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The Physical Chemistry of Energy-saturated Media

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The physicochemical properties of ultradispersed media, as a particular case of energy-saturated media, have been reviewed. The size dependence of the temperatures of fusion, polymorphic transformation, and sintering, the diffusion coefficients, and the chemical activity of ultra-small particles have been explained from a single viewpoint. Methods for obtaining ultradispersed powders, and methods for producing an ultradispersed structure in metals and alloys, have been described. The bibliography contains 96 references.

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I. INTRODUCTION

Energy-saturated media are media into which an excess of energy, comparable with the internal energy of the equilibrium condensed medium, has been introduced by some means. An energy-saturated medium can be produced by dispersal of the substance, plastic deformation of solids, quenching of a metastable structure or a supersaturated solution in alloys, irradiation of solids with a beam of neutrons or hard γ-radiation, etc.

In practice, a combination of these methods is most frequently used. Irrespective of the method used to obtain the dispersed system, its excess energy is determined either by the surface energy or by the formation of metastable solutions (in particular by an increase in the limiting solubility of inert gases in small particles). At the lower limit of the particle size of dispersed systems (<5 nm), that is in ultradispersed (UD) media, the contribution of these forms of energy is comparable with the internal energy, so that the definition of energy-saturated media is satisfied, in particular, by UD media.

Cooling a melt sufficiently rapidly (up to 10^6 K s^{-1}) makes it possible to fix metastable structures (phases), supersaturated solid solutions, and systems with dispersed phase components.

The deformation of metals and alloys leads to the appearance of dislocations, disclinations, and vacancies, and hence to saturation by an excess of energy if the relaxation time is sufficiently long.

The irradiation of a solid by neutrons, a beam of charged particles, or hard electromagnetic radiation produces radiation defects: vacancies and interstitial atoms, accumulations of vacancies, and impurity atoms (on neutral irradiation or as a result of ion implantation), again leading to energy saturation.

All states of this kind are non-equilibrium states. In some cases they are metastable states (when the system is at an intermediate energy minimum), and in other cases they are kinetically hindered states. The present review deals only with states for which the relaxation time is sufficiently long for local equilibrium to be established, and in a number of cases a thermodynamic approach can be used to discuss these systems. The chief characteristics of these media will be discussed for the case of UD media.

Ultradispersed media (UDM) represent unique states of condensed substances—macroscopic ensembles of ultra-small particles with dimensions reaching about 10 nm. The unusual properties of UD systems may be due both to the characteristic features of the individual ultra-small particles present in the ensemble and to their collective behaviour, determined by the nature of the interaction between them. In UDM, the surface states acquire particular importance, since in an ultra-small particle the number of atoms on the surface becomes comparable with the number of atoms in the bulk, so that the contribution of the surface energy to the total energy of the particle becomes comparable with that of the bulk energy. Thus for the liquid droplets of aluminium at 10^3 K, the proportion of excess (surface) energy relative to the bulk energy increases from 9% to 45% with decrease in the particle size from 10 nm to 20 nm.[1] The developed surface influences the lattice and electronic subsystems of the UDM, changing the spectra of various elementary excitations sensitive to change in the symmetry and the boundary conditions. The interaction of the particles in the system determines those physical properties of the UDM resulting from the correlation of the electronic and phonon states of the system. Finally, the presence of a large excess of energy in the ultra-small particles leads to an increase in their chemical activity, and this on the one hand must be taken into account in their preparation (the problem of "passivation") but on the other hand can be used in various technological processes.

A basis for the physical chemistry of UDM is provided by the theory of heterophase fluctuations,[2] the physicochemical mechanics of materials,[3] the thermodynamics of "small" systems,[4,5] and the fundamental postulates of thermodynamics and statistical physics.[6]

In the last 10 years, the properties of ultradispersed metal particles and powders (UDP) have been actively studied,[7-9] the properties of clusters in ultra-fine channels, in particular in the pores of zeolites, have been studied,[10] plasma-chemical methods for obtaining UDP [11-14] and methods for the thermal decomposition of solid substances[15] have been developed, new properties of ultradispersed carbon materials have been studied,[16,17] the thermodynamics of metastable states and methods for producing ultradispersed structures in compact solids under synthesis conditions and with plastic deformation,[17-21] and the technology of the production of heat-resistant amorphous alloys,[22] have been developed, and the physicochemical properties of materials with ultradispersed structures have been studied.[23]

An important methodological addition to the physicochemical analysis of metastable (ultradispersed) systems is the need to take account of not only the composition and physicochemical and mechanical properties but also the structural characteristics of the reaction products. An important structural characteristic of a material is its degree of dispersion. The three-term formula of classical physicochemical analysis, "composition–structure–property", can be supplemented by the additional term "degree of dispersion". This is particularly obvious for materials with degrees of dispersion at the lower limit of the size of the structural fragments. Thus in compact form the extended equation of physicochemical analysis[24] has the following form:

Composition	Structure	Degree of dispersion	Property
Atomic, molecular (mass) from 0 to 100%	Determined by X-ray diffraction or spectroscopy (infrared, NMR, Mössbauer, EPR, etc.), and also determination of structural defects (dislocations, defects, associations of defects)	From monoatomic or molecular to single crystals, including the colloidal state	All measurable properties (physics, thermodynamics, mechanics, resistance of materials)

The introduction of the degree of dispersion into the basic equation of physicochemical analysis requires firstly the accumulation of the appropriate experimental data. This is done using the methods of modern experimental physics: X-ray, electron, and neutron diffraction, Auger, photoelectron, and infrared spectroscopy, secondary ion mass spectrometry, nuclear and electronic magnetic resonance, and the methods of crystal chemistry.

The effects of size on physicochemical properties, clearly revealed in ultradispersed systems, are used in various practical technological processes. For example, the production of a system of ultrafine channels from powders makes it possible to use capillary effects in low-temperature soldering processes. Ultradispersed powders can provide a basis for the production of pastes for the permanent joining of materials of different kinds, and also for the development of composition materials with improved physicomechanical properties for the production of tungsten-free hard alloys and special optical and other materials. The use of UDM as additives in powder metallurgy (for example in sintering) decreases considerably the energy of the activation processes. Promising possibilities are provided by the electrophysical properties of powdered pure metals and their compounds (nitrides, carbides, borides, etc.), which can be used as superconducting and semiconducting materials and as getters, catalysts, and filters with improved properties. The products of a stable ultradispersed structure in compact materials leads to an increase in their strength up to the theoretical value and to increased values of the hardness and toughness.

The use of energy-saturated and in particular ultradispersed media is now one of the most important conditions for the development of the new technology in various branches of the national economy. The importance of this field is the reason for the development of intensive studies in the USSR and other countries (West Germany, Japan, the USA, France, Sweden, etc.).

The solution of the problems associated with the technological application of energy-saturated media, leading to direct "production of materials", is not a remote possibility. The comprehensive development of this field of study is therefore now necessary.

II. THE PHYSICOCHEMICAL PROPERTIES OF ENERGY-SATURATED MEDIA

1. The Thermodynamics of Small Systems. The Minimum Size of Particles with the Characteristics of the Phase

The thermodynamic and statistical-mechanical approaches to the study of the theory of UDM have developed fruitfully in recent years. In the thermodynamic approach, difficulties arise, associated with the limiting change to small systems. Classical thermodynamics and statistical physics no longer "operate" with decrease in the particle size to 1 nm.

When the degree of dispersion is introduced into the thermodynamic description, the energy of the system is no longer a linear homogeneous function of its variables;[5] an additional degree of freedom appears, namely the size of the particles in the ensemble, or in other words the degree of dispersion. According to the criteria adopted, this requires additional coordinates in the equilibrium diagrams. The physicochemical analysis of inorganic materials is therefore complicated considerably, particularly in the case of multi-component systems.

The non-additivity of the thermodynamic functions, due to the contribution of the phase interface, is taken into account in Gibbs thermodynamics by introducing the surface tension σ, related in definite fashion to the chosen interface surface, and leads to size effects of first order for the principal thermodynamic quantities. The extension of the thermodynamic approach to the range of small particle sizes (r < 5–7 nm), which is justified in the examination of ensembles of these particles, makes it necessary to take account of the size dependence $\sigma(r)$, and hence leads to second-order size effects for the principal thermodynamic quantities characterising the small system. It will be shown that σ decreases with decrease in r, leading to the lowered values of the Laplace pressure p_L, that is to a decrease in the proportion of the surface energy, which is characterised by p_L, relative to the bulk energy, compared with the result of the calculation for $\sigma = \text{const}$. Thus the first-order size effects are due to the basic non-additivity of the thermodynamic functions, whereas the second-order effects based on them are due to the elimination of this non-additivity and the approach of the bulk and surface states in a small particle. The second-order size effects represent the most characteristic feature of the physical chemistry of UDM. Their introduction makes it possible to extend considerably the range of applicability of the thermodynamic description to particles with small dimensions.

