Phase Diagram of Nanoparticles of Palladium-Platinum Alloys

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Abstract. Melting and crystallization temperatures of mesoscopic metal particles have been calculated within the framework of thermodynamics of surface phenomena and the electron-statistical method, for which it is necessary to take into account the dimensional dependences of the surface and interphase energies. All estimates were carried out in the model of heterogeneous melting in the presence of a skin layer. Phase diagrams have been constructed for binary Pd-Pt nanoparticles with solid core linear dimensions of 5 and 8 nm and a skin layer thickness of 2 nm. The surface and interfacial energies, as well as their temperature and size dependences, were estimated by a modified electronic statistical method. A comparative analysis of the results obtained using different expressions for the size dependence of the specific heat of fusion of nanoparticles is carried out. It was found that the shape of the diagram has significant differences from the phase diagram for the bulk phases of the metals under consideration. The main reason for the difference is the melting-crystallization hysteresis and the appearance of a smooth maximum on the liquidus and solidus lines. The maximum on the lines of melting and crystallization temperatures can be explained by a more pronounced size dependence of the interfacial characteristics of platinum. In accordance with the criterion that determines the more surface-active component, it can be concluded that with a change in the melting point ratios of pure components and lower values of the surface energy of palladium, a core (Pd) - shell (Pt) structure will form in nanoparticles.

1. Introduction
Phase analysis is an informative and most frequently used method for researching and predicting the behavior of two- and multicomponent systems. For a large number of binary systems, such diagrams are constructed [1]. However, when passing to nanomaterials, their use does not seem correct, since the melting-crystallization phase transition temperature depends on the particle size and has a hysteresis [2-11].

The first work in which the melting point of nanoparticles was studied was published over a hundred years ago [2]. It was shown in it that with a decrease in the particle size, the melting temperature decreases, since the contribution of the surface energy to the free energy of the particle increases and the surface energy of a liquid is always lower than that of a solid.

In [8], the experimental phase diagrams of binary systems of different types have been constructed and it is shown that the transition from the bulk to form nanoscale state diagrams may be changed, since there is a decrease of phase transition temperature and change in the position of components solubility limit lines.
The aim of this work was to construct a phase diagram for nanoparticles of a binary alloy with unlimited solubility of components in the solid and liquid states.

The palladium-platinum system was chosen as the object of research, since the properties of these metals are well studied, their phase diagram has a simple form [1]. Also, this system is widely used in various industries.

2. Calculation method

There are several significantly different models of the phenomenon of melting-crystallization of particles, including homo- and heterophase [2, 8-14]. We considered the case of nanoheterogeneous melting of a particle, when melting begins from the surface with the formation of a liquid shell – solid core structure [13].

The palladium-platinum system forms a continuous series of solid solutions [1]; therefore, in the calculations, it was assumed that the physical parameters of solid solutions obey Vegard’s rule. Autoadsorption was not taken into account.

To calculate the melting point, we used the expressions [13]

\[
T_m(r) = T_m \left[ 1 + \frac{(2/3)\sigma_s(r)(v_l - v_s) - (5/3)v_s\sigma_{sl}(r)}{L - \frac{2T_m}{r} \left( v_l - v_s \left( \frac{d\sigma_s}{dT} - \frac{d\sigma_l}{dT} \right) \right) - (5/3)v_s\left( \frac{d\sigma_s}{dT} - \frac{d\sigma_l}{dT} \right)} \right],
\]

\[
T_m(r) = T_m \left[ 1 + \frac{(2/3)\sigma_l(r)(v_l - v_s) - (5/3)v_l\sigma_{sl}(r)}{L - \frac{2T_m}{r} \left( v_l - v_s \left( \frac{d\sigma_l}{dT} - \frac{d\sigma_s}{dT} \right) \right) - (5/3)v_s\left( \frac{d\sigma_s}{dT} - \frac{d\sigma_l}{dT} \right)} \right].
\]

Here \(T_m\) - the melting point of a massive body, \(L\) - the specific heat of melting of a bulk metal, \(\delta\) - the thickness of the skin layer, \(\sigma_s(r)\) and \(\sigma_l(r)\) are the surface tensions of the liquid and solid phases, \(\sigma_{sl}(r)\) - the interfacial tension, \(\rho_l\) and \(\rho_s\) - the densities of the liquid and solid phases, \(v_l\) and \(v_s\) - the specific volumes of the liquid and solid phases, respectively.

