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08

Comparative atomistic simulation of structure and structural transformations in Ni—Ag and Ni—Cu nanoalloys

© A.Yu. Kolosov, K.G. Savina, N.I. Nepsha, S.S. Bogdanov, D.N. Sokolov,
R.E. Grigoryev, N.Yu. Sdobnyakov

Tver State University,
Tver, Russia

E-mail: nsdobnyakov@mail.ru

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The structure and structural transformations of binary Ni-Ag and Ni-Cu nanoparticles with a size of 3.2 nm were studied. The molecular dynamics method was used as a method for simulation the thermally induced effect. It was shown that the surface segregation of Ag and Cu atoms, respectively, is characteristic of binary Ni-Ag and Ni-Cu nanoparticles. Based on the analysis of caloric curves of the potential part of the specific internal energy and the energy spectrum of binary Ni-Ag and Ni-Cu nanoparticles, the features of the segregation behavior of Ag and Cu atoms were revealed. Similarities and differences in the processes of structure formation under thermally induced effects corresponding to heating and cooling are described.

Keywords: binary nanoparticles, molecular dynamics, tight binding potential, structural transformations, core—shell structure.

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The interconnection between the structure and the physical and chemical characteristics of binary metal nanoparticles (NPs) manifests itself much stronger with the account of size effect, change of the composition or their configuration [1]. Papers [2–4] are dedicated to the study of the thermally induced structural transformations in binary NPs based on Ni. Papers [5,6] present the results of atomistic molecular-dynamic modeling that demonstrated that in the binary NPs Ni-Cu the copper atoms tend towards surface segregation. Apart from the factors mentioned in [2–4], nickel-containing binary NPs are of interest for the reason that the inversion of surface segregation in NPs Ni-Cu was found there when the binary system was doped with carbon, i. e. transition from surface segregation of Cu to surface segregation of Ni [7]. In [8] the method of molecular dynamics (MD) studied the effect of the size, temperature and cooling speed at the formation of the structure and pattern of the phase transitions in the equiatomic ternary alloy Ag-Cu-Ni (containing three components in equal fractions). The results demonstrated the presence of the nucleus—shell structure in all cases, and increased temperature of modeling and reduction of the cooling speed help to crystallize the ternary clusters of Ag-Cu-Ni. Paper [9] studied the effect of size non-conformity at the structural transformations in binary NPs Ni-Ag, Co-Ag, Cu-Ag, Co-Pt, Ni-Pd, Rh-Au and Ni-Cu. Note that the development of nickel-based catalysts faces such problems as low-temperature activity and NP sintering. A potential solution studied by [10] is inclusion of second transition metals or noble metals into such catalysts. Another problem for synthesis of binary NPs is slow kinetics of diffusion in solid bodies and poor mixing of precursors, the solution to this problem was proposed in [11].

The objects of the study are binary NPs Ni-X (where $X = \mathrm{Ag, Cu}$, i. e. nickel serves as a basic component, and the second component is selected from the copper subgroup). Since in practice the most common variant of the binary NPs synthesis result is even distribution [12], in this paper we review NPs of equiatomic composition to find out the degree of metal atom segregation from the copper subgroup. The objective of this paper is to compare the patterns in structural transformations of Ni-Ag and Ni-Cu nanoalloys under thermally induced exposure.

The MD method was used to study the thermally induced structural transformations in NPs with the initial even distribution of components with diameter of 3.2 nm (2000 atoms). In process of modeling the NPs were heated from 300 to 1500 K, then cooled down to 300 K, in process of such thermally induced exposure their local structure and energy spectrum were analyzed (i. e. distribution of NP atoms by the value of specific potential energy). Within the computer experiment based on using the MD method, the following parameters were used: time of relaxation of nanoparticles was 15 ps, speed of temperature variation for heating and cooling was 0.3 K/ps.

MD-modeling was carried out using in-house software, which uses the strong coupling potential, the parameters of which for monometallic bonds are taken from paper [13]. To obtain the cross parameters, the so called Lorentz–Berthelot rule was used: parameters A, ξ are found as geometric mean values, and parameters p, q, r_0 — as arithmetic mean ones (see table). The parameter of strong coupling

