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PRODUCTION AND PROPERTIES OF ULTRAFINE INORGANIC POWDERS IN AN ELECTRIC ARC PLASMA

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The article generalizes the results of investigations carried out by the present author in the field of plasmochemical production of ultrafine inorganic powders under conditions of electric arc low-temperature plasma. The results of a comprehensive study of specific chemical and physicochemical properties of synthesized ultrafine powders are considered.

Introduction. One of the trends in the practical application of an electric arc low-temperature plasma is its use for producing ultrafine powders: metals, oxides, nitrides, carbides, catalysts, etc. [1, 2]. Bearing in mind the specific features of the properties of fine materials that depend on the mean particle diameter, we think it advisable to introduce the following classification: ultrafine materials (including clusters) ranging in size from 1 to 50 nm, fine materials from 50 to 500 nm, micron-sized powders measuring 0.5 to 100 μm, and coarse materials of above 0.1 mm in size [3].

By their properties ultrafine powders differ substantially from both massive solid bodies and liquids. They constitute a specific form of the condensed state of matter. They are used in production of pressed articles (in powder metallurgy, metal ceramic), for hardening certain metals and alloys, in production of special ceramics, parts for electronic engineering, and they are also applied as abrasives, catalysts, pigments, etc.

The high energy parameters of a low-temperature plasma, high rates of the processes of evaporation and condensation, possibilities for automatization, optimization, and simulation of the plasmochemical technology and processes, predetermine the practical advisability of the use of a low-temperature plasma for obtaining ultrafine powders.

Investigations of the use of quasi-equilibrium or nonequilibrium low-temperature plasmas for obtaining ultrafine powders with specific properties, primarily those that cannot be obtained by traditional methods, have been carried out in the world for the past twenty-five years (our works along these lines also have more than a 25-year history).

A number of problems in the field of plasmochemical production of ultrafine powders are still waiting solution. This concerns both the study of the processes occurring in a plasmochemical reactor and the choice of criteria for evaluating the expediency (economical, technical-economical, etc.) of applying the plasmochemical method to the synthesis of one or another substances in the ultradisperse state. These problems can be solved only when the properties of the ultrafine powders produced have been exhaustively studied. For this purpose, it is necessary to considerably extend both theoretical and experimental investigations, in particular, for the formation of particles with specified chemical and granulometric composition, morphology, and the structure of the surface, and with a purposeful change of these characteristics in the process of their production.

The development of scientific foundations for the plasmochemical method of the production of ultrafine powders in jet plasmochemical reactors is a topical problem whose solution will promote the creation of new effective plasmochemical technologies for obtaining a wide range of ultrafine powders and will ease an integrated design of plasmochemical plants. The current interest in the problem is also explained, in particular, by the indisputable advantages of plasmochemical processes: they proceed at high rates for very short time intervals (of the order of milliseconds); the number of technological stages is reduced; in some cases it is possible to use cheap raw material,

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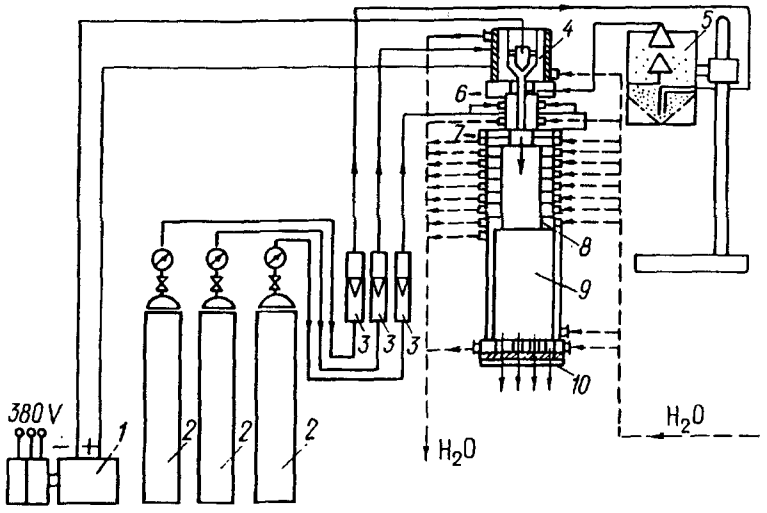

