Study of thermal stability of disordered alloy Ag_xCu_{1-x} nanoparticles by molecular dynamic simulations

V S Baidyshev, I V Chepkasov, N D Artemova

Katanov Khakas State University, Lenina Av., 90, Abakan, 655000, Russia
E-mail: bayd_vs@mail.ru

Abstract. In this paper melting processes of particles of disordered AgCu alloy in the size range of D=3-5 nm were investigated. The simulation was carried out with molecular dynamics, using the embedded atom potential. It was defined that for nanoparticles of D=3 nm, the melting process is connected with the formation of the outer layer consisting of Ag atoms as well as with the further transition of the particle into an amorphous state. The increase of the particle size to D=5 nm did not show the processes of redistributing Ag atoms on the particle surface.

1. Introduction
Bimetal nanoparticles (nanoalloys) often have unique chemical, optical and magnetic properties that may be determined by the chemical composition and a structure. As a result, the use of these particles includes the catalysis field that shows improved activity and selectivity of chemical reactions during the nanoalloy usage [1], the magnetism field where alloying effects can be used to increase magnetic crystalline anisotropy in nanostructured devices [2] and the optics where fine-tuning of localized surface plasmon resonance is possible in the spectrum of optical absorption of bimetal nanoparticles [3].

The binary system of AgCu is an example of immiscible phases in the bulk. Consequently, a phase separation will also be characteristic of AgCu nanoparticles. Two common types of chemical ordering have been revealed by the experiment and they were predicted theoretically for this system. Small AgCu nanoparticles have a core-shell structure with Ag segregation on the surface [4]. This structure contributes to the lower surface energy of Ag. According to work [5], the second type of ordering is the ordering with an explicit phase separation with the structure type of a Janus particle, which is typical of nanoparticles of more than 12 nm.

On the other hand, in work [3], AgCu bimetal nanoparticles are gained with the method of thermal deposition into the Teflon matrix; the optical properties of these particles were analyzed. So, one peak was noted for the small sizes in the absorption spectrum, which corresponds to the structure of a homogeneous solid solution. When the size of the nanoparticle was increased, a second peak was observed, which indicates the formation of the phase separated structure, presumably, of the core-shell particle. The effect of increased segregation of phases was detected after thermal annealing.

From the practical point of view, the research interest is focused on the stability of the received particles, possible structural transformations and phase segregation effects under thermal influence. However, the experimental analysis of the structures formed in AgCu nanoparticles synthesized with this method is a hard task. On the other hand, the study of the thermodynamic stability and structure of
this type of particles can be performed with the computer simulation [6-9].
Thus, the main purpose of the work was to study the thermodynamic stability of spherical nanoparticles of Ag\textsubscript{x}Cu\textsubscript{1-x} disordered alloy of various composition and size.

2. Computer simulation
The molecular dynamics method has been chosen as a method of study. The simulation of thermal effects on Ag\textsubscript{x}Cu\textsubscript{1-x} nanoparticles was carried out when using a many-body potential based on the "embedded atom method" (EAM potential) [10]. Spherical Cu clusters cut from the ideal FCC structure were considered as starting items. In these clusters, the fraction (x) of Cu atoms was randomly changed into Ag atoms to simulate in this way an unordered solid solution Ag\textsubscript{x}Cu\textsubscript{1-x}. There were considered particles of D=3-5 nm with Ag as impurities in the range of 0.1-0.9.

At the beginning of the modeling phase, all the nanoparticles were relaxed at T=300 K, heating performed with Nose-Hoover thermostat, heating velocity being equal to \(2.6 \times 10^{11} \text{K/s}\). The Verlet algorithm was used for numerical integration of the motion equations, the time interval being \(\tau=1 \text{ fs}\). The simulation was carried out with the package of the molecular-dynamic researches LAMMPS [11].

3. Results and Discussion
The AgCu system in a bulk refers to eutectic systems with partial miscibility of its components. According to [12], the eutectic temperature is 1051 K, while the eutectic concentration is 60.1 % (at.) Ag. In addition, the temperature of the crystal-fluid phase transition for this high-volume system is not a linear function of the composition. Therefore, the nanoparticles will be characterized by even more complex behaviour. In this regard, there were considered heating processes for AgCu spherical bimetal nanoparticles in a solid solution state, characterized by the random distribution of impurity atoms.

The simulation results showed that during heating a classical phase transition was observed with small particles of D=3 nm and 0-20 and 80-100 % of Ag atoms, with a typical leap of potential energy at the melting point (see Figure 1, a).

In this case, the dependence of nanoparticles melting temperatures on Ag atoms concentration is
qualitatively consistent with the phase diagram for the bulk materials of AgCu and is not linear. Particles containing the percentage of Ag atoms in the range over 30-70 % showed a completely different situation under the thermal impact. In that case, the calorimetric curves did not demonstrate an explicit leap of the potential energy corresponding to the nanoparticle melting (see Figure 1, b).

**Figure 2.** Structures of Ag$_{x}$Cu$_{1-x}$ nanoparticles with diameter D= 3 nm for different heating temperatures and fraction of Ag atoms (x): a, b, c – x=10 %; d, e, f – x= 50%; a, d – initial state, T=300 K; b, e – pre-melting state, T~Tm; c, f – liquid drop, T>Tm; Tm – melting temperature.

**Figure 3.** Structures of Ag$_{x}$Cu$_{1-x}$ nanoparticles with diameter D= 5 nm for different heating temperatures and x - fraction of Ag atoms: a, b, c – x=10 %; d, e, f – x= 40%; a, d – initial state, T=300 K; b, e – pre-melting state, T~Tm; c, f – liquid drop, T>Tm; Tm – melting temperature.

The melting process was as follows: at some temperature, there was a mass yield of Ag atoms to the nanoparticle surface to form the outer layer (see Figure 2), which led to the reduction of the surface energy of the nanoparticle and its transfer into an amorphous state.

The further heating made the particles of this size gradually transfer into a liquid state. This effect
was not observed with the size increase of nanoparticles to D=5 nm (see Figure 3). In this situation, the melting processes were classical for all the concentrations considered, with the leap of the potential energy at the phase transition point (see Figure 4).

4. Conclusion
To summarize, computer simulations were used to examine thermal influence on AgCu nanoparticle alloy of various compositions that initially are in a solid solution state and have a size of D=3-5 nm.

The heating process for small nanoparticles of D=3 nm is associated with the yield of Ag atoms to the nanoparticle surface and the formation of the outer layer. Further heating caused the particles transition into an amorphous state. The size increase of particles to D=5 nm did not show this effect, with the melting processes realized by a mechanism typical of nanoparticles.

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