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Structural, phase and morphological features of plasmachemically synthesized ultradispersed particles

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An attempt has been made to characterize and explain some physical and physicochemical, including structural, phase and morphological features, of ultradispersed particles (UDP) of nitrides (Si_3N_4, AlN, TiN), oxides (Al_2O_3, FeO, Fe_3O_4, Fe_2O_3), metals (Fe) and catalysts (catalyst for ammonia synthesis), synthesized under electric arc low-temperature plasma (LTP) conditions. A relative decrease in the value of the crystal lattice period of up to 0.9% has been observed in ultradispersed powders with particle sizes up to 50 nm. For ultradispersed powders with admixtures, the crystal lattice period may decrease under the influence of the Laplace pressure or increase due to the introduction of admixtures in the main phase crystal lattice. The plasmachemically synthesized ultradispersed powders are built up by the respective high-temperature modifications which have minimum free surface energy, i.e. by phases with a maximum compact crystal lattice.

1. Introduction

One of the lines for practical application of low-temperature plasma (LTP) is its use for the synthesis of ultradispersed powders – metals, oxides, nitrides, carbides, catalysts, etc. [1, 2]. Different terminology has been used in specialized scientific literature to characterize the powder substances, depending on the mean diameter of their particles: ultradispersed, highly dispersed, finely dispersed, submicrometre, micropowders, etc., which complicates the determination of their physicochemical properties. Taking into account first and foremost the features of the physical and chemical properties of the dispersed materials, we consider the following classification (depending on the mean diameter of the particles) to be expedient: ultradispersed (including clusters) – 1–50 nm; high-dispersed (finely dispersed) – 50–500 nm; powders of micrometre sizes – 0.5–100 μm, roughly dispersed – > 0.1 mm.

The plasmachemical methods, based on the formation of ultradispersed particles (UDP) with the participation of chemically reacting HF, microwave plasma jets or arc discharge, have undeniable advantages over the classical condenser methods, particularly in the cases where there is a need for large-scale production of UDP from not readily meltable metals or other substances (nitrides, borides, carbides, oxides, etc.).

The present work attempted to characterize and explain some physical and physicochemical, including structural, phase and morphological features, of UDP synthesized under the conditions of quasiequilibrium electric arc LTP.

2. Experimental procedure

The ultradispersed powders were synthesized under conditions of an electric arc LTP [1–7] on installations described previously. The electric power consumption reaches 15 kW for a plasma-forming gas, predominantly argon with (depending on the nature of the process) argon, nitrogen, air, oxygen, etc., as a powder carrier. The output reaches 150 g h^{-1}. The quenching is achieved by the cold walls of the powder trapping chamber and/or cold gas jets (air, argon, nitrogen), depending on the process features. The ultradispersed powders obtained were analysed using chemical analysis to determine the purity of the desired product, electron microscope analysis to determine the size and the shape of the UDP, the Klijachko-Gurvich [8] method to measure the specific surface of the powders, and X-ray structural and phase analysis to define the phases and the crystal lattice periods.

3. Results and discussion

Some structural, phase and morphological features of a number of ultradispersed powders with particle sizes predominantly under 50 nm (metals, oxides, nitrides, catalysts for obtaining ammonia), synthesized under LTP conditions and the same characteristics for samples of large size, are shown in Tables I and II.

3.1. Structural features of UDP, synthesized under LTP

In UDP, the relative number of surface atoms with respect to the total number of atoms, is much greater

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TABLE I Structural, phase and morphological characteristics of plasmachemically synthesized ultradispersed powders and solid substances