Fig. 1. Schematic diagram of a plasmochemical installation for obtaining ultrafine powder: 1) d.c. generator, 2) tanks with plasma-forming dust-carrying and quenching gases, 3) flow meters, 4) electric-arc plasmatron, 5) vibrational dust-delivering device, 6) water-cooled plasmochemical reactor, 7) gas quenching of reaction products, 8) quencher, 9) dust-trapping chamber, 10) filter.

as well as industrial and habitational wastes; the production of ultrafine powders with valuable and sometimes unique properties, etc.

The aim of the present work was to determine the optimum parameters of plasmochemical processes (mean-mass temperature, form and geometry of plasmochemical mixers and reactors, quenching, capture of condensed phases, etc.) occurring in a neutral, reducing, oxidizing, and redox media when obtaining desired condensed products with regulated particle size, chemical activity, phase composition, crystalline lattice defects, etc., as well as to give a comprehensive characteristic of certain chemical, physicochemical, physical, and other properties of plasmochemically synthesized ultrafine powders.

Experimental Investigations. The synthesis of ultrafine powders was carried out on a plasmochemical electric-arc d.c. installation with a controlled electric power of up to 15 kW and with a capacity of up to 150 g/h. A diagram of the installation is shown in Fig. 1. Argon was used as a plasma-forming gas, and argon, nitrogen, air, oxygen, hydrogen, etc., as carrier gases, depending on the character of the process. The quenching was accomplished on the cold walls of a dust-trapping chamber and/or by cold gas jets (air, argon, nitrogen), depending on the specific features of the process. The ultrafine powders obtained were then subjected to chemical analysis for determining the shape of the desired product, to electronic microscopic analysis for determining the size and shape of the ultrafine particles, to measurements by the Klyachko-Gurvich method [4] for determining the specific surface of the ultrafine powder, as well as to x-ray structural and phase analyses* for determining phases and the change in the crystalline lattice period. Moreover, we also applied infrared and Mössbauer spectroscopy, emission-spectrum derivometric, thermomagnetic, chemical, etc., methods of analysis.

Results of Experiments and Discussion. On the basis of the developed thirty-two plasmochemical processes with products in a condensed ultrafine phase produced in a neutral (Ar, He), reducing (H_2, C, CO, NH_3, CH_4, C_3H_8, and C_4H_{10}), oxidizing (O_2, CO_2, air), nitrogen, and redox media, the optimum parameters of plasmochemical processes (mean-mass temperature, form and geometry of plasmochemical mixers and reactors, means and rate of quenching, dust trapping, etc.) were determined for obtaining the desired products with regulated particle size (specific surface), chemical activity, morphology (crystal lattice defects), and phase composition [5]. Tables 1 and 2 list the developed plasmochemical processes characterized by the principal gross-reaction, desired

* The x-ray and phase analyses were carried out by R. Radanov (Candidate of Technical Sciences) at the Sofia Technological University on a TUR-M62 apparatus.

TABLE 1. Plasmochemical Processes for Producing Ultrafine Inorganic Powders Under the Conditions of Electric-Arc Low-Temperature Plasma

