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Analysis of internal structure management methods for binary nanoparticles Ag-Cu

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Binary nanoparticles of a copper and silver alloy are of great practical interest due to the possibility of fine-tuning their physicochemical properties by changing the composition, size, shape and structure of the nanoparticles. In the presented work, the processes of formation of the internal structure of Ag-Cu nanoparticles with a diameter of 2.0–8.0 nm during their crystallization were studied using the molecular dynamics method. The features of this process were found depending on the target chemical composition of nanoparticles, their size and the intensity of thermal energy removal. Based on the analysis of available experimental data and the results of computer modeling, it was concluded that it is possible to control the internal structure and shape of Ag-Cu nanoparticles. In particular, it was shown that as a result of crystallization of binary Ag-Cu nanoparticles from a melt, metastable states that are quite stable at room temperature are captured.

Keywords: binary alloys, copper, silver, nanoparticles, structure, molecular dynamics, tight-binding.

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1. Introduction

Due to their quite unusual catalytic, optical, magnetic, electric and mechanical properties, bimetal nanoparticles (NP) start playing a very important role in various modern technological applications [1]. Particularly actively, they are applied in catalysis, and in some cases it is the bimetal nanoparticles that have much high activity in comparison with the macroparticles of a usual alloy [2].

In addition to the higher catalytic activity, the binary NPs have a wide spectrum and other interesting peculiarities [3]. Addition of the second metal into the nanoparticle results in substantial change of its physical and chemical properties, which is often manifested in the change of its internal structure, too. At the same time, the nanoalloys can have a more variable spectrum of the external structure as well, including irregular morphology (triangular, hexagonal, quasi-elongated plates, etc.) [4].

Moreover, the nanoalloys can have a large variety of segregation models (of chemical ordering), which can be mixed or phase-separated ones. Distinguishing the nanoparticles with the maximum possible phase separation shows „core-shell“ structures, wherein the core of one atomic sort is covered by the shell of the second kind, and Janus-type structures, wherein metals are separated in two halves of the nanoparticle. The models of segregation of the real systems can have intermediate features between these extreme types.

It is especially important to have fine tunability of the properties of such particles by purposefully changing

not only their size or shape, but their target chemical composition as well. We also note that the structure of these nanoparticles is one of the important characteristics, which define their physical and chemical properties.

Of the entire plurality of chemical compounds, which are presently used in nanotechnologies, we focus our attention only on the Ag-Cu nanoalloy, which is one of the widely studied binary systems. Thus, it has been experimentally shown that the Ag-Cu nanoparticles were better catalyzers for oxygen reduction reactions [5] than respective pure nanoparticles. The Ag-Cu nanoparticles are also used as low-melting solders [6], plasmon particles, etc.

Recent experiments and calculations [3] have shown that in the Ag-Cu nanoparticle the chemical ordering largely depends on the target composition. For the compositions with a high content of Ag atoms, it is a preferable option to have the core-shell structure with a shifted center. In this sample, the Cu core is asymmetrically located in the nanoparticle, which is covered by a very thin Ag layer on one side, which is often called the quasi-Janus morphology. The Janus and quasi-Janus morphology are common for the various binary metal systems. But, icosahedral clusters of the Ag alloys are predictably excluded from this behaviour due to special nature of interatomic interaction forces. Moreover, some studies have demonstrated that the Ag-Cu nanoparticles observed during gas-phase synthesis were exactly various non-crystal structures, which belonged to the icosahedral type with the chemical ordering of the „core-shell“ type [7].

Besides, the nanoparticles of the Ag-Cu binary alloy are often observed as well as in an implicit metastable state [8,9], which is characterized by a totally different internal structure in relation to the optimized structures with a minimum energy value. This state is characterized by its thermal stability, which results in the fact that the metastable Ag-Cu nanoparticles could be observed for a long time in the wide range of the temperatures.

It is decisively important to understand and control the metastability conditions in the nanoscale systems for developing technological application of these materials. Actually, the nanoparticles are very often produced in largely non-equilibrium conditions, which is especially typical for physical techniques of the synthesis. It results in formation of the kinetically captured metastable structures as a final result of the synthesis process [10,11], which was experimentally observed both for the pure metals (Ag, Au, Fe [12–15]), and for some binary metal nanoparticles [16–21].

