SIMULATION OF THE THERMAL STABILITY AND MELTING OF THE Ag@Pd, Au@Pd BIMETALLIC NANOPARTICLES

МОДЕЛИРОВАНИЕ ТЕРМИЧЕСКОЙ СТАБИЛЬНОСТИ И ПЛАВЛЕНИЕ БИМЕТАЛЛИЧЕСКИХ НАНОЧАСТИЦ Ag@Pd, Au@Pd

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Abstract: Within the framework of the molecular dynamics methods the simulation of the temperature stability of the metallic nanoparticles with the core-shell structure was performed and the melting temperature of the sample was determined. During the simulation of the dynamic behavior of nanoparticle the calculation of forces of interatomic interactions was carried out within the embedded atom method. To simulate the melting process the temperature of the sample was gradually increased by scaling the corresponding atomic velocities using the Berendsen thermostat. The Lindemann index was used as a numerical parameter describing changes in the structure of the nanoparticle. According to the results of the study, the temperature dependences of the Lindeman index and the average potential energy were obtained, as well as the radial distribution functions for the nanoparticles. From the simulation results, atomistic configurations of the sample were built and the dynamics of changes in its structure was investigated. Spatial distribution of the atoms on Lindeman index within the volume of the sample around melting temperature was also calculated.

KEYWORDS: MOLECULAR DYNAMICS, CORE-SHELL, METALLIC NANOPARTICLE, MELTING, LINDEMMANN INDEX

1 Introduction

Bimetallic nanoparticles are given considerable attention by researchers of nanoscale systems, since they allow the design of new structures with individual properties that are not observed in monometallic and bulk materials [1–3]. Particularly in demand from theoretical and practical aspects were nanomaterials with a core@shell structure, due to the wide range of applications in optoelectronics, semiconductors, quantum dots, biological marking, and nanocatalysis [4–6].

Among the objects of nanosystems are different types of forms and structures [1]. It is known that by changing the type and parameters of a shell, one can control the properties of these systems, at the same time as the shell, in turn, protects the kernel from external influence [7]. Thus, by correlating the structure and properties of the core and shell material, especially the shape and size, the expansion of the functionality of these nanosystems is ensured [8]. As a material for core-shell nanostructures, a wide range of combinations of inorganic and organic materials is used.

The development and production of nanoparticles with individual characteristics requires an understanding of their structural and thermodynamic properties [9–11]. Numerous methods of synthesis of nanoparticles with different structure, size and shape were proposed [1, 5]. However, some experimental techniques that are widely used in material science, not always can be applied to investigate the structure and behavior of the nanoscale objects [12], thus, various theoretical and computational investigations [13, 14] can be an additional tool in studying of nanostructures.

The purpose of this work was to study the behavior of bimetallic nanoparticles Ag@Pd, Au@Pd (Ag/Au is core; Pd is shell) during melting within molecular dynamics methods.

2 Model and simulation configuration

Within the framework, Ag@Pd and Au@Pd nanoparticles were investigated, which had a spherical shape with a core (Ag/Au)-shell (Pd) structure. In the experiment the total number of atoms was 16 757 for Ag@Pd, where 14 634 (87.3 %) atoms were palladium and 2 123 (12.7 %) atoms were silver, and the total number of atoms was 46 049 for Ag@Pd, where 40 274 (87.5 %) atoms were palladium and 5 775 (12.5 %) atoms were aurum for Au@Pd. The initial diameters of Ag@Pd and Au@Pd nanoparticles were 7.4 nm (core diameter ~4.0 nm) and 13.0 nm (core diameter ~7.0 nm), respectively. The simulation was performed with the support of an ideal vacuum at free boundary conditions in three directions. OVITO software package was used to obtain images of atomistic configurations [15]. For example, the initial atomic configuration of the Ag@Pd modeled nanoparticle is presented in Fig. 1.

During the simulation of the melting process, the sample temperature was gradually increased by scaling the corresponding atomic velocities using the Berendsen thermostat. The Lindemann index was used as a numerical parameter describing changes in the system and calculation of parameters were realized after the temperature reached equilibrium value.