Ordinal No.	Principal reaction	Desired product (yield)
	I. Neutral medium – destruction, precondensation	
1	$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow Mn$	Mn
2	$MoO_3 \rightarrow MoO_2 \rightarrow Mo$	Mo
3	$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$	α-Fe, γ-Fe
4	$ZrSiO_4 = ZrO_2 + SiO_2$	ZrO_2, SiO
5	$\alpha - Al_2O_3 \rightarrow \gamma$ -, δ-Al_2O_3	γ-, δ-Al_2O_3
	II. Reducing medium – reduction	
6	$(MnO_2, Mn_2O_3, Mn_3O_4) + H_2 \rightarrow Mn + H_2O$	Mn (53%)
7	$MoS_2 + 2H_2 = Mo + 2H_2S$	Mo (90–93) %
8	$MoO_2 + 2H_2 = Mo + 2H_2O$	Mo (90–93) %
9	$CoO + H_2 = Co + H_2O$	Co (100%)
10	$ZnO + H_2 = Zn + H_2O$	Zn (100%)
11	$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$	α-, γ-Fe (100%)
	III. Oxidizing medium – oxidation	
12	$SiCl_4 + O_2 = SiO_2 + 2Cl$	SiO_2 (100%)
13	$SiCl_4 + 2H_2O = SiO_2 + 4HCl$	SiO_2 (100%)
14	Fe FeO Fe_3O_4 Fe_2O_3	Fe_2O_3, Fe_3O_4
15	$4Al + 3O_2 = 2Al_2O_3$	γ-Al_2O_3 (100%)
16	$2CoS + 3O_2 = 2CoO + 2SO_2$	CoO (100%)
17	$(Ni, Al) + O_2$ $NiO + Al_2O_3 + NiAl_2O_4$	Catalyst for reforming CH_4,
18	$(Cu, Zn, Al) + O_2$ $CuO(Cu_2O) + ZnO + Al_2O_3$	catalyst for converting CO with H_2O,
19	$3Fe + 2O_2 = Fe_3O_4$	synthesized (regenerated)
20	$4Fe + 3O_2 = 2Fe_2O_3$	catalyst for synthesizing NH_3
21	$2Fe + O_2 = 2FeO$	
	IV. Nitrogen medium – formation of nitrides	
22	$2Al + N_2 = 2AlN$	AlN (100%)
23	$3Si + 2N_2 = Si_3N_4$	α-, β-Si_3N_4-48%, 97% after purification
24	$3Mg + N_2 = Mg_3N_2$	Mg_3N_2 (73%)
	V. Redox medium	
25	$SiO_2 + C = SiO + CO$ (I)	
26	$2SiO + O_2 = 2SiO_2$ (II)	SiO_2 (100%)
27	$NiO + H_2 = Ni + H_2O$ (I)	synthesized (regenerated) catalyst
28	$2Ni + O_2 = 2NiO$ (II)	for reforming CH_4; synthesized
29	$(CuO, ZnO, Al_2O_3) + H_2 \rightarrow (Cu, Zn, Al) + H_2O$ (I)	(regenerated) catalyst for
30	$(Cu, Zn, Al) + O_2 \rightarrow CuO(Cu_2O) + ZnO + Al_2O_3$ (II)	converting CO with H_2O;
31	$Fe_2O_4 + 4H_2 = 3Fe_2 + 4H_2O$ (I)	same to synthesize ammonia
32	$3Fe + 2O_2 = Fe_3O_4$ (II)	

TABLE 2. Parameters of Plasmochemical Processes

Ordinal number	Temperature range, K	Characteristics of the product		Region of applicability
		dimensions of particles, nm	specific surafce, m^2/g	
1	3500–4000	<100	40–70	Powdery metallurgy, metallurgy, metal ceramic, production of paints
2	4000–5000	<100	up to 300	
3	2000–3000	<100	up to 100	
4	4000–5000	<500	up to 50	
5	3500–4500	<500	30–50	
6	2500–4000	<100	up to 80	
7	2500–4000	<100	20–380	Powdery metallurgy, metal ceramic, chemical industry, microelectronics
8	3000–4000	<100	up to 300	
9	3000–4000	<100	up to 160	
10	3000–4000	<100	up to 160	
11	2000–4000	10–100	up to 160	
12	up to 10,000	<100	60–200	Chemical, pharmaceutical, rubber industry, powdery metallurgy, pigments, catalysts for converting CH_4, CO, catalysts for synthesizing ammonia, industrial catalyst
13	up to 11,000	<100	90–400	
14	1200–2200	10–50	90–150	
15	1200–7000	6–45	120–420	
16	1000–3000	–	up to 60	
17	2000–3000	10–30	up to 110	
18	up to 5100	10–40	45–51	
19	1100–3400	20–60	10–40	
20	1300–3500	20–60	20–40	
21	1500–3500	<100	up to 40	
22	3300–3800	50–70	60–100	Chemical industry, coatings
23	3000–3500	10–60	up to 250	
24	2000–2500	10–60	up to 180	
25	5000–10,000	50–500	50–400	Microelectronics, nutritional industry, regenerated catalyst for converting CH_4 and CO, catalyst for synthesizing ammonia
26	10,000–300			
27	1000–4000	<100	up to 150	
28	4000–300			
29	1000–4000	<100	up to 40	
30	4000–300			
31	1000–4000	10–30	up to 50	
32	4000–300			

products of the process, optimum temperature conditions in the plasmochemical reactor, dimensions of the particles of ultrafine powders, magnitude of their specific surface, and region of applicability.

