$_{2686}$ cluster with increasing temperature: a) $T = 100$ K, b) $T = 300$ K, c) $T = 500$ K, d) $T = 700$ K, e) $T = 900$ K, f) $T = 1100$ K.

**Figure 3.** Evolution of a Cu$_{1771}$ cluster with increasing temperature: a) $T = 77$ K, b) $T = 100$ K, c) $T = 500$ K, d) $T = 800$ K, e) $T = 1000$ K, f) $T = 1200$ K.
condensation from gaseous phase often possess segments with icosahedral structure. In order to verify this assumption, we have studied other nonunified clusters. It was found that, in the overwhelming majority of cases, these clusters comprised combinations of several icosahedral clusters that agglomerated at very low temperatures (below 100 K). The competition of these structures in a cluster leads to further formation of an amorphous-like layer between the particle parts.

Thus, the results of computer simulations of the thermal treatment of copper clusters synthesized from the gas phase suggest that a rather high temperature of agglomeration is the key factor. If the agglomeration took place at the initial stages of development, a high ambient temperature favored the agglomeration of primary clusters into almost unified particles. If the agglomeration proceeded at low temperatures, the kinetic energy of collision was insufficient to fuse the primary particles together. As a result, the parts of the cluster merely stuck together, predominantly due to interatomic interaction forces. In this case, the initial shape of the cluster changed during its thermal treatment and acquired a chainlike or wormlike structure.

4. Conclusions
In this paper the processes of copper atoms condensation with formation of nanoparticles of various form and structure were modeled with the method of molecular dynamics with using of tight-binding modified potential TB-SMA. To define the mechanism of external form and internal structure evolution, the copper nanoclusters condensed from gaseous phase were influenced by thermal treatment.

As a result of thermal treatment modeling we have found that in case of 70% of observed clusters there was full ordering of internal structure and external form. The remaining 30% has failed to form unified shape and structure in the process of thermal-activated relaxation and was presented as competing parts of one particle with comparable energies of surface and chemical potentials. The analysis of the evolution of clusters synthesized from a gaseous medium suggests, that it is necessary to restrict the temperature of cooling of the working gas mixture to a level of 400 - 500 K to obtain a large fraction of spherical metal nanoparticles with a unified crystalline structure. Cooling the mixture by liquid nitrogen according to the commonly accepted practice leads to the formation of a considerable fraction of weakly bound (because of the small area of contact) icosahedral clusters. Upon subsequent heat treatment, these clusters form wormlike nanoparticles consisting of segments with different crystalline structures.

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