Using the thermodynamic approach, Tolman[25] obtained the following expression for $\sigma(r)$:

$$\ln\frac{\sigma(r)}{\sigma_s}=\int_{\infty}^{r}\left\{\frac{2\sigma}{r^2}\left[1+\frac{\delta}{r}+\frac{1}{3}\left(\frac{\delta}{r}\right)^2\right]\right\}dr\Big/\left\{1+\frac{2\delta}{r}\left[1+\frac{\delta}{r}+\frac{1}{3}\left(\frac{\delta}{r}\right)^2\right]\right\} \quad (1)$$

where σ_s is the surface tension of the planar phase interface, and $\delta = r_e - r$ the difference between the radii of the equimolar surface and the tension surface. In the general case the $\delta(r)$ relationship is not known. The determination of the $\delta(r)$ relation requires the statistical-mechanical calculation of the profiles of the density and the pressures of the interphase region for a real spherical structure corresponding to the given supersaturation. These calculations are fairly complex, and require the selection of some "single equation of state", by means of which, given the supersaturation of the vapour, it is possible to calculate the parameters of the pressure of the macroscopic condensed phase in equilibrium with it at a given temperature, to determine the density profile of the spherical formation, and to find the position of the equimolar surface and, from the profile of the basic pressures, the position of the tension surface. In addition, in the statistical-mechanical calculation it is necessary to make various assumptions associated with the description of the inter-phase region.

The following method for the closure of Tolman's expression (1) has been proposed.[26] The difference between the equimolar volume $V_e = 4\pi r_e^3/3$ and the tension volume $V = 4\pi r^3/3$ is related to the dispersion of the equimolar volume:

$$(\overline{(\Delta V_e)^2})^{1/2} = (kT\varkappa_T V_e)^{1/2}, \text{ that is } \quad V_e - V = a(kT\varkappa_T V_e)^{1/2} \quad (2)$$

where a is a correction factor, and $\varkappa_T$ the isothermal compressibility. Expressing r_e from Eqn.(2) in terms of r gives a $\delta(r)$ relationship of the form:

$$\delta(r)=\frac{r_0}{6^{1/3}}\left\{1+\left[1+6\left(\frac{r}{r_0}\right)^3\right]^{1/2}\right\}^{2/3}-r,\quad r_0=\left(\frac{9kT\varkappa_T a^2}{8\pi}\right)^{1/3} \quad (3)$$

Integrating Eqn.(1) with allowance for Eqn.(3) gives the explicit form of the expression for $\sigma(r)$:

$$\frac{\sigma(r)}{\sigma_s}=\left(\sqrt{1+y}+\frac{\sqrt{y}}{3}\right)^{1/3}\left(\sqrt{1+y}-\sqrt{y}\right);\quad y=\frac{1}{6}\left(\frac{r_0}{r}\right)^3 \quad (4)$$

In the range of small dimensions ($r \ll r_0$), Eqn.(4) gives a physically justified linear relationship $(\sigma(r)/\sigma_S) = r/r_0 + \ldots$, and the slope of the straight line is determined by the characteristic dimension r_0. At high $r \gg r_0$, the approach of σ to σ_S is described by the approximation

$$\frac{\sigma(r)}{\sigma_s}=1-\frac{2}{3}\left(\frac{2}{3}\frac{r_0}{r}\right)^{3/2}+\ldots$$

that is the influence of slight curvature on the surface tension is proportional to $r^{-3/2}$, in complete agreement with the results of statistical-mechanical calculations.[27]

Since Eqn.(2) contains the unknown factor a, the parameter r_0 can be found only by comparing the experimental $\sigma(r)$ relationship. These experimental data are not available, however. Another possibility is to consider data on the spinodals of the substance. This procedure[28] is based on the assumption that at the boundary of stability of the homogeneous original phase, that is on the spinodal defined by the condition $(\partial p_0/\partial v_0)_T = 0$, both the radius r of the tension surface of the critical nucleus of the new phase and the tension corresponding to this surface σ become zero. Here, v_0 is the volume corresponding to one mole of the vapour.

The radius of the tension surface of the critical nucleus of the competing phase satisfies the equations

$$\begin{cases} p_1 - p_0 = \dfrac{2\sigma}{r} & (5) \\ \mu(p_1, T) = \mu_0(p_0, T) & (6) \end{cases}$$

where 1 and 0 are the indices of the parameters of the liquid and vapour respectively. On going deeper into the metastable range as $p_0 \to p_2$ (the pressure on the spinodal), the size of the critical nucleus $r \to 0$, but the decrease in $\sigma(r) \sim r$ leads to the final value of the left-hand side of Eqn.(5). The approximation of Eqn.(4) in the range of small dimensions gives the expression

$$(p_1 - p_0)|_{p_0 \to p_2} = \frac{2\sigma}{r}\Big|_{r\to 0} = \frac{2\sigma_s}{r_0} \quad (7)$$

When $p_2(T)$ is known, the difference between the pressures in the left-hand side of Eqn.(7) can be determined from Eqn.(6). For two infinitely close states of equilibrium of the critical nucleus with the metastable vapour it is possible to write

$$d\mu_1(p_1, T) = d\mu_0(p_0, T)$$

or at constant temperature

$$\int_{p_s}^{p} v_1 dp_1 = \int_{p_s}^{p_0} v_0 dp_0 \quad (8)$$

The index s relates to quantities on the binodal. Neglecting the compressibility of the liquid ($v_1 = v_{1S} = \text{const}$) and regarding the vapour as an ideal gas ($v_0 p_0 = p_S v_{0S}$), Eqn.(8) with allowance for Eqn.(5) yields:

$$\frac{2\sigma}{r} = \frac{p_s v_{0s}}{v_{1s}} \ln\frac{p_0}{p_s} - (p_0 - p_s) \quad (9)$$

If in Eqn.(9) the last term is neglected and $p_S v_{0S}$ is replaced by kT, it is possible to obtain the familiar Kelvin equation: $\ln(p_0/p_S) = 2\sigma v_{1S}/kT$. The ideal-gas approximation is fairly crude in the metastable range, but the proposed[29] relation of the isotherm of an ideal gas not to the far range of the true isotherm, where they are in fact similar, but to the condensation point, reduces the error of the approximation considerably.

Equating p_0 in Eqn.(9) to p_2, and allowing for Eqn.(7), gives for the parameter $r_0(T)$ an expression of the form:

$$r_0 = 2\sigma_s \Big/ \left[\frac{p_S v_{0S}}{v_{1S}} \ln\frac{p_2}{p_s} - (p_2 - p_s)\right] \qquad (10)$$

If in Eqn.(3) $r = 0$, then $\delta_0 = (2/3)^{1/3} r_0$.

Thus the fluctuation approach, supplemented by the spinodal procedure, makes possible not only the closed calculation of the $\sigma(r)$ relationship but also the estimation of the minimum spinodal diameter of the competing phase $2\delta_0$.

The problem of finding the minimum size of the nucleating phase is related to the fundamental problem of determining the size limit of applicability of the thermodynamic description of small systems. A rigorous definition of thermodynamic concepts is possible only in the limit $N, v \to \infty$, $N/v \to$ const, that is for a large system. The use of the thermodynamic concepts of small systems is justified only in the examination of not an individual small particle but an ensemble consisting of n identical particles. As $n \to \infty$, the ensemble becomes a macroscopic system, no matter how small its component subsystems, and the use of the thermodynamic approach becomes fully justified. The minimum size of the new formation and the deviation from homogeneity which would make it possible to speak of the appearance of a new phase can be considered. As already shown, the systematic extension of the Gibbs–Tolman ideas to the range of small dimensions leads to the boundary condition $\sigma = 0$ with the disappearance of the tension surface ($r = 0$). The radius of the equimolar surface is non-zero and equal to δ_0. Since this radius characterises most accurately the size of the physical inhomogeneity, it is natural to regard it as the minimum size, beyond which the separation of the system into different phases loses meaning. The condition of disappearance of the tension surface corresponds to the disappearance of the nucleus of the new formation, that is the entire small "particle" is an interphase particle, so that it is now not a particle of a new phase, but a cluster. The same condition can alternatively be called the spinodal limit of stability of the homogeneous phase with respect to the appearance in it of the nucleus of a competing phase, since the work of nucleus formation also becomes zero. A clear boundary is thus drawn between homogeneous and heterogeneous states.