No.	Substance	Chemical composition (%)	Particle shape and size (nm)	Specific surface ($m^2 g^{-1}$)	Phase	Crystal lattice	Crystal lattice periods			Relative change in the lattice period $a_R = \frac{a_s - a_p}{a_s} \times 100\%$	
							a (nm)	c (nm)	c/a	a_R	c_R
1.	Silicic nitride	I Si_3N_4 – 100	Solid	–	I α-Si_3N_4	Hexagonal	0.7818	0.5591	0.7151	–	–
	sol.[a]	II Si_3N_4 – 100	Solid	–	II β-Si_3N_4	Hexagonal	0.7595	0.2902	0.3821	–	–
2.	Silicic nitride	I Si_3N_4 – 95.6	Spherical and	181	I β-Si_3N_4	Hexagonal	0.7592	0.2904	0.3825	0.04	− 0.04
	pl.[b]		hexagonal		I α-Si_3N_4	Hexagonal	0.7800	0.5572	0.7143	0.23	0.34
		II Si_3N_4 – 94.9	10–60	173	II β-Si_3N_4	Hexagonal	0.7651	0.2877	0.3760	− 0.74	0.86
					II α-Si_3N_4	Hexagonal	0.7822	0.5600	0.7159	− 0.05	− 0.16
		III Si_3N_4 – 95.6	After caking	–	III β-Si_3N_4	Hexagonal	0.7660	0.2910	0.3799	− 0.86	− 0.27
3.	Al nitride, sol.	AlN – 100	Solid	–	AlN	Hexagonal	0.3111	0.4975	1.5992	–	–
4.	Al nitride pl.	AlN – 99	Spherical and hexagonal	82	AlN	Hexagonal	0.3100	0.4950	1.5968	0.35	0.50
	Al nitride, pl. caked	AlN – 99	Solid after caking	–	AlN	Hexagonal	0.3119	0.4986	1.5986	− 0.26	− 0.22
5.	Titanium nitride, sol	TiN – 100	Solid	–	TiN	fcc	0.4243			–	–
6.	Titanium nitride, pl[c].	TiN – 92.4	Cubic and tetrahedron 10–80	43	TiN	fcc	0.4235			0.19	
	Titanium nitride, pl. caked	TiN – 92.4	Solid after caking	–	TiN	fcc	0.4253			− 0.24	
7.	Aluminium oxide, sd.	I Al_2O_3 – 100	Solid	–	I α-Al_2O_3	Rhombohedra	0.512	α = 55.25°		–	–
		II Al_2O_3 – 100	Solid	–	II γ-Al_2O_3	Tetragonal	0.5620	0.7800	1.3879	–	–
8.	Aluminium oxide, pl.	Al_2O_3 – 100	Spherical 5–40	145	γ-Al_2O_3	Tetragonal	0.5570	0.7700	1.3931	0.89	0.51
9.	Iron, sol.	I Fe – 100	Solid	–	I α-Fe	bcc	0.286645			–	–
		II Fe – 100	Solid	–	II γ-Fe	fcc	0.3656			–	–
10.	Iron, pl.	I Fe – 50	Spherical	150	I α-Fe	bcc	0.2841			0.89	
	Iron, pl.	II Fe – 50	10–50	150	II γ-Fe	fcc	0.3631			0.68	
11.	Iron oxide, sol.	FeO – 100	Solid	–	FeO	Cubic	0.4357			–	–
			Spherical								
12.	Iron oxide pl.	FeO	10–50	160	FeO	Cubic	0.4336			0.48	
13.	Ferriferrous oxide, sol.	Fe_3O_4 – 100	Solid	–	Fe_3O_4	Cubic	0.8390			–	
14.	Ferriferrous oxide, pl.	Fe_3O_4 – 94	Spherical 10–50	160	Fe_3O_4	Cubic	0.8360			0.36	
15.	Ferric oxide, sol.	I Fe_2O_3 – 100	Solid	–	I α-Fe_2O_3	Trigonal	0.5420	α = 55.28°		–	
	Ferric oxide, sol.	II Fe_2O_3 – 100	Solid		II γ-Fe_2O_3	Cubic	0.8339			–	
16.	Ferric oxide, pl.	I Fe_2O_3 – 100	Spherical	190	I α-Fe_2O_3	Trigonal	0.5400			0.37	
	Ferric oxide, pl.	II Fe_2O_3 – 100	5–40	185	II γ-Fe_2O_3	Cubic	0.8310			0.35	

[a] sol. = solid
[b] pl. = plasma
[c] The titanium nitride was synthesized in the Laboratory of Plasma Processes, Institute of Inorganic Chemistry, Latvian Academy of Sciences.

