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About the temperature of melting of metallic nanoparticles

Different approaches to the determination of temperature are considered. Thermodynamic consideration of clusters takes into account not only the energy of thermal motion of atoms, but also the potential energy of interaction of atoms in the cluster, including the energy of configuration excitation. The thermodynamic determination of the temperature of clusters is more complete and accurate. Thermodynamic consideration of clusters, taking into account their total internal energy and entropy, allows us to describe many processes occurring during structural transitions, and gives a deeper and more detailed understanding of the physics of phase transitions in clusters. In this paper we review various models of the melting temperature of nanoparticles and propose a quantum-statistical analysis of the melting of nanoparticles. To explain the change in the melting temperature of nanoobjects, the most widely used thermodynamic approach is based on taking into account the increasing role of surface energy with a decrease in the characteristic size. The dependence of the melting temperature of metal nanoparticles on size is also explained on the basis of the criteria proposed by Lindemann. According to Lindemann's ideas, the crystal melts when the root-mean-square displacement of atoms in the crystal becomes larger than the fraction of intraatomic distances. The molecular dynamics method allows one to study structural transitions, thermodynamic parameters, transport properties, and electronic states in complex systems. The increasing computing power of computers constantly expands the range of possible applications of the molecular dynamics method. At present, the behavior of quite complex systems containing tens of thousands of atoms is successfully modeled. With the help of nonequilibrium statistical thermodynamics, a connection was found between the microscopic (quantum) processes of interaction of primary fields (the parameters of which can be controlled and varied over a wide range) with the macroscopic characteristics of the physical object. In all cases, the size dependence of the melting temperature of nanoparticles is determined.

Keywords: temperature, thermodynamics, melting, atom, cluster, nanoparticle.

Introduction

In the molecular-kinetic theory of an ideal gas, the concept of temperature is closely related to the concept of thermal equilibrium. Bodies that are in contact with each other can exchange energy. The energy transferred by one body to another during thermal contact is called the amount of heat. Thermal equilibrium is a state of a system of bodies in thermal contact, in which no heat transfer occurs from one body to another, and all macroscopic parameters of the bodies remain unchanged. Temperature is a physical parameter, the same for all bodies in thermal equilibrium. The possibility of introducing the concept of temperature follows from experience and is called the zero law of thermodynamics.

The cluster temperature (nanoparticles) is determined by the energy of the random movement of the constituent atoms or molecules relative to its center of mass. If the rotational and translational degrees of freedom of the cluster are «frozen», then the internal temperature of the cluster T_{cl} is determined by the relation [1]:

$$\frac{3N}{2}k_B T_{cl} = \left\langle \sum_{i=1}^{N} \frac{m_i(\upsilon_{cm}-\upsilon_i)^2}{2} \right\rangle, \qquad (1)$$

where m_i and υ_i are the mass and velocity of the constituent atoms (molecules), υ_{cm} is the velocity of the cluster's center of mass, N is the number of particles in the cluster, and k_B is the Boltzmann constant.

Relation (1) is the kinetic determination of the cluster temperature. The cluster temperature can also be defined as a thermodynamic quantity:

$$T_{cl} = \frac{dE}{dS}, \qquad (2)$$

where *E* and *S* are respectively the total internal energy and entropy of the cluster. The temperatures determined by the relations (1) and (2) are in general different quantities, and their difference can lead to fundamental consequences (see, for example, refs. 2 and 3 and references therein). Thermodynamic consideration of clusters takes into account not only the energy of thermal motion of atoms, but also the potential energy of interaction of atoms in the cluster, including the energy of configuration excitation. Thus, for a cluster consisting of N atoms with pair interaction:

$$E = U + K = \sum_{ij} u(r_{ij}) + \frac{m}{2}\sum_{i}\left(\frac{dr_i}{dt}\right)^2. \tag{3}$$

Here, U is the total potential energy, K is the total kinetic energy of the atoms, and $u\ (r_{ij})$ is the interaction potential of two atoms at a distance between them $r_{ij} = r_i - r_j$, where r_i, r_j are the coordinates of the atoms, and m is the atomic mass. For the entropy of a cluster, in this case we can take the general expression for entropy [4]:

$$S = -\langle \ln P \rangle = -\sum_{i} P_i \ln P_i, \tag{4}$$

where the subscript i characterizes the state of the cluster and P_i is the probability of finding a cluster in this state $\left(\sum_i P_i = 1\right)$. By configurational excitation we mean transitions from the ground state of the cluster to local minima of the multidimensional space of the potential energy surface. In particular, it is the configurational excitations that lead to a change in the structure and aggregate state of the clusters [2–6].