2. Change in the Phonon Spectrum with Decrease in the Particle Size

It is natural to try to describe the properties of an ultra-small particle by the methods of statistical physics. If the atoms in a cluster can undergo vibrations about equilibrium positions, and the cluster as a whole can undergo rotations and translations, then the partition function can be represented as the product of the translational Z_{tr}, rotational Z_{rot}, and vibrational Z_{vib} partial partition functions:

$$Z(N, T) = Z_N^{rot}(T) Z_N^{tr}(T) Z_{vib}(N, T) e^{-U_0(N)/kT} \qquad (11)$$

Here, $U_0(N)$ is the minimum value of the potential energy of the cluster. To calculate $Z_N^{tr}(T)$ it is necessary only to know the mass of the cluster; $Z_N^{rot}(T)$—the moment of inertia of the cluster (that is it is necessary to have an idea of the shape of the cluster); and $Z_{vib}(N, T)$—the frequencies ν_i of the normal vibrations of the system, which can be found from the expression for the potential energy of the system:

$$U(N) = \sum_{i}^{N} \sum_{j \neq i}^{N} U(r_{ij}) \qquad (12)$$

where $U(r_{ij})$ is the potential of the interaction between the atoms, of the Lennard–Jones or Morse type.

By expanding $U(N)$ in a series with respect to powers of the Cartesian coordinates of small displacements of the atoms from their equilibrium positions and restricting to harmonic terms, it is possible to calculate the magnitude of the forces acting on the atoms and to write the equations of motion of the atoms. Changing from Cartesian to normal coordinates gives a system of $3N - 6$ independent equations, whose determinant gives the frequencies of the $3N - 6$ modes. A knowledge of the spectrum of the normal vibrations (the phonon spectrum) makes it possible to calculate $Z_{vib}(N, T)$, and hence the thermodynamic characteristics of the cluster.[30]

Direct mechanical methods (of molecular dynamics) of calculating the properties of the clusters are also used. In this case, for each atom, a system of ordinary equations of motion under the influence of the forces is written,

$$\overline{F}_i = -\sum_{j=1}^{N-1} \nabla U(r_{ij}),$$

where $U(r_{ij})$ is also the pair interaction potential. The magnitude of the calculation increases in avalanche fashion with increase in the number of particles, so that the possibilities of the method are determined by the possibilities of the computers used.[31] The machine methods also include the Monte Carlo method.[32]

The phonon spectrum of small particles show low-frequency modes which are not present in the spectrum of large crystals.[33–35] These "soft" modes are related to the surface vibrations, and change irregularly with change in the size of the cluster: the spectrum depends on the geometry of the equilibrium configuration. The thermodynamic characteristics also change irregularly. The "soft" surface modes lead to increased values of the heat capacity for small particles at low temperatures, as follows from the form of the vibrational part of the partition function

$$Z_{vib}(N, T) = \prod_{i=1}^{3N-6} \exp\left(-\frac{h\nu_i}{2kT}\right)[1 - \exp(-h\nu_i/kT)]^{-1} \qquad (13)$$

The change in the low-frequency part of the phonon spectrum is due to the fact that the longest wavelength of elastic vibrations should not be greater than twice the maximum dimension of the crystal and is determined by the shape of the solid, the boundary conditions, and the wave velocities. The density of the frequency spectrum of a small cube with edge dimensions a can be written in the form:[30]

$$g(\nu) = 4\pi a^3 w^{-3} \nu^2 - a^2 w^{-2} \nu - 0{,}125 a w \qquad (14)$$

where $w^{-3} = w_l^{-3} + 2w_t^{-3}$ is the average rate (defined in terms of the rates of the longitudinal w_l and transverse w_t vibrations), and the total number of these normal vibrations is

$$3N = \int_{\nu_{min}}^{\nu_{max}} g(\nu)\, d\nu.$$

For a large crystal, the second and third terms in $g(\nu)$ can be neglected, $\nu_{min} = 0$. Thus $\nu_{max}^3 = 9Nw^3/4\pi a^3$, and the Debye frequency $\theta = h\nu_{max}/k$. For a small particle it is

necessary to take account of the low-frequency cut-off of the spectrum ($\nu_{min} \neq 0$), and in this case the use of the familiar relationship

$$E = \int_{\nu_{min}}^{\nu_{max}} h\nu g(\nu) [\exp(h\nu/kT) - 1]^{-1} d\nu \quad (15)$$

gives the dependence of the heat capacity $C_\nu = (\partial E/\partial T)_\nu$ on size in terms of ν_{min}, and also, with change in the interatomic distances, in terms of ν_{max}. The Debye temperature θ for a small spherical particle depends on the radius R:[36]

$$\theta \approx \theta_\infty + \theta_\infty (2G\sigma\varkappa - 3w/16\nu_{max})/R \quad (16)$$

where $G = -\partial \ln \theta_\infty / \partial \ln \nu$ is the Gruneisen constant, $\varkappa$ the isothermal compressibility, and σ the surface tension. This description of the phenomena is naturally qualitative. For gold particles with $R = 10$ nm, $\theta = 0.966\theta_\infty$, and for $R = 1$ nm, $\theta = 0.92\theta_\infty$. The same trend is observed experimentally.[37]

3. Phase Transformations in Ultra-small Particles

If the size of the cluster exceeds the minimum spinodal diameter, a particle of a new phase is produced. The morphology of relatively large metal particles does not differ from Wolff polyhedra, but for very fine particles the deviations become appreciable. The particles of face-centred cubic metals with dimensions up to 20 nm have dodecahedral and icosahedral forms. A dodecahedral particle can be represented as a combination of five tetrahedra. Twenty tetrahedra with a common vertex give the other stable configuration, that is the icosahedron. The presence in these crystals of five-fold symmetry axes, not characteristic of the massive crystals, indicates that at a definite size of this repeatedly twinned particle, a polymorphic transformation should take place to give the structure characteristic of large particles of the given metal. Repeated twinning of tetrahedra cannot give a continuous "framework", and between some of the twins, gaps filled with an amorphous phase, or stresses distributed through the entire particle, will be produced. The stability of small metal particles with dimensions of 1.5–1.6 nm has been examined theoretically.[33] It was found, for example, that particles of gold, silver, and copper with a diameter smaller than 10.7, 7.6, and 6.8 nm respectively have an icosahedral structure, and that larger particles have the normal face-centred cubic structure. Aerosil particles of most substances with dimensions $\geq$ 20 nm in fact have the structure of the massive crystal.[30] Thus after the growing particle reaches a certain size, a phase transformation from the icosahedral to the usual structure takes place.

Calculations by the methods of molecular dynamics[38] of the temperature dependence of the total energy show that the temperature–energy diagram contains a section corresponding to heating, a horizontal plateau corresponding to a phase transformation, and a section corresponding to supercooled states of the liquid. This indicates that the concepts of "solid" and "liquid" are also applicable to very small particles. Measurements on UDP show that particles with $R \cong 5$ nm melt at 200–400 K.[37,39,40] This also applies to polymorphic transformations. An example is provided by the transition metals W, Mo, and Nb. The massive specimens have a body-centred lattice (β-phase), but thin films (and small particles) have a face-centred cubic structure (α-phase).[41]

An expression can be written for the chemical potentials of the melt (L) and the α- and β-phases with allowance for the dimensions of fragments of the corresponding phase of n atoms

$$\mu_L = \mu_\beta^0 + \lambda\left(1 + \frac{T}{T^0_{fusion}}\right) + \frac{2}{3}\alpha_L\sigma_L v_L^{2/3} n^{-1/3}$$
$$\mu_\beta = \mu_\beta^0 + \frac{2}{3}\alpha_\beta\sigma_\beta v_\beta^{2/3} n^{-1/3}$$
$$\mu_\alpha = \mu_\beta^0 - \lambda_{\alpha\beta}\left(1 - \frac{T}{T^0_{\alpha\beta}}\right) + \frac{2}{3}\alpha_\alpha\sigma_\alpha v_\alpha^{2/3} n^{-1/3} \quad (17)$$

Here, α_i ($i = L$, α, β) are the form coefficients, σ_i the surface energy, and v_i the volume per atom in the melt and in the α- and β-phases respectively; λ and T^0_{fusion} the heat and temperature of fusion; and $\lambda_{\alpha\beta}$ and $T^0_{\alpha\beta}$ the heat and temperature of the $\alpha-\beta$ transformation of the massive specimen. Since μ_L and μ_β are equal on the equilibrium line, an expression is obtained for the dependence of the melting point of the particle on the size n, the shape α_β, and the density ρ_β:

$$\frac{T^0_{fusion} - T_n}{T^0_{fusion}} = \frac{2m_0^{2/3}}{3\lambda}\left(\frac{\alpha_\beta\sigma_\beta}{\rho_\beta^{2/3}} - \frac{\alpha_L\sigma_L}{\rho_L^{2/3}}\right) n^{-1/3} \quad (18)$$

Here, m_0 is the mass of the atom, and T the melting point of a particle containing n atoms. Since $\rho_\beta \cong \rho_L$, $\sigma_\beta > \sigma_L$, and, usually, $\alpha_\beta > \alpha_L$ (faceting takes place), then $T_n < T^0_{fusion}$, that is the melting point of the ultra-small particles is lowered.

