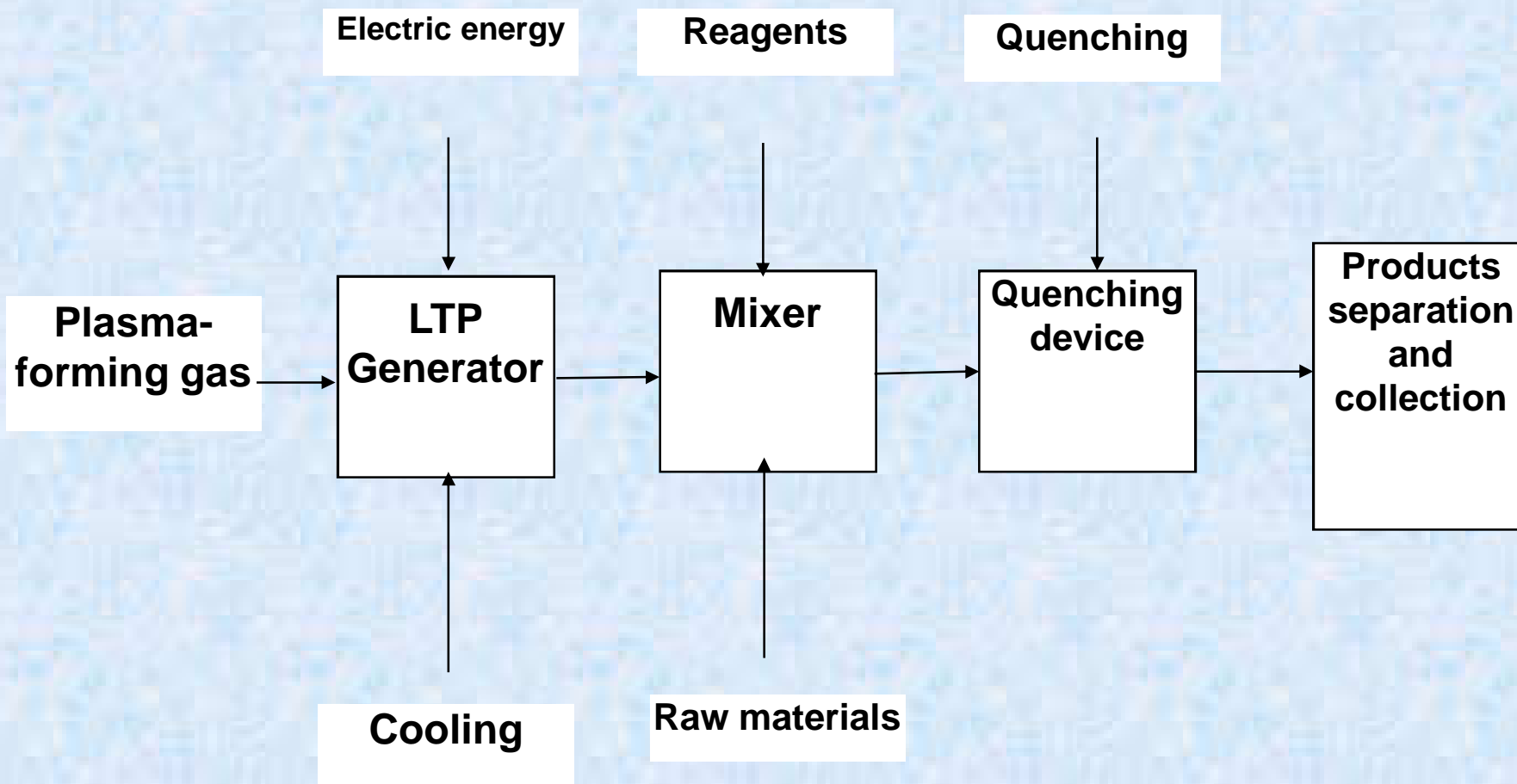
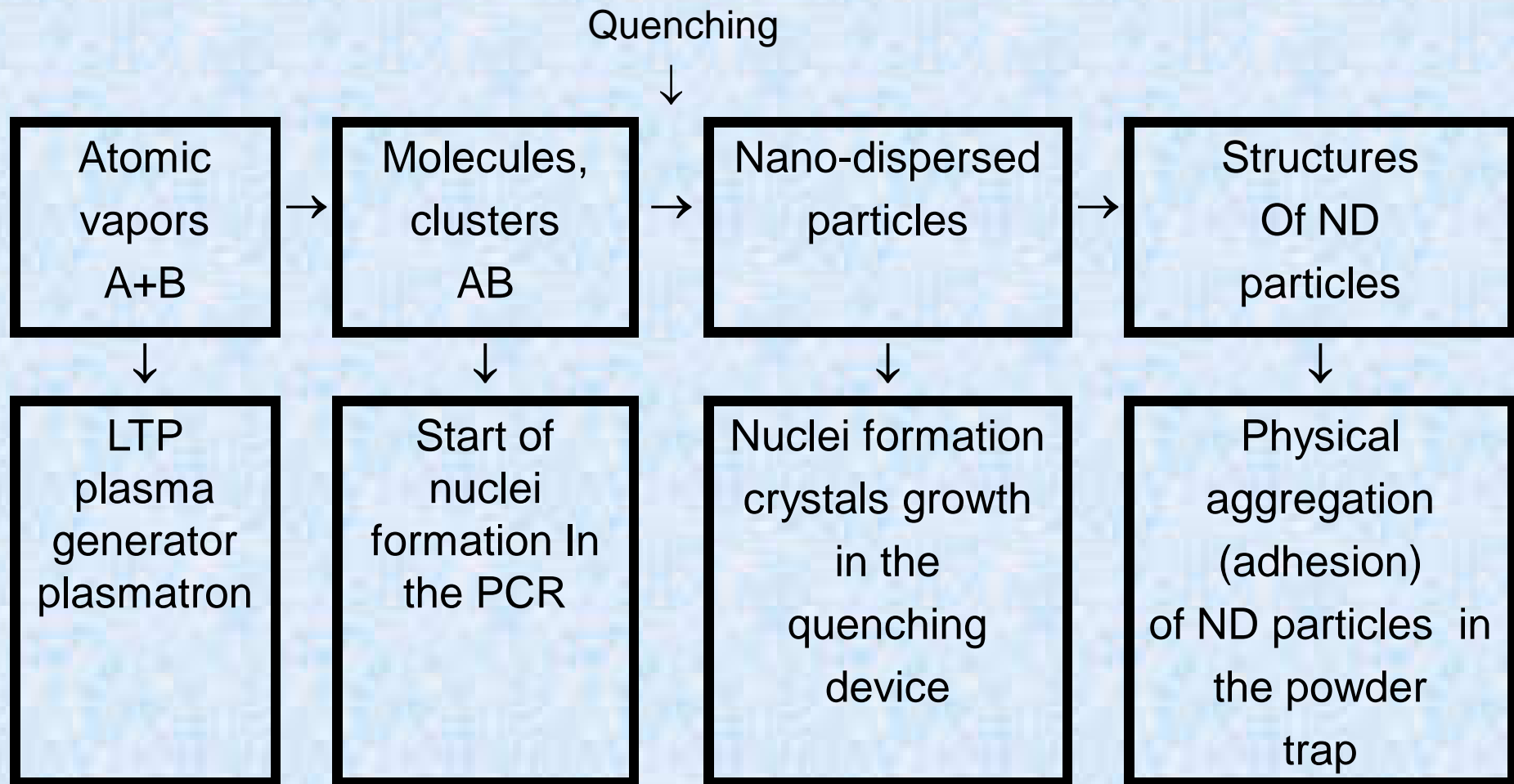


# **NANOPOWDERS – PLASMACHEMICAL SYNTHESIS AND