The thermodynamic determination of the temperature of clusters is more complete and accurate. Thermodynamic consideration of clusters, taking into account their total internal energy and entropy, allows describing many processes occurring during structural transitions, and provides a deeper and more detailed understanding of the physics of phase transitions in clusters [2–6]. Thus, on the basis of thermodynamic considerations, it was predicted, for example, the possibility of the existence of a negative heat capacity of the cluster near the melting point [7–10].

The most important results of the solid-liquid phase transition studies in clusters and nanoparticles are: 1) the coexistence of two phases in a certain temperature range in the vicinity of the thermodynamic equilibrium temperature; 2) representation of the solid-liquid phase transition in clusters as configurational excitation; and 3) the possibility of the negative heat capacity of the cluster near the melting point.

In this paper we review various models of the melting temperature of nanoparticles and propose a quantum-statistical analysis of the melting of nanoparticles.

Thermodynamic approach

To explain the change in the melting temperature of nanoobjects, the most widely used thermodynamic approach, which goes back to Pavlov's work [11], is based on taking into account the increasing role of surface energy with a decrease in the characteristic size.

Strictly speaking, the concept of a phase transition for small particles makes sense only as an approximation, since true phase transitions can occur only in infinitely large systems. It is in this context that Pavlov's statement [11] needs to be understood that, as the particle size decreases, the melting temperature Tm decreases. The corresponding result is easily obtained by equating to each other the chemical potentials of the solid and liquid phases for which expression (5) with the appropriate parameters is used, and decomposition of these potentials by temperature and pressure near the melting point of a bulk sample:

$$\delta F / \delta N_C = \mu_0(p_g + p_i) - \mu_g(p_g) = 0. \tag{5}$$

Then, using the thermodynamic relations

$$s_i = \partial\mu_i / \partial T, \quad n_i^{-1} = \partial\mu_i / \partial p,$$

where s_i is the entropy per atom in the i-th phase, we obtain:

$$\frac{T_m}{T_{m_0}} - 1 = \frac{2}{Q}\left[\frac{\sigma_2}{n_2 R_2} - \frac{\sigma_1}{n_1 R_i}\right], \tag{6}$$

$$Q = T_{m_0}(s_2 - s_1),$$

where T_{m_0} is the heat of fusion of the bulk sample. The surface tension σ_2 for a liquid is much lower than for a crystal σ_1 but the densities of both phases are close to each other, from which Pavlov's assertion follows.

On the basis of Pavlov's approach, the simplest types of phase diagrams for nanoobjects are considered in [12] and it is shown that in the general case for small samples the relative change in the temperature of the phase transformation is determined by expression:

$$\frac{\Delta T}{T_s}=\frac{\Delta\Omega}{\lambda}\cdot\frac{k}{d}, \tag{7}$$

where k is the shape factor equal to 6, 4 and 2 for a particle, a thin filament and a film respectively, λ is the heat of conversion, $\Delta\Omega$ is the change in the specific surface energy for the phase transformation of a small object with a characteristic dimension d (particle diameter or fine filament, films).

Various modifications of this approach are presented in [13–26].

A completely different physical picture of the melting of small particles was proposed in [27]. It consists in that clusters with a given number of atoms in them exhibit a sharp lower temperature limit for the thermodynamic stability of the liquid form and a sharp upper limit T_m for the stability of the solid form. The set of identical clusters behaves like a statistical ensemble, which within a certain temperature and pressure region consists of two types of clusters: solid and liquid. The ratio of their numbers in thermal equilibrium is equal to the difference of free energies in the solid and liquid states. But this equilibrium is dynamic, each individual cluster changes the form in which it is located. However, the frequency of the transition between these phases is sufficiently low, and equilibrium properties can be established for each phase. The results of [27] were obtained analytically by analyzing the density of cluster states.