Similarly, since μ_β and μ_α are equal on the equilibrium line,

$$\frac{T^0_{\alpha\beta} - T_{\alpha\beta}}{T^0_{\alpha\beta}} = \frac{2m_0^{2/3}}{3\lambda_{\alpha\beta}}\left(\frac{\alpha_\alpha\sigma_\alpha}{\rho_\alpha^{2/3}} - \frac{\alpha_\beta\sigma_\beta}{\rho_\beta^{2/3}}\right) n^{-1/3} \quad (19)$$

Since $\alpha_\alpha \cong \alpha_\beta$, $\sigma_\alpha \cong \sigma_\beta$, and $\rho_\beta < \rho_\alpha$, the difference in brackets is negative, and the temperature of the polymorphic transformation of the ultra-small particle $T_{\alpha\beta}$ is higher than $T^0_{\alpha\beta}$ for the massive specimen. From this it is clear that in a certain range of temperatures, as the film becomes thinner, the β-phase may be converted into the α-phase, metastable with respect to the massive equilibrium specimen, as observed in experiments with films of W, Mo, and Nb.[41]

As far as the mechanism of the fusion of the particles is concerned, Petrov,[30] for example, considers that the most acceptable model is the cluster model, according to which any single crystal, when heated to pre-fusion temperatures, breaks down into clusters separated by amorphous layers of atoms. With increase in temperature, the thickness of the amorphous layers increases, and at the moment of fusion, rupture of the bonds between the clusters takes place. X-Ray diffraction has shown[40] that lead particles with $r \cong 10$ nm on fusion break down to give clusters with an edge length approximately seven times the lattice parameter; with increase in the temperature of the melt by 300 K, the cluster dimensions decrease by a factor of only 1.5, and the structure of the gas is acquired only at the temperature of the liquid–vapour transformation.

The size dependence of diffusion in small particles has been studied.[42,43] A relationship has been established between the activation energy of diffusion θ and the melting point of the substance T_m: $\theta = \alpha T_m$.[44] If it is assumed that this relationship is preserved for a given substance in the UD state, that is that the relationship $\theta_r = \alpha T_r$ is also applicable for particles with radius r, then eliminating the factor α gives $\theta_r = \theta T_r/T_m = \theta - \theta\Delta T/T_m$, and the

diffusion coefficient in a particle of radius r will be

$$D_r = A\exp\left(-\frac{\theta_r}{kT}\right) = A\exp\left(-\frac{\theta}{kT}\right)\exp\left(\frac{\theta}{kT}\frac{\Delta T}{T_m}\right) = D\exp\left(\frac{\theta}{kT}\frac{\Delta T}{T_m}\right)$$

The experimental values of the melting points of the particles should be substituted in this equation. Since $\Delta T = T_m - T_r$ increases with decrease in the particle size, D_r also increases, and for dimensions of 10 nm it differs from the diffusion coefficient D in the macro-phase by several orders of magnitude.[43]

4. The Energy Saturation and Reactivity of a Medium

A very important characteristic of UD media is their high chemical activity. This is also related to the high energy saturation of dispersed particles, in particular due to the contribution of the surface energy. Thus the equilibrium constant in a closed system is given by the expression[45] $K_e = \exp(-\Delta\Phi^0/RT)$, where the change in the Gibbs potential in the standard state is

$$\Delta\Phi^0 = \Phi_2^0 - \Phi_1^0 = \sum_j \nu_j^1 \Phi_{Bj}^0 - \sum_i \nu_i \Phi_{Ai}^0$$

This equation is applicable for equilibrium with respect to the reaction

$$\sum_i \nu_i A_i \rightleftarrows \sum_j \nu_j^1 B_j$$

for given P and T. If the starting materials and products are dispersed, the change in the thermodynamic potential is:

$$\Delta\Phi = \Delta\Phi^0 + \sum_j \nu_j^1 \Delta\Phi_j^1 - \sum_i \nu_i \Delta\Phi_i$$

where the summation is carried out over the dispersed reagents. Recalculation to one dispersed particle of n atoms gives $\delta\Phi = \alpha\sigma v^{2/3} n^{2/3}$. It is assumed that the reaction is forbidden under standard conditions ($\Phi_2^0 > \Phi_1^0$). If in the dispersed state

$$\Phi_2^0 + \sum_j \nu_j^1 \Delta\Phi_j^1 < \Phi_1^0 + \sum_i \nu_i \Delta\Phi_i,$$

then the reaction becomes possible, and the equilibrium constant of the reaction can be calculated from the equation

$$K_e = K_e^{(\infty)} \exp\left[\left(\sum_i \nu_i \Delta\Phi_i - \sum_j \nu_j^1 \Delta\Phi_j\right)/RT\right]$$

When the reaction products are more highly dispersed than the starting materials, the entropy factor will facilitate an increase in the displacement of the process towards the formation of the products, since $\Delta\Phi^0 = \Delta H^0 - T\Delta S^0$.

As a result of the extremely high reactivity of UDP, they react even with inert gases. On the freshly formed surfaces of finely divided solids[46] there is appreciable irreversible adsorption not only of oxygen, nitric oxide, and the products of the dissociation of the liquids in contact with it, but also of inert gases at ordinary pressure and temperature. The gas molecules form strong bonds with the surfaces of the solid particles; the bond energy, estimated from thermal data, is 2–4 kJ mole^{-1}.

The passivation of metals by inert gases is possible in the cold plasma of a glow discharge.[47] For example, the simultaneous bombardment of an aluminium surface by argon and hydrogen ions from the plasma leads to the irreversible penetration of the atoms of these gases not only into the surface layer (5–10 nm) but also into the bulk of the metal, with the formation of a metastable metal–inert gas substitutional solid solution. The concentration of absorbed argon may reach several percent.

It has been established experimentally that the limiting concentration of dissolved argon in aluminium c_0 is 0.3 at.% at 400 K. At a higher concentration, the metastable solution breaks down with the formation of gas-filled bubbles. The lattice parameter increases practically linearly with increase in the inert gas concentration from 0.40496 nm for pure Al to 0.40533 nm for Al containing 0.3 at.% Ar. If this macroscopic solution is described in the regular approximation and it is assumed that the free energy of argon in the solution is equal to that of the argon ions, then at $T = 400$ K and $c_0 = 0.003$ the energy of mixing ΔH is 1.5×10^6 J g-atom^{-1}.

If the solution is a system of small particles, the equilibrium concentration is increased. Using the Ostwald–Freundlich relationship and assuming that the concentration of Ar in the macroscopic solution is 0.003 at $T = 400$ K, and that the surface tension of the macroscopic solution–gas boundary is ~1 J m^{-2}, gives for particles with dimensions of 10, 3, and 2 nm, the argon concentration values 0.54, 2.20, and 6.10 at.% and the values of the excess energy of solution 0.76, 3.66, and 8.10 respectively in units of $\Delta H/\Delta H_m$, where $\Delta H_m = 10.68$ J mole^{-1} is the heat of fusion of aluminium. Thus the solution is formed with a huge expenditure of energy. On its relaxation (breakdown), this excess energy of mixing will be liberated, and at the lower limit of the UDM it may be appreciably greater than the heat of fusion of aluminium. In Ref. 48, tablets (diameter 6 mm and height 1.2 mm) were compressed and heated at a rate of ~200 K min^{-1} in an inert gas atmosphere (under a pressure of 0.13 Pa) from powders obtained by the electrical explosion of wires (r = 0.03–1.3 μm). At 720–820 K the tablet of copper powder began to glow brightly, and its temperature rose to 1200 K. The temperature of the aluminium tablets increased spontaneously to 940 K, which corresponds to the melting point. Thus for powders with the degree of dispersion indicated, the excess energy is sufficient to maintain the self-propagating process of sintering and even fusion.