TABLE II Structural, phase and morphological characteristics of plasma chemically synthesized or regenerated catalysts for the synthesis of ammonia type CA-1 and of a solid sample

No.	Type of catalyst for ammonia synthesis	Chemical composition (mass %)	Fe^{2+}/Fe^{3+} ratio	Particle shape and size (nm)	Specific surface ($m^2 g^{-1}$)	Main phases and crystal lattice	Crystal lattice periods for some of the main phases		Relative change in the lattice period $a_R = \frac{a_s - a_p}{a_s} \times 100\%$
							Phase	a (nm)	
1.	CA-1 standard fraction < 50 μm	FeO 29, Fe_2O_3 65, Al_2O_3 3.0, K_2O 0.8, CaO 2.0, SiO_2 0.2	0.44	Irregular < 50 μm	1.6	Fe_3O_4 cubic	Fe_3O_4	0.840	$a_{Fe_3O_4}$: 0.12
2.	CA-1, regenerated in argon medium	FeO 27–29, Fe_2O_3 64–65, Al_2O_3 3.4–3.5, K_2O 0.8, CaO 2.0, SiO_2 0.3, α, γ-Fe	0.41–0.45	Cubic 20–80	14–22	Fe_3O_4 cubic α-Fe bcc γ-Fe fcc FeO cubic	Fe_3O_4 α-Fe	0.83788 0.28657	$a_{Fe_3O_4}$: 0.13 $a_{\alpha\text{-}Fe}$: 0.03
3.	CA-1, synthesized in air medium (reactor "cold" walls)	(Fe_3O_4 + Fe_2O_3 + FeO) 94, Al_2O_3 3.0, K_2O 0.8, CaO 2.0, SiO_2 0.2	0.26–0.30	Spherical 20–60	21–33	Fe_3O_4 cubic γ-Fe_2O_3 cubic FeO cubic	Fe_3O_4	0.83761	$a_{Fe_3O_4}$: 0.17
4.	CA-1, synthesized in technical nitrogen medium (5% O_2) (reactor "cold" walls)	Fe_3O_4 75–80, Fe_2O_3 13–18, Al_2O_3 2.8–3.0, K_2O 0.8, α, γ-Fe CaO 2.0, SiO_2 0.3	0.32–0.41	Spherical 20–60	20–30	Fe_3O_4 cubic α-Fe bcc γ-Fe fcc FeO	Fe_3O_4 α-Fe	0.8369 0.28664	$a_{Fe_3O_4}$: 0.25 $a_{\alpha\text{-}Fe}$: 0.00
5.	CA-1, synthesized in air medium (reactor "hot" walls)	Fe_3O_4 49.6, Fe_2O_3 44, Al_2O_3 3.0, K_2O 0.6, CaO 1.8, SiO_2 0.6, MgO 0.4	0.26	Spherical 20–45	45	Fe_3O_4 cubic γ-Fe_2O_3 cubic FeO cubic	Fe_3O_4	0.8373	$a_{Fe_3O_4}$: 0.20
6.	CA-1, synthesized in technical nitrogen medium (5% O_2) (reactor "hot" walls)	Fe_3O_4 70.5, Fe_2O_3 23, Al_2O_3 3.1, K_2O 0.6, CaO 1.8, SiO_2 0.6, MgO 0.4, α, γ-Fe	0.32	Spherical 20–45	50	Fe_3O_4 cubic α-Fe bcc γ-Fe fcc Fe_2O_3 cubic FeO cubic	Fe_3O_4 α-Fe	0.8390 0.28655	$a_{Fe_3O_4}$: 0.00 $a_{\alpha\text{-}Fe}$: 0.03

than that of the highly dispersed (finely dispersed) particles. The surface atoms in the UDP have fewer neighbours in comparison to the atoms located in the central area of the particle. This leads to a disturbance in the equilibrium and in the distribution symmetry of the forces of attraction which results in a change in the interatomic distances in comparison with those of the solid substances. It is well known that close to the surface where there is a certain curvature (calculations show that for particles with sizes of the order of 10–30 nm the formation of walls, characteristic of crystals, is not yet stable and there is a trend towards the formation of particles with a spherical shape, the ribs and the tips being rounded and the walls becoming convex) the surface layers of the atoms create a superpressure determining the surface tension forces. This pressure is described for any surface point by the Laplace formula

$$P = \alpha(1/R_1 + 1/R_2) \qquad (1)$$

where R_1 and R_2 are the radii of surface curvature at a given point in two reciprocally perpendicular planes, α is the surface tension.