However, it can be assumed that over time the metastable structures will develop towards thermodynamic equilibrium, so their properties including structural ones can change. That is why determination of the technological conditions for obtaining the metastable configurations of the nanoparticles is of great practical importance, but there is almost no experimental studies of these problems.

In terms of computer simulation of the Ag-Cu nanosystem, this problem has been solved by means of the Monte Carlo techniques [22] and molecular dynamics (MD) [8–10]. The simulation [22] has studied full evolution of a cuboctahedral form from an initial chemically-unordered configuration to equilibrium chemical ordering of Cu@Ag. The MD simulation [8–10] has been done only for strictly defined chemical compositions and sizes, which is still an insufficient technological basis for identifying ways of creating the metastable configurations.

Thus, the binary particles of the copper and silver alloy are of great practical interest due to fine tunability of their physical and chemical properties via changing the composition, size, shape and structure of the nanoparticles. So, the present study was aimed at investigating the processes of formation of the internal structure of the AgCu-alloy nanoparticles using the computer simulation methods, depending on the target chemical composition, size and intensity of thermal impact.

2. Simulation system

The experimental determination of many substance properties in the nanometer range can be often aided by the computer simulation, which plays a key role in detailed description of the characteristics of these systems. Indeed, such simulation has a lot of advantages. First of all, it can study the nanoparticle on the atomic level and on the very short time scales, which is not always possible when conducting the real experiments. Besides, the available

experimental techniques are clearly insufficient for understanding the peculiarities of atomic motion mechanisms, which determine the resultant properties of the clusters, especially, the structural ones. In this regard, the computer analysis of the processes in the nanoparticles is very useful, since it can provide information to deeply understand these mechanisms [9].

We think that the most adequate technique for studying the above-described processes can be a molecular-dynamic approach, which is based on calculation of the classic (Newton) trajectories of object motion in the phase space of the coordinates and pulses of its atoms. This method can quite accurately determine the structural and thermodynamic properties of the clusters as well as trace the dynamics of nanoparticle atoms with change of the various external factors, such as the temperature, pressure, etc.

The MD simulation is also advantageous in creating the completely physical trajectories of atoms instead of somewhat artificial dynamics of the Monte Carlo schemes [10]. Moreover, such simulation covers the quite long time scales, since most models of our paper have duration of dozens of nanoseconds. This time scale is enough for studying the processes of origin of the significant structural changes in the nanoparticles of the size studied by us, when they are solidified from a melt, and completion of the structural evolution at room temperatures.

In order to simulate the thermal impact on the Ag-Cu nanoparticles by the method of molecular dynamics, we have used the MDNTP software designed by Dr. Ralf Meyer, University Duisburg Germany. The interatomic interaction forces have been calculated using the strong-binding potential TB-SMA based on the parameters, which are calculated in [23]. This potential is selected based on an assumption that the big group of the properties of the transition metals and the alloys thereof can be fully determined from the density of states of the external d — electrons

The ongoing processes were analyzed in a computer in the microcanonical NVE-ensemble. The temperature was determined by the average kinetic energy of atoms, which was calculated based on the speed Verlet algorithm with a time step $h = 1$ fs. The initial objects were selected to be spherical clusters produced by cutting out of the ideal Ag crystal lattice, wherein a part of the silver atoms was randomly substituted with copper atoms in a target percent ratio, which was of interest for us.

The first interval included smooth heating of the simulated systems to 1200 K and holding thereof for 1.0 ns for full disappearance of residues of the crystal structure. The upper limit of 1200 K is enough for melting the modelled particles as the melting temperature for the Ag clusters significantly reduces with decrease in the particle size in comparison with the bulk material ($T_{\text{melt}} = 1235.1$ K).

Then, based on the Andersen thermostat, the procedure of smooth cooling of the Ag-Cu nanoparticles was performed to the room temperature at three various rates of thermal energy removal. Possible structural transitions

occurring thereat were determined by means of a radial distribution function and a plot of temperature change of potential energy. The most stable cluster structure was determined by taking an ensemble of the same-size nanoparticles. Then, the visualizers OVITO and xmakemol were used for finding the real appearance and structure of the nanoparticles under study.