A whole series of papers describe the experimental observation of an increase in the chemical activity of energy-saturated media. It has been reported[49] that in two-layer oxide hetero-structures, reactions of the type

$$MgO + Nb_2O_5 \rightarrow MgNb_2O_6$$

take place spontaneously at temperatures 800–1000 K lower than the usual temperatures for the reactions in the massive state. Many examples from the work of Boldyrev and co-workers have demonstrated the activation of solid-phase reactions under the influence of mechanical subdivision,[50] a shock wave,[51], X-rays,[52] and a stream of protons.[53] Finally, recent studies have revealed the high biological activity of highly dispersed metal powders at all levels, from the general indices of the metabolism of the organism to the influence on the activity of individual biological systems and biomacromolecules.[54,55] The antimicrobial activity of various metal powders has been established. Progress in this field is being held up by the lack of satisfactory methods for introducing the metals into the organism. A possible solution is the introduction of the required metals into the organism as UD powders, particularly since their activity increases with decrease in size. This topic lies outside the scope of the present review, however, and will not be discussed in detail here.

III. METHODS FOR OBTAINING ULTRADISPERSED POWDERS OF METALS AND COMPOUNDS

1. Mechanical Methods of Dispersing Solid Metals

Ultradispersed powders can be obtained by the mechanical dispersal of solids, the decomposition, precipitation, and reduction of chemical compounds, and the condensation of metal vapours. A combination of these methods is often used.

In powder metallurgy, coarsely dispersed materials are often obtained by mechanical sub-division in ball, rod, or other mills or in disintegrators,[56] and also by electrohydraulic impact. When a certain degree of dispersion has been achieved, however, a dynamic equilibrium is established between the processes of dispersal and coagulation of the particles. To obtain particles with micron dimensions it is necessary to carry out the sub-division at very low temperatures, at which the material is more brittle,[57] to use ultrasonic dispersal,[58] or to add surface-active substances, which lower the surface energy and strength of the particles.

Sputtering of melts in liquid or gas streams, and ultrasonic[59] and other methods can also be used to obtain powders, but in these cases the products are coarsely dispersed.

The above methods can apparently be used only as an intermediate stage in the production of UD powders. Ultrasonic treatment can be applied to prepared UDP (to break down conglomerates, for mixing, and to produce more compact pressings).

There is however a form of mechanical treatment which creates conditions both for the synthesis of the desired products (diamond) and for their dispersal, namely the action of a shock wave.[60] Diamonds are obtained by the shock-wave treatment of mixtures of graphite and metals at 20–40 GPa and a shock-wave duration of 10–20 μs. The structure and composition of the resulting powders have been studied.[61] The average particle size of the diamonds was ~4 nm.

2. Physical Methods of Obtaining UD Powders Based on Volatilisation and Condensation Processes

The simplest and most natural method for obtaining UD metal powders is by volatilising the metals and condensing their vapours. This method was used to obtain UDP in early studies.[62] Assemblies using the volatilisation–condensation principle may differ in the method of introducing the material to be volatilised, the method of introducing the energy required to volatilise the metal, the nature of the working medium, the organisation of the condensation process, and the system for collecting the powder.

The metal is either volatilised from a crucible or fed to the heating system in the form of a powder, wire, or stream of liquid, through special devices.

Energy can be supplied to the metal to be volatilised through a conductor,[63] by high-frequency induction heating[64] or superhigh-frequency currents,[65] by electric-arc discharge in a plasma,[66] by a laser light flash, etc.

The processes of volatilisation and condensation may take place in a vacuum, in a stationary inert gas, or in a stream or gas (in particular in a plasma stream).

In the production of UD powders, the condensation process is the decisive stage. The physical principles of the theory of the condensation of metals is fairly well developed,[67,68] and methods have been proposed[67,69,70] for calculating the particle size distribution of metal aerosols. The numerical solution of the equations of the kinetics of bulk condensation for this model has been carried out:[70] the vapour–gas mixture in the condensation zone moved in a channel with a constant cross-section of 118.7 mm^2 at a constant velocity of 150 m s^{-1}, the axial temperature gradient due to cooling of the stream was 200 K min^{-1}, the pressure in the channel was constant and equal to atmospheric pressure, and the boundary layer was not taken into account; the argon consumption was 3.5 m^3 h^{-1} (6.24 kg h^{-1}), and the consumption of tungsten powder volatilised 2 kg h^{-1}. These values of the parameters correspond to those of a real assembly. The kinetic analysis showed that it is theoretically possible to obtain tungsten powder with an average particle size of 3–5 nm (without allowance for coagulation). The length of the coagulation zone (90 mm) is much less than the length of the nucleation zone (~4 mm); this makes it possible to protect the powder formed from coagulation, for example by removing it from the condensation zone.

Methods of condensation have been discussed in detail.[71] The vapour–gas mixture at a temperature of 5000–10 000 K can simply be passed into a chamber of large cross-section filled with a cooled inert gas, in which condensation takes place. In improved assemblies, two coaxial streams are passed into a channel; the inner axial stream contains the vapour–gas mixture, and the outer annular stream contains a cold inert gas. As a result of turbulent mixing, the temperature of the metal vapour is lowered, the supersaturation increases, and rapid condensation takes place. The width of the condensation zone in this assembly changes along the longitudinal coordinate, however, and this gives a broad particle size distribution function. Nevertheless, detailed analysis and allowance for the characteristic features of the turbulent mixing of non-isothermal coaxial streams in a channel[73] makes it possible to decrease considerably the thickness of the temperature layer and to obtain UDP with a narrow fractional composition. UDP of copper, aluminium, iron, nickel, and other metals have been obtained in this way in a laboratory assembly.[71] The average particle size of the powders obtained was 7–20 nm at a production rate of 40–50 g h^{-1}, depending on the material and the operating conditions.

If the vapour–gas mixture is directed into a channel with a cooled wall, hydrodynamic, temperature, and concentration boundary layers are established at the surface of the channel. Under turbulent conditions, the thickness of the boundary layer and hence of the condensation zone is proportional to the longitudinal coordinate to the power 0.2.[71] The resulting particles, under the influence of thermophoresis forces, are displaced across the boundary layer to the wall. The temperature gradient in the boundary layer (~10^5 K m^{-1}) is higher than in the layers of the stream, and this makes it possible to obtain particles with smaller dimensions (less than 1 μm). The particles settling out, however, accumulate on the wall surface and partly coagulate and cake to form agglomerates. The growth of the layer of particles on the wall of the channel increases the thermal resistance of the layer and the temperature of the outer layer, and this in turn leads to sintering of the particles with the formation of a crust and overgrowths. Special methods of cleaning the surface have to be used to prevent this phenomenon.

The most favourable conditions for the condensation of metal vapours (to obtain UD powders with a narrow particle size distribution) are apparently produced on adiabatic expansion in a Laval nozzle.[71,72] With sufficiently rapid expansion of the mixture, a temperature gradient of

~10^8 K s^{-1} is created,[13] and the vapour of the metal (for example aluminium) condenses almost instantaneously to give UDP with an average particle size of 50–60 nm. The temperature of the walls of the nozzle should be greater than the melting point of the metal, to avoid the deposition of metal particles on the wall and the production of a metallic crust.

The UDP obtained are usually collected on special filters or by centrifugal deposition. In some assembles, the particles are either deposited on a rotating drum or endless belt, after which the surface is cleaned with a scraper, or trapped in a liquid film.

3. Chemical Methods for Obtaining UD Powders

Chemical methods include precipitation, the reduction of oxides and other compounds of the metals, and thermal decomposition. The chief condition for obtaining dispersed powders by chemical methods is that the reaction should take place at a distance from equilibrium, with a high rate of formation of the nuclei of the new phase, combined with a low rate of their growth. These conditions are ensured by selecting a temperature at which the chemical reaction takes place sufficiently intensively, but transfer through the gas phase is still retarded.