A characteristic feature of the ultradispersed state (for UDP of average size < 50 nm, Tables I and II) is the inducement of crystal lattice defects under the influence of the Laplace pressure, i.e. the mean interatomic distance is changed (crystal lattice period, Tables I and II), related to the relative change in volume

$$\Delta V/V = k\frac{2\sigma}{r} \qquad (2)$$

where k is the volume contraction coefficient, r is the UDP radius and $2\sigma/r$ is the Laplace pressure (the surface tension, α, should be considered for crystals).

The numerical evaluation shows that, for example, for an UDP size of 10 nm (10^{-8} m) $\sigma \cong 1\ \mathrm{J\,m^{-2}}$, the volume change will be $\sim 10^{-2}$, which corresponds to a relative change in the interatomic distance of 3×10^{-3}, i.e. $\sim 0.3\%$. Thus, for example, for a cobalt UDP [9] the lattice parameter a decreases from 0.3533 nm to 0.3517 nm, i.e. 0.45%, with a decrease in the particle size from 120 nm to 15 nm. If that is compared to the solid cobalt, where the parameter of the face centred cubic crystal lattice (β-Co) is $a = 0.3544$ nm, the relative change in the parameter a would then be 0.76% for particle sizes 15 nm, i.e. $a_R = 0.76\%$. The formula

$$a_R = \frac{a_{\text{solid smpl}} - a_{\text{UDP}}}{a_{\text{solid smpl}}} \times 100\% \qquad (3)$$

is used to compute a_R. The latter gives a quantitative picture for the relative change of the crystal lattice parameter in the UDP. If $a_R > 0$, then $a_{\text{UDP}} < a_{\text{mass.smpl}}$; if $a_R < 0$, then $a_{\text{UDP}} > a_{\text{mass.smpl}}$ (refer to Tables I and II).

The atoms in the UDP surface layer have fewer close neighbours compared to those in the volume. As a result there is a disturbance in the symmetry in distribution of the mass and the forces acting on each surface atom. The positions taken by these atoms in the ordinary solid crystal do not correspond to minimum energy. Aiming at minimum energy, the atoms move to new positions, i.e. there is the so-called surface structural relaxation. The thickness of the surface layer where these shifts take place is probably of the order of a number of interatomic distances. For plasmachemically synthesized UDP, where the dimensions are approximately some tens of nanometres, this is a value reaching up to 15% of the volume.

For UDP with sizes from 2–10 nm, the numbers of the surface and inside atoms are approximately equal. This is the most interesting and the least studied area of the UDP. The basic anomalies in the UDP physical properties are observed in this area.

The particles with sizes 10–30 nm are a transition area with an increasing number of internal layers in the centre of the particle with a shielding beginning to correspond to the structure of the concrete compact substance (metal, nitride, oxide, etc.). For particles with sizes > 30 nm, some of the surface atoms compared to the total number of atoms in these particles are < 0.01 and the respective effect of the surface energy is very small. Although such particles still differ in a number of properties from the compact substance, their internal structure corresponds to the crystal structure of that substance.

The structure parameters and the UDP surface properties depend on their dispersion. Substantial lack of order in the crystal structure (AlN, TiN, Si_3N_4) is observed in UDP and some are amorphous (SiO_2). It is assumed [10] that for dimensions under 50 nm, a reorganization in the position of the atoms and a change in the type of interatomic bonds takes place which results in a structural, phase and concentration heterogeneity. The strict spatial regularity of atom disposition characteristic of monocrystals is disturbed. The interatomic distances decrease in the transition from the particle centre to the surface. These characteristics should differentiate the UDP from the other types of condensed state for matter: amorphous, liquid, glassy, polycrystal.

The analysis of the results for the UDP sizes obtained under LTP conditions, shown in Tables I and II give grounds to assume that the degree of control of the plasmachemical processes from the point of view of obtaining a set distribution according to UDP size, is much lower than for the classical methods. The difficulties are related first and foremost to the fact that the particles are formed in mixing gas dynamic high-temperature flows with the participation of chemical reactions, taking place in spatial non-uniform concentration and temperature fields under conditions distant from the thermodynamic equilibrium, etc. Our investigations [3] show that under explicit conditions, UDP obtained under LTP medium have normal logarithmic distribution. The histograms are plotted after statistical processing of the electron micrographs. For each UDP type there are at least 10^3 particles processed. Analysis of the statistical error shows that the deviation of the experimental distribution from the normally logarithmic does not exceed 5% [3].