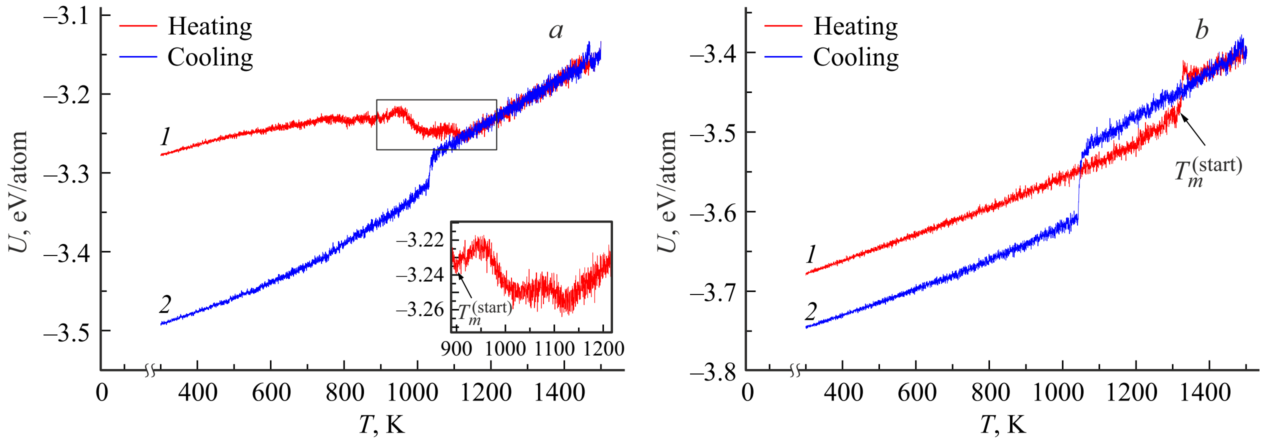

Figure 1. Dependence of the potential part of the specific internal temperature on temperature: *a* — Ni-Ag, *b* — Ni-Cu. Curve *1* — heating, curve *2* — cooling.

Strong coupling potential parameters

System	A, eV	ξ, eV	p	q	r_0, Å	r_{cut}, Å
Ag-Ag	0.1028	1.178	10.928	3.139	2.889	7.55
Ni-Ag	0.0622	1.1227	13.9635	2.164	2.6904	7.55
Cu-Cu	0.0855	1.224	10.96	2.278	2.556	7.55
Ni-Cu	0.0567	1.1444	13.9795	1.7335	2.5239	7.55
Ni-Ni	0.0376	1.07	16.999	1.189	2.4918	7.55

potential cutting r_{cut} complies with the conditions proposed in paper [13]. Such approach to finding cross parameters of strong coupling potential was tested in papers [1–6].

A soft stochastic thermostat [14,15] was applied, which was a Nose–Hoover thermostat with addition of random noise to improve ergodicity. Contrary to Langevin dynamics, where noise is added directly to every physical degree of freedom, the scheme of this thermostat is based on indirect link with one Brownian particle. Despite the stochastic nature, the thermostat weakly affects the physical dynamics measured by disturbance of temporary autocorrelation functions. Kinetic energy is well controlled even at early modeling stages. The method selected to integrate the motion equations was Verlet algorithm in the speed form, since it has quite good precision, is „self-starting“ and does not require knowledge of coordinates and speeds at the previous moment of time. To model certain nanoparticles, periodical boundary conditions were used. The analysis of the structure of studied NPs was carried out with OVITO software complex by the method of comparison of polyhedral templates [16].

Figure 1 presents curves of dependences of the potential part of the specific internal energy on temperature for binary NPs Ni-Ag (*a*) and Ni-Cu (*b*). Analysis of the curve sections that correspond to the start of heating and the end of cooling, shows that the initial configuration with the even distribution of components is not optimal for any nanosystem, which is evidenced by a higher value of the specific energy on the curve that corresponds to heating. The nature of behavior The nature of behavior of temperature dependences of the potential part of the specific internal energy U, corresponding to the heating of binary NPs Ni-Ag and Ni-Cu, differs greatly in the melting area. It is due to the fact that the atoms of silver in the process of heating form an NP shell, but at the same time some silver atoms are present in the central part of NPs. At the same time the nickel atoms occupy the peripheral area relative to the nucleus and do not surface (see Figure 2,*a*), i.e. actually in this temperature interval an onion-like structure is formed [17]. In process of melting (Figure 1,*a*) the considerable energy drop is observed, which is due to the active process of surface segregation of the silver atoms. This process continues even after melting up to 1120 K, which is confirmed by the progress of the temperature dependence U (see insert in Figure 1,*a*). Temperatures corresponding to the start of melting differ greatly: for Ni-Ag the melting starts at temperature of 903 K, and for Ni-Cu — at 1313 K. For NPs it is specific that phase transitions corresponding to melting and crystallization both for mono- and binary NPs occur in a certain temperature interval [1,18]. Such feature is due to different segregation behavior of silver and copper atoms both in the process of heating and after melting. End configurations corresponding to heating of binary NPs, are characterized by the presence of the surface segregation of silver and copper atoms, i.e. NPs are formed with nucleus–shell structure for Ni@Ag and Ni@Cu (see Figure 2). The results of atomistic modeling of the Ni-Cu system [5,6] predict similar behavior of copper atoms in process of segregation, which may be explained by the difference in the surface energies of nanoalloy components. Besides, papers [5,6] contain a conclusion on the fact that segregation reduces as temperature grows and particle size decreases. The results of the experiments [19,20] using the methods of