PROPERTIES**

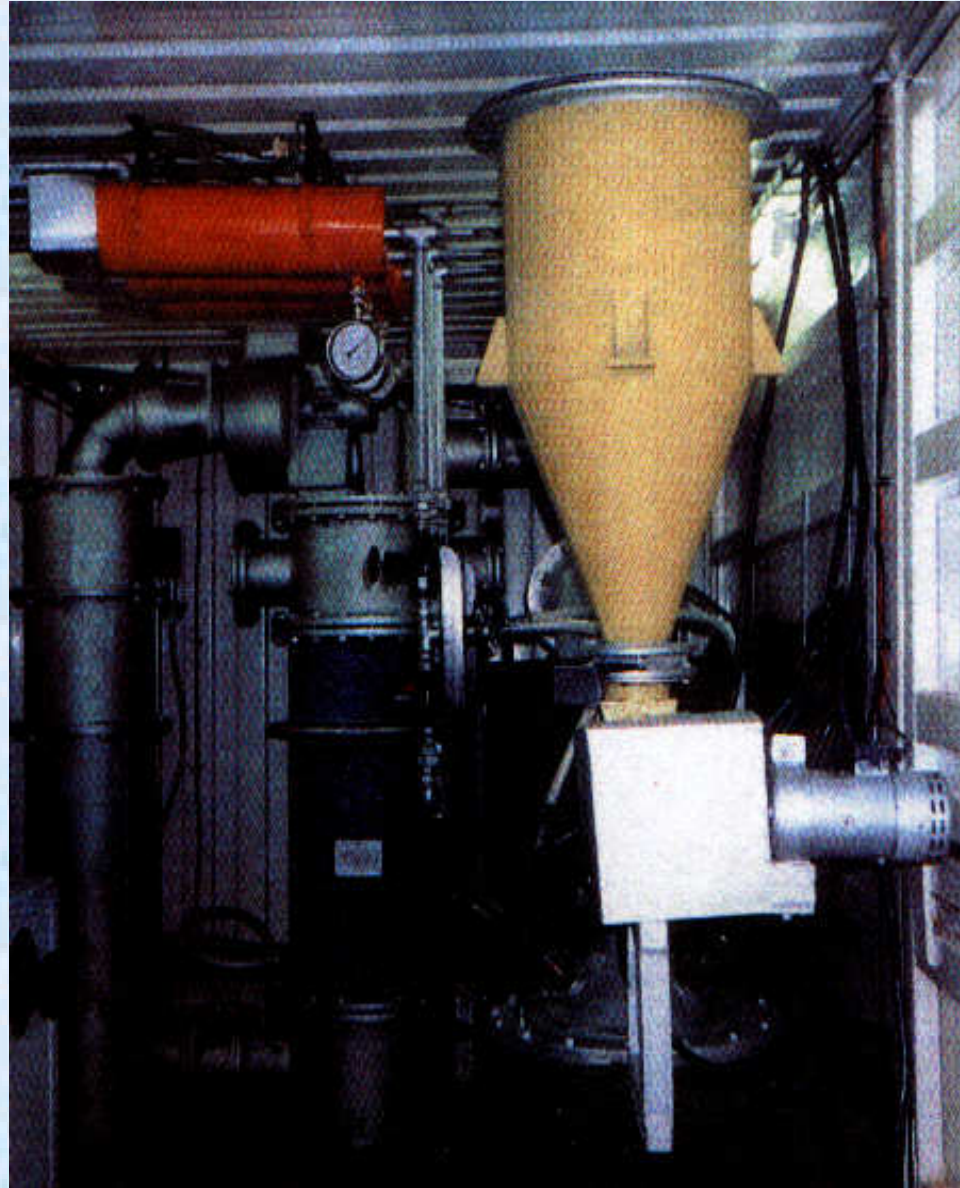
**Prof. G.P. VISSOKOV, Ph.D, D.Sc.**



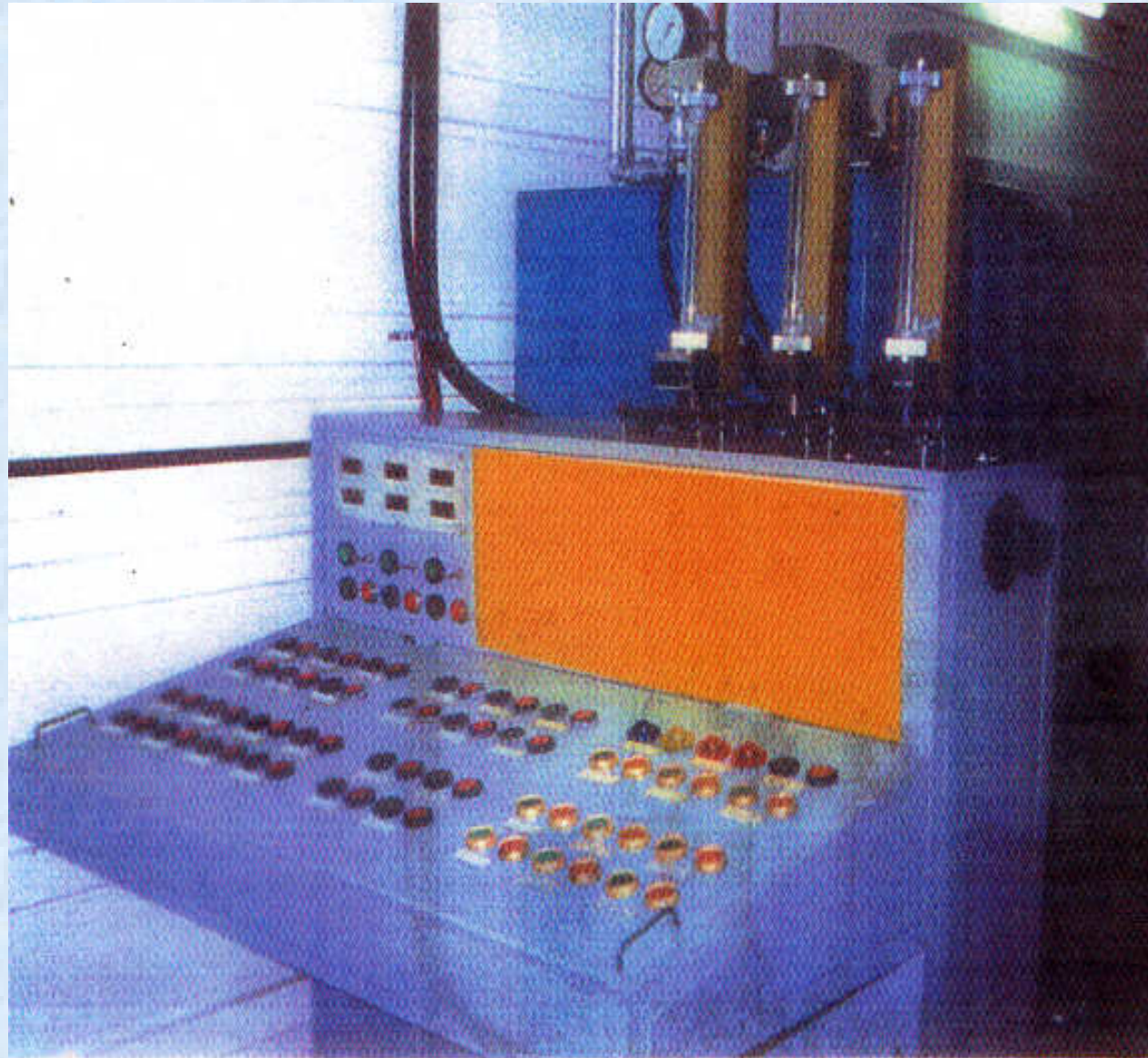
