Physics of the Solid State, 2023, Vol. 65, No. 1

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Thermal profile analysis in simulation of the initial stage of synthesis of Cu-Au nanoparticles from the gas phase

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Received September 26, 2022
Revised October 2, 2022
Accepted October 3, 2022

The production of particles from the gas phase is one of the main physical methods for the synthesis of nanostructured materials, the obvious advantages of which include good control of the target composition of the resulting nanomaterial. However, the determination of clear dependences between the initial parameters of experimental setups and the size of nanoparticles is not an easy task, requiring a detailed study of the processes of formation, growth, and agglomeration of nanoclusters. Another problem is that metal nanoparticles of identical chemical composition and size can be in different structural states or have different levels of defects. The processes underlying the formation of the structure of such nanoparticles are also not completely clear, especially at the very initial stage of synthesis from the moment of decomposition of precursors to the formation of primary stable nuclei. Therefore, in the presented work, the molecular dynamics method was used to simulate the process of synthesis of Cu-Au nanoclusters of various target compositions from the high-temperature gas phase. Based on the data obtained, conclusions were drawn about the main stages of the evolution of the model system. It is shown that the initial stage of synthesis consists of five different stages, gradually leading to the formation of primary spherical Cu-Au binary alloy nanoparticles with a clear extrusion of gold atoms to the surface.

Keywords: nanotechnology, synthesis, nanopowders, computer simulation, tight binding, nanoparticles, copper, gold.

DOI: 10.21883/PSS.2023.01.54969.483

1. Introduction

Synthesis from a gaseous medium is considered the most economically attractive method of creating nanostructured materials on an industrial scale, suitable for the vast majority of chemical elements and compounds. Its undoubted advantage is a fairly good control of the parameters of experimental installations and the relative simplicity of production in comparison with traditional chemical methods. In recent decades, significant progress has been made in the development of various variants of such synthesis, the study of underlying physical and chemical processes and the determination of the properties of the resulting nanoparticles and ultrafine nanopowders [1–6].

Parallel to the real experiments, simulation experiments were also conducted to analyze the features available both at the atomic level and at the level of the already formed primary nanomaterial. In this case, the methods of *ab initio* were used to assess the dynamic processes of formation and growth of nanoparticles computing or molecular dynamics. The knowledge gained during modeling could then be used to make changes to the synthesis technology or even to the design of installations.

The peculiarity of condensation from a gaseous medium is that bulk precursors in a high-temperature state are transferred to the phase of a metastable supersaturated gas, which leads to the formation and growth of nanoparticles. At the same time, the initial atomic vapor, even in the case of a binary mixture, is observed in a homogeneous state, and is not a nanocomposite with any given composition [7]. That is why, in gas-phase synthesis, in contrast to chemical methods, there is almost complete control of the target composition of the resulting nanomaterial [8,9].

Another important characteristic of the resulting nanoparticles is the size, which is one of the reasons for their unique physicochemical properties. However, the determination and control of this value in the synthesis process is no longer a simple task that requires a detailed study of the formation, growth and agglomeration of nanoclusters. Only on the basis of such data it is possible to purposefully influence many very important characteristics of the nanoparticles synthesized in the end.

Another problem may be the fact that metal nanoparticles, even of identical chemical composition and size, may be in different structural states (polymorphism), have different levels of defects, or even be observed in a thermodynamically stable amorphous state [10]. If the desired target chemical composition can be easily controlled by choosing: the initial chemical composition of the evaporated precursors, the transport (buffer) gas, its temperature and feed rate into the synthesis chamber, then the creation of an isomorphic crystal structure is not a solved task. The processes underlying the formation of the structure of nanoparticles are also not completely clear, in particular, the features of the formation of nanoparticles at the very initial stage of synthesis from the moment of decomposition of precursors to the formation of primary stable nuclei are not understood.

However, it has now become obvious that it is the morphology of metal nanoparticles, in addition to their size, that has a significant impact on the properties used in catalysis, optics, magnetism, etc. Therefore, the development of gas-phase synthesis methods is currently aimed at finding ways to obtain nanoparticles with a certain external shape (spherical, cubic, planar, etc.) and the required crystal structure. It is the combination of these two factors that can become a key technology in many areas of modern industry using nanoparticles.

It should be noted that the problem of preparing free nanoclusters, especially in the form of an ultrafine powder, is much more complex than the usual deposition of nanoparticles on a substrate. The costs of production and storage of such particles are higher, due to their possible surface contamination with related substances. The preparation of simpler methods for creating metal nanoparticles with a certain external shape, structure and surface uncontaminated with impurities is very important in terms of the development of high-precision selective catalysis of chemical reactions used in industry [1], but this requires a theoretical and practical study of all processes occurring during gas-phase synthesis.