Taking into account the above statements, it can be assumed that the predominant mechanism in the growth of some UDP (e.g. of metals Fe, Co, Mo, Ni) [2] in LTP after quenching, is similar to a liquid coalescence. This is indirectly confirmed by the spherical shape of the particles in the electron micrographs. For example, in the production of a catalyst for ammonia synthesis, a deviation is observed in the experimental dependence from the theoretical, which increases with increasing particle size where the number of large particles is smaller than predicted by the normal logarithmic distribution. This means that the coagulation processes in this particular case do not play a substantial part and grow through the incorporation of atoms using the vapour–crystal mechanism predominates. This is supported by the presence of particles surrounded by walls in the electron micrographs (Table I, 2, 4, 6; Table II, 2). In this way, during crystallization of UDP from LTP and electric arc discharge medium, there is a correlation between the morphology of the particles and the type of distribution by size which shows the different role of coagulation in the process of particle growth.

During plasmachemical synthesis and/or regeneration of catalysts for ammonia synthesis, a bidisperse distribution of particles is observed by sizes with a maxima at 25 and 40 nm [4]. This experimental fact may be due to two circumstances. First, under the conditions of electric arc LTP there is no total evaporation of the particles from the raw material so that particles which are not fully evaporated appear as crystallization centres of the condensing phase, and second, the complex composition of the catalyst causes the crystallization of various components at different rates.

3.2. Phase features of LTP-synthesized UDP

Crystal structures may be built up in UDP with particle sizes 10–100 nm, metastable for solid materials of the same composition from the view point of the temperature interval of their existence or generally not characteristic for substances in the solid condition. This can be related to the change in the conditions of thermodynamic balance in UDP compared to the solid substances, as well as to the conditions for producing the particles, e.g. with the quenching of high-temperature compounds.

The physical and the physicochemical properties of UDP are, to a larger degree, determined by their crystal structure. This is the reason why the study of the dependence of the UDP phase composition on the particle size and the conditions for their production is of interest from a scientific, as well as from a practical, point of view, e.g. for the development of criteria for the "certification" of UDP.

The thermodynamic conditions of the phase equilibria are changed in plasmachemically synthesized UDP due to the surface energy influence. New phases may be formed there, which are not characteristic of the particular substance in the solid state, and in cases when in the solid state there is a polymorphic transformation, its temperature (and/or composition) in the UDP may change. With decrease in the sample size from a given substance to very small (nanometric) dimensions, the surface share increases

$$F_s = \sigma(s/v) \tag{4}$$

in the free energy

$$F = F_v + F_s \tag{5}$$

where F, F_v, F_s are the free energy, volume and surface part of the free energy, respectively, and σ is the surface energy.

In the final analysis it may turn out that if, in the solid samples, phase 1 is stable at a given temperature, i.e.

$$F_v^{(1)} < F_v^{(2)} \tag{6}$$

with a decrease in size and taking into account F_s, the condition [11] may be fulfilled where

$$F_{v_2} + (\sigma_2 s_2/v_2) \leqslant F_{v_1} + (\sigma_1 s_1/v_1) \tag{7}$$

so that for sufficiently small dimensions phase 2 will be stable.

From the phase balance condition (Equation 7) an expression can be obtained for the relative change in the temperature of the phase transition in UDP, T_{12}, compared to the solid sample, T_{12}^{∞}. Having in mind that

$$F_{v_2} - F_{v_1} = \lambda\left(1 - \frac{T_{12}}{T_{12}^{\infty}}\right) \tag{8}$$

where λ is the phase transition heat, we obtain

$$\frac{T_{12}^{\infty} - T_{12}}{T_{12}^{\infty}} = \frac{1}{\lambda}\left(\frac{\sigma_1 s_1}{v_1} - \frac{\sigma_2 s_2}{v_2}\right) \tag{9}$$

The determination of the phase transition temperature in the UDP requires one to take into account the surface energy at the Laplace pressure (which, at particle sizes 10–1 nm, is 10^8–10^{10} Pa) the influence of different defects and admixtures in the particles, as well as the electric and magnetic fields.