The phonon model

The dependence of the melting temperature of metal nanoparticles on the size is also explained on the basis of the criteria proposed by Lindemann [28]. According to Lindemann's ideas, the crystal melts when the root-mean-square displacement $\langle u\rangle$ of atoms in the crystal becomes larger than the fraction of intraatomic distances. An increase in temperature leads to an increase in the amplitude of the oscillations. At a certain temperature they become sufficiently large, they destroy the crystal lattice, and the solid begins to melt. Atoms of the surface are less strongly bound, and under real conditions this can lead to large oscillation amplitudes at the same temperature as for the atoms in the bulk of the particle. This effect can be described as the mean square displacement of atoms on the surface of a particle $\langle u_S^2\rangle$ and $\langle u_V^2\rangle$ inside it. The fraction of surface atoms in spherical nanoparticles measuring 3 nm reaches about 50%, and their oscillations strongly influence the Lindemann criterion. This circumstance was used to describe the dependence of the melting temperature of nanoparticles on their size without using the concepts of thermodynamics. The phonon model, which considers the decrease in the temperature of nanoparticles with a decrease in their size, is developed in [29]. To describe the properties of nanoparticles

$$\frac{T_m(r)}{T_m(\infty)}=\exp\left[-(\alpha-1)\left(\frac{r}{3d}-1\right)^{-1}\right], \tag{8}$$

where $T_m(r)$ and $T_m(\infty)$ are the melting points (K) of a nanocrystal and a compact metal, respectively; d is the height of the monolayer of atoms in the crystal structure; r is the radius of the particle, α is the ratio of the root-mean-square displacements at the surface and in the volume of the nanoparticle (the value of α varies in most cases from 2 to 4).

Nanothermodynamics

The foundations of nanothermodynamics were laid by T. Hill [30]. The fundamental equations have the form:

$$dE=TdS-pdV+\mu dN; \tag{9}$$

$$E=TS-pV+\mu N+W, \tag{10}$$

In nanothermodynamics, in contrast to classical thermodynamics, there are two chemical potentials, «integral» $\hat{\mu}$ and «differential» μ, for which:

$$G=N\hat{\mu}; \tag{11}$$

$$N\left(\frac{\partial G}{\partial N}\right)_{p,T}=N\mu, \tag{12}$$

where G is the free Gibbs energy, N is the number of molecules in the nanoparticle. The difference between the potentials $\hat{\mu}$ and μ is related to the nonzero value W:

$$\widehat{\mu}-\mu=\frac{1}{N}W. \tag{13}$$

When the number of molecules is N → ∞, the chemical potentials $\widehat{\mu}$ and μ tend to one limit μ_0. It is shown in [31] that the chemical potentials for a fixed mass of a particle satisfy the following equations:

$$\widehat{\mu}-\mu_0=\frac{m_0}{\rho}\frac{3\sigma}{r}; \tag{14}$$

$$\mu-\mu_0=\frac{m_0}{\rho}\left(\frac{2\sigma}{r}+\frac{\partial\sigma}{\partial r}\right), \tag{15}$$

where m_0 is the mass of the molecule, ρ is the density of the nanoparticle, σ is the surface tension, r is the radius of the equimolecular surface.

Formulas (14)–(15) can be used both in liquid and in solid states; it should be taken, μ_0 describing the corresponding macroscopic phase. For nanoparticles that are capable of solidifying or, on the contrary, melting, there are four chemical potentials: two «differential» chemical potentials μ and two «integral» chemical potentials $\widehat{\mu}$. Further, the indices s and l correspond to the solid state and the liquid state.

Hill [30] showed that the phase transition occurs when the «integral» chemical potentials coincide:

$$\widehat{\mu}_s=\widehat{\mu}_l. \tag{16}$$

According to Hill, the melting point of the nanoparticle is:

$$T_m=T_0+\frac{N^{-1/3}\Delta a}{\Delta S_0}, \tag{17}$$

where T_m is the melting point of the nanoparticle, T_0 is the melting point of the macroscopic (large) crystal, ΔS_0 is the change in the specific entropy upon melting of the crystal (per molecule), N is the number of molecules in the nanoparticle:

$$\Delta a=N^{-2/3}(\sigma_l A_l-\sigma_S A_S). \tag{18}$$

σ_l and σ_S are the surface tension of liquid and solid particles of the same mass, and A is the surface area of the particle. In this case, the quantity Δa <0.

Computer Models

The regularities and mechanisms of melting-crystallization hysteresis in transition metal nanoparticles (gold, nickel, silver, and copper) were studied in papers [32–40] using molecular dynamics (MD) and the strong-coupling potential. MD allows us to study structural transitions, thermodynamic parameters, transport properties, as well as electronic states in complex systems. The increasing computing power of computers constantly expands the range of possible applications of the MD method. At present, the behavior of quite complex systems containing tens of thousands of atoms is successfully modeled.