The nanometer-sized compounds Cu-Au studied by us in this work are now being studied quite actively [11–21] because of their potential applications in the field of catalysis and optics. A nanoalloy Cu-Au is usually obtained by standard chemical methods, however, in this case, nanoparticles can vary greatly in size, percentage of chemical elements or the structure being formed, because of which it is not always possible to find an explicit relationship between the initial conditions of the experiment and the final result. In comparison with chemical methods, physical methods offer better control of the composition of synthesized bimetallic nanoparticles, but in the absence of dimensional and morphological uniformity.

Thus, in all the experiments conducted, the most diverse external and internal structure of Cu-Au nanoparticles was observed without a clear understanding of what kind of structure, shape and chemical composition can be formed as a result of a particular synthesis method. In this paper, we will focus on the analysis by computer simulation methods of only one of the physical methods for the production of binary nanoparticles Cu-Au, namely, synthesis from a high-temperature gas phase. For the first time, a detailed study of the dependence of the processes of atomic ordering of Cu-Au particles on the concentration of gold atoms in a sufficiently voluminous model medium will be carried out on the basis of a multiparticle tight-binding potential that is sufficiently complex for modeling large systems. Based on the data obtained, we plan to draw conclusions about possible mechanisms for the synthesis of binary nanoparticles Cu-Au and conduct a general analysis of the simulated system at different stages of its evolution.

The thing is that a wide variety of particles are required for different technical applications. If we consider catalysis, then particles with a developed surface are needed here, that is, worm-like clusters, usually obtained at the final stages of synthesis during agglomeration processes. If synthesized particles are used in microelectronics, for example, when creating PCM memory cells (Phase Change Memory), then spherical clusters are required. If we consider optics (plasmon applications) — clusters with the maximum number of angles are needed for the occurrence of plasmon resonance and etc.

Therefore, the presented work did not focus on the production of particles of any one form. The main goal was to determine the technological conditions for the preferential production of particles of a particular morphology, for which the analysis of all stages of gas-phase synthesis is carried out. A whole series of works on this topic is planned and this article is only the beginning. The volume of information obtained during modeling is very large, and it is simply not possible to present all the results in one article.

2. Computer model

One of the simplest methods of gas-phase synthesis is the evaporation of precursors in an atmosphere of cold inert gas, usually He or Ar with a low density (pressure of the order of 1 mbar). The convection flow of inert gas passes through the evaporation zone of precursors and transfers the vaporized substance in the direction of collecting filters or substrates. The walls of the reactor zone are cooled with liquid nitrogen, water or other substance, depending on what rate of thermal energy removal is required to create. An increase in the pressure or molecular weight of an inert gas leads to an increase in the average particle size. This method (Inert Gas Condensation) is widely used for the commercial production of a wide range of nanomaterials.

In the molecular dynamics method we use to simulate such a gas-phase synthesis, the microcanonical or NVE ensemble is considered the basic one. In this case, the number of simulated particles N, the volume of the system V and its total energy E are unchanged throughout the simulation process. However, this standard approach is well applicable only for a homogeneous system, preferably of macroscopic size, having a number of limitations in the presence of phase changes. So, if we consider the formation of a condensation embryo from atomic vapor, then due to the union of atoms among themselves into dimers, trimmers, etc., the potential energy released in this case turns into kinetic energy, which leads to a sharp increase in the temperature in the synthesis chamber [1,22].

If no measures are taken to remove thermal energy from the system, an uncontrolled increase in the velocity of the nuclei atoms will occur, again leading to its evaporation. Consequently, the heat released when combined into cluster fragments must be somehow removed from the simulation cell, for which various kinds of thermostats are used.

In our case, an Andersen thermostat with a constant rate of thermal energy removal (NVT ensemble) was used to cool the binary atomic vapor. The chosen method allows model atoms to experience random collisions with virtual particles of this thermostat. The result of collisions is that the velocity of the simulated atoms decreases stochastically with respect to the distribution of atoms in velocities (Maxwell-Boltzmann law) at the previous simulation step. For condensation from a high-temperature gas medium, such interactions simulate a cooling inert gas used in real experiments on the synthesis of nanoclusters by the gas-phase method.

