The general mechanisms of Cu cluster formation in the processes of condensation from the gas phase

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Abstract. Technological applications of metallic clusters impose very strict requirements for particle size, shape, structure and defect density. Such geometrical characteristics of nanoparticles are mainly determined by the process of their growth. This work represents the basic mechanisms of cluster formation from the gas phase that has been studied on the example of copper. The process of Cu nanoclusters synthesis has been studied by the molecular-dynamics method based on tight-binding potentials. It has been shown that depending on the size and temperature of the initial nanoclusters the process of nanoparticle formation can pass through different basic scenarios. The general conditions of different types of particles formation have been defined and clear dependence of the cluster shape from collision temperature of initial conglomerates has been shown. The simulation results demonstrate a very good agreement with the available experimental data. Thus, it has been shown that depending on the specific application of the synthesized particles or in electronics, where particles of a small size with a spherical shape are required, or in catalytic reactions, where the main factor of effectiveness is the maximum surface area with the help of temperature of the system it is possible to get the realization of a certain frequency of this or that scenario of the shape formation of nanocrystalline particles.

Keywords. Condensation; computer simulations; tight-binding potential; copper; nanoclusters; diffusion.

1. Introduction

The interest concerning the development of new and already existed methods of getting nanodispersed materials has significantly increased for last years. This is due to the fact that this particular class of technological materials is increasingly used as a feedstock in the production of a wide variety of ceramic and composite compounds, superconductors, data carriers, filters, catalysts and nanoelectronic devices.^{1–3} This is primarily because of the fact, that a decrease in the particle size to a nanometre level favours the manifestation of cardinal new properties of the particles, i.e., thermodynamic, chemical, mechanical, magnetic, etc.

Such a change of physicochemical properties could not but arouse the interest in applied science. However, at the same time a very important problem of obtaining of nanoparticles of a given size, shape (polyhedral, spherical or chain) and achievement of the internal structure perfection has not been solved. However, the commercial production and the use of nanoparticles is seriously limited by the insufficiently developed theory of their nucleation, growth and substructure formation.⁴ The present-day state of the art in nanoparticle technology meets no longer the growing demands of various industries with respect to shape, size and properties of nanoclusters and nanoparticles. Commercially available

nanopowders are in most cases polydisperse despite all attempts to control particle size by various technical means. The obtained particles are with a single (but variable) crystalline structure or polycrystalline nanoparticles with a large variety of exterior shapes.

As the direct experimental methods are difficult to use for detailed investigation of the formation and evolution of individual nanoclusters, we have performed computer simulation and the synthesis analysis of metallic nanoparticles on a copper example and their subsequent heat treatment. There are various approaches to solve this task. We believe that the most promising is the molecular dynamics (MD) method based on the modified tight-binding potentials. Using MD simulations, it is possible to determine the influence of external conditions on the structure and shape of synthesized nanoparticles quite exactly.

In the present study, we used the MD method to study the process of ultrafine dispersed material production by condensation from the gas phase, which plays an important role in the commercial synthesis of various nanomaterials. Using this method of synthesis, it is theoretically possible to obtain nanoparticles with controlled chemical composition, defect density, internal structure, and preset distribution of particle size.^{5,6} In the first (preliminary) stage, we simulated the condensation of copper nanoparticles from a high-temperature gas phase in order to obtain the physically and technologically correct computer prototype of gas

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synthesized nanoparticles. In the second (main) stage, we have studied the base mechanisms responsible for Cu nanoclusters formation at processes of real synthesis for the purpose of definition of formation laws of copper particles with the demanded external form.