**Schematic diagram of a plasma-chemical installation for ND powders preparation**



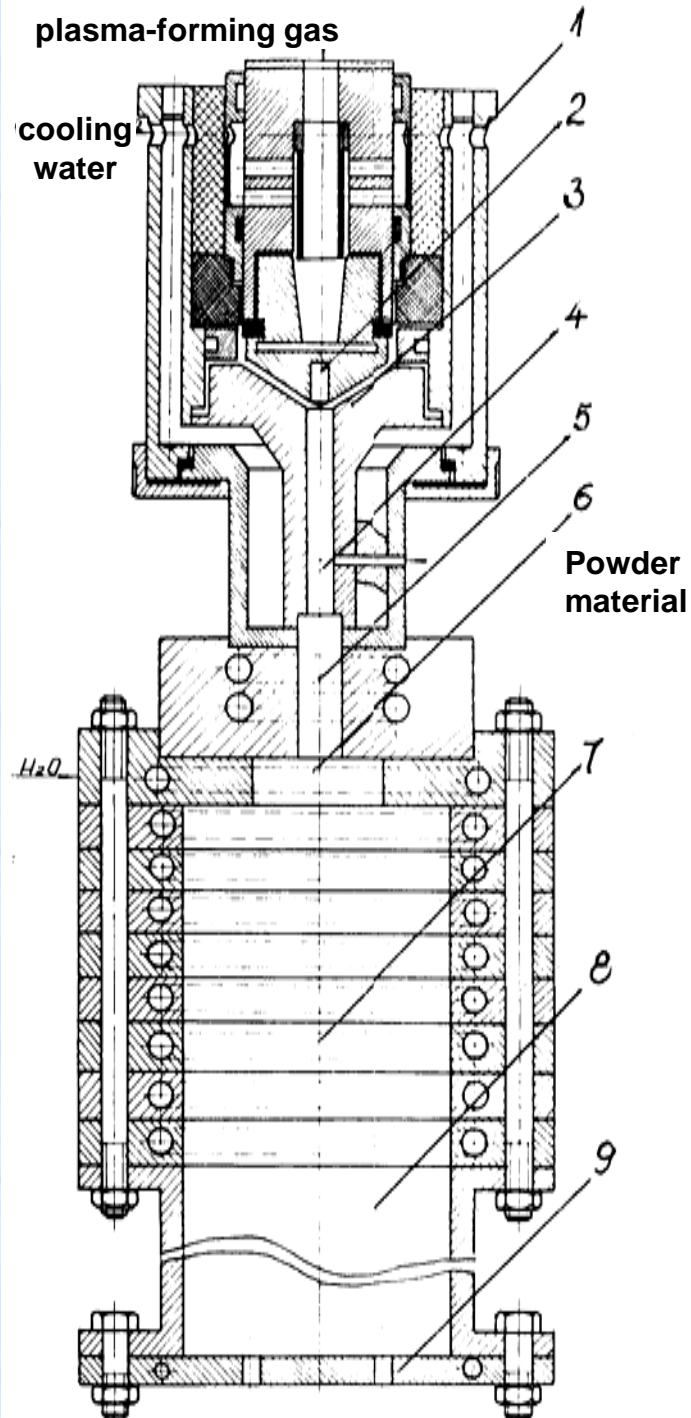
**Scheme for formation of structures of ND particles**



**General view of plasmachemical instalation for preparation of NDP**