The region created for the numerical experiment had a regular cubic shape with a face length of 1350 Bohr radii a_{B} with the presence of periodic boundary conditions and contained a total of 91124 copper and gold atoms evenly distributed in space with an average distance between them of 30 Bohr radii. The choice of the initial distribution of atoms (cubic lattice) does not have much influence on the results, since the distance between the atoms turns out to be greater than the radius of the cutoff of the interaction potential ($r_c = 11.1\,a_{\mathrm{B}}$). In addition, a sufficiently high value of the initial temperature $T_i = 1000\,\mathrm{K}$, characteristic of the region of primary cluster reactions, was set. All this gives reason to believe that the simulated system very quickly loses its memory of its initial distribution, which makes it possible to achieve a situation of random placement of atoms in the synthesis zone.

The inert gas created by the Andersen thermostat and diverting thermal energy from the main gas binary mixture had a temperature of 77 K, which simulated a fairly standard situation of cooling the system with liquid nitrogen. The equations of motion of atoms were solved on the basis of a high-speed Verlet scheme with an integration step of $h = 1\,\mathrm{fs}$. The choice of the distance between atoms (initial density) was determined by the tasks set in the experiment. If it is necessary to obtain only small particles at the outlet of the installation, then the initial density of metal vapor in the synthesis chamber should be much less than the density of the inert gas. Such a simulation simulates the situation in a shock tube (*shock tube*), in which metal molecules at the initial stage are largely diluted by an inert gas atmosphere.

If it is necessary to produce sufficiently large clusters with a diameter of several nanometers, a completely different initial density is required. Our set of parameters was chosen in such a way as to more accurately simulate the conditions of condensation in an inert gas (*Inert gas condensation*). In such installations, super-saturated metal vapor is observed, which then moves into the surrounding inert atmosphere.

A modified tight-binding potential was used to calculate the forces of interatomic interaction [23] with a fixed cutoff radius corresponding to the fifth coordination sphere inclusive. The method is based on the fact that a large group of properties of transition metals can be completely determined from the density of states of external d-electrons. It is this method, in which the ion-ion interaction is described taking into account the band nature of the bond and the short-range repulsive pair potential, in our opinion, that is able to correctly describe some of the characteristic features of small metal nanosystems. In addition, we note that this type of representation of the potential energy of atomic clusters is widely used in computer simulation of both macroscopic bodies and nanoparticles.

3. Results and discussion

The kinetics of the interaction of precursor atoms and the processes of initial formation of nanoparticles strongly depend on temperature. The temperature change in the synthesis chamber is one of the most important quantities characterizing the evolution of the entire system as a whole. Temperature is also indispensable as an input and control parameter for conducting realistic modeling, including highly temperature-dependent chemical kinetics.

However, when the mechanisms of gas-phase interactions obtained as a result of experiments in rarefied atmospheres begin to be applied to synthesizing reactors, strong differences are often found indicating the importance of heterogeneous reactions in which precursors or early intermediates interact with a large and highly reactive surface area of a freshly generated nanoparticle. But because of the experimental complexity of studying such processes, there is a serious lack of information in the theoretical basis of gas-phase production of nanoparticles.

For the problem of estimating the evolution of the binary system Cu-Au during condensation from a gaseous medium, it is the cooling rate that is of the greatest importance in terms of the dispersion and size of the resulting nanopowder. Thermal energy is discharged here by a flow of transport gas cooled by the surfaces of the synthesis chamber. This technique allows you to obtain a temperature gradient of more 10^5 K/s, which is sufficient for the synthesis of refractory metal powders with particle sizes of $50-100$ nm. At cooling rates 10^5-10^8 K/s powders Al, Ni, Cu, Au with particle sizes $0.5-50$ nm and specific surface area $(70-30) \cdot 10^3\,\mathrm{m^2/kg}$ can be obtained.

The rate of temperature decrease set by us in the model corresponds to the nanosecond range of creating nanopowders Cu-Au, at which the size of the synthesized particles cannot exceed $30-40$ nm. With the selected size of the simulated system, such a heat removal rate allows us to adequately reflect the situation of a direct experiment with respect to the average value of the particles produced [9].