The deposition is carried out in a solution, a stream of gas, or a plasma. For example, titanium dioxide is obtained by precipitation as a result of the hydrolysis of titanyl sulphate with heating. The fresh precipitate is amorphous. Transformation to the rutile structure is achieved by subsequent heating to 1000–1300 K.[74] Methods for obtaining powdered iron, cobalt, nickel, and alloys of palladium have been described (see Ref.71 for bibliography). The particle size of these powders varies from 5 nm to 3 μm.

Oxides and halides are usually reduced using hydrogen or carbon monoxide. Powdered iron, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten with an average particle size of 0.1 μm have been obtained by this method at 750–1600 K.[75]

Powdered nickel, iron, chromium, copper, etc. are obtained by the thermal decomposition of the carbonyls, formates, oxalates, and other compounds at 500–700 K. These methods have been reviewed in detail.[7,74]

General unsatisfactory features of methods for obtaining metal UDP by low-temperature processes are the formation of comparatively large particles (0.03–10 μm), a wide particle size distribution, a high concentration of impurities in the powder, and a complex, multi-stage, non-universal technology. In a number of cases, however, the large-scale production of powders can be organised using these processes.

A significant increase in the degree of dispersion of the powders can be achieved by carrying out the process at high temperatures, in particular in a low-temperature plasma generated by an arc or induction discharge. This method can be used to obtain practically all refractory carbides, nitrides, borides, oxides, etc., and also more complex compounds. UD titanium nitride powders with a particle size of <0.5 μm are obtained by reducing the chlorides with hydrogen in a flux of nitrogen plasma.

Thermodynamic calculations for the systems M–Cl–H–N, where M = Ti, Zr, or Hf, show that at the stoichiometric ratio of the original components of the reaction

$$2MCl_4+4H_2+N_2=2MN+8HCl$$

the equilibrium throughout the temperature range (400 to 3500 K) is characterised by the presence of chlorides, so that the degree of transformation of MCl_4 into MN is slight, but a combined excess of hydrogen and nitrogen ensures a nitride yield of 100% over a wide temperature range.[12] The combined reduction of $TiCl_4$ and thermal decomposition of hydrocarbons in a nitrogen plasma is used to obtain titanium carbide nitrides which in the composition range from $TiN_{0.98}$ to $TiC_{0.4}N_{0.6}$ form single phases and consist of a series of solid solutions of carbon in titanium nitride with the NaCl structure. The average particle size of these powders is ~50 nm.[76]

The carbides of titanium, zirconium, hafnium, vanadium, tungsten, and other metals with an average particle size of 0.01–0.1 μm have been obtained in the plasma of an arc discharge using the corresponding metal chlorides and hydrocarbons as starting materials.[77,78]

UD copper powder has been obtained[81] by reducing copper chloride with hydrogen in the stream of argon plasma of an electric-arc discharge. A thermodynamic calculation for the Cu–Cl–H system showed that it is possible to obtain copper in a yield close to 100% in the temperature range 500–1800 K with more than ten-fold dilution of the system with hydrogen, relative to the stoichiometric quantity. The assembly gave copper powder with a particle size <0.1 μm and a relatively narrow particle size distribution.

The reduction of nickel monoxide in a high-enthalpy stream of gas obtained by the complete oxidation of propane by air:

$$C_3H_6+1.5\,O_2+5.64\,N_2=3\,CO+4\,H_2+5.64\,N_2$$

has been studied.[82]

Thermodynamic analysis showed that in a 1.2-fold excess of the reducing agent in the temperature range 800–6000 K, complete reduction of the oxide to the metal is achieved. The experiments gave nickel powder with an average particle size of 0.1–0.4 μm, containing 0.2–3% carbon and 1.5–6% oxygen.

Silicon carbide powders can be obtained from quartz sand and a propane–butane mixture[79] or from a mixture of silanes and halogen derivatives of hydrocarbons in a hydrogen plasma at 2800–3800 K. The average particle size is 0.05 to 0.02 μm.

UDP of tungsten have been obtained by reducing tungsten trioxide in an argon–hydrogen plasma.[80]

An unsatisfactory feature of thermal decomposition and reduction methods is the low selectivity of the process; the reaction product usually consists of a mixture of the desired product and other compounds.[14]

Overall, however, assembles with a low-temperature plasma at present provide one of the most efficient, productive, and universal means of obtaining UDP of metals and compounds.

4. The Electrical Explosion of Wires

One version of the volatilisation–condensation method involves the production of UDP by the electrical explosion of wires. This method is dealt with separately because of its practical importance.

In the electrical explosion of wires (EEW), the materials of the wire breaks down under the influence of a powerful current pulse; part of the material of the wire may volatilise, while the rest is scattered as liquid droplets.[83] As a result of volatilisation at the expense of condensation in the stream of rapidly expanding vapour, particles with very small dimensions are formed, but the solidified droplets give larger particles. The ratio of these components depends on the nature of the breakdown of the wire, which is determined by the process used to introduce the energy into the wire.

The quantities characterising the electrical explosion of wires are functions of the parameters:[84]

$$E = CU_0^2 n^{-2} d^{-4} Z^{-1},\ \lambda = ln^{-1} d^{-2} Z^{-1},\ \nu = L^{1/4} C^{1/4} d^{-1}$$

where l is the length, d the diameter, and n the number of the exploding wires, Z the wave resistance, L the inductance, C the capacity of the circuit, and U_0 the initial voltage at the condenser. The parameters of the explosion are selected using these variables.

The results of the study of copper powders obtained at an inert gas pressure of 200 Pa have been described.[63] The size of the spherical copper particles depends to a significant extent on the density of the energy introduced and the rate of its introduction. It is possible to obtain a powder with a maximum size distribution in the region of 20 nm for copper exploded in air, or in the region of 50 nm for aluminium in argon.

5. Freeze Drying

Ultradispersed powders of metals and compounds can be obtained by freeze drying. The starting materials, in particular metal salts, are used to prepare a solution with the required composition, which is rapidly frozen by spraying into a chamber containing a cryogenic medium. The pressure of the gaseous medium above the frozen granules is then decreased until it is lower than the equilibrium pressure for the multi-component system formed on cooling, and the material is heated with continuous evacuation to sublime the solvent. The product consists of very fine porous granules with identical composition. Heating the granules in air gives the oxides, reduction gives the metal powders, and selective reduction gives a mixture of the oxides and the metals. The UD compositions Pb–10% MgO, W–S, W–25% Re, Cu–ThO_2, Cu–W, $NiZnFe_2O_4$, etc. with a particle size of 10–60 nm have been obtained in this way.[85,86]

The reduction of ammonium paratungstate in solution by hydrogen gives a finely dispersed tungsten powder with a particle size of 0.2–0.8 μm, and the product acquires a completely new structure.[87] Ammonium paratungstate has several crystalline hydrated forms, each of which gives a characteristic X-ray diffraction pattern. When the paratungstate obtained by freeze drying was examined by X-ray diffraction, however, no diffraction lines were observed.

Sub-micron nickel powders are obtained by this method from solutions of nickel chloride and nitride.

IV. ENERGY-SATURATED MEDIA AS MATERIALS OF PRESENT-DAY TECHNOLOGY

1. Materials with an Ultradispersed Structure—A Unique Form of Composite Material

Attempts to eliminate the gap between the requirements to be satisfied by constructional materials for present-day technology and the possibilities provided by the usual alloys of materials science are being made by developing and applying composite materials.[24] The complexity of this problem lies in the fact that elements of different kinds (for example metal and non-metal), combined in the same composite material, must function as a single whole. For a long time these difficulties could not be overcome, so that in the past, materials consisting of one substance were preferred.

Composite materials may be of three main types: metal + metal; ceramic + ceramic; and metal + ceramic. The components either do not react, or react with one another during use. In the first case the system is a purely mechanical system, whose behaviour under working conditions can be predicted from mechanical data with allowance for the scale factor. In the second case, the components of the composite materials react to form a new product at the interface. This practically always takes place, since during use the materials are subjected to high temperatures and pressures and other influences. For inorganic materials used at sufficiently high temperatures, the first case need not be considered.

The reaction "within" the composite material may give chemical compounds corresponding to the complete range of possible oxidation states of the metal, including sub-compounds, complex compounds, compounds formed by ceramic + ceramic and metal + metal (intermetallic compounds) combination, and also phases of variable composition of the solid solution type. Thus the "spectrum" of components of a composite material is complicated considerably when the corresponding material starts to be used at high temperatures. This makes it difficult to calculate accurately the behaviour and capacity of the material at different stages of its use, and its examination is usually restricted to the determination of the dependence of the properties, in particular the strength characteristics of the material, on the intensity of the reaction with time. These phenomenological data have now been collected for a whole range of composite materials, and their amount is increasing rapidly. The generalisation of this experience still lags behind practice. A tendency to move to the "molecular level" in the examination of the mechanisms of the reactions of the components of composite materials is gradually being observed, in spite of the considerable difficulty of these questions.