2. Simulation technique

In our work we have performed molecular-dynamics simulations of a Cu–Ar gas mixtures. For our molecular-dynamics consideration, Newton's equations of motion are numerically solved for each atom in the force field of the remaining atoms. To calculate the forces acting between them, an interaction potential of a particular form should be used. The choice of a potential is determined by the character of the formulated problem and by the properties that should be studied. The time scale accessible to simulation and the confidence level of the results obtained also depend on the form of the potential. After our analysis of various representations of the potential energy, we used a modified tight-binding potential⁷ with a fixed cutoff radius corresponding to the fifth coordination sphere inclusive to calculate the forces acting between atoms. The potentials developed by Cleri and Rosato⁷ proved to be very good in simulating systems in a crystalline state and passed a detailed successful test based on many indicators. Clearly, more complex models similar to the *ab initio* method are more realistic, but it turns out to be just impossible to simulate clusters consisting of several hundred or thousand atoms by this method even in the current state of the art of computer technology. On the other hand, the potentials developed by Cleri and Rosato⁷ were successfully applied in a number of cluster studies^{8,10–13} and are currently among the main potentials for calculating the properties of metallic clusters.

According to this model, the potential energy of the atomic system is calculated using the following expression:

$$E = \sum_i \left[- \left(\sum_{i \neq j} \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta} (r_{ij}/r_{\alpha\beta}^0 - 1)} \right)^{1/2} + \frac{1}{2} \sum_{i \neq j} A_{\alpha\beta} e^{-p_{\alpha\beta} (r_{ij}/r_{\alpha\beta}^0 - 1)} \right], \quad (1)$$

where r_{ij} is the distance between i th and j th atoms and subscripts α and β indicate various types of atoms. In the case of the Cu–Cu interaction values of specific parameters $\xi_{\alpha\beta}$, $p_{\alpha\beta}$, $A_{\alpha\beta}$, $q_{\alpha\beta}$ and $r_{\alpha\beta}^0$ were directly taken from the study by Cleri and Rosato.⁷ For the Ar–Ar and Cu–Ar interaction, however, we chose our own parameters. Clearly, the tight-binding second moment potential is in general not the best choice for the description of the interactions of inert gases and a Lennard–Jones potential might be a better choice. However, the Cu atoms condensate at relatively high temperatures compared to the weak attractive interaction of the inert gas atoms. For this reason and in order to facilitate the

calculations, we opted to use one and the same functional form for all interactions. By setting the prefactor $\xi_{\alpha\beta}$ to zero we eliminated the many-body part from the interactions of the Ar atoms (making the parameter q pointless). The remaining parameters $A_{\alpha\beta}$, $p_{\alpha\beta}$ and $r_{\alpha\beta}^0$ were then chosen in such a way that the remaining pairwise repulsive potential resembles the repulsive part of the Lennard–Jones interaction.

Our simulation was designed in order to mimic the conditions in an inert gas condensation (IGC) cluster source. In such a source the supersaturated metal vapour is produced by thermal evaporation or DC sputtering. This leads to an initially dense metal vapour that subsequently expands into a surrounding inert gas atmosphere. The starting point of the condensation process was a spatial configuration consisting of 85,000 Cu atoms, which were uniformly distributed in a region of space with a volume of $V = 42,600 \text{ nm}^3$ and periodic boundary conditions. In order to avoid premature coagulation of atoms at the very early evolution stages, the average interatomic distance was set greater than the potential cutoff radius. 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. The rather high initial temperature and random velocity distribution give grounds to believe that the model system would rapidly lose memory of the initial spatial distribution. Subsequently, the system was cooled with some fixed rate to a pre-specified final temperature. The final temperature of the chosen particles corresponded to the temperature of liquid nitrogen (77 K), which is used in real experiments on the aerosol synthesis of nanoclusters to cool the high-temperature gas medium. The equations of motion were then integrated with the help of the velocity from of the Verlet algorithm¹⁴ using a time step $h = 2 \text{ fs}$. The partial pressure of the Ar gas was approximately 1 bar. A more complete description of the approach to simulating the condensation process was given earlier.^{8,11,15}