3. Results and discussion

The crystallization processes are of primary importance in many techniques of synthesis of materials, which are often prepared initially at a high temperature in the liquid phase, and then cooled to achieve operating temperatures, which is especially typical for obtaining nanoscale objects via the physical techniques. However, despite the importance thereof, the crystallization processes are insufficiently studied at the nanolevel. In particular, very little is known about crystallization of the binary metal nanoparticles. In addition to the thermodynamic factors, the kind of chemical ordering can be strongly affected by conditions of a cooling process, i.e. kinetic peculiarities of the system behavior. So, it is even more important to study crystallization of the binary particles than in the nanoparticles of the pure metals.

It is extremely difficult to determine ways of nanoscale crystallization on the experimental level due to small time scales of the ongoing processes and, as a rule, high temperatures. For this reason, the data of computer simulation can be very useful, since it is this simulation that can reproduce the respective mechanisms on the atomic level [8].

Now, let us move to an issue of determining the internal structure of the Ag-Cu nanoparticles obtained in our MD simulation. The analysis was performed on the selected Ag-Cu nanoparticles of the diameter of $2.0 \leq D \leq 8.0$ nm with the percent content of the copper atoms therein within 10–50%. As the technique of vacuum and thermal formation of the Ag-Cu nanoparticles was simulated [24,25], the primary nanoparticles were in a melted (amorphous) state with the maximum possible spherical form available. Then, these primary nanoparticles were subjected to the procedure of cooling to the room temperature with a various pace of thermal energy removal as corresponding to the cooling time $\tau = 0.5; 1.5$ and 2.5 ns.

The analysis has been conducted to show that regardless of the percent content of the copper atoms (10–50%) in the binary Ag-Cu particles and their size ($2.0 \leq D \leq 8.0$ nm), the two highest rates of cooling ($\tau = 0.5$ and 1.5 ns) always had the nanoparticles recorded with the disordered structure only (Figure 1).

In case of more detailed consideration of the nanoparticles at the various stages of thermal evolution, we can notice expected separation of the chemical elements (segregation) according to a core-shell scenario. However, it is this binary alloy that is characterized by incompleteness of such a process. Indeed, the Ag atoms were pressed out of the

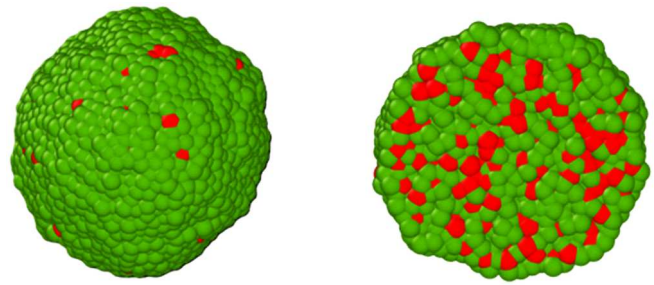


Figure 1. Nanoparticle of the $\text{Ag}_{70}\text{Cu}_{30}$ alloy of the diameter of $D = 6.0$ nm, as obtained by cooling from the melt to the room temperature for the time $\tau = 0.5$ ns. The silver atoms are shown in green, so are the copper atoms in red. Amorphous structure. The nanoparticle is shown in section on the right side.

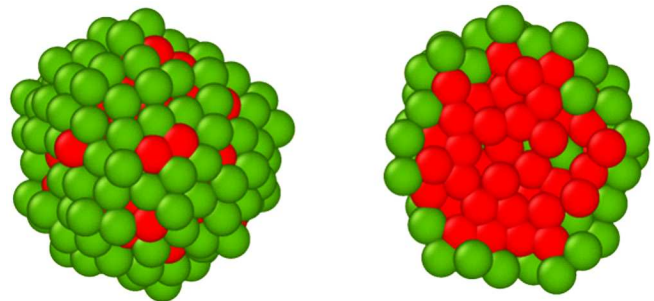


Figure 2. Nanoparticle of the $\text{Ag}_{50}\text{Cu}_{50}$ alloy of the diameter of $D = 2.0$ nm, as obtained by cooling from the melt to the room temperature for the time $\tau = 1.5$ ns. The silver atoms are shown in green, so are the copper atoms in red. Amorphous structure. The nanoparticle is shown in section on the right side.

center of the Ag-Cu particle, predominantly to its surface, but an evident core of the Ag-Cu nanoparticle was not still observed (Figure 1). Instead, the central part of the Ag-Cu nanoparticle had a mixture of atoms of the various sort within the quite wide volume.