The MD method calculates in the phase space the trajectories of a set of molecules, each of which obeys the classical laws of motion. Usually the MD method uses Newton's equations:

$$\frac{d\mathbf{r}_i}{dt}=\boldsymbol{\upsilon}_i; \tag{19}$$

$$\frac{d\upsilon_i}{dt}=\mathbf{a}_i=\frac{1}{m_i}F_i, \tag{20}$$

where r_i are the coordinates of the i-th particle, v_i is the velocity, m_i is the mass, a_i is the acceleration, F_i is the force acting on the particle i from the side of all other particles.

The forces acting in the system are determined through the potential energy of the interaction of the particles V:

$$\mathbf{F}_i=-\frac{\partial V}{\partial\mathbf{r}_i}. \tag{21}$$

To calculate the trajectory of molecules it is necessary:

1) choose a numerical scheme for approximating the equations of motion;
2) define the potential of interparticle interaction;
3) define the boundary and initial conditions.

For the numerical solution of the equations of motion (19, 20), the derivatives are replaced by finite differences. Usually, numerical schemes based on the expansion of the coordinates and velocities in the Taylor series with respect to the time step Δt are used for this purpose. The preservation in the Taylor series of terms containing the first power Δt leads to the Euler method. The accuracy of Euler's method is not high. Its local error (error in step) has the value O $[(\Delta t)^2]$, but the accumulation of error from step to step leads to a global error of the order O (Δt).

Another widely used numerical scheme is the Verlette velocity algorithm (Verlet algorithm):

$$\begin{aligned}\mathbf{r}_i^{(n+1)} &= \mathbf{r}_i^{(n)} + \boldsymbol{\upsilon}_i^{(n)}\Delta t + \frac{1}{2}\mathbf{a}_i^{(n)} \cdot (\Delta t)^2; \\ \boldsymbol{\upsilon}_i^{(n+1)} &= \boldsymbol{\upsilon}_i^{(n)} + \frac{1}{2}(\mathbf{a}_i^{n+1)} + \mathbf{a}_i^{(n+1)})\Delta t.\end{aligned} \qquad (22)$$

The circuit (22) is self-starting and has the third order of global error in coordinate and second in speed.

The correct choice of the interaction potential is the most important condition for an adequate simulation of the properties of the system under study. There are two basic approaches to the description of the molecular dynamic model of a physical system: classical and quantum mechanical. The classical approach treats atoms as material points, which have mass and charge, without taking into account the complex structure of atoms. The interaction between atoms and molecules is described by formulas that have an empirical character and contain a number of adjustable parameters. This approach makes it possible to determine stable configurations of the simulated system, to study the kinetics of the course of phase transitions. The quantum-mechanical approach takes into account the electronic subsystem of atoms and allows calculating the energy levels of the simulated system, the configuration of electronic orbitals, absorption spectra, etc.

It is known that a lot of methods are used to produce nanoparticles, but the problem of preparing clusters with a certain size, shape, structure and physical properties has not been solved yet. Some of the methods for producing nanoparticles are amenable to direct computer modeling and, in particular, the synthesis of nanoclusters from the gas phase by condensation.

There are many different approximations that differ both in the level of complexity of the mathematical apparatus and in the degree to which the interaction features are taken into account. The theoretical foundations for constructing the most effective interatomic interaction potentials used in MD modeling (Lennard-Jones, effective medium methods, immersed atom and strong coupling) are laid. Successful use of the modified strong-coupling potential (TB-SMA) with a fixed cut-off radius corresponding to the fifth coordination sphere inclusive [41]. These potentials are widely used in computer modeling, both macroscopic bodies and clusters. In this case, there is a positive experience of their use even in the analysis of very small 13-atom clusters, for example, Ni-Al alloy. This potential is able to carefully consider the processes of particle formation and structure on time scales characteristic for nucleation and further particle growth processes and take into account the main features of the interatomic interaction in nickel and copper. In addition, the potentials developed by Clery and Rosato are very well proven in the modeling of systems in the crystalline state and have undergone a detailed successful verification [41] in many respects. In particular, a number of parameters of point defects (vacancies, interstices and their small complexes) were compared with experimental data, a number of thermodynamic properties of metals (melting point, heat of transition, heat capacity, thermal expansion coefficient, Grüneisen constant, etc.), and the same phonon spectra.