The crystallization temperature was calculated using the formula [14]:

\[
T_c(r) = T_m \left( 1 - \frac{v_s}{L\delta} \left[ \sigma_s(r) - \sigma_l(r) \right] \right).
\]

In (1) - (5) should also be borne in mind dependence of the specific heat of fusion of the particle size, which can be calculated from expressions [5] and [15]:

\[
L(r) = L \left( 1 - \frac{L}{r} \right)^3,
\]

\[
L(r) = \frac{3}{r} \left( \frac{\sigma_s(r)}{\rho_s} - \frac{\sigma_l(r)}{\rho_l} \right) - \frac{C_{ps}(T) - C_{ps}(T)}{T_m(r)}dT.
\]

Here, the parameter has the meaning of the thickness of the skin layer, \(C_{ps}(T)\) and \(C_{ps}(T)\) - the specific heat capacity at constant pressure of the metal in the liquid and solid states.

The calculation of the values of the surface energies of a solid particle and melt and interfacial tension, taking into account their size and temperature dependences, was carried out by a modified electron-statistical method [17-20]. In calculating these values used concentration of the liquid and solid phases, determined by using the experimental diagram of segments rules.

In the calculations according to (1) - (7), we take into account the particle size dependence of the density and the melt via loosening factor inversely proportional to particle size.
To obtain the values of the melting and crystallization temperatures of macroscopic alloys, the experimental diagram [1] was digitized in the Origin program. The size of the solid core was chosen to be 5 and 8 nm. The skin layer thickness was fixed at 2 nm. We did not take into account the change in the particle shape during melting.

![Figure 1. Phase diagram of the palladium-platinum binary metal system [1]](image)

3. Results and discussion

Figures 2 and 3 plot the temperature lines of phase transitions of binary Pd-Pt nanoparticles, obtained by us according to (1) - (5), which can be considered analogs of the liquidus and solidus lines of the bulk phase diagram. Comparison of Fig. 1 with fig. 2 and 3, not only changes the position of the phase transformations lines in the diagram, but also its shape. However, the form of the diagram remained the same - with unlimited solubility of the components in liquid and solid states. There are three regions on it - melt, solid solutions, and a two-phase region of coexistence of liquid and solid phases. The latter should be interpreted as a region of pronounced premelting, that is, the process of formation of a nanoheterogeneous core-shell system [12].

The size dependence of the specific heat of fusion was taken into account in two different ways in order to identify a more correct version of the assessment $T_m$ and $T_c$, according to expressions (4) and (5). Taking into account the dimensional dependence according to (4) in (1), (2) and (3) leads to a significant decrease in $T_m$ and $T_c$. The phase transition temperatures for the "palladium" part of the diagram are reduced by almost 50% of the bulk metal, and in the "platinum" part - below normal conditions. This contradicts the experimental data for the case of homogeneous melting of palladium particles with $r = 4$ nm [21] and the results of molecular dynamics simulation for platinum nanoparticles [22]. Thus, we can conclude that the complex application of (4) and (1) - (3) is not correct. The use of (5) leads to a decrease in $T_m$ and $T_c$ by several degrees in comparison with the data obtained without taking into account the size dependence of the specific heat of fusion of metals.