Probably, if subjecting these nanoparticles to the high-thermal annealing procedure at the temperatures about $T = 800\text{--}1000$ K during several dozens of minutes, then intense diffusion processes will make it possible to obtain the binary Ag-Cu nanoparticles with a much more shaped core-shell structure. Thus, we can have technological controllability of the internal structure depending on whether it is necessary to create a particular kind of the structure of the Ag-Cu nanoparticles.

However, this theoretical assumption can not be proved by the methods of the computer MD simulation performed by us, which is limited by a nanosecond range of the real time and requires additional experimental investigation. Our hypothesis can be confirmed by data on the smallest of the nanoparticles studied by us ($D = 2.0$ nm) with the target composition $\text{Ag}_{50}\text{Cu}_{50}$. Only in this limit case, we could obtain the expressed core-shell structure (Figure 2).

But even this behavior was found only in 20% of the computer simulations performed and only at $\tau = 1.5$ ns. At $\tau = 0.5$ ns, no copper core was observed in the Ag-Cu nanoparticle. In case of cooling from the melt the nanoparticles of the diameter of $D = 2.0$ nm with the same target composition $\text{Ag}_{50}\text{Cu}_{50}$ for $\tau = 2.5$ ns, the percent of appearance of the core-shell structure was increased 30%, thereby indicating correctness of the proposed assumption.

Thus, it can be concluded that at the high cooling rates ($\tau = 0.5$ and 1.5 ns) crystallization of the Ag-Cu nanoparticles of the diameter of $2.0 \leq D \leq 8.0$ nm and with the copper atoms content of at most 50% therein almost in all the cases results in capture of evident metastable states, which apparently can exist for quite long time.

Below, we comparatively analyze the data of our computer simulation with the results available in other studies. Thus, [3] has demonstrated that in the simulated Ag-Cu nanoparticles with the total number of 100–300 atoms, for the compositions with the big Ag content it is a preferable option to have the core-shell structure with possible availability of the icosahedral structure. We note that this structure has been obtained by the authors of [3] under the condition of thermodynamic equilibrium (the minimum value of the cluster energy), i.e. in quite idealized conditions, which may be absent in the real NP crystallization.

The results of [3] seem to be quite clear to us. Indeed, with such sizes of the binary nanoparticles, the effect of pressing larger atoms out to the surface in the course of the temperature-induced diffusion was an expected one. We recorded it in the Au-Cu-alloy nanoparticles [26]. Thus, [26] has found that heating of the Au-Cu nanoclusters induced typical changes of its structures, which resulted in the atoms starting gradually escaping the crystal lattice sites $L1_2$ and occupying energetically more favorable positions, which is called the „order-disorder“ transition.

However, we have demonstrated in [26] that with further increase in the temperature the initially homogeneous chemical composition of the Au-Cu nanoparticles started changing due to the process of pressing the Au atoms out to the surface layer, while the segregation process rate increases with the temperature. So, after the thermal relaxation procedure the Cu-Au cluster was actually a particle with the copper center and the surface enriched with the gold atoms.

If all these processes are conditioned by a small size of the nanocluster ($N < 300$ atoms), then the icosahedral structure can be formed, wherein it can have the surface energy minimum in comparison with other polytype modifications. It can be also noted here that availability of the atoms with substantial difference in the effective interaction diameter in one nanocluster can significantly facilitate the processes of diffusion reconstruction of the nanoparticle structure, thereby making it possible to result in formation of the icosahedral phase.

Indeed, the binary Ag-Cu alloy is characterized by very weak mixability in the bulk state and lattice mismatch

above 10%, wherein the element with a larger atomic size (Ag) also has a lower surface energy. These peculiarities are a driving force of phase separation in the Ag-Cu nanoparticles, thereby resulting in surface Ag segregation and, finally, formation of Cu@Ag [10]. These structures will be in equilibrium, if the nanoparticle composition is quite enriched with a shell element to fully cover the core. However, the experiments have exhibited other types of the structures, such as structures with mixed chemical ordering, with inverted „core-shell“ arrangement or a multi-shell structure. These structures are probably outside the equilibrium [27], and, really, it has been clearly shown that the mixed structures were often metastable during experimental annealing [10], which had been confirmed by our MD-simulation analysis, as well.