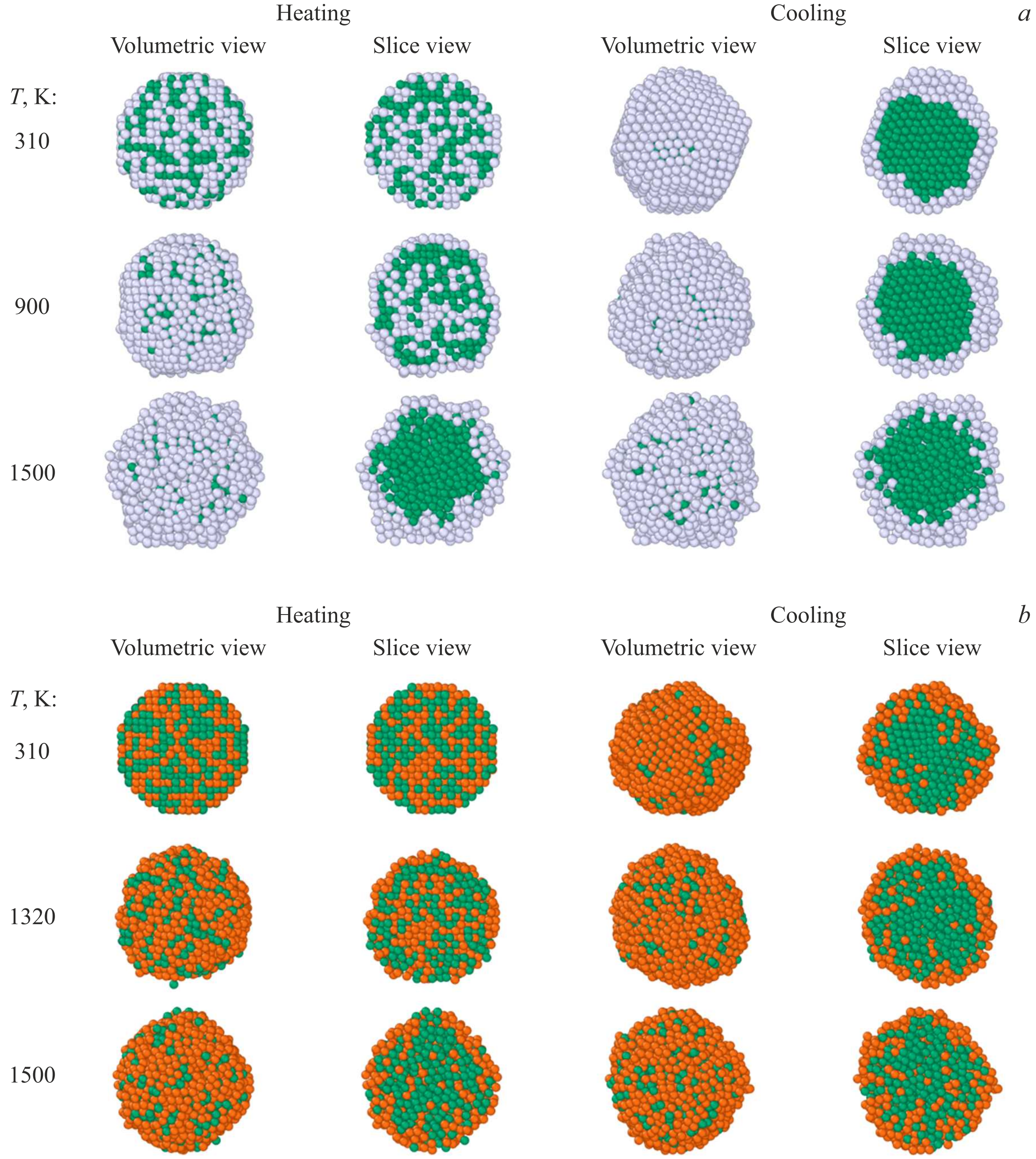

Figure 2. Instant configurations of NPs Ni-Ag (*a*) and Ni-Cu (*b*) with he initial even distribution of atoms at various temperatures. Dark-green is for Ni atoms, grey — Ag atoms, brown — Cu atoms.