The modified embedded-atom method (MEAM) was used to calculate the forces of interatomic interaction [17]. MEAM is known to reliably reproduce the basic properties of materials and is widely used in the metal alloys modelling by classical molecular dynamics (MD) techniques. The simulation was performed using the LAMMPS software package [18].

The complete algorithm for particle motion calculations used in molecular dynamics simulations involves obtaining analytical expressions for the forces of interatomic interaction $F(r)$, based on the given dependences for the potential energy, through the equation

$$F(r) = -\frac{\partial U}{\partial r}$$

and further numerical integration of the equations of motion

$$m \frac{d^2r_i}{dt^2} = F_i(r_i) = -\frac{\partial U}{\partial r}$$

for each atom $i$.

Within the MEAM, the total potential energy of a metallic crystal can be presented as a sum of two components, each of which describes the corresponding mechanisms of interaction:

$$U = \frac{1}{2} \sum_{i>j} \varphi(r_{ij}) + \sum_i F_i(r_i),$$

where $\varphi(r_{ij})$ is the pair energy between atoms $i$ and $j$ at a distance...
\[ r_{ij} \]; \( F(\rho_i) \) is the local embedding energy of the \( i \)-atom in the space domain, that is characterized by the electronic density \( \rho_i \).

For each term in equation (3), the analytical expression was proposed through approximating the data obtained from the calculations from the first principles [19]. Thus, the pair energy of the interatomic interaction can be written in the form

\[
\varphi(r) = \frac{A e^{-\beta r}}{1 + \left( \frac{r}{\alpha} \right)^{\gamma}} - \frac{B e^{-\gamma r}}{1 + \left( \frac{r}{\beta} \right)^{\alpha}},
\]

(4)

where \( r_e \) is the equilibrium distance between the two atoms of the given type; \( A, B, \alpha, \beta, \gamma \) are the approximation parameters; \( \kappa, \lambda \) are the additional parameters for ensuring zero energy of interaction at significant interatomic distances.

The local embedding energy as a function of electron density \( F(\rho_i) \) is calculated in several steps. Firstly, the electronic density \( \rho_i \) is calculated as

\[
\rho_i = \sum_{j \neq i} f(r_{ij}),
\]

(5)

where \( f(r_{ij}) \) is the local electron density in the atomic region of atom \( i \), calculated through the following expression

\[
f(r_{ij}) = \frac{f_{e} e^{\beta r_e(r - 1)}}{1 + \left( \frac{r}{\epsilon} \right)^{\alpha} r_e}.
\]

(6)

that has the same form as the second term in formula (4) with the same values of parameters \( \beta, \lambda \) and \( r_e \). Then the electronic density function \( F(\rho_i) \) should be calculated from three following equations, depending on the value of \( \rho_i \)

\[
F(\rho) = \sum_{i=0}^{3} F_{e} \left( \frac{\rho_i}{\rho_0} - 1 \right), \quad \rho < \rho_n, \quad \rho_n = 0.85 \rho_e, \quad (7)
\]

\[
F(\rho) = \sum_{i=0}^{3} F_{e} \left( \frac{\rho_i}{\rho_0} - 1 \right), \quad \rho_n < \rho < \rho_0, \quad \rho_0 = 1.15 \rho_e, \quad (8)
\]

\[
F(\rho) = F_{e} \left( 1 - \ln \frac{\rho}{\rho_0} \right) \left( \frac{\rho}{\rho_0} \right)^{\gamma}, \quad \rho_0 \leq \rho. \quad (9)
\]

Such method for determining the electronic density function \( F(\rho) \) is necessary for the realistic approximation of the embedding energy and for reproducing the properties of the material in a wide range of values \( \rho \).

The forces between different types of atoms can be calculated using the MEAM model for alloys [19]. Within mentioned approach the pair energy \( \varphi^{ab}(r_{ij}) \) between atoms of type \( a \) and \( b \) can be calculated as

\[
\varphi^{ab}(r) = \frac{1}{2} \left( \frac{f^{aa}(r)}{f^{ab}(r)} \varphi^{aa}(r) + \frac{f^{bb}(r)}{f^{ab}(r)} \varphi^{bb}(r) \right). \quad (10)
\]

Thus, using equations (1)-(10), it is possible to investigate the dynamics of metallic nanoparticles under the external influences.