Since we are interested in the processes occurring at the earliest stages of the formation of nanoparticles, we considered the behavior of the system in the time interval up to 10.0 ns. First of all, let's analyze the thermal development of the simulated area. The initial temperature was 1000 K for all the target chemical compositions simulated by us, but already at 0.1ns there was a significant difference

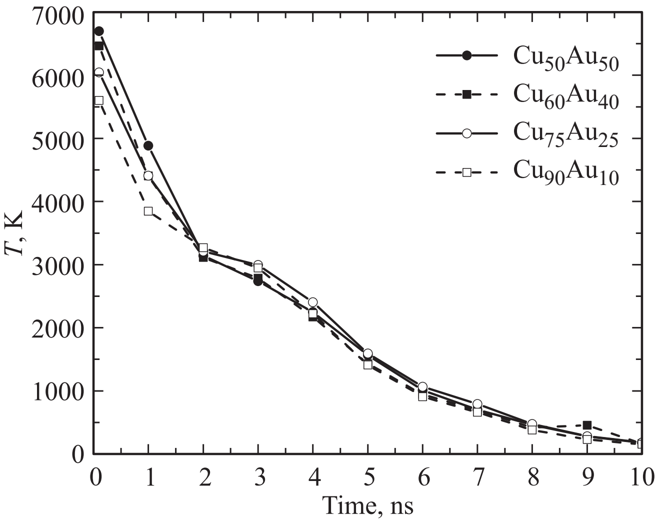

Figure 1. The dependence of the temperature of the synthesis region on the simulation time for different target compositions.

in this very important indicator. So for $Cu_{90}Au_{10}$, it was minimal and amounted to 5600 K, with an increase in the percentage of gold atoms in the initial gas medium, the temperature gradually increased, reaching a maximum value of $T = 6700$ K for the target composition with the highest simulated gold content ($Cu_{50}Au_{50}$). That is, an increase in the binary system of gold atoms by 1number of atoms chosen by us corresponded to an increase in the temperature of the system by about 27.5 K (Fig. 1).

This result is a direct consequence of the fact that during the formation of one dimer of gold, 0.32 eV of energy [24] is additionally released in relation to the formation of the Cu dimer, which, in part, leads to the temperature increase of the model system that we observed. In addition, the different atomic mass of the metals imitated by us is also of great importance. The cooling process in such systems is carried out through elastic interactions of metal atoms and a transport gas having a constant final temperature. And when metal vapors with large atomic masses are cooled, compared with the atomic mass of gas, the system cools much more slowly, since the number of elastic interactions of gas-metal atoms to cool the system increases by one kelvin, which is a direct consequence of the law of conservation of momentum of the system. Gold has a large atomic mass relative to copper, which leads to slower cooling of the system with its increased content.

We will consider the proportion of temperature change found by us to be the base one, since it describes two extreme simulated cases: the lowest and the highest concentration of gold atoms. To verify this assumption, we present the data obtained for the case of pure copper condensation under similar conditions of a computer experiment. Here, at the simulation time $t = 0.1$ ns, the temperature of a system of a similar size was approximately 5320 K [25], which fits into the dependence that we have found. Undoubtedly, due to the random nature of the formation of dimers, trimers and larger cluster fragments, the formation of bonds Au-Au, Au-Cu or Cu-Cu occurs stochastically, because of what with other simulated target compositions ($Cu_{75}Au_{25}$, $Cu_{60}Au_{40}$) some deviations were observed, but in general the found proportion was observed within 10% of error. This trend persists until the time $t = 1.0$ nsbecause of which this time interval can be considered as the first stage of the general evolution of the binary system Cu-Au. If we analyze „instantaneous“ snapshots of the model area with different target compositions simulated by us, then there is practically no difference between the case of $t = 0.1$ ns and $t = 1.0$ ns. Everywhere there was a pattern of chaotic distribution of single Cu and Au atoms, as well as their very small formations. But at $t = 1.0$ ns, the temperature in all model systems, due to interaction with cold transport gas (Andersen thermostat), drops by about 1800–2000 K, which makes a decisive contribution to the processes of further development of the binary gas medium.

The second stage of the evolution of the Cu-Au system, in our opinion, occurs in the time interval $t = 1.0{-}2.0$ ns. As can be seen from Fig. 1, at this time interval there is a reduction in the difference in temperatures of all simulated target compositions, with the completion of the process precisely to $t = 2.0$ ns. Let us try to understand the reasons for such a change in the behavior of the simulated system. A simple visual analysis of „instantaneous“ snapshots of the model area at a given time interval does not allow us to come to any unambiguous conclusions. Only the processes of primary formation of cluster fragments are clearly visible, observed by increasing the „transparency“ of the model region (Fig. 2). That is, the primary, almost chaotic distribution of single atoms begins to be replaced by a picture of the placement of atomic compounds in the space of the synthesis chamber, including various kinds.

Therefore, the calculation of the number of forming clusters and cluster fragments depending on the time of evolution was carried out further (Fig. 3). For the calculation, a technique was used in which a cluster fragment was understood to be the union of at least four atoms into a single whole. That is, single atoms, dimers and trimers were excluded from consideration.

