Numerical modeling of interface diffusion during heating of spherical metal heterostructure

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This work is a pilot one and addresses to the development of a physical and mathematical model of alloy formation; this model permits conducting a micro-level detailed study of the influence imposed by the ratio of the thermophysical parameters of the matrix and nanoclusters materials, as well as external controlled parameters on the physical properties of the alloys. The article presents the developed methodological approaches for the numerical simulation of alloys formation with the help of molecular dynamics method (MDM).

1. Introduction
Necessity to have nano-modified alloys with prescribed properties causes the need in a developed physical and mathematical model of the atomic-level formation of such alloys and in the analysis of the influence of combination of matrix nanocluster materials, as well as the effect of external conditions on the alloy properties.

In recent decades, interest to the molecular-dynamic modeling (MDM) of alloy formation on the atomic level has begun to grow. There are quite a lot of works where the ready alloy is used as the initial data [1]. The cycle of papers [2 – 5] approaches better to the authors’ paper by the nature of investigations. The major difference is in the following: the liquid film formed initially as a stoichiometric mixture, and was then melted through with the aid of the modeling of the impulse atom distribution in accordance with the Maxwell distribution. The system temperature is increased abruptly in 100 K. This approach does not permit modeling the process of heat transfer during the heating and cooling which, as we know from experiment, dictates the final structure of the alloy. In [6 – 7] there is the MD modeling of the structural and dynamic properties of the alloy Cu-Ni on the liquid and solid interface.

The main difference of this paper from the above mentioned ones is that we use the free boundary conditions which permits modeling the effect of the nanoparticle size, taking into account the influence of the nanoparticle surface. Moreover, the purpose of the work is to model the formation of the alloys, not only analysis of the thermophysical properties of the ready (formed) alloys, which is the fundamental difference from the works of other scientific teams.
2. Physical system and calculation method
The studied system presents a sphere of one material covered with a spherical layer of another material; such a system can be referred to as a “spherical heterostructure”.

Copper and silver were used at the stage of methodology refinement. To model the interaction between atoms in this system, we used the Voter potential [8] obtained by the embedded atom method (EAM), which has successfully been used in many tasks. To prepare the system and bring in the stationary equilibrium state in the potential energy minimum, the artificial viscosity method was used [9]. Then, the found values of coordinates and momenta were used as the initial data for the system heating up to the needed temperature. To do this, we used the stochastic momenta method [10]. The following heating parameters were applied for every system atom: the random momentum amplitude \( \Delta p = 4 \) (in program units), and the interval between absorption of momenta by atoms is \( \Delta N = 20 \) numerical time pitches. In this calculation, in every 25 K of the system temperature growth, the coordinates and momenta arrays were output.

The velocity Verlet algorithm [11] is used in every calculation of this paper, the chosen time pitch is \( \tau = 10^{-16} \) s.

Below there are the results for the case when the inner copper sphere radius is 20 Å, whereas the external silver sphere is 40 Å (i.e. the silver layer thickness is 20 Å). This system consists of 2899 atoms of copper and 12784 atoms of silver. Totally there are 15683 atoms in the system. All of them are located in the nodes of a perfect FCC lattice, the constants of the copper (\( a_{\text{Cu}} = 3.6149 \) Å) and silver lattice (\( a_{\text{Ag}} = 4.09 \) Å) are used. The origin of the laboratory system of coordinates lies in the sphere center.

3. Numerical cooling of the system
The cooling procedure results in the fact that the system evolves into the state with the temperature close to the absolute zero, the potential energy of the total system and each Cu and Ag subsystem decreases and takes the constant equilibrium values, the atoms in the Cu-Ag interface shift toward the more energetically advisable position. A layer of 5 Å was cut in the equatorial plane for the better visualization of the processes in the inner volume of the heterostructure.

The system temperature is calculated through the kinetic energy of the chaotic motion of the atoms, the kinetic energy of the mass center is ignored (figure 1).

Figure 1 – (c) presents the change of the potential energy of the copper subsystem \( \Delta U_{\text{Cu}} \) (the calculation is such as if there is no silver subsystem), change of the potential energy of the silver subsystem \( \Delta U_{\text{Ag}} \) (the calculation is such as if there is no copper subsystem). Opposite to the full potential energy \( U_i \), which decreased during the cooling (figure 1 – b), the potential energies of the subsystems rise. The bound energy between two subsystems is the key characteristic of the heterostructure; it is found as follows:

\[
U_b = U_i - (U_{\text{Cu}} + U_{\text{Ag}}).
\]

Reduction of the full potential energy at the simultaneous increase of \( \Delta U_{\text{Cu}} \) and \( \Delta U_{\text{Ag}} \) is possible owning to the reduction of the bound energy (figure 1 – d). Coordinates and pulses of the system resulting from the cooling process, were then used for the system heating.

4. Modeling of diffusion during the heating of the spherical heterostructure

4.1. Heating of the spherical heterostructure
After the heating which technique is briefly described in chapter 2., every characteristic of interest was averaged by thermal fluctuations within 1,000 calculation steps (or 0.1 ps). After the heating, all necessary characteristics were analyzed during the relaxation of the closed and isolated system. It turned out that the heterogeneous system needs much more time to get into the thermodynamically
equilibrium state. The system containing only copper atoms gets into the equilibrium state after the heating within approximately 500 calculation pitches (0.05 ps). Whereas the spherical heterostructure Cu-Ag needs about 500,000 calculation pitches to equalize the temperatures of the silver and copper subsystems (see figure 2).