Below we consider the data, which we have received by reducing the rate of thermal energy removal (the cooling time $\tau = 2.5$ ns). In this case, a number of interesting peculiarities was found, but only under a condition of minimum alloying of the silver nanoparticles with the copper atoms ($\approx 10\%$). In other target compositions with the higher percent content of the copper atoms ($\geq 20\%$), the external and internal appearance of the Ag-Cu nanoparticles fully complied with the above-considered cases of the higher crystallization rate. I.e., at the room temperature $T = 300$ K, the final interval of this process has exhibited the binary nanoparticles of an approximately spherical form in the amorphous structural state without the completed core-shell structure.

Before passing to our results, we provide the data of [28]. Thus, for the larger Ag-Cu nanoparticles ($D = 3-5$ nm), using the computer simulation methods of [28], too, it has been found that the very low alloying levels could cause sharp restructuring of the metal nanoparticles. I.e., the introduction of the impurities with a small atomic radius into the matrix of the larger atoms causes a structural transition from the FCC crystallites to the icosahedrons. Stabilization of the unexpectedly sized icosahedrons means that the probability of presence of such a five-part structure can be significantly increased in the nanoalloys in comparison with the single-metal nanoparticles. The data of [28] have been also obtained under the condition of the minimum energy of the binary nanoparticle.

Experimentally, this fact was already noticed in 1984 by the future Nobel Prize winner Daniel Shechtman when studying the Al alloy with 10–14 at.% Mn, Fe or Cr [29]. He found that under the condition of very fast cooling, even in quite big samples of the size up to $2\mu\text{m}$, it is possible to form the clearly expressed five-part structure shaped as the icosahedron.

The stabilization of the Ih-phase can be explained by alloying the elements of a different atom size, since this mismatch can compensate for deformation in the icosahedral shells, which is available due to an increasing difference between the atomic distances along the radial and tangential directions.

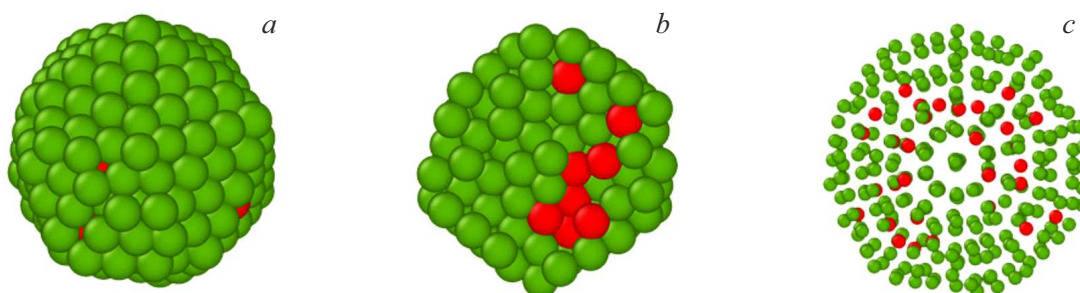


Figure 3. Nanoparticle of the $\text{Ag}_{90}\text{Cu}_{10}$ alloy of the diameter of $D = 2.0$ nm, as obtained by cooling from the melt to the room temperature for the time $\tau = 2.5$ ns. Icosahedral structure. The silver atoms are shown in green, so are the copper atoms in red. *a* — the general view of the nanoparticle; *b* — the nanoparticle in section; *c* — the nanoparticle atoms are shown in flat projection and with a reduced size.