From Fig. 3, it becomes clear that the selection of the time interval $t = 1.0{-}2.0$ ns as the second stage of evolution, but from other physical positions. It is up to the time $t = 2.0$ ns that absolutely all simulated target compositions reach the maximum value of the number of primary clusters. Further, this number begins to decrease rapidly exponentially due to the processes of coalescence, and then agglomeration. We note that the second process becomes possible only at much lower temperatures, at which the initially molten nanoparticle crystallizes during the removal of thermal energy by the transport gas, and in this state combines with neighboring ones, forming cluster compounds of the most diverse external shape and internal structure.

Thus, the second stage of evolution can be observed up to the simulation time $t = 2.0$ ns, a typical feature of

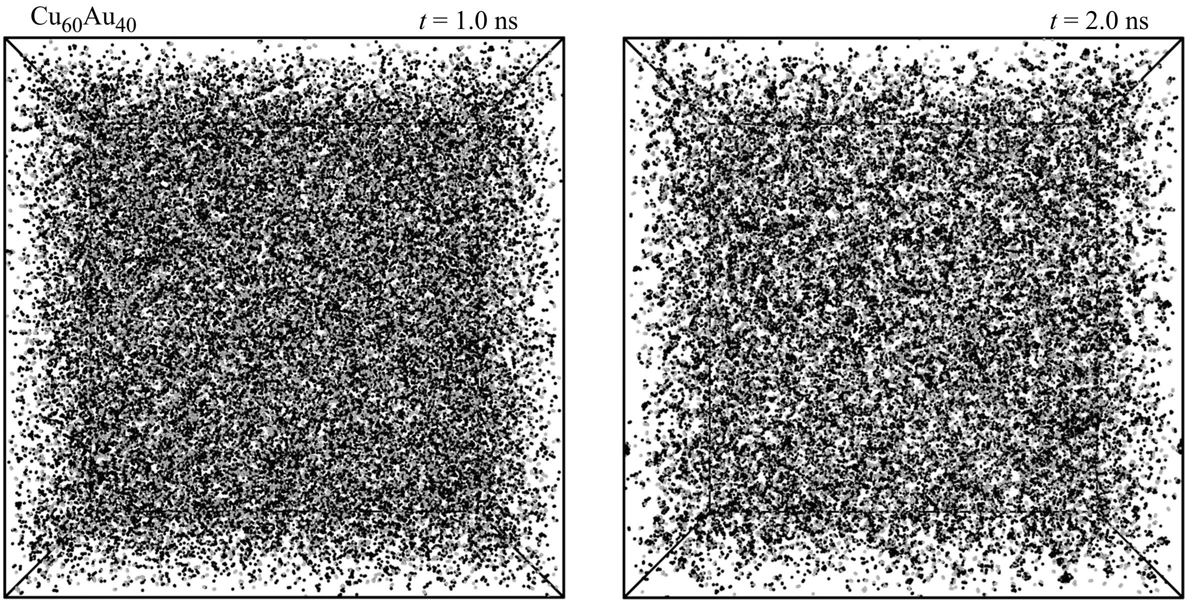

Figure 2. „Instant“ snapshots of the model system of the target composition $Cu_{60}Au_{40}$ at different times of evolution. Copper atoms are shown in black, gold atoms in gray.

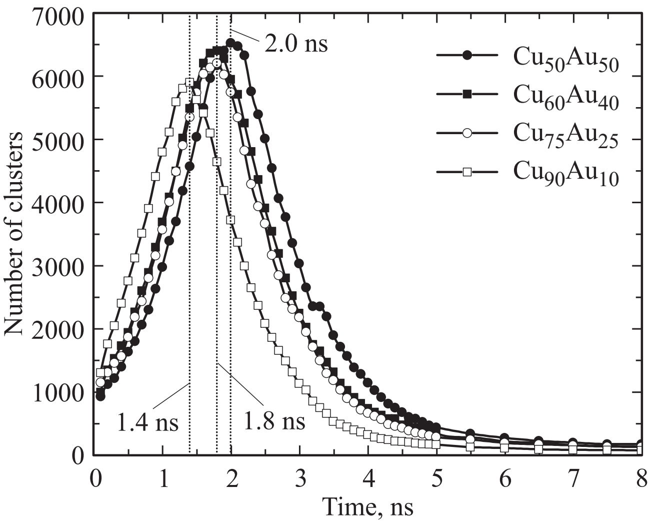

Figure 3. Dependence of the number of clusters formed on the synthesis time for different target compositions. Number of clusters t, ns.

which is the practical equalization of temperature in all four simulated target compositions (Fig. 1). As can be understood from Fig. 3, this is a consequence of the simulated systems achieving approximately the same level of binding energy release when combining atoms. An interesting feature of this graph is a fairly clear dependence of the number of clusters and the rate of their formation on the chemical composition. Namely, an increase in the percentage of gold atoms in the gas binary mixture clearly suppresses the rate of cluster formation at all the considered stages of the evolution of the binary system.