Nonequilibrium quantum thermodynamics

To measure any physical property of the object under investigation, it is necessary to act on it by some primary field (magnetic, electrical, etc.) and measure the secondary field (the response of the system), the value of which carries information about the object. Since the process of interaction of the object with the field usually proceeds rather quickly (the time of single-particle relaxation is ≈ 10-12 s), it is clear that this process is far from equilibrium.

On the other hand, the characteristics of the secondary field carry information about an object that is in certain thermodynamic conditions and possesses thermodynamic parameters that are directly related to its structural, chemical and physical properties.

Thus, using nonequilibrium statistical thermodynamics, one can find the connection between the microscopic (quantum) processes of interaction of primary fields (the parameters of which can be controlled and varied over a wide range) with the macroscopic characteristics of the physical object.

Consider defects (elementary excitations), as a system of non-interacting particles, immersed in a thermostat. Quantum transitions due to the interaction of defects with a thermostat will be dissipative (with probability P), in contrast to interaction with an external field (with probability). Dissipative processes lead to the fact that the secondary field Z2 is always smaller than the primary Z1.

Since the subsystem of defects exchanges only the energy with the thermostat, the ensemble of particles corresponding to them will be canonical [4]. Then the expression for the statistical entropy has the form:

$$S = -k\sum_i f_i \ln f_i, \tag{23}$$

where f_i is the distribution function; k is the Boltzmann constant.

Differentiating (23) with respect to time and transforming, we obtain:

$$\frac{dS}{dt} = \frac{k}{2}\sum_{i,j}\left(lhf_i - \ln f_j\right)\left(P_{ij}f_i - P_{ji}f_j\right), \tag{24}$$

where P_{ij} is the transition probability from the initial i (with energy E_i) to the excited state j (with energy E_j).

For dissipative processes, the principle of detailed equilibrium has the form:

$$\frac{g_i P_{ij}}{g_j P_{ji}} = e^{\frac{E_j - E_i}{kT}}, \tag{25}$$

where g_i and g_j are the statistical weights for the levels E_i and E_j.

Then (24) takes the form:

$$\frac{dS}{dt} = \frac{k}{2}P_{ij}\left(\ln f_i - \ln f_j\right)\left(f_i - \frac{g_i}{g_j}f_j e^{-\frac{E_i - E_j}{kT}}\right), \tag{26}$$

The canonical distribution function [4]:

$$f_{ij} = \frac{1}{Z}e^{-E_{ij}/kT}, \tag{27}$$

where the partition function:

$$Z = e^{-G/kT}, \tag{28}$$

where G is the potential (free energy) of the Gibbs system of thermostat + system.

Let us assume that the nonconfigurational part of the Gibbs potential depends linearly on the concentration of N defects:

$$e^{-G/kT} = \sum_N h(N), \tag{29}$$

$$h(N) = \omega(N)\cdot e^{-G/kT}; \tag{30}$$

where ω (N) is the statistical weight.

After cumbersome but simple calculations, it can be shown that the function h (N) is the Gaussian distribution near the equilibrium value with a small variance, i.e.

$$h(N) = h(\bar{N})e^{-\Delta\bar{N}^2/N}. \tag{31}$$

Substituting (31) into (29), we have:

$$e^{-G/kT} = h(\bar{N})\sum_{\Delta N} e^{-\Delta\bar{N}^2/\bar{N}}. \tag{32}$$

To estimate the sum in (32), we replace it by the integral:

$$\sum_{\Delta N} e^{-\Delta\bar{N}^2/\bar{N}} = \int_{-\infty}^{+\infty} e^{-x^2/\bar{N}}dx = \sqrt{\pi x}.$$

Then (32) takes the form:

$$e^{-G/kT} = h(\bar{N})(\pi\bar{N})^{1/2}. \tag{33}$$

Using (29) and taking the logarithm from (33), we find:

$$G/kT = -\ln\omega(\bar{N}) + \frac{G(\bar{N})}{kT} + \frac{1}{2}\ln(\pi\bar{N}), \tag{34}$$

where $G(\bar{N})$ is part of the total Gibbs potential associated with the concentration of magnetic dipoles. From the estimate of the first logarithmic term:

$$\ln \omega(\bar{N}) = N \ln\left(1+\frac{\bar{N}}{N}\right) + \bar{N}\ln\frac{N+\bar{N}}{N} . \tag{35}$$