It has been shown with electronographic analysis for the determination of the phase composition of the surface layers of UDP from plasmachemically obtained Al_2O_3, that these layers of particles for all fractions studied are enriched at the high-temperature phase by γ-Al_2O_3 [12]. Our investigations of the phase composition plasmachemically synthesized under conditions of electric arc LTP from aluminium and oxygen UD Al_2O_3 [3], show that the UDP are built up by γ-Al_2O_3 (high-temperature phase), γ-Al_2O_3 (low-temperature), α-Al_2O_3 (corundum) and θ-Al_2O_3. The investigations on Al_2O_3 with particle sizes 6–45 nm show that all UDP, except the smallest, are multiphase; the change in dispersity leads to a change in the particle phase composition, i.e. in the studied size interval (6–45 nm), the particle structure depends on their size. Part of the high-temperature phase (γ-Al_2O_3) in the composition of the particles (Table I, 8) increases with the decrease in their size; the surface layers of the particles are enriched with high-temperature particles, therefore with the most symmetric modifications. This is related to the fact that the decrease in the entropic member in the free energy of these layers is more substantial than the increase in the internal energy of the particles during stabilization of the high-temperature phases. The plasmachemically synthesized ultradispersed silicon nitride from silicon and nitrogen is built up of a mixture of β-Si_3N_4 (hexagonal, high-temperature phase); α-Si_3N_4 (hexagonal, low-temperature phase) and Si_3N_4 (orthorhomboid) (Table I, 2). The plasmachemically obtained catalyst for ammonia synthesis type CA-1 is built up of Fe_3O_4, Fe_2O_3, α-Fe, γ-Fe and promoting admixtures.

It follows from the equilibrium conditions (Equations 7 and 8) that with the decrease in the particle size there is a preference for the formation of phases with smaller surface energy, i.e. denser packing. For example, for two of the most widespread fcc and bcc crystal lattices for metals, the first may turn out to be more advantageous because its specific volume and surface energy are smaller. This is why, if in the solid state the densely packed fcc phase is stable, it will exist with the decrease in the particle size until it passes to an amorphous or a liquid phase. If in the solid state at a given temperature, the relatively "friable" bcc phase is stable, a phase transition with the formation of a denser lattice of the fcc modification is possible with the decrease in particle size. For instance, our investigations of the production of iron under electric arc LTP conditions show (Table I, 10) that during reduction of iron oxides there is obtained up to 50% γ-Fe together with α-Fe, while during classical reduction with hydrogen, only α-Fe is obtained. Therefore, during plasma reduction there is also obtained the high-temperature modification γ-Fe, which has a more compact fcc crystal lattice than that for the α-Fe (bcc) (Table I, 10).

The stabilization in UDP of structural modifications, differing from those observed in the same substances in the solid state, and the change in the interatomic distances (and therefore of the density) can have the corresponding thermodynamic explanation [12]. If the relation $F_1 < F_2$ is fulfilled for the macrosamples, i.e. the free energy, corresponding to the structural modification 1 is lower (which means that the thermodynamic stability of this modification for the UDP taking into account the part of the surface energy, σ) the opposite condition may be fulfilled

$$F_1 + (\sigma s/v)_1 > F_2 + (\sigma s/v)_2 \qquad (10)$$

This happens when the addition element to the volume part, due to the excess surface energy for structure 1 turns out to be more than for structure 2.

The stabilization at low temperatures of amorphous and liquid phases is also related to the situations where there is broadening of the area of existence of the high-temperature phase. Such is the case for the lowering of the UDP melting temperature. For example, our investigations [7] show that the caking of UDP from AlN obtained by the plasmachemical method starts at 1000 K, and at 1600 K the samples reach zero porosity. The lowering of the optimum caking temperature of AlN synthesized under plasma conditions is also due to its unusually high activity, which itself is due to the high specific surface area (60–$120\ m^2\ g^{-1}$) and to the fixed structural defects during quenching. The high chemical activity of the ultradispersed AlN makes its use possible for the production, using the methods of powder metallurgy, of qualitatively new articles with very high performance characteristics.