It can be seen (Fig. 3) that the fastest evolution takes place for the target composition $Cu_{90}Au_{10}$ with a minimum value of the number of gold atoms in the system. This can be seen more clearly in the „instant“ snapshots shown in Fig. 4. At the same simulation time, the $Cu_{90}Au_{10}$ system shows a much more advanced stage of nanoparticle formation. With such a chemical composition, the number of formed particles is about 70% less than for the case of $Cu_{50}Au_{50}$, which makes them significantly larger in size. This leads to a rather unexpected conclusion that at the initial stages of synthesis, the formation of a pair Au-Au, Au-Cu or Cu-Cu it is not equally probable and pairs of Cu-Cu are formed the fastest.

In our opinion, the result obtained is a consequence of the fact that the volume binding energy of the chemical elements and their compounds chosen by us changes in the following order: $\mathrm{Au}-3.81\,\mathrm{eV} > \mathrm{CuAu_3} - 3.75\,\mathrm{eV} > \mathrm{CuAu} - 3.74\,\mathrm{eV} > \mathrm{Cu_3Au} - 3.64\,\mathrm{eV} > \mathrm{Cu} - 3.49\,\mathrm{eV}$ [24]. That is, as mentioned above, during the formation of one Au dimer, 0.32 eV of energy is additionally released in relation to the formation of the Cu dimer, which leads to the increased temperature increase observed by us in the model system with an increased content of gold atoms.

Thus, at the simulation time $t \leq 2.0$ ns in the model binary gas system, we recorded an autocorrective feedback between the type of chemical element and the rate of formation of initial nanoclusters of the corresponding composition. Thus, the formation of a Au-Au pair leads to an increased release of binding energy, which, in turn, leads to a greater increase in temperature in the synthesis chamber. A high temperature increases the kinetic energy of the atoms of the Au-Au pair, which leads to its decay. In this case, the Au-Cu or Cu-Cu pairs of energy are released less,

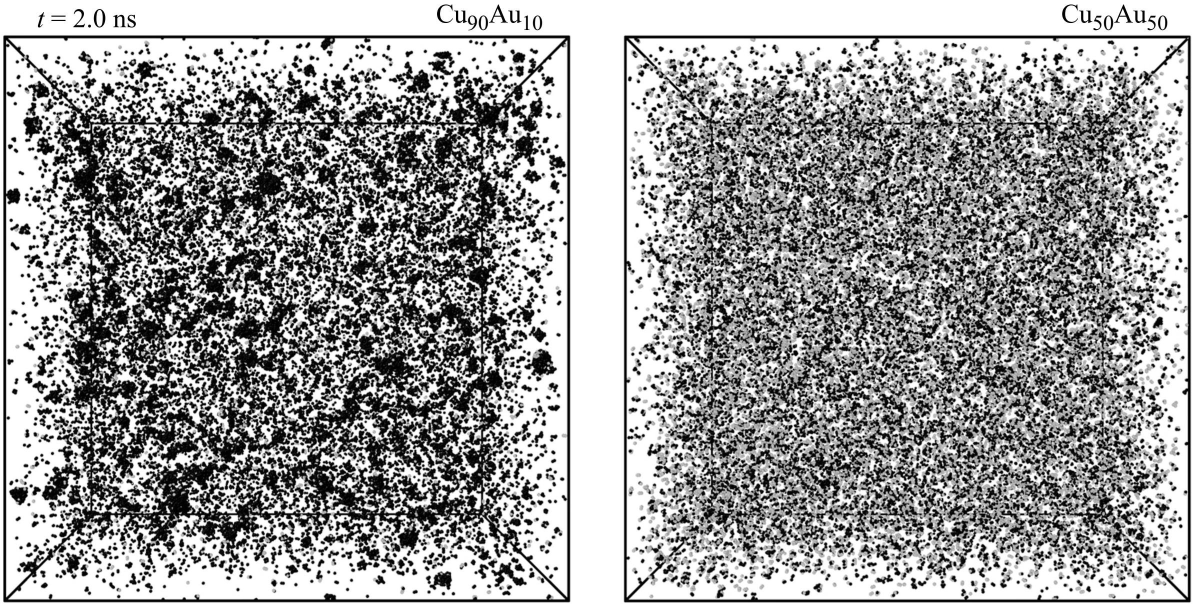

Figure 4. „Instant“ snapshots of the model system of the target composition at different times of evolution $t = 2.0$ ns. Copper atoms are shown in black, gold atoms in gray.

the temperature does not grow as fast and the probability of saving the Au-Cu or Cu-Cu pair increases accordingly. This feedback will be observed until the transport gas removes excess energy from the system and the temperature at different target compositions takes approximately the same value. In our case, this happens at $t = 2.0$ ns (Fig. 1).