4.2. Detection of the diffusion on the interface
Initially, the diffusion on the interface between Cu and Ag is found visually. For better evidence, the atomic layer of 5 Å thick is shown for different temperatures; it is cut out from the spherical heterostructure in the equatorial plane. Figure 3 presents as an example the physical system at $T = 1700$ K. This visualization clearly shows both the beginning and the developed diffusion process.

Figure 1. System characteristics versus time during the cooling. (a) temperature; (b) variation of the full potential energy of the system; (c) variation of the potential energy of copper (black line) and silver (grey line) subsystems; (d) variation of the bound energy between the copper and silver subsystems.

Figure 2. Change of the temperature of the heterostructure system component versus relaxation time. $T$ is the average temperature of the total system, $T_{Cu}$ is the copper subsystem temperature, $T_{Ag}$ is the silver subsystem temperature.

Figure 3. Position of atoms in the YZ plane during the heating. $T = 1700$ K. Layer thickness is 5 Å.
4.3. Meso-analysis

It is necessary to have the distribution of a number of characteristics inside the spherical heterostructure. To do this, the technique of meso-analysis has been developed. The logics of space division to subsystems depends on both the geometry of the studied object and the processes occurring in it. In the case of spherical heterostructure heating, the optimal division of the space is to split it to spherical layers between two radiuses \( r \) and \( (r+\Delta r) \), where \( \Delta r \) – the layer thickness. The center of these inserted spheres coincides with the studied object center.

The distance between the layers is \( \Delta r = 5 \, \text{Å} \), the radius of the most inner meso-cell is also 5 Å. For the chosen size of the studied system \( R=40 \, \text{Å} \), the lattice of spherical inserted meso-cells up to 80 Å is assigned. Such a stock is used to take into account the metal expansion during the heating, and even possible evaporation of the atoms from the surface.

The files with data arrays about the coordinates and momenta of each atom of the system obtained with the aid of the program on the spherical heterostructure heating are used as the initial data in the calculation program of the meso-analysis.

The temperature distribution over the meso-cells has been obtained (figure 4). Certain temperature decrease from the center toward boundary meso-cells is observed, which vindicates the need to increase the time of relaxation of the heterogeneous system during the heating.

The distribution has been calculated about the relative amount of the atoms of each kind (copper and silver in this task) for the meso-cells at different temperatures of the system heating. It is found as the relation of the substance (copper or silver) atom amount in the certain meso-cell at the chosen temperature to the total amount of the atoms (both copper and silver) in the same meso-cell at the same temperature. Figure 5 shows the results for \( T = 1100 \, \text{K} \).

Every graph contains for better visualization the initial (in the cooled system) boundary of the inner copper sphere and external silver sphere \( R_{Cu} \), and the external system boundary \( R_{Sp} \) (actually, the radius of the external shell from silver).

![Figure 4](image1.png)  ![Figure 5](image2.png)

**Figure 4.** Temperature distribution over meso-cells. The heated system temperature \( T=1100 \, \text{K} \).

**Figure 5.** Distribution of the relative amount of copper atoms (black line) and silver atoms (grey line) over meso-cells at the heating temperature \( T=1100 \, \text{K} \).

4.4. Calculation of the parameters characterizing the diffusion on the interface

The algorithm of parameters calculation has been developed; these parameters characterize the diffusion through the medium interface and through the external interface (which in fact corresponds to the thermal expansion of the substance). The essence is that in certain moments during the heating we determine the position of copper and silver atoms in respect to the initial position of the interface between the inner copper sphere and external silver layer. In the same way we detect, if copper (and silver) atoms have crossed the external boundary of the system, and what is was before the heating.
The amount of atoms of each substance is summed up and their content in percent from the total amount of the atoms of the same substance is determined. Thus the qualitative development of the diffusion during the heating becomes clear (figure 6). At the temperature of 1100 K, atoms diffusion is still weak, which is proven by the results below.

Figure 6. Diffusion of copper (black line) and silver (grey line) atoms through the external system boundary (the interface with the external medium) (a) and interface between the substances (b).

It is evident that the diffusion of copper atoms through the inner interface begins from about 600 K. Note that the diffusion of silver atoms through the initial external interface of the system begins also from 600 K. I.e., the thermal expansion becomes noticeable at the temperature about 600 K. Insignificant amount of silver atoms from the external shell get into the inner sphere of Cu (figure 6 – b, grey line), but even at the copper melting temperature which is higher than the silver melting point the diffusion of Ag atoms from the external shell through the inner interface toward the center remains negligibly low (about 1% of all Ag atoms), whereas the thermal expansion of the whole system makes about 10% of the total amount of atoms at the copper melting temperature (figure 6 – a grey line, figure 6 – b black line). I.e., the diffusion of both copper and silver from the spherical heterostructure center dominates over the diffusion toward the system center.

5. Conclusions
- The technique of the numerical simulation of the heating of the heterogeneous system has been developed on the example of the spherical heterostructure: the inner sphere from Cu, the external shell from Ag up to the temperatures above the melting point of the heterostructure components.
- The approach has been developed to perform the meso-analysis of the spherical structure for the better visualization of the physical parameters distribution in the system.
- On the base of the meso-analysis, the temperature profile distribution has been found in the spherical heterostructure, as well as the distribution of the relative amount of the atoms of each substance for the meso-cells. The resulting graphs demonstrate how the compound profile changes as the temperature grows.
- The algorithm has been developed for the qualitative analysis of the diffusion in the system. It is shown that the dominating diffusion is that which coincides in direction with the atoms motion at the thermal expansion of a substance.

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7. References

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