X-ray photoelectron spectroscopy and Auger-spectroscopy also demonstrated the presence of surface segregation of copper in the Ni/Cu system in process of nickel film deposition on the copper substrate at room temperature and during thermal treatment in the vacuum. At the same time, these results confirm that segregation reduces the surface energy. For the Ni-Ag system the patterns of formation of the nucleus–shell structure and assessment of stability of such systems were studied by us in [2] also using the method of molecular dynamics and strong coupling potential. It was shown that for bimetallic nanoparticles $Ni_{675}@Ag_{3325}$ (the lower index specifies the number of atoms) the processes of surface segregation of nickel atoms were less pronounced, while in the $Ag_{675}@Ni_{3325}$ nanoparticle the silver atoms actively segregated on the nanoparticle surface. At the same time the numerical results [21], received by method of global optimization for NP Ni-Ag with size of up to 300 atoms, predict the formation of the shell from silver atoms only. Note that the temperature interval, where binary Ni-Ag and Ni-Cu NPs are crystallized,

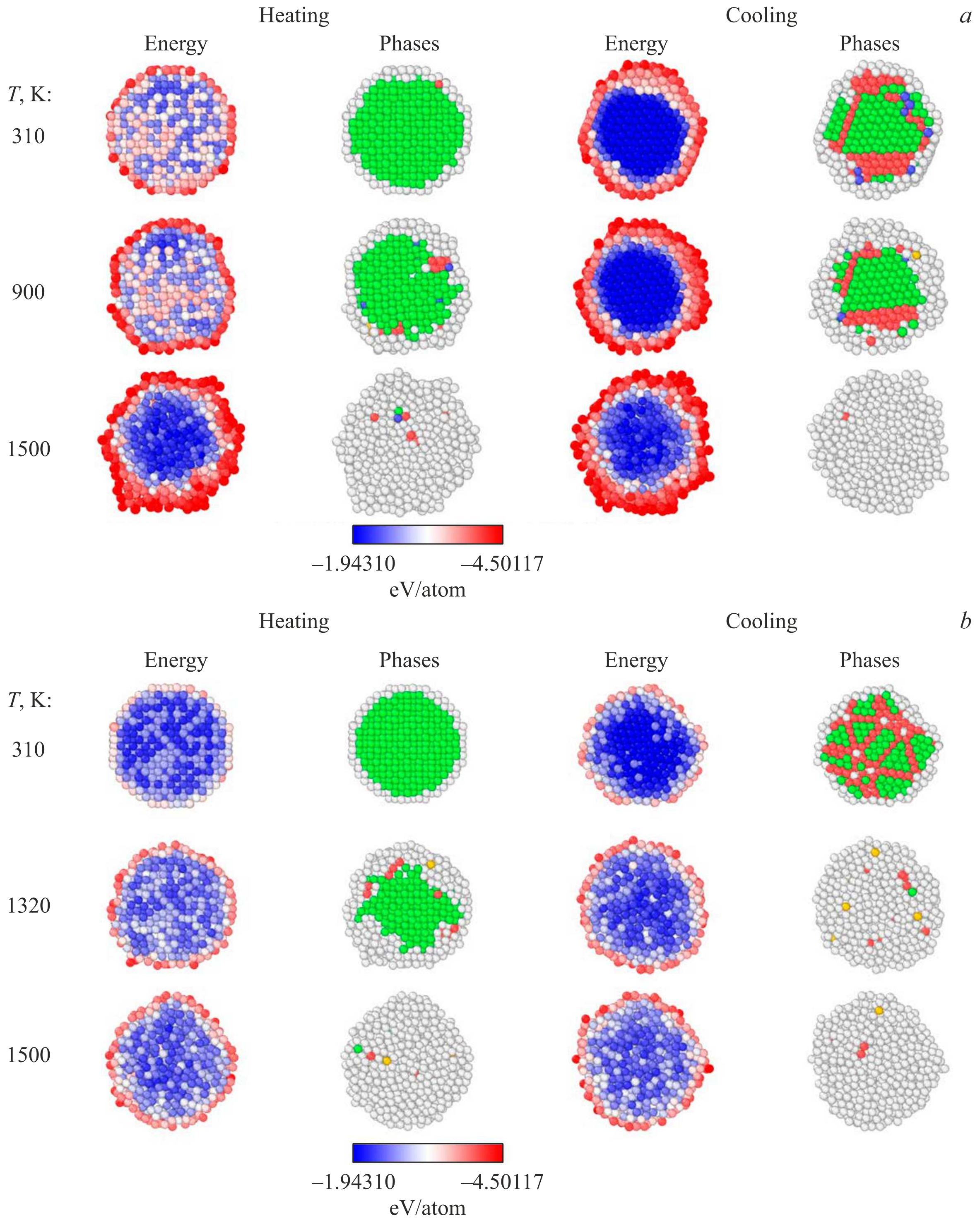

Figure 3. Evolution of energy spectrum and local structure in heating and cooling processes. Green corresponds to local face-centered cubic (FCC) structure, red — to local hexagonal close-packed (HCP) structure, blue — to local body-centered cubic (BCC) structure, yellow — icosahedral nuclei, white — atoms that belong to unidentified structures.