An important point for simulations of condensation phenomena is the coupling of the system to a heat bath. Since considerable amounts of binding energy are released as clusters are formed, such a coupling is necessary in order to avoid unphysical temperature increases. In the experimental situation this coupling is provided by the inert gas atmosphere. For cooling of Ar atoms to the temperature required according to experimental conditions, the Nosé–Hoover and Andersen thermostats can be used.¹⁴ The main idea of the Nosé–Hoover thermostat is the introduction of an additional degree of freedom s that controls the energy input from the thermal reservoir. The Nosé–Hoover control mechanism lies in the fact that the equations of motion obtain an additional force that can take on various values, including negative ones, depending on whether the actual kinetic energy is greater or less than the required kinetic energy of the system. Through the velocity normalization, the thermostat parameter s lowers or raises the kinetic energy and, consequently, the instantaneous temperature. The advantage of this technique is a very good stabilization of a fixed temperature: the deviations from this value are at most one per cent.

In the simulations described in this work we have employed the stochastic Andersen thermostat method^{14,16} to cool the Ar atoms to a given heat-bath temperature. The energy released by the condensation of the Cu atoms is then transferred by atomic collisions to the Ar gas, from which it is removed by the thermostat. This molecular dynamics (MD) method is used for a closed system with a fixed number of particles N , system volume V and total energy E (NVE ensemble). The advantage of this approach consists in the fact that the Andersen thermostat can imitate the technique of cooling of nanoclusters at various rates. According to this stochastic method, metal atoms exhibit random collisions with certain virtual particles so as to model the interaction with atoms of the cooling inert gas, the temperature of which under the adopted experimental conditions corresponded to liquid nitrogen temperature. The simulating cooling rate ($\sim 10^8$ K s⁻¹) was appropriate or was a little bit higher than the speed of thermal energy removal that is technically already exists nowadays in gas-phase condensation processes.

The processes of condensation were simulated using the MDNTP program developed by Dr Ralf Meyer (University of Duisburg, Germany).

3. Cluster growth mechanism

The properties of nanoparticles are largely determined by their structure resulting from the actual particle growth scenario. The processes contributing to particle synthesis may widely differ, depending on details of the technique employed. This is particularly true for the production of metal nanoclusters.¹⁷ In the inert-gas-metal-vapour mixture used to produce Cu nanoclusters by gas-phase condensation, the inert gas is mainly required to cool the metal vapour 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 vapour fills the condensation region.

The cluster growth mechanism depends on the vapour density and temperature. When the supersaturation is low, clusters are created via homogeneous nucleation (random formation of nuclei).¹⁸ Since the spectrum of density fluctuations in the supersaturated region is wide, a nucleus either grows into a stable liquid particle (if it is larger than a critical size) or vapourizes. After the nucleation stage, clusters can grow by several mechanisms. Surface growth is a gradual process in which atoms join a cluster one by one. Cluster-cluster collisions may lead to growth via aggregation or coalescence.¹⁸ Aggregation does not change the shapes of the colliding clusters, whereas coalescing clusters merge into a particle whose shape is different from the cluster shapes prior to the collision.¹⁸ In the course of further growth, the particle shape may change due to single atom migration. With increasing density of the metal vapour, the energy barrier for aggregation of atoms decreases and spontaneous growth of nanoparticles by passing nucleation becomes possible. The final

particle morphology depends on the relative contributions of these mechanisms.¹⁸ Therefore, it is important to study cluster growth processes and their influence on the state of the entire system. Understanding of nanoparticle growth mechanisms can help in producing clusters of size, shape and structure required to obtain desired physical and chemical properties.

To our mind, the main mechanism, that influences the formation and clusters growth from the gas phase is the process of merging (coagulation) of the primary particles. The most stable structures are received when the primary particles merge into a single cluster of a spherical shape. It is possible if in the course of the synthesis the surface diffusion of collided particles leads to a massive transfer of matter, and as a consequence, to the complete unification of the primary clusters.