We comprehensively characterized a number of the properties of plasmochemically synthesized ultrafine or fine powders: physical (morphology, structure, mechanical properties, specific surface or size, bulk weight, magnetic, thermal, etc.) [1-6]; chemical (chemical activity – pyrophoric nature, viscosity, pH, hydrophilic nature, phase composition) [1-7]; physicochemical (catalytic activity and the degree of the reduction of oxides in the composition of catalysts, distribution of impurities within ultrafine particles and on their surface) [1-12].

TABLE 3. Some Technological Characteristics and Physicochemical Properties of Chemically Active and/or Pyrophoric Ultrafine Powders Synthesized in an Electric-Arc Low-Temperature Plasma

Ordinal number	Ultrafine substance	Principal reactions of plasmochemical synthesis	Temperature range in plasmochemical reactor, K	Dimensions of particles, nm	Specific surface, m^2/g	Passivator	Composition of a protecting layer
1	Mn	$Mn_xO_y + yH_2 \rightarrow xMn + yH_2O$	2000–4000	100	up to 80	N_2	Mn_3N_2,, Mn_4N, Mn_2N
2	Mo	$MoS_2 + 2H_2 \rightarrow Mo + 2H_2S$	2000–4000	100	20–380	CO	$Mn(CO)_6$
3	α-Fe, γ-Fe	$Fe_xO_y + yH_2 \rightarrow xFe + yH_2O$	2000–3000	10–100	up to 160	$N_2(0.5O_2)$, CO	Fe_xO_y,$Fe(CO)_5$, $Fe_2(CO)_9$
4	Catalyst for synthezing ammonium CA-1	$3Fe + 2O_2 \rightarrow Fe_3O_4$	1100–3500	20–60	10–40	N_2(05-2%O_2) CO_2(2%O_2)	Fe_xO_y, Fe_xO_y
5	Catalyst for low-temperature conversion of CO by steam	(Cu, Zn, Al) + $O_2 \rightarrow$ CuO(Cu_2O) + ZnO + + Al_2O_3	up to 5100	10–40	45-51	N_2(1%O_2)	CuO, Cu_2O
6	Catalyst for reforming methane	(Ni, Al) + $O_2 \rightarrow$ NiO + Al_2O_3	2000–3000	10–30	up to 110	N_2(1-2%O_2)	NiO
7	AlN	$2Al + N_2 \rightarrow 2AlN$	3300–3800	50–70	60–100	Annealing to 1000 K	–
8	Mg_3N_2	$3Mg + N_2 \rightarrow Mg_3N_2$	2000–2500	10–60	up to 180	Annealing to 1000 K	–

We discovered a relationship between certain properties (size, specific surface, crystal lattice parameters) of ultrafine condensed inorganic powders and the operation parameters of plasmochemical processes: magnitudes of current and voltage, electric power input, efficiency, flow rate, ratio between the reagents and the place of their delivery, kind and flow rate of plasma-forming and dust-carrying gases, mean-mass temperature and enthalpy of the active portion of the arc and of a plasmochemical reactor, temperature profile and gradients in the reaction volume, time of contact between the reagents, kind, rate, and place of quenching of reaction products, means of trapping ultrafine powders, etc. The relationship established between the unique properties of ultrafine powders and the parameters of a plasmochemical process allow one to carry them out in conditions close to optimal ones.