It should be noted, in particular, that the view that the composition of the products of the reaction in composite materials is determined by data from the corresponding equilibrium diagrams cannot be fully accepted, since composite materials are generally non-equilibrium systems. Thus kinetics must be added to present-day methods for their physicochemical analysis. Composite materials are "living" systems, and kinetic questions become fundamental in their study during use. The equilibrium diagrams in the case being considered are of major importance if they are constructed from data obtained in experimental studies with allowance for kinetics. The question of the importance of obtaining "kinetic" equilibrium diagrams is not new,[88] but it has not found extensive practical application. The possible reason may be that up to the present, physicochemical analysis has been applied chiefly to substances as such, when there has been no particular need to study the kinetics of the corresponding processes. Moreover, in the examination of composite materials it is necessary to take account of the degree of dispersion of the starting material and the products formed when the materials are used.

It is usually assumed that composite materials are artificial systems made up of the corresponding macro-components, namely the matrix, which is a compact material (metal or ceramic) of any dimensions, and the reinforcing material, in the form of fibres or filaments, ceramic or metallic, and best of all in the form of single crystals. Since a sharp boundary cannot be drawn between macro- and micro-states, the concept of composite material can apparently be extended to include in this category materials having components with atomic or molecular degrees of dispersion, placing arbitrary boundaries between individual groups.

It is appropriate to divide each of these three types of composite material into three groups, in which the components differ in their degree of dispersion.

1) Composite materials made up of two parts ("blocks") of any dimensions, each of which has independent functions. In this case the area of contact between the blocks is negligibly small compared with the blocks themselves, and at high working temperatures (not exceeding their melting points) the behaviour of the corresponding composite material can be regarded as a function of the behaviour of its component parts, and the "events" at the interface are of secondary importance, the interface functioning only as a means of holding the blocks together.

2) Composite materials in which the degree of dispersion of the reinforcing particles is relatively high: fine single-crystal filaments, short (1–5 mm) fibres, and fine crystals. Here, the components cannot behave independently, and the mass of the interphase formations may be comparable with that of the original components. The behaviour of this most widely encountered classical type of composite material ($Al + Al_2O_3$; $Mg + MgO$; etc.) must be examined in a known temperature range as a system which is the usual object of physicochemical analysis.

3) Composite materials at the level of mixing of components with atomic or molecular dimensions. These are ordinary chemical compounds of the type AB, AB_2, A_2B, etc., up to double salts and complex compounds, and also phases of variable composition. Materials with these components are not usually regarded as composite materials, but in principle this is not quite correct, since there may also be external factors influencing the material (for example radiation, defect-forming influences), when its component atoms or molecules behave "independently" and influence the working properties of the material.

The proposed classification may possibly be disputed, but it covers all types of composite material, if they are classified according to the particle size of the components. Moreover, account must be taken of the fact that at sufficiently high temperatures (for example close to the melting points of the components), their mutual diffusion will take place so rapidly that a composite material of type 2 begins to function as a composite material of type 3. It is always necessary to take into account the extent to which this transformation of one type of material into another is permissible from the viewpoint of the application of the composite material.

2. The Relationship Between the Energy Saturation, Structure, and Mechanical Properties of Materials

The characteristic feature of ultradispersed particles discussed in the previous sections also appear in compact materials with an ultradispersed structure. In this case the degree of dispersion is determined by the average dimensions of the defect-free regions (structural fragments) and the angles of disorientation between them. Here, the relationship between the ultradispersed structure and the physicomechanical properties of the materials is of the greatest importance.

In these materials it is possible to distinguish three levels of structural organisation:[21] granules with dimensions of 10^3–10^4 nm, angles of disorientation 1–90°; sub-granules with dimensions of 50–10^3 nm, angles of disorientation 5′–3°; and blocks with dimensions of 3–100 nm, angles 5′–5″. The energy saturation of a structure of this kind depends on the dimensions of the elements of the structure and the energy of the interfaces. The energy of the interfaces, calculated by the Shockley–Read method, for example for nickel, varies from 0.0014 J m^{-2} ($\theta = 30''$) to 1.1 J m^{-2} ($\theta = 57°$).[21]

Analogous calculations of the excess values of the chemical potential for gold show that for dimensions of the structural fragments of 4.5 nm and large-angle interfaces between them, the state of the structural fragments corresponds to the state of the macro-system at the melting point, and that for dimensions of ~10 nm and large-angle interfaces it corresponds to the state of the macro-system at a temperature of 0.6 T_{fusion}. Since at this temperature relaxation processes (of the crystallisation type) take place actively in metals, a dispersed system with these parameters will not apparently be stable.

For low-angle boundaries, an analogous state is reached at structural fragment dimensions of ~3 nm. It is evidently possible to speak of a limiting attainable level of dispersion of a polycrystalline system.

Accordingly to the familiar Oding diagram, the greatest strength is shown either by materials with a low density of dislocations (single crystals) or materials with a dislocation density of 10^{13}–10^{14} m^{-2}. The strength properties of metals are influenced not only by the density of dislocations, but also by the nature of their distribution in the volume. Distribution of the dislocations in the form of networks of block boundaries is thermodynamically favourable. Assuming that all the dislocations lie at the boundaries between the blocks, the size of the blocks L is related to the density of dislocations ρ by the expression:[89]

$$L = (a/\rho)^{1/2}$$

where a is a parameter of the order of 1, defining the degree of regularity of the distribution of the dislocations. For $\rho = 10^{15}$ m^{-2}, the dimensions of the blocks lie in the range 4–5 nm.

The relationship between the structure and the strength characteristics is given qualitatively by the Hall–Petch relationship,[90] according to which the strength of a metal is proportional to $L^{-1/2}$, where L is the size of the granules for materials with a coarsely granular structure, and the size of the blocks for materials with highly developed fragmentation of the structure.

By changing the sub-structure of the materials (the size of the structural fragments and the angles of disorientation), it is possible to control their physicomechanical properties.[90,91] For example, the strength of U-8 steel increases from 1.4 GPa to 2.8–3.2 GPa with decrease in the size of the structural fragments from 30 nm to 10 nm. The yield point of TsM-6 molybdenum alloy increases from 400 MPa to 750 MPa with decrease in the particle size from 160 μm to 1 μm. With decrease in the size of the granules of the sub-structure, the impact strength also increases. Thus for 45 steel it changes from 0.62 kJ m^{-2} to 1.5 kJ m^{-2} with decrease in the size of the granules from 60 μm to 6 μm.

An important feature is that with the increase in strength, a sufficient reserve of plasticity is retained, since the temperature of cold brittleness is lowered. For example, for molybdenum it is lowered from 600 K to 415 K with decrease in the size of the granules from 7.3 μm to 1.2 μm.

The temperature of the transition from viscous to brittle breakdown (the temperature of cold brittleness) is a structure-sensitive property, and decreases with decrease in the size of the elements of the sub-structure.[23] The formation and growth of cracks of critical dimensions in an UD material is hindered because of the small size of the structural fragments and the presence of a large number of boundaries, so that the breakdown viscosity of the UD material is increased.

Lowering the temperature of cold brittleness and increasing the breakdown viscosity are important aims for most constructional materials, particularly refractory materials,

intermetallic compounds, and metal–ceramics. The possibilities provided by traditional methods (metallurgical, thermal, thermomechanical) in this area have been practically exhausted. To solve the problems of improving further the physicomechanical properties of materials it is necessary to look for new methods of producing ultradispersed structures.

3. The Production of Highly Dispersed States in the Synthesis of Titanium Carbide Under Bulk Combustion Conditions

The mechanism of the formation of a dispersed structure in the synthesis of titanium carbide under non-isothermal conditions can be considered. It has been shown[17,91,94,95] for the Ni–C, Al–Si, and other systems that the presence of ultradispersed components in the original system gives metastable equilibrium diagrams. Thus the temperature of eutectic formation in the Zr–C system is lowered by 500 K when the form of carbon used is coke with an excess energy of about 8.4 kJ mole^{-1}.