In the work,¹⁶ the processes of coagulation of the particles depending on the time have been examined. The authors of this work believe that if coalescence processes occur much faster than the time between the further collisions of the primary cluster fragments, then the particles have time for development of their external shape into a spherical one (figure 1a). On the contrary, if the processes of coalescence are slow, then the primary particles stick together without merging and in the final particle the initial clusters remain identifiable as shoots. The slowdown of coalescence can occur in that case if for the system of two collided particles and partially joined particles the third one will join. Such a collision leads to a 'freeze' of the process of a shared cluster formation.¹⁹

This effect can be explained by the fact that during the diffusion of surface atoms by coalescence, the emergence of another junction causes redistribution of atoms on the surface of the primary particle that slows down the process of merging (figure 1b). The greater effect of slowing down of a single cluster formation can be observed in that case if the particle A collides with a system of two clusters B+C nearby the place of their unification.¹⁹ In this case, the particle A actually becomes a layer between the particles B and C (figure 1c). All the mechanisms of merging that have been

Figure 1. Different mechanisms of the cluster formation in the processes of condensation from the gas phase.

described above are being observed in our computer simulation of synthesis of copper particles from the high temperature gas phase. Figure 2 shows the formation of the cluster Cu_{766} ($N = 766$ atoms) during the collision and association of the primary particles Cu_{321} ($N = 321$ atoms) and Cu_{445} ($N = 445$ atoms). The formation of a single shape in a merged particle was caused by the collision of primary clusters Cu_{321} and Cu_{445} that were in the early stages of condensation (after about 0.2 ns simulation time). At that time a rather high temperature value still existed in the system and because of that the collided particles completely changed their shape due to the atoms diffusion.

Also in the process of simulation of copper atoms condensation the mechanisms of particle growth were observed when the joining of the third particle froze the process of

merging of the first two clusters. Such a mechanism is graphically demonstrated in figure 3, where particle formation of Cu_{1856} occurs in the process of connection to a rather large cluster Cu_{1459} of smaller particles Cu_{218} and Cu_{179} . Between these two successive collisions a quite long period of time has passed (exactly 0.7 ns). During this time, the cluster Cu_{218} was able to fasten the primary particle Cu_{1459} and change its structure (from icosahedral to fcc). In the collision of these particles in the system a stable low temperature has been observed. The association of Cu_{218} and Cu_{1459} was at $T_{\text{col}} = 95.5$ K and Cu_{1677} at $T_{\text{col}} = 80.2$ K, that did not allow the primary clusters to form a conglomerate with a single spherical shape, as there was not enough energy for atoms for surface self-diffusion.

The colours of the atoms denote the result of a CNA²⁰ analysis as follows: atoms drawn in blue (green) have a local crystalline fcc (hcp) environment; it implies that the number of neighbours for these atoms in the first coordination sphere is $Z = 12$, the number of neighbours in the second sphere equals to 6, and, respectively, in the third sphere it makes 24 (fcc) or 2 (hcp). Yellow atoms have no identified structure, however their coordination number is $Z = 12$, that is the number of neighbours in the second coordination sphere < 6 . Atoms with coordination numbers $Z < 12$ are drawn in red.

The most common variant in the simulation process is the variant of merging of particles under condensation from high-temperature gas phase shown in figure 4. In this case the formation of the final particle Cu_{2912} goes through phased engagement of the primary clusters one by one, forming in the long run, a 'wormlike' shape of a conglomerate. Such conglomerates can be represented through very long chain

Figure 2. Cu_{766} cluster formation as the result of Cu_{321} and Cu_{445} clusters merging at $T_{\text{col}} = 2060$ K.

Figure 3. Cu_{1856} cluster formation in the process of merging of the primary particles.

Figure 4. Cu_{2912} cluster formation in the process of merging of the primary particles.

Figure 5. Cluster of Cu_{4467} atoms received by synthesis simulations from a gas phase.

Figure 6. Transmission electron microscopy image of (a) Cu nanoparticles and (b) Co nanoparticles condensated from the gas phase.

particles formed by the merging of more than 20 primary clusters with one another. The example of such particle is shown in figure 5, where the final cluster is the result of consecutive merging of 15 clusters with different shapes and internal structures.