Further, we can distinguish the third main stage of the development of binary nanoparticles synthesized from the gas medium CuAu. This stage occurs approximately by the time $t = 3.0$ ns, when the temperature in the model systems decreases to a value at which thermal energy is no longer sufficient to separate cluster fragments into individual atoms and they begin to combine with each other, forming full-fledged binary particles. A characteristic feature of such clusters is their loose structure with the presence of a diverse external shape. That is, at this stage, clusters are not yet subject to thermal relaxation processes that lead to optimization of the internal and external structure.

We begin to fix such optimization only at the time $t = 4.0$ ns and the temperature of the systems is approximately $2200-2400$ K (the fourth stage of primary evolution). It is clearly noticeable here that the shapeless cluster „lumps “ begin to turn into rather spherical formations located in a cloud of individual atoms and cluster fragments. Further, these fragments are absorbed by the cluster surface, which leads to even greater sphericity of the resulting particles. At the fifth, final stage of the initial evolution of the model system ($t = 6.0$ ns), the final transformation of the forming primary nanoparticles occurs, consisting in the almost complete disappearance of the initial atomic atmosphere with the formation of spherical binary nanoparticles, the characteristic feature of which is the displacement of gold atoms to the surface (Fig. 5).

This fact is not unexpected, since in a number of our earlier works it was already noticed that the initially homogeneous chemical composition of CuAu particles corresponding to the structure $L1_2$ begins to change due to the process of displacement of Au atoms into the surface layer [26–28], and the speed of the segregation process is expected increases with temperature, which is confirmed experimentally by [29]. It is generally assumed that surface segregation depends on the interaction between atomic radii, coupling energy, surface energy and electronegativity of core and shell materials.

As a rule, it can be expected that metals with a smaller atomic radius and greater surface energy will tend to occupy the core region. At high temperatures, Au atoms begin to diffuse to the surface of the nanoparticle CuAu due to lower surface energy and Au cohesion energy. Consequently, it can be concluded that the processes of atomic mixing and separation are determined by many factors. These are minimization of surface energy, reduction of internal stresses, the efficiency of atomic packaging and the presence of a certain structure, which can make energetically advantageous Au-Au or Au-Cu interactions, in relation to the creation of a pair Cu-Cu.

Thus, at the fifth stage of the initial evolution, a situation of greater stability is already observed for macroscopic bodies, namely pairs Au-Au or Au-Cu, which is the opposite for earlier stages of the formation of binary nanoclusters CuAu. This circumstance allows us to assume that at this point the primary stage of synthesis is completed and then the creation of nanoparticles takes place according to the usual laws, mainly characteristic of three-dimensional objects.

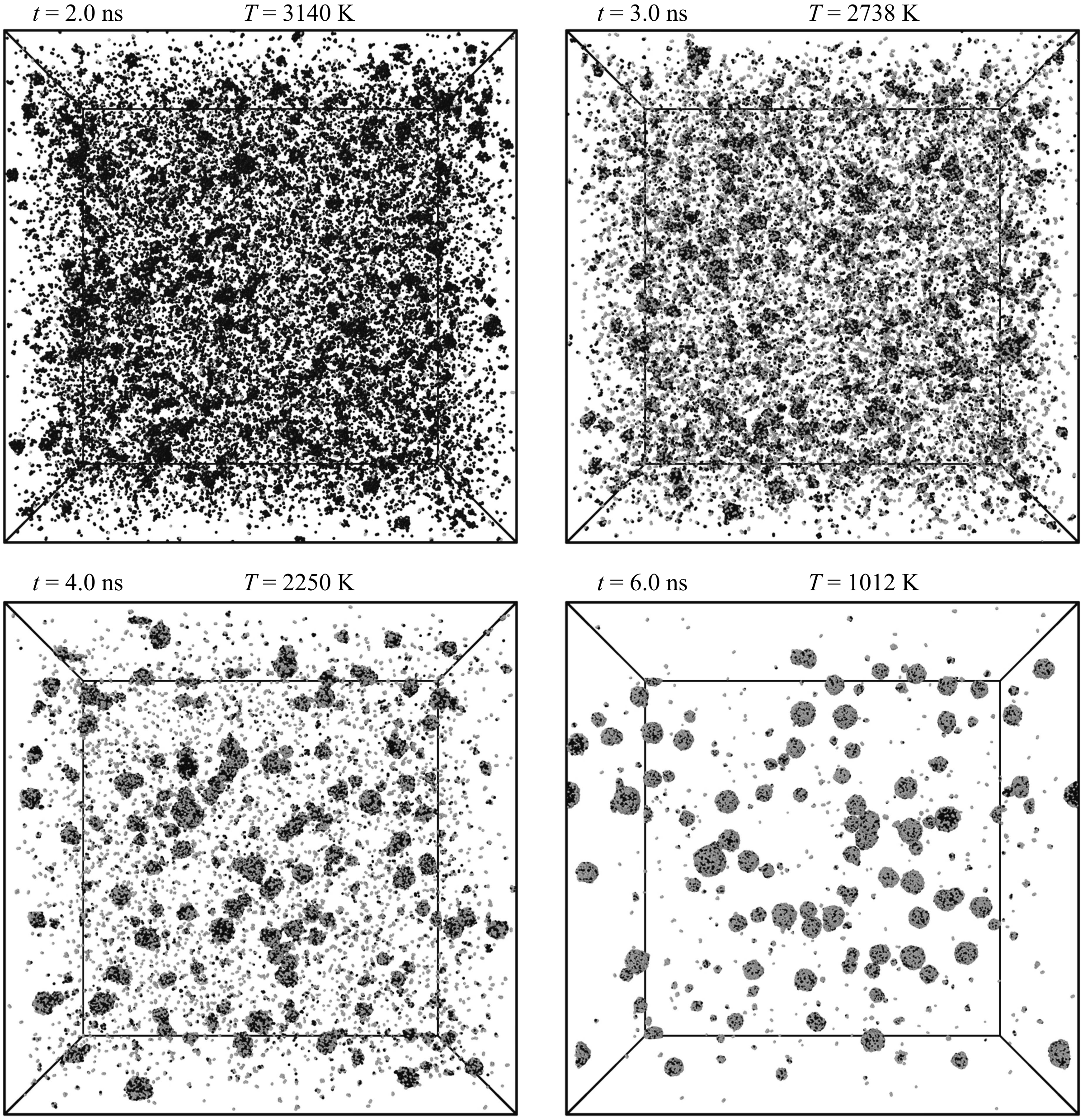

Figure 5. Time evolution of the simulated binary system $Cu_{50}Au_{50}$ (black shows Cu atoms, gray — Au).

4. Conclusion

Despite the progress made in recent years in the synthesis of nanomaterial from a gaseous medium, provided by both empirical methods and theoretical research methods, a wide range of issues of this problem still needs to be studied in the future. And here special attention should be paid to the processes occurring at the initial stage, that is, in the high-temperature phase. To understand this requires, first of all, the presence of a large set of thermodynamic and kinetic data, which can not always be presented experimentally, because of what great hopes are pinned on computer simulation.

Although many of the results already obtained by science can be transferred from the burning theory, this synthesis technique still has a significant gap in understanding the very initial stage of particle formation (nucleation), cluster growth processes and the possible strong influence of heterogeneous reactions involved in this process, observed, for example, in the synthesis of binary systems.

However, gas-phase synthesis has a number of very important advantages in relation to other methods. So one of the promising aspects may be the direct, single-stage formation of complex materials, where it is theoretically possible to achieve the required chemical composition, the necessary crystal structure and appearance. But all this requires the most thorough study of all the features of the behavior of small cluster fragments, the processes of their unification and the possible restructuring of the internal and external structure.

Therefore, in the presented work, a number of aspects of such gas-phase synthesis with respect to the binary system Cu-Au of various target composition were analyzed by the method of MD computer simulation at the earliest stage of the formation of such nanoclusters. Five possible general stages of the development of such model systems were identified, typical features were analyzed and conclusions were drawn about the reasons for their appearance in connection with the amount of thermal energy available in the synthesis chamber.

Funding

The study was carried out at the expense of a grant from the Russian Science Foundation No. 22-29-20018, https://rscf.ru/project/22-29-20018 / with the parity financial support of the Government of the Republic of Khakassia.

Conflict of interest

The authors declare that they have no conflict of interest.

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