Approximating the logarithm in the first term on the right-hand side of (35) by the first term of its series expansion, and the second term, expressing in terms of the Gibbs potential of the system of magnetic dipoles G^f, we obtain:

$$\ln \omega(\bar{N}) = \bar{N} + \bar{N}G^f/kT . \tag{36}$$

Substituting (36) into (34) and neglecting the term $1/2\ln\left(\pi\bar{N}\right)$ in comparison with $\bar{N}$, we obtain:

$$G = G(\bar{N}) - \bar{N}G^f - \bar{N}kT. \tag{37}$$

As above, assuming that the thermodynamic potential $G(\bar{N})$ depends on the equilibrium number of defects C^f in a linear fashion, i.e:

$$G = G^0 + \bar{N}G^f, \tag{38}$$

where G^0 is the thermodynamic potential of the thermostat, we find:

$$G = G^0 - \bar{N}kT. \tag{39}$$

With the aid of (38), expression (28) is transformed to the form:

$$Z = e^{-G^0/kT}e^{\bar{N}}. \tag{40}$$

Substituting (40) into (26), we find:

$$\frac{dS}{dt} = \frac{k}{2}\sum_{i,j} P_{ij} e^{G^0/kT} e^{-\bar{N}} e^{-E_i/kT}\left(\frac{E_j - E_i}{kT}\right)\left(1-\frac{g_i}{g_j}e^{2\frac{E_i-E_j}{kT}}\right). \tag{41}$$

Neglecting the small terms and replacing the sum in (41) by an integral (as is true for a continuous spectrum of values of the energy of defects), we obtain:

$$P = \frac{2\Delta S}{k\tau}\exp\left\{-\frac{E_m - G^0/N}{kT}\right\}, \tag{42}$$

where ΔS is the entropy change in the dissipative process; Em is the mean value of the ground-state energy of the defects; τ is the relaxation time.

The response function of the system to the external action is:

$$\Omega = \frac{F}{F+P}, \tag{43}$$

where $F = 1/\tau$.

Equation (43) can be reduced to a linear form and written down:

$$\Omega(r) = \Omega_0\left(1-\frac{d}{r}\right), \tag{44}$$

where $d = 2\sigma\upsilon/RT$, σ is the surface tension, υ is the atomic volume, R is the gas constant, and T is the temperature.

If we take the melting temperature T_m as the response function in (44), we obtain:

$$T_m(r) = T_0\left(1-\frac{d}{r}\right), \tag{45}$$

T_0 is the temperature of a massive sample.

Equation (45) coincides with the Tolman equation [42], but the parameter d has a different physical meaning and coincides with the thickness of the surface layer.

In recent years, studies of multi-element (highly entropic) alloys and coatings based on them have begun to develop intensively in a number of countries (see, for example, reviews [43–47]). This is due to their unique physical properties and opens the prospect of obtaining new construction materials for the needs of various industries.

We also started work on the synthesis of multi-element (high-entropy) coatings and obtained good results on hardening, anticorrosive, thermally and radiation-resistant coatings [48-54].

The following results were obtained:

– a relationship between the surface energy and the melting point of a metal and its compounds was obtained [55], as well as the universal dimensional dependence of the physical properties of nanomaterials [56];

– a method for determining the surface tension of deposited coatings was first proposed [57, 58];

– on the basis of our studies [55–58], it was possible to predict for the first time the physical properties of nanocrystalline and functional coatings [59, 60].

The novelty of the proposed technology is as follows:

– using the results of our studies [61, 62], we select nanoparticles of pure metals or their compounds of such dimensions, whose melting point is practically the same, but almost 1000 °C below the melting point of bulk samples [63];

– when melting such a mixture of nanoparticles, a single-phase structure with unique physical properties should be obtained [43–45];

– from such an alloy cathodes and targets for the application of high-entropy coatings.

Conclusion

In Kazakhstan, special steels are not produced for the manufacture of most parts of machinery and machinery of industrial enterprises. The proposed technology for applying high-entropy coatings gives products from simple steel grades that are produced in Kazakhstan, performance characteristics that are not inferior to products made from special steels. This leads to a decrease in the cost of production by about 5–12 times.