The calculation results show that there is a significant decrease in the temperatures of phase transitions for nanoparticles in the entire concentration interval compared to bulk materials. In particular, for palladium it decreases by 26%, for platinum - by 35.3% (Fig. 3b). The melting and crystallization temperatures of pure components for a given size of the system do not coincide ($T_c < T_m$, $\Delta T(Pd) \approx 3.5 K$, $\Delta T(Pr) \approx 5.8 K$), which is consistent with the data of works devoted to the study of melting hysteresis [5, 7-10].

The values $T_m$ of platinum are in agreement with the results of molecular dynamics modeling [21]. Comparison with the experimental and calculated values $T_m$ of palladium in the case of homogeneous
melting of a particle with a radius of 4 nm [20] shows good agreement between our results for the melting – crystallization phase transition temperatures of solid particles (r = 5 nm) in the presence of a skin layer 2 nm thick.

**Figure 2.** Phase diagram of palladium-platinum binary metal particles: a) calculation without taking into account (4) 1 - r = 8 nm according to (1) and (3); 2 - r = 8 nm, according to (2) and (3); 3 - r = 5 nm, according to (1) and (3); 4 - r = 5 nm, according to (2) and (3); b) calculation taking into account (4) 1 - r = 8 nm according to (1) and (3); 2 - r = 8 nm, according to (2) and (3); 3 - r = 5 nm, according to (1) and (3); 4 - r = 5 nm, according to (2) and (3)

**Figure 3.** Phase diagram of palladium-platinum binary metal particles: a) 1 - r = 8 nm according to (1), (3) and (5); 2 - r = 8 nm, according to (2), (3) and (5); b) 1 - r = 5 nm, according to (1), (3) and (5); 2 - r = 5 nm, according to (2), (3) and (5)

Calculations show that, for nanoparticles, the difference between the melting / crystallization temperatures of pure components decreases. For bulk metals, it is 214 K, for nanoparticles with r = 8 nm, 70.2 K and 81.7 K, respectively, which can be interpreted as an expansion of the region of existence of the melt (without taking into account the change in the temperatures of evaporation and sublimation). The temperature interval between the conditional lines of liquidus and solidus is significantly narrowed. For example, for a component concentration of 60% Pd-40% Pt, the difference between and is 8.5 K for a bulk alloy and 3.5 K and K for nanoparticles with a radius of 10 and 5 nm.

The lines of phase transformations (Figs. 2a and 3) have a smooth maximum in the range from 50 to 60%Pt for the crystallization process and 55-60%Pt for the melting process.
The presence of a maximum on the liquidus and solidus lines can be explained by the fact that the size dependences of the specific heat of fusion, surface and interfacial energies of platinum are much more pronounced than that of palladium. On the other hand, according to the criterion for choosing a surface-active component of a binary alloy [22], for bulk phases, palladium is a surfactant in the Pd – Pt system. Our calculations showed that, in the case of nanoparticles, the interfacial characteristics of palladium are also smaller in magnitude than those of platinum. Consequently, palladium remains a surfactant in the palladium-platinum system with a solid particle size of 5 and 10 nm and a skin layer thickness of 2 nm. Qualitative criteria for surface activity are also qualitative criteria for surface segregation. Thus, with a significant decrease in the melting and crystallization temperatures and their values approaching, one can expect that a core-shell structure (core - Pt, shell - Pd) will be formed in a binary particle of the Pd - Pt system due to the phenomena of segregation, which is consistent with experimental data [23].

4. Conclusion
In this work, using the electronic statistical method and thermodynamic expressions for the melting and crystallization temperatures, a phase diagram was constructed for nanoparticles of a palladium-platinum binary alloy. Melting and crystallization points are significantly reduced compared to bulk material. It is shown that when the dimensional effects of the surface characteristics and specific heat of fusion are taken into account, the diagram changes its shape, but does not change its type. At a size of 5 nm, the ratio between the phase transition temperatures of pure components changes (and), which should cause segregation in the nanoparticle and the formation of a core-shell structure.

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