3.3. Influence of the admixtures on the UDP structure

The question, however, arises whether the surface phenomena are the only cause of the change in the interatomic distances in the UDP. In the first place one can point out the influence of the various admixtures. In the synthesis of UDP under LTP, the dissolved atoms of gases (in the process of intense gas quenching), as admixtures of incorporation, may only cause an increase in the interplanar distances. Other admixtures in the crystal lattice of the plasma-synthesized UDP may be the atoms of the raw material which did not react (e.g. aluminium in AlN or Al_2O_3, silicon in Si_3N_4, etc.). On the other hand, in the plasmachemical synthesis and catalyst regeneration, some of the promoting admixtures are of the order of a few percent (e.g. in the catalyst for ammonia synthesis K_2O 0.5%, CaO 2.0%, SiO_2 0.2%, Al_2O_3 3.5%) some of which are incorporated into the crystal lattice of the main phase (e.g. for the ammonia synthesis catalyst Al_2O_3 is incorporated into the magnetite lattice). The analysis of the Mössbauer spectra of the samples (catalysts for ammonia synthesis, promoted by Al_2O_3 and K_2O, synthesized under LTP conditions) shows [13, 14] that Al_2O_3 is incorporated into the magnetite crystal lattice and increases the quantity of ferric ions in a tetrahedron coordination with respect to the stoichiometric quantity. This incorporation has an effect on the defects in the crystal lattice of iron after reduction.

If the relative changes in the lattice periods of the substances, shown in Tables I and II, are considered, one can draw a general conclusion that for comparable phase dispersity (sizes < 50 nm), the absolute value of these changes depends directly on the purity of the respective substances in the ultradispersed state (Table I: 4, a_{AlN} 0.35%, c_{AlN} 0.50%; 8, $a_{\gamma Al_2O_3}$ 0.89%, $c_{\gamma Al_2O_3}$ 0.51%; 16, $a_{\alpha Fe_2O_3}$ 0.37%, $a_{\gamma Fe_2O_3}$ 0.35%). Conversely, the more admixtures there are in the UDP, the smaller the absolute value of the relative change in the lattice period (decrease in the value of the period under the influence of the Laplace pressure) (Table I: 2, $a_{\beta Si_3N_4}$ 0.04%; 6, a_{TiN} 0.19%; Table II: 2, $a_{Fe_3O_4}$ 0.13%, $a_{\alpha Fe}$ 0.03%; 3, $a_{Fe_3O_4}$ 0.17%; 4, $a_{Fe_3O_4}$ 0.25%, $a_{\alpha Fe}$ 0.00%; 5, $a_{Fe_3O_4}$ 0.20%; 6, $a_{Fe_3O_4}$ 0.00%). Even for some UDP the value of a_R is zero or near zero (Table II: 4, $a_{\alpha Fe}$ 0.0%; 6, $a_{Fe_3O_4}$ 0.0%, $a_{\alpha Fe}$ 0.03%), and for other UDP, due to the incorporation of admixtures in the crystal lattice of the respective phase, the relative change in the lattice period assumes a negative value (Table I: 2, $c_{\beta Si_3N_4}$ $-$ 0.04%, $a_{\beta Si_3N_4}$ $-$ 0.74%, $a_{\alpha Si_3N_4}$ $-$ 0.05%; $c_{\alpha Si_3N_4}$ $-$ 0.16%), i.e. an increase is registered in the interatomic distance. This is proved by the change in the lattice period of the substances in the ultradispersed state, as compared to those with the same chemical composition in the solid state (after caking of the UDP, Table I, 2, 4 and 6). It is seen that for β-Si_3N_4 (95.6%) that a increases from 0.7592 nm to 0.7660 nm, c increases from 0.2904 nm to 0.2910 nm; for AlN (99%) a increases from 0.3100 nm to 0.3119 nm, c from 0.4950 nm to 0.4986 nm, and for TiN (92.4%) a increases from 0.4235 nm to 0.4253 nm. In all three cases the values are higher than the respective values for the pure substances in the solid state.

The thermodynamic calculations show that the fcc lattice is stable in the solid state sample, the formation of a new modification in the UDP is less probable. If the bcc lattice is stable in the solid sample, the formation of an fcc lattice is possible in the UDP [15].