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Металл нанобөлшектердің балқу температурасы туралы

Температураны анықтаудың әртүрлі тәсілдері зерттелді. Кластерлердің термодинамикалық қарастырылуында атомдардың жылу қозғалысының энергиясы ғана емес, кластердегі атомдардың өзара әрекеттесуінің әлеуетті энергиясы, сонымен қатар конфигурациялық қоздыру энергиясы да ескерілді. Кластерлердің температурасын термодинамикалық анықтау неғұрлым толық және дәл болып табылады. Кластерлердің термодинамикалық қарастырылуында олардың жалпы ішкі энергиясын және энтропиясын ескере отырып, құрылымдық ауысулар кезінде орын алған көптеген процестерді сипаттауға мүмкіндік береді және кластерлердегі фазалық ауысу физикасына тереңірек және толық түсінік береді. Мақалада нанобөлшектердің балқу температурасының әртүрлі үлгілері қарастырылған және нанобөлшектердің балқуының кванттық-статистикалық талдауы ұсынылған. Нанообъектілердің балқу температурасының өзгеруін түсіндіру үшін, сипатты мөлшерінің азайтылуымен беттік қуаттың рөлінің өсуін ескере отырып, термодинамикалық әдіс кеңінен пайдаланылады. Металл нанобөлшектерінің балқу температурасының мөлшеріне тәуелділігі Линдеманн ұсынған критерийлердің негізінде де түсіндіріледі. Линдеманның идеясына сәйкес, кристалдағы атомдардың орташа-квадраттық жылжуы ішкі атомдық қашықтықтардың үлесінен үлкен болған кезде кристалл ериді. Молекулярлық динамика әдісі құрылымдық ауысуларды, термодинамикалық параметрлерді, көшіру қасиеттерін және күрделі жүйелердегі электрондық күйді оқып үйренуге мүмкіндік береді. Компьютерлердің артушы есептеуіш қуаты молекулалық динамика әдістерінің ықтимал қосымшалар спектрін үнемі кеңейтеді. Қазіргі уақытта он мыңдаған атомды қамтитын өте күрделі жүйелердің тәртібі табысты үлгіленуде. Айнымалы статистикалық термодинамиканың көмегімен физикалық объектінің макроскопиялық сипаттамалары бар бастапқы диапазондардың өзара әрекеттесуінің микроскопиялық (кванттық) процестері (олардың параметрлерін кең ауқымда бақылауға және өзгеруге болады) арасында байланыс анықталған. Барлық жағдайларда нанобөлшектердің балқу температурасының біркелкі тәуелділігі анықталды.

Кілт сөздер: термодинамика, балқу температурасы, атом, кластер, нанобөлшек, молекулярлық динамика әдісі.

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О температуре плавления металлических наночастиц

В статье рассмотрены различные подходы к определению температуры. При термодинамическом рассмотрении кластеров учитывается не только энергия теплового движения атомов, но и потенциальная энергия взаимодействия атомов в кластере, в том числе энергия конфигурационного возбуждения. Термодинамическое определение температуры кластеров является более полным и точным. Термодинамическое рассмотрение кластеров с учётом их полной внутренней энергии и энтропии позволяет описывать многие процессы, происходящие при структурных переходах, и даёт более глубокое и детальное понимание физики фазовых переходов в кластерах. В настоящей работе дан обзор различных моделей температуры плавления наночастиц и предложено квантово-статистическое рассмотрение плавления наночастиц. Для объяснения изменения температуры плавления нанообъектов наиболее широко используется термодинамический подход, основанный на учете возрастающей роли поверхностной энергии с уменьшением характерного размера. Зависимость температуры плавления наночастиц металлов от размера объясняется также на основе критериев, предложенных Линдеманом. Согласно представлениям Линдемана, кристалл плавится, когда среднеквадратичное смещение атомов в кристалле становится больше доли внутриатомных расстояний. Метод молекулярной динамики позволяет изучать структурные переходы, термодинамические параметры, свойства переноса, а также электронные состояния в сложных системах. Возрастающая вычислительная мощность компьютеров постоянно расширяет спектр возможных приложений метода молекулярной динамики. В настоящее время успешно моделируется поведение достаточно сложных систем, содержащих десятки тысяч атомов. С помощью неравновесной статистической термодинамики найдена связь между микроскопическими (квантовыми) процессами взаимодействия первичных полей (параметры которых можно контролировать и изменять в широких пределах) с макроскопическими характеристиками физического объекта. Во вех случаях определена размерная зависимость температуры плавления наночастиц.

Ключевые слова: термодинамика, температура плавления, атом, кластер, наночастица, метод молекулярной динамики.

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