We considered the mechanisms of some of the plasmochemical processes realized. Characteristic of plasmochemical processes is a high degree of transformation of ingredients in the product desired. Plasmochemically synthesized ultrafine powders (metals, oxides, nitrides, pigments, catalysts, etc.) are characterized by an extended specific surface (up to several hundreds of m^2/g), by a correspondingly small size (the mean nominal diameter of particles usually does not exceed 100 nm and in some cases it is below 50 nm). Usually, ultrafine particles have a normal logarithmic size distribution, small bulk weight ($0.5-0.05$ g/cm^3), a tendency toward caking, a crystalline (with defects on the surface and inside the crystal lattice) or amorphous (predominantly of spherical or spheroidal form) structure, and an increased chemical activity (Table 3). For example, the sintering temperature of various ultrafine powders is lower by about 500 K than the maximum sintering temperature of a corresponding substance with micron-sized particles.

The chemical composition of ultrafine metal oxides in a corresponding metal with more than one degree of oxidation (for example, in iron oxides) depends on the mean-mass temperature in the plasmochemical reactor, the excess oxidizer relative to the stoichiometric content, and the time of the corresponding reaction.

The degree of raw material evaporation, rate of quenching, and the efficiency of the prevention of high chemical activity (in particular, pyrophoric nature for metals) determine the practical degree of thermal destruction to the elements of complex substances under the conditions of a low-temperature plasma.

We selected suitable sorbates for decreasing the high chemical activity of certain ultrafine particles exhibiting itself in certain cases in pyrophoric behavior. Such sorbates are: nitrogen for manganese; carbon monooxide for molybdenum; nitrogen with 0.5 vol.% of oxygen for iron (Table 3). The elevated reactivity of certain ultrafine powders (for example, aluminum and magnesium nitrides) is remedied by thermal treatment in an inert (argon, helium) or hydrogen media, as well as in vacuum (Table 3).

Plasmochemically synthesized single-component ultrafine powders (metals, oxides, nitrides) whose particles do not exceed in size 50 nm are characterized by a relative decrease in the crystal lattice period to 0.9%. For ultrafine powders involving impurities, the crystal lattice period may be decreased under the influence of Laplace pressure or be increased by building-in impurities into the basic phase [3, 5, 11].

Effective quenching of desired products leads to the formation of phases (usually high-temperature modifications with a minimum free surface energy, i.e., with the greatest possible compact crystal lattice), that have no analogs in massive specimens [3, 5, 11].

Using the Delmont method of layer-by-layer dissolution of the surface of ultrafine particles, it is shown that elementary impurities are distributed in conformity with a priori notions about successive condensation of components depending on the magnitudes of condensation (boiling) temperatures. High-temperature impurities are distributed in the interior of ultrafine particles (for example, tungsten), and low-temperature ones, on the surface (for example, potassium oxide in the composition of the ultrafine particles of a catalyst to synthesize ammonia) [5].

In Bulgaria, installations were developed and built for the first time with a capacity of 5 ton per year and a power of up to 100 kW for plasmochemical production of ultrafine inorganic powders (metals, oxides, nitrides, pigments, catalysts, etc.) by treating ingredients with a certain purity (metals, oxides, salts, etc.) and/or raw materials of inorganic (metallurgical) waste: mineral salts, deactivated used-up catalysts, pyritic waste, various concentrates, cakes, etc. [5].

Different variants of electric arc plasmatrons, plasmochemical mixers, and reactors (cylindrical, conical, with "cold" and "hot" walls), dust-delivering apparatuses (with a fluidized bed, with a piston, with pneumatic

transport), dust trappers (chamber-like, louvered, precipitators, mechanical filters) and electric filters, cyclones), etc. were designed and manufactured.

Conclusion. The obtained experimental results on the technological parameters of plasmochemical processes for obtaining ultrafine powders can be used in designing pilot plants, keeping in mind simulation criteria, and in some cases industrial installations (for example, for producing silicon oxide by vaporization of quartz sand). For application to practice, it is necessary to test some of the thirty-two developed plasmochemical processes under industrial conditions. The incorporation into industry can be realized in any chemical or metallurginal plant interested in the production of ultrafine powders with unique properties. The plasmochemical method offers promise if there is no alternative for producing ultrafine powders with specific properties.

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