The process of particle formation also can occur due to regular collisions with primary particle cluster fragments. During the time between collisions of particles, the primary cluster completely absorbs a joined fragment, but only up to a certain moment. When the primary particle of a certain maximum size is reached the uniform growth of spherical cluster ends, the particle is no longer able to fully absorb any joining cluster fragments. Then only the process of adhesion and partial merging of clusters is observed. This mechanism of phased particle growth is clearly observed in the other works concerning condensation of metal atoms, for example, in Krasnochtchekov *et al.*²¹

Finally, we want to compare the results of our simulations with corresponding experimental findings. To this end, we present in figure 6 electron-microscopy images of real Cu and Co nanoparticles condensated from the gas phase. The electron microscopy images were made at Institute of Theoretical and Applied Mechanics (Novosibirsk, Russia) in the group of Prof. SP Bardakhanov. Despite the fact that before their deposition these particles were sintered at high temperature and despite the fact that these particles are approximately 10 times larger, the resemblance between the shape of these particles and our simulation results is striking.

At Institute of Theoretical and Applied Mechanics has been used an industrial accelerator operating with a power of 100 kW (see, for example, Bardakhanov *et al.*²²). A specific feature of the accelerator is the high energy of electrons (1.4 MeV), as well as the possibility of releasing the beam into the atmosphere. The electrons move with relativistic velocities and their mean free path, for example, in air,

Figure 7. Stages of growth of a 1697-atom Cu cluster (MD simulations).

can reach 6 m. The power density can be as high as 5 MW cm⁻², which makes it possible to evaporate high-melting substances at normal conditions and to perform synthesis in a high-temperature 'gaseous' phase. The other advantages of this method are the high efficiency of the process due to the direct conversion of the electric energy into the thermal energy inside the material, the heating rate exceeding 1000 K s⁻¹, and the 'chemical purity' of the electron beam. The evaporation of the initial solid material is performed inside the reactor; then, the vapour is transported from the heating zone and is simultaneously diluted and cooled by air (or by any other carrier gas). Then, condensed and solidified nanoparticles are captured in the corresponding parts of the facility and accumulated in the form of a powder. The studies of the methods used for preparing a metallic nanopowder were performed during its evaporation in an argon atmosphere at a pressure slightly above the atmospheric value.

The diagram of cluster formation of Cu₁₆₉₇ in the various processes of growth is shown as a typical example in figure 7. In the initial stages of condensation clusters growth is dominated. All these mechanisms are clearly seen in figure 6. Until the time $\sim t = 0.4$ ns high temperature values are kept in the system that allows for the primary clusters when merged to form a single spherical particle. However, by gradually lowering of the temperature in the system to replace the process of clusters growth, the agglomeration and coagulation processes are coming. As a result, at the collision of the clusters they do not form uniform particles but form some agglomerates with dumbbell and chained shapes. Then these agglomerates also combine with each other forming three-dimensional clusters mainly with a chained shape.

4. Conclusion

In this work with the help of molecular-dynamics method the process of synthesis of copper nanoparticles from the gas phase has been modelled and the basic mechanisms of the clusters formation in different stages of modelling have been examined. It has been stated that depending on the temperature and size of the merging primary particles the process of a single nanocluster formation can pass through several scenarios. If the primary particle collision occurs in the early stages of condensation at relatively high temperatures values in the system then there is a prevailing probability that particles can form a single cluster mainly of spherical shape with the help of the intensive processes of self-diffusion of surface atoms at the collision point of the primary particles. If the merging is at relatively low temperatures, then the joining of particles to the primary cluster goes at the chain-like scenario. That is, each subsequent particle is joined to the place of adhesion of the primary particles. In this case, in the agglomeration process rather large clusters are formed with clearly defined wormlike shapes.

Depending on the specific application of the synthesized particles or in electronics, where particles of a small size with a spherical external shape are required, or in catalytic

reactions, where the main factor of effectiveness is the maximum surface area with the help of regulating temperature parameters of the system, it is possible to get the realization of a certain frequency of this or that scenario of the shape formation of nanocrystalline particles.

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