3.4. Some peculiarities in the physical and physicochemical properties of LTP-synthesized UDP

A summary of the results of the structural and phase features studied of the plasmachemically synthesized UDP may explain their application in powder metallurgy and in metal ceramics for the production of specialized small-grained materials and ceramic goods exhibiting superplasticity, unique density and strength, chemical and thermal stability and special electrophysical properties (in particular they exhibit high transition temperature in the superconducting state).

The crystal structure and the properties of the UDP have distinctive features. The individual particles in the UDP composition are most often monocrystals or their agglomerates, with surface defects or defects in the crystal lattice which makes it possible to use them as catalysts (active components of catalysts) and also in the pressing of ceramic articles. In addition, they are used as alloying additions in the production of special steels, for the abrasive processing of optical glass, as pigments, fillers of plastics and rubbers, in the production of cutting and structural ceramics, etc.

The ultra- and the highly dispersed powders have a large specific surface (from a few to some hundred $m^2 g^{-1}$), low loose mass (0.5–0.05 $g cm^{-3}$) and increased chemical (catalytic) activity. The initial caking or oxidation temperature for non-oxygen UDP is up to 500 K lower than for powders of micrometre dimensions. The high caking rate and the substantial lowering of the caking temperature [16] is usually related to the large increase in the UDP surface. In the UDP pressing processes, the importance of such factors as particle shape, size distribution of particles, surface condition, etc., is greater than for the coarse dispersed particles. These factors, as well as the low flowability which practically excludes the automatic charging of the press forms and the low pouring mass, complicate the practical application of UDP in areas traditional for powder metallurgy.

The adsorption capacity of UDP for vapours and gases from the environment is related to their high surface activity. For example, the plasmachemically obtained metal powders exhibit, during contact with air, substantial affinity towards oxygen (pyrophorosity) [2]. Depending on their function, these powders may be passivated in a suitable atmosphere or prerefined by heating in an inert atmosphere or vacuum. Our investigations show that for the ultradisperse manganese, molybdenum and iron, there can be used as passivators nitrogen, carbon monoxide and nitrogen 0.5% O_2, respectively [2]. The UDP high activity causes difficulties for their storage and transport, due to the pyrophorosity, etc. considered above.

A characteristic feature of UDPs is their aggregation property. The smaller the particles, the more profound is this property. For example, the plasmachemical synthesis of ultradispersed SiO_2 by hydrolysis or oxidation of silicon tetrachloride with water vapour and oxygen, leads to a product with a specific surface area up to 600 $m^2 g^{-1}$ (spherical amorphous particle size 1–50 nm) which agglomerate in conglomerates, etc. [1]. This facilitates the organization of UDP trapping with the help of ordinary mechanical (sleeve, cassette, etc.) filters, i.e. agglomeration is a property useful from the point of view of plasmachemical technology. On the other hand, if particle pasting together has to be prevented, they are processed with some molecules which can interact with the surface of the individual UDP. In this manner, a layer of ligand molecules is formed on the particle surface, which impedes their aggregation.

4. Conclusion

The plasmachemically synthesized single-component UDP (metals, oxides, nitrides) with particle sizes normally not exceeding 50 nm, are characterized by a relative decrease in the value of the crystal lattice period to 0.9%. In the plasmachemically synthesized powders from ultradispersed substances also containing admixtures (e.g. multipromoted catalysts), a slight change is observed in the value of the crystal lattice period in the main phase (it can decrease or increase) due to the opposing effect of two main factors. As a result of the effect of the Laplace pressure there is a decrease in the crystal lattice period but, on the other hand, the period increases due to the incorporation of admixtures in the crystal lattice of the main phases (e.g. Al_2O_3 in the magnetite crystal lattice in the plasmachemical synthesis of the catalyst for obtaining ammonia).

In the UDP synthesis under LTP conditions, after the effective quenching of the desired products, phases are obtained (usually high-temperature modifications) with minimum free surface energy, i.e. with a maximum compact crystal lattice, which may be without analogues in the solid samples.

The specific physicochemical properties of the plasmachemically synthesized UDP are a good prerequisite for their multiform application in industry.

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