The Ti–C system has been studied.[92] It contains an intermediate titanium carbide phase (subsequently denoted σ). The equilibrium diagram can be divided into two regions, Ti + σ and σ + C. The thermodynamic potentials in the left-hand and right-hand regions will have the form:

$$\Phi^{\mathrm{Ti}+\sigma} = (1-x)\,\Phi^0_{\mathrm{Ti}} + x\Phi^0_{\mathrm{C}} + (x/x_0)\,\Delta\Phi^\sigma,$$
$$\Phi^{\sigma+\mathrm{C}} = (1-x)\,\Phi^0_{\mathrm{Ti}} + x\Phi^0_{\mathrm{C}} + [(1-x)/(1-x_0)]\,\Delta\Phi^\sigma$$

The thermodynamic potential of the σ-phase can be estimated by the published method:[93]

$$\Delta\Phi^\sigma = x(1-x)\,W_0 + (1-x)(1-2x)\,W_1 + x(1-2x)\,W_2 + RT\{A_1x + A_2x^2 + (1-x)\ln[(1-x)/(1-2x)] - x\ln[x/(1-2x)]\}$$

where for titanium carbide $A_1 = 0.62$, $A_2 = -0.32$, $W_0 = -368\times 10^6$ J kmole^{-1}, $W_1 = 117\times 10^6$ J kmole^{-1}, $W_2 = 92\times 10^6$ J kmole^{-1}. Substituting gives $\Delta\Phi^\sigma = (92\times 10^3 - 1.9T)$ J kmole^{-1}.

The liquid phase can be described in the approximation of regular solutions

$$\Phi^L = (1-y)\,\Phi^L_{\mathrm{Ti}} + y\Phi^L_{\mathrm{C}} + RT[y\ln y + (1-y)\ln(1-y)] + y(1-y)\,\Delta L$$

where ΔL is the interaction parameter in the liquid solution,

$$\Phi^L_{\mathrm{Ti}} = \Phi^0_{\mathrm{Ti}} + \Delta H_{\mathrm{Ti}}(1-T/T_{\mathrm{Ti}}), \quad \Phi_{\mathrm{C}}{}^L = \Phi_{\mathrm{C}}{}^0 + \Delta H_{\mathrm{C}}(1-T/T_{\mathrm{C}}),$$

and the temperatures and enthalpies of fusion of the components have the values $T_{\mathrm{Ti}} = 1940$ K, $T_{\mathrm{C}} = 4000$ K, $\Delta H_{\mathrm{Ti}} = 15.47\times 10^6$ J kmole^{-1}, and $\Delta H_{\mathrm{C}} = 104.5\times 10^6$ J kmole^{-1}.

For simplicity it will be assumed that the homogeneity range extends to a line around $x = 0.5$; the formation potential $\Delta\Phi^\sigma$ at the point of congruent fusion is related to $x = 0.5$; the range of solubility of titanium in carbon (α-solution) and the influence of pressure are neglected, and the data on the fusion of carbon are taken for $P = 10^7$ Pa.

Using the condition $\Phi^{\sigma+\mathrm{C}} = \Phi$ on the right-hand eutectic of the equilibrium diagram ($x = 0.643$, $x_0 = 0.5$, $T_e = 3049$ K) gives $\Delta L = -258.6\times 10^6$ J kmole^{-1}. The lowering of the right-hand eutectic as a result of the dispersal of carbon can now be estimated. In this case it is necessary to add to the left-hand side of the condition $\Phi^{\sigma+\mathrm{C}} = \Phi^L$ the term $\Delta H_{\mathrm{excess}}(x - x_0)/(1 - x_0)$ reflecting the contribution of the excess energy. For $x - y$ this gives the equation

$$[(1-x)/(1-x_0)]\,\Delta\Phi^\sigma + [(x-x_0)/(1-x_0)]\Delta H_{\mathrm{excess}} = (1-x)\,\Delta H_{\mathrm{Ti}}(1-T/T_{\mathrm{Ti}}) + x\Delta H_{\mathrm{C}}(1-T/T_{\mathrm{C}}) + RT[x\ln x + (1-x)\ln(1-x)] + x(1-x)\,\Delta L$$

By specifying a series of values of $\Delta H_{\mathrm{excess}}$ and looking for the minimum $T = T(x)$ it is possible to find the positions of the eutectic for different carbon materials (CM). The estimates give downward temperature displacements of the right-hand eutectic of 540 K for coke, 1200 K for carbon black, and 1800 K for "amorphous" carbon, with a simultaneous displacement to the right along the concentration axis.

Since the carbide phase formed is also dispersed, it is also possible, by estimating the excess energy of the σ-phase and making use of the condition $\Phi^\sigma = \Phi^L$, to determine the decrease in the temperature of congruent fusion and then to construct the entire metastable equilibrium diagram, as described in Ref.91, including the left-hand side (with allowance for the degree of dispersion of titanium).

The characteristic features of the M–C diagram determine the mechanism of the reaction of fine-crystalline mixtures of a metal and CM. In the reaction of Ti with imperfect forms of carbon, nuclei of the carbide phase, which will give the titanium–carbide eutectic, are formed first at the Ti–C interface. Because of the dispersal of Ti and the carbide, the temperature of the titanium–carbide eutectic will be lowered. The metal, penetrating into the channels of the CM, accumulating in the micro-pores, and reacting with carbon, gives new TiC nuclei, and Ti and TiC give a metastable eutectic. The front of this eutectic is displaced towards the imperfect CM, leaving perfect forms behind it, that is "processing" of the CM takes place. When $T \geq T_e$ for the right-hand metastable eutectic is reached, as a result of spontaneous heating of the mixture, the same processing of the CM begins, but now with the carbide–carbon eutectic, with simultaneous precipitation of the carbide phase. This stage determines the yield of carbide. These processes are based on the phenomenon discovered by Elyutin and co-workers.[16] There are many reaction channels, but the system tends to lower its energy, so that the basic reaction is the processing of the imperfect forms of CM.

Since the new phase appears on the metastable equilibrium lines, it is strongly supercooled, as it were "self-quenching" takes place, and an ultradispersed structure is produced because of the retardation of the relaxation processes at low temperatures. This method can also be used to obtain UD structures in the non-equilibrium processes of the combustion of powdered exothermic mixtures in the synthesis of intermetallic compounds, carbides with metallic bonding, and other materials.[94,20]

4. The Production of an Ultradispersed Structure in the Plastic Deformation of Titanium Nickelide

One method for the intensive treatment of solids involves a combination of high pressure and shear deformation. Available data indicate that this leads to physical and chemical processes which cannot be initiated by other methods.

The fine structure of titanium nickelide formed by the action of high pressure and shear deformation, various physicomechanical properties of the intermetallic compound, and the stability of its structure when heated have been studied.[18,96] The original specimen was a TiNi strip with thickness 200 μm, annealed at 770 K for 1 h.

Analysis of the X-ray spectra shows that the diffraction reflections become broader and merge to give a single diffuse reflection on going from the centre to the periphery of the specimens; with increase in the angle of rotation of the anvils, these differences in the structure are less clearly defined. This is due to the increase in the degree

of dispersion and defect character of the structure. The dimensions of the structure are approximately 3–1.5 nm.

Electron microscope studies showed that at low degrees of deformation the granular structure of the material is close to the original structure, that is deformation takes place within the structural fragments, and the distinct boundaries between them are retained. At high deformations, dispersal takes place and the range of coherent scattering of X-rays decreases.

With increase in the deformation and pressure, the microhardness of the specimens increases and reaches 9 GPa. which is almost ten times that of the material in the annealed state.

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Energy-rich media have a number of valuable physicochemical properties, which determine the possible fields of their technological application.

Such properties of UD powders as the lowered temperatures of phase transformations, the increased coefficients of diffusion in the particles, the lowered sintering temperatures, etc. make them particularly attractive for the synthesis of materials with unique properties by sintering, reactive sintering, hot pressing, and hot isostatic pressing; for preparing pastes for low-temperature soldering and welding, etc.

The chemical activity of UDP, including biologically active materials, is finding a number of useful applications.

The properties of energy-saturated solids (metals and alloys) are equally valuable. These include increased strength, hardness, and toughness, and lowered cold brittleness threshold, for materials with an ultrafine fragmentation structure.

A number of technologies have been developed, and experience gained, in the construction and use of experimental assemblies for the production of UDP of metals and compounds. Experience has also been gained in the storage, transportation, mixing, and compaction of UDP.

All this makes the problem of the technological application of energy-saturated media in industry and the national economy of the greatest importance.

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