The description of changes in nanoparticle structure was based on the use of the Lindemann numerical parameter [20]. The local Lindeman index of the \( i \)-th atom was determined through the following formula:

\[
q_i = \frac{1}{N - 1} \sum_{j \neq i} \left[ \frac{|r_{ij} - \langle r_{ij} \rangle|^2}{\langle r_{ij} \rangle} \right],
\]

(11)

where \( r_{ij} \) is the distance between \( i \) and \( j \) atoms; corner brackets are time averaging at a constant temperature value.

The quantitative characterization of the changes in the sample structure is carried out by the calculated radial density functions \( g(r_n) \), which are defined as the relative probability of finding a pair of atoms at some distance from each other. \( g(r_n) \) was calculated through the equation [21]:

\[
g(r_n) = \frac{v_{h_n}}{2\pi N_n^2 r_n^2 \Delta r}, \quad (12)
\]

where \( v_{h_n} \) is the volume of the sample; \( h_n \) is the number of atomic pairs \( (i, j) \) for which the condition \( \left( n - 1 \right) \Delta r \leq r_{ij} \leq n \Delta r \) is satisfied; \( N_n \) is the total number of atoms; \( \Delta r \) – parameter of sampling of interatomic distances \( (\Delta r \) has sufficiently small values); \( r_n = (n - 1/2) \Delta r \) is the value of the interatomic distances.

### 3 Results

Temperature dependences of the Lindemann index calculated for the Au@Pd and Ag@Pd nanoparticles under investigation are shown in Fig. 2. As it can be seen from the figure, the obtained values on the dependences \( Q(T) \) and \( E(T) \) increase monotonically in the temperature range \( T \leq 1500 \) K. After that, the Lindemann index and the potential energy start to rise rapidly at a temperature value of \( T \approx 1600 \) K, which may be a start of the melting process.

The value of the Lindemann index for the Ag@Pd nanoparticles was \( Q_* = 0.01 \) and for the Au@Pd nanoparticles was \( Q_* = 0.015 \). At temperatures \( T > 1700 \) K, there is a slow, almost linear increase in the values of \( Q \) and \( E \) (Fig. 2, Fig. 3).

To detect the changes in the structure of the nanoparticles, the radial distribution functions were calculated at the initial temperature of 300 K (Fig. 4, Fig. 5). As can be seen from the figure for Ag@Pd, at temperatures \( T = 300 \) K and \( T = 1050 \) K, the sample has clearly expressed peaks corresponding to the crystalline structure of silver and palladium. At \( T = 1050 \) K, the \( g(r_n) \) is
characterized by a decrease in the height (intensity) of the peaks. At $T = 2000$, only the first peak corresponding to the equilibrium distance between atoms is visible on the radial distribution function, and there are no other peaks. This kind of radial distribution function is typical of an amorphous state.

The cross sections and general views of the Ag@Pd nanoparticle at the melting point and the maximum temperature of the computer experiment are shown in Fig. 6. As it follows from visual analysis, temperature growth lead to increasing spacing between atoms, resulting in destruction of the initial crystal structure. It is noticeable that above the melting temperature core-shell structure of the nanoparticle is also destroyed, due to the increased velocity of the diffusion processes.

4 Conclusion
In the work melting behavior of the bimetallic Ag@Pd, Au@Pd nanoparticles with core-shell structure investigated by classical molecular dynamic simulations. According to the simulation results, the numerical parameters were obtained for the samples and the dynamics of the structural changes were analyzed. The approximate melting point for nanoparticles was 1600 K. At that point the Lindemann indexes exceed the critical values $Q_c \approx 0.01$ and $Q_c \approx 0.015$ for Ag@Pd, Au@Pd respectively. Initial core-shell structure of the nanoparticle is preserved up to the melting point. With the temperature growth, the volume of the nanoparticle is also increasing due to the larger spacing between atoms, which lead to the destruction of the initial crystal structure and the core-shell diffusion became more intense. It should be noted that the model presented here allows us to investigate the behavior of nanoparticles of another chemical composition during heating and melting (depending on the presence of a parameterized interatomic interaction potential), size and shape.

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6 Literature


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