practically coincides and makes for Ni-Ag 1028–1043 K, and for Ni-Cu — 1037–1053 K. This reflects in the nature of the energy spectrum, in particular, the gradual reduction of the specific energy value is well traced in the transition to the central part of the NP (see Figure 3). The energy spectrum of Ni-Ag NPs varies rather strongly in the process of heating, which is a manifestation of structural instability, contrary to Ni-Cu NPs, where changes of energy related to lattice rearrangement are practically fully absent. Analysis of configurations received in process of cooling shows that for binary Ni-Cu and Ni-Ag NPs the prevalent local structure is FCC, and the local HCP structure is formed as planes.

Despite certain similarity, for binary Ni-Cu NPs the end local internal structure is more complicated. It seems that a more complex local HCP structure is also formed due to the presence of copper atoms in the inner part of NPs. For the studied NPs, the nucleus is formed by nickel atoms, but if in Ni-Ag NPs the full segregation of components takes place (nickel — nucleus, silver — shell), then in the Ni-Cu particle it is not so unambiguous. Copper atoms create a „loose“ shell around the nickel nucleus, enabling its atoms to surface, in its turn nickel „lets through“ certain copper atoms into the nucleus. Such effect for Ni-Cu NPs is presumably related to a lower value of the coefficient of size discrepancy for the atoms compared to Ni-Ag NPs. In Ni-Ag NPs the value of the potential part of the specific internal energy of silver atoms is practically three times higher than in nickel atoms, which makes the full segregation of silver atoms near the surface energetically beneficial (see Figure 3, *a*).

In subsequent cycles of recrystallization for the Ni-Cu system the type of hysteresis of melting and crystallization and accordingly temperatures of phase transitions do not change practically, which is explained by the presence of the second heating cycle in the initial configurations in the central part of the copper atoms. For the Ni-Ag system the hysteresis of melting and crystallization is also recorded, but at the same time, since in the first cycle of heating and cooling the Ni@Ag structure was formed (this fact is confirmed, in particular, by the results of [21]), the caloric dependences of the potential part of the specific internal energy record the pre-melting of the shell made of silver (as the least hard-melting metal in the pair) at temperatures close to the value specified in Figure 1, *a*, and then the nucleus from nickel melts.

Despite the fact that in the binary Ni-Ag and Ni-Cu NPs the surface segregation of copper subgroup atoms (Cu or Ag) is observed, the nature of distribution of copper and silver atoms in the central part of the NPs differs. At the same time the Ni-Cu NPs demonstrate more diversity when the local structure is formed in process of cooling and are more thermally stable from the point of view of the spatial atom distribution compared to the Ni-Ag NPs. It is necessary to take into account both their structural stability [1] and the value of the specific energy of end configurations, since it is the potential energy that makes the dominant contribution to the free energy, analysis of behavior of which is most accurate method from the thermodynamic point of view to justify the stability of the studied configurations, compared to the entropy contribution, even at high temperatures. The methods to control the final energy of NPs in the process of crystallization that may be considered include both cooling speed [1,8] and the presence of the external pressure [22]. It should be noted that the non-equilibrium nature of nanoparticles, for instance, as in the case of the Ni-Ag system with even distribution, will not always prevent practical use of both ensembles of such nanoparticles and materials on their basis [12]. From the point of view of practical applications, in many cases it is quite sufficient that micro- and nanostructures are stable at specific times necessary for specific application [23].

Therefore, when comparing the structural transformations in binary nanoparticles, one of components of which coincides, one should expect that the fixed features of the structural transformations will be determined exactly by the segregation behavior of the second component atoms. At the same time, there are results already for the binary Cu-Ni nanoparticles, which describe the inversion of segregation [7]. But such process is activated only when the binary nanoparticle is doped with the third component. To conclude, note that whenever the problem of stability of binary and especially multi-component metal nanoparticles is studied, other factors must be taken into account, apart from the stability of the integral and mesoscopic structure, the attempt to classify which was made in [24].

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Conflict of interest

The authors declare that they have no conflict of interest.

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