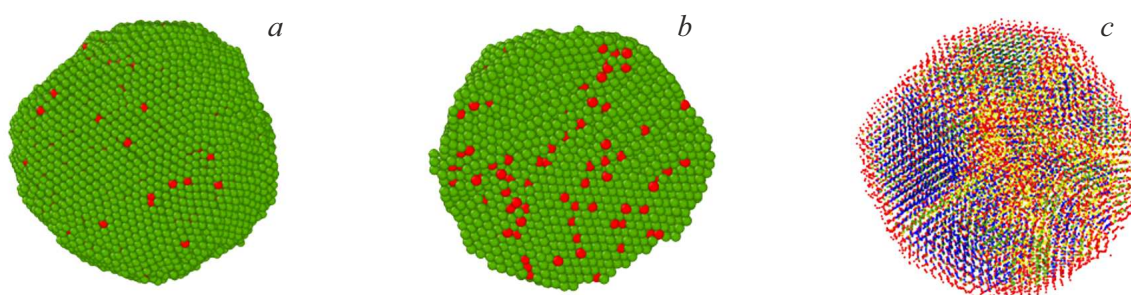


Figure 4. Nanoparticle of the $\text{Ag}_{90}\text{Cu}_{10}$ alloy of the diameter of $D = 8.0$ nm, as obtained by cooling from the melt to the room temperature for the time $\tau = 2.5$ ns. The silver atoms are shown in green, so are the copper atoms in red. *a* — the general view of the nanoparticle; *b* — the nanoparticle in section; *c* — the nanoparticle atoms are shown in flat projection with a reduced sized based on the standard CNA technique (common neighbors analyze).

Thus, in terms of the theory, the ideal Ih-cluster of the binary Ag-Cu alloy must have an enriched copper core and a surface with predominant arrangement of the silver atoms. It agrees with the fact that the icosahedron core is compressed, which makes it energetically more favorable for smaller atoms to be arranged therein. Consequently, the Ih surface of the nanoparticle is stretched, so that it is impractical for the small atoms to be arranged therein.

Another important issue may be a specified pace of the thermal energy removal. Our earlier studies of the crystallization processes for the nanoclusters of the pure chemical elements (Cu, Ni) have found that with the different cooling rate it exhibited predominant formation of either the FCC structure or the icosahedral structure [30–32]. I.e., the kinetic factors can play a decisive role in determining an atom arrangement's order resulting from the crystallization process, which can result in capturing the stable metastable states, too.

The similar results were also detected in our MD experiments, with a clearly expressed size effect. Thus, for the ensemble of the Ag-Cu nanoparticles of the diameter of $D = 2.0$ nm, about 30% of the nanoparticles really had an icosahedral structure (Figure 3).

The other nanoparticles ($\approx 70\%$) have been found to have a disordered structure. With increase in the nanoparti-

cle diameter to 4.0 nm, there was significant reduction of the nanoparticles in the amorphous or quasi-amorphous state ($\approx 40\%$). Of the nanoparticles, which had any clearly expressed crystal structure, about 30% had the five-part symmetry (Ih, Dh), while the other ones had the FCC structure, which is typical for the very fast cooled macroscopic samples of the Ag-Cu alloy. With $D = 6.0$ nm, no Ag-Cu nanoparticle in the amorphous state was detected. I.e., all our simulated nanoparticles of the given size and target composition under such crystallization conditions (the cooling time $\tau = 2.5$ ns) already had enough time for reconstruction towards formation of either the icosahedral modification ($\approx 20\%$), or towards the FCC phase. In the last studied ensemble of the binary Ag-Cu nanoparticles of the diameter of $D = 8.0$ nm, all the nanoparticles of the last simulation stage ($T = 300$ K) had predominantly the FCC structure (Figure 4 shows it in blue), although with presence of quite big amorphous areas (Figure 4 highlights them in yellow).

Thus, based on the performed computer simulation of the process of crystallization of the Ag-Cu nanoparticles with the several different paces of the thermal energy removal, it can be concluded as follows. During the processes of the physical synthesis of the Ag-Cu nanoparticles, for example, when creating SERS substrates [24,25] or when

producing the nanoparticles from the high-temperature gas medium [33,34], the real internal structure of such binary nanoparticles is radically different from the structure of the Ag-Cu nanoparticles obtained in the conditions of thermodynamic equilibrium, i.e. based on analyzing the structures with the least possible energy value.

Consequently, as a result of crystallization of the binary Ag-Cu nanoparticles, due to intense kinetic phenomena, the metastable states, which are quite stable at the room temperature, are captured. However, at the low levels of copper alloying in the Ag-Cu nanoparticles of the size up to 8.0 nm and with the slow process of crystallization, it is still possible to form the five-part symmetry of the FCC structure even in the conditions of no evident thermodynamic equilibrium. The diameter of $D = 8.0$ nm for the Ag-Cu nanoparticles is apparently a limit, starting from which there is exhibition of an effect of almost entire stabilization, which is not inherent in the eutectic Ag-Cu alloy of the polytype FCC modification.

4. Conclusion

The metallic nanomaterials are already widely used in many branches of science and technology owing to their special catalytic, magnetic, optical and mechanical properties. One of the most interesting applications thereof may be nanooptics, namely, using a phenomenon of localized surface plasmonic resonance (LSPR), which provides for freedom of technical use thereof. However, these peculiarities of behavior of the metallic nanoparticles largely depend on the form, size, internal structure, composition and chemical stability.

The binary particles of the copper and silver alloy are here of great practical interest due to LSPR tunability via changing the composition, size, form and structure of the nanoparticles. Using the methods of MD simulation, the present study has investigated the processes of formation of the internal structure of the Ag-Cu-alloy nanoparticles depending on the target chemical composition, size and intensity of thermal impact.

Based on the results of computer analysis, it has been found that in most cases, regardless of the target chemical composition, the simulated Ag-Cu particles of the diameter of up to 8.0 nm, inclusive, demonstrated at the final stage of thermal evolution the amorphous structure with quite wide distribution of the Cu atoms inside the central area of the binary nanoparticle and with partially pressing the Ag atoms out predominantly to its surface. We note that such pressing of the Ag atoms out to the surface promotes protection of the Cu atoms against atmospheric oxidation, thereby resulting in preservation of plasmon effects.

Besides, it has been simulated to find that at the low levels of copper alloying the Ag-Cu nanoparticles can still form the five-part symmetry, and record the conditions of origin of this effect. It has been also determined that $D = 8.0$ nm for the Ag-Cu nanoparticle is apparently a size limit, starting

from which there is exhibition of the macroscopic effect of stabilization of the FCC structure of the eutectic alloy under the condition of very fast quenching of the sample.

Thus, based on the results of analysis of the available experimental data and the data of the performed computer simulation, it has been concluded the internal structure and the form of the Ag-Cu nanoparticles could be controlled depending on technical necessity for creating a particular kind of the structure.

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References

- [1] R. Ferrando, A. Fortunelli, G. Rossi. *Phys. Rev. B* **72**, 085449 (2005).
- [2] Zh. Lia, X. Yanga, Ch. Liua, J. Wanga, G. Li. *Prog. Nature Sci.: Mater. Int.* **26**, 477 (2016).
- [3] D. Bochicchio, R. Ferrando, E. Panizon, G. Rossi. *J. Phys.: Condens. Matter* **28**, 064005 (2016).
- [4] M. Khan, Kh. Al-hamoud, Z. Liaqat, M.R. Shaik, S.F. Adil, M. Kuniyil, H.Z. Alkhathlan, A. Al-Warthan, M. Rafiq H. Siddiqui, M. Mondeshki, W. Tremel, M. Khan, M.N. Tahir. *Nanomaterials* **10**, 1885 (2020).
- [5] K. Shin, D.H. Kim, S.C. Yeo, H.M. Lee. *Catal. Today* **185**, 94 (2012).
- [6] S.J. Kim, E.A. Stach, C.A. Handwerker. *Appl. Phys. Lett.* **96**, 144101 (2010).
- [7] E. Panizon, D. Bochicchio, G. Rossi, R. Ferrando. *Chem. Mater* **26**, 3354 (2014).
- [8] D. Nelli, El Yakout El Koraychy, M. Cerbelaud, B. Crespin, A. Videcoq, A. Giacomello, R. Ferrando. *ACS Nano* **17**, 587 (2023).
- [9] D. Rapetti, C. Roncaglia, R. Ferrando. *Adv. Theory Simul.* **6**, 2300268 (2023).
- [10] D. Nelli, R. Ferrando. *Nanoscale* **11**, 13040 (2019).
- [11] I.K. Razumov, Yu.N. Gornostyrev. *FTT* **61**, 2462 (2019). (in Russian).
- [12] D.M. Wells, G. Rossi, R. Ferrando, R.E. Palmer. *Nanoscale* **7**, 6498 (2015).
- [13] Y. Xia, X. Xia, H.-C. Peng. *J. Am. Chem. Soc.* **137**, 7947 (2015).
- [14] J. Zhao, E. Baibuz, J. Vernieres, P. Grammatikopoulos, V. Jansson, M. Nagel, S. Steinhauer, M. Sowwan, A. Kuronen, K. Nordlund, F. Djurabekova. *ACS Nano* **10**, 4684 (2016).
- [15] D.M. Foster, R. Ferrando, R.E. Palmer. *Nature. Commun.* **9**, 1323 (2018).
- [16] T. Wen, K.M. Krishnan. *J. Phys. Chem. C* **114**, 14838 (2010).
- [17] P. Andreazza, C. Mottet, C. Andreazza-Vignolle, J. Penuelas, H. Tolentino, M.D. Santis, R. Felici, N. Bouet. *Phys. Rev. B* **82**, 155453 (2010).
- [18] S. Liu, Z. Sun, Q. Liu, L. Wu, Y. Huang, T. Yao, J. Zhang, T. Hu, M. Ge, F. Hu, Z. Xie, G. Pan, S. Wei. *ACS Nano* **8**, 1886 (2014).

- [19] V. Dupuis, A. Hillion, A. Robert, O. Loiselet, G. Khadra, P. Capiod, C. Albin, O. Boisron, D. Le Roy, L. Bardotti, F. Tournus, A. Tamion. *J. Nanopart. Res.* **20**, 128 (2018).
- [20] M. Schnedlitz, M. Lasserus, R. Meyer, D. Knez, F. Hofer, W.E. Ernst, A.W. Hauser. *Chem. Mater.* **30**, 1113 (2018).
- [21] T.-W. Liao, A. Yadav, K.-J. Hu, J. van der Tol, S. Cosentino, F. D'Acapito, R.E. Palmer, C. Lenardi, R. Ferrando, D. Grandjean, P. Lievens. *Nanoscale* **10**, 6684 (2018).
- [22] F. Berthier, A. Tadjine, B. Legrand. *Phys. Chem. Chem. Phys.* **17**, 28193 (2015).
- [23] A. Rapallo, G. Rossi, R. Ferrando, A. Fortunelli, B.C. Curley, L.D. Lloyd, R.L. Johnston. *J. Chem. Phys.* **122**, 19, 194308 (2005).
- [24] S.V. Dubkov, A.I. Savitskiy, A.Yu. Trifonov, G.S. Yeritsyan, Yu.P. Shaman, E.P. Kitsyuk, A. Tarasov, O. Shtyka, R. Ciesielski, D.G. Gromov. *Opt. Mater. X* **7**, 100055 (2020).
- [25] D.G. Gromov, S.V. Dubkov, A.I. Savitskiy, Yu.P. Shaman, A.A. Polokhin, I.A. Belogorokhov, A.Yu. Trifonov. *Appl. Surf. Sci.* **489**, 701 (2019).
- [26] Y. Gafner, S. Gafner, L. Redel, I. Zamulin. *J. Nanopart. Res.* **20**, 2, 51 (2018).
- [27] A.Yu. Stroev, O.I. Gorbatov, Yu.N. Gornostyrev, P.A. Korzhavyi. *Comput. Mater. Sci.* **218**, 111912 (2023).
- [28] E. Panizon, D. Bochicchio, G. Rossi, R. Ferrando. *Chem. Mater.* **26**, 3354 (2014).
- [29] D. Shechtman, I. Blech, D. Gratias, J.W. Cahn. *Phys. Rev. Lett.* **53**, 1951 (1984).
- [30] S.L. Gafner, Yu.Ya. Gafner. *ZhETF* **134**, 4(10), 831 (2008). (in Russian).
- [31] Yu.Ya. Gafner, S.L. Gafner, P. Entel'. *FTT* **46**, 7, 1287 (2004). (in Russian).
- [32] S.L. Gafner, L.V. Redel', Yu.Ya. Gafner. *FMM* **104**, 2, 189 (2007). (in Russian).
- [33] Y.Ya. Gafner, S.L. Gafner, D.A. Ryzhkova, A.V. Nomoev. *Beilstein J. Nanotechnology* **12**, 72 (2021).
- [34] I.V. Chepkasov, Yu.Ya. Gafner, S.L. Gafner. *J. Aerosol Sci.* **91**, 33 (2016).

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