Molecular dynamic simulation of melting copper-silicon nanoparticles

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Abstract. The research defines parameters of thermal stability of core-shell copper-silicon composite nanoparticles of different sizes and structures by means of molecular-dynamic calculations. The researchers found temperature points of the sudden change of the potential energy for the particles under study. Such changes are shown to be associated with the nanocomposite structure break. It was determined that the temperature rise initiates the copper atoms diffusion to the surface, which causes the reversing structure of the particle.

1. Introduction
The study of the composite nanoparticles is one of the most intensively developing areas of nanotechnology. The main reason for such a heightened interest is that if compared with conventional, single-component nanoparticles, the properties of nanocomposites strongly depend not only on the size, but also on the structure, shape and composition, which provides more possibilities to monitor physical and chemical peculiarities of their behavior and, accordingly, expands the potential application areas [1-4]. The two-component nanoparticles under study can be divided into homogeneous nanoparticles consisting of one phase (of a disordered alloy or intermetallic metal with a clear crystalline structure) and two-phase nanoparticles. Herewith, two-phase particles can have various structures, of a core-shell type or of Janus type.

Two-phase particles consisting of a nucleus and an outer thin shell are actively used as quantum dots [5], magnetic-fluorescent nanoparticles [6] and highly efficient anodes in lithium-ion batteries [7, 8] due to the peculiarities of their structure. The non-organic shell on the metal particle often contributes to significant improvement of the thermal stability of the nucleus and reliably protects its surface from oxidative-restorative reactions under hermetic coating [9]. Core-shell particles of another type are actively used as a matrix to produce hollow particles when the nucleus being removed by dissolving or firing. Such particles can be used as microvessels, adsorbents [10], light construction materials [11-12], thermal and electric insulators [13].

From the technical point of view, Cu@Si systems are very promising due to their special optical properties [1], since optically transparent silicon changes its position and intensity of the plasmon absorption band [14]. In particular, the addition of Cu/ Si composite nanoparticles increases luminescence intensity of luminous centres of ions of various lanthanides (Pr$^{3+}$, Nd$^{3+}$, Ho$^{3+}$, Er$^{3+}$) by more than an order [15]. The active use of Cu-Si compounds in chemical reactions is caused by the unique catalytic activity of Cu@SiO$_2$ nanoparticles in the hydrolytic dehydrogenation of ammonia borane (NH$_3$BH$_3$) and borane hydrozine (N$_2$H$_4$BH$_3$) under atmospheric conditions and room temperature [16].
Lately, to produce core-shell particles scientists have widely applied a gas-phase synthesis method [17], which forms two-component nanoparticles through the primary formation of the nucleus and the subsequent coating [18]. The authors of work [19] used a method based on substance evaporation with a relativistic electron beam and subsequent vapor condensation in the stream of the inert gas carrier to experimentally get Cu@Si particles. However, the investigation of the thermal stability of Cu@Si nanoparticles proved to be very challenging if obtained by experimental methods. So, the detailed analysis can be applied only to the results received after the completion of all the processes of the thermal influence, without full understanding of the physical phenomenon of the thermal evolution. From this point of view, it is the computer simulation that allows revealing the basic laws of the structural evolution of the two-component system at the atomic level, when physically substantiated interatomic potentials are used.

2. Computer simulation
In this work the simulation of the thermal influence on Cu@Si particles of various sizes was carried out with the molecular dynamics (MD) method in LAMMPS program package (Large-scale Atomic/Molecular Massively Parallel Simulator). MD method is widely used for the investigation of structural phase transitions in metals and alloys since it allows computing dynamical characteristics of simulated system [20, 21]. According to the literature, thermodynamic properties and interaction between atoms in nanoparticles can be successfully described by various many-body potentials, namely, Sutton–Chen, Cleri-Rosato and Embedded Atom Method (EAM). In this work, the authors carry out MD simulations with modified multiparticle embedded atom potential MEAM (Modified Embedded Atom Method), earlier this potential was successfully used in calculating the interfaces of Cu-Si system [22].

Molecular dynamics studies of nanoparticles that were experimentally obtained by the authors [19] (the average size of 119 nm) appear to be very challenging because even the smallest particle of D=46 nm consists of more than 4 million atoms; so the systems of such sizes are not available to calculate with the molecular dynamics method of even when using supercomputers. Accordingly, this work investigates relatively small particles of Cu@Si to find the basic regularities of the thermal impact. For this purpose there were selected particles containing from 2000 up to 8000 atoms with nucleuses of various sizes (1205, 2899, 5473 atoms of Cu) and the changing amount of atom layers of the silicon shell (from 3 to 6).

3. Results and Discussion
In Figure 1a is show potential energy of the Cu1205Si1062 particle in the heating process from T = 100 K to T = 1600 K (t = 10 ns). It is clearly seen from the graph that no significant changes in the particle occur in the temperature range T = 100-700 K, and starting from a temperature T = 700 K, a sharp change in the energy caused by the melting of the shell consisting of three atomic layers of silicon was observed. When the temperature reached T = 1000 K, the integrity of the shell was destroyed and through the resulting hole the atoms of the core (Cu) diffusion to the nanoparticle surface. This process led to the formation of a Janus-like structure, and a decrease of the potential energy. With further heating, the diffusion of Cu atoms on the surface of the nanoparticle was observed (see Figure 1b).

With an increase in the number of atomic silicon layers (from 3 to 4), the formation of a Janus-like particle was not observed. In this case, the shell is melt at a higher temperature T = 1080 K, which caused fast increase of the potential energy (see Figure 2a). A further heating led to the destruction of bonds between the atoms in core, as a result of which its melting was observed at a temperature of T = 1200 K. After the shell and the core lost the crystal structure, the liquid droplet retained the core-shell structure up to temperature T = 1400 K. With further heating, the diffusion of Cu atoms through the silicon shell was observed. However, because of the thickness of the silicon shell, even when the particle is heated to a final temperature of T = 1600 K, the copper core never fully diffusion through the shell to the surface of the Cu1205 @ Si1606 nanoparticle (see Figure 2b).
Figure 1. a - dependence of the potential energy on the temperature in heating a Cu_{1205}@Si_{1062} particle; b - structure of an amorphous Janus-particle at temperature $T = 1250$ K.

Figure 2. a - dependence of the potential energy on the temperature in heating a Cu_{1205}@Si_{1660} particle; b, c – the structure of a liquid drop.
4. Conclusion
Thus, based on the results of the computer simulation of heating Cu @ Si particles, it can be concluded that their thermal stability is only in the region of relatively small temperatures, depending on the size of a composite particle and the silicon shell thickness. At a thickness of the silicon shell of less than 4 atomic layers, the formation of Janus-like particles occurs during the heating process. With increasing thickness of the outer shell, this effect is not observed. In this case, as the temperature rises, the shell also goes into a liquid state, but retains its integrity. At a certain temperature, the diffusion of copper atoms to the surface begins, which can lead to a reversal of the structure of the particle and the formation of a particle of the Si-Cu type, apparently unattainable in the usual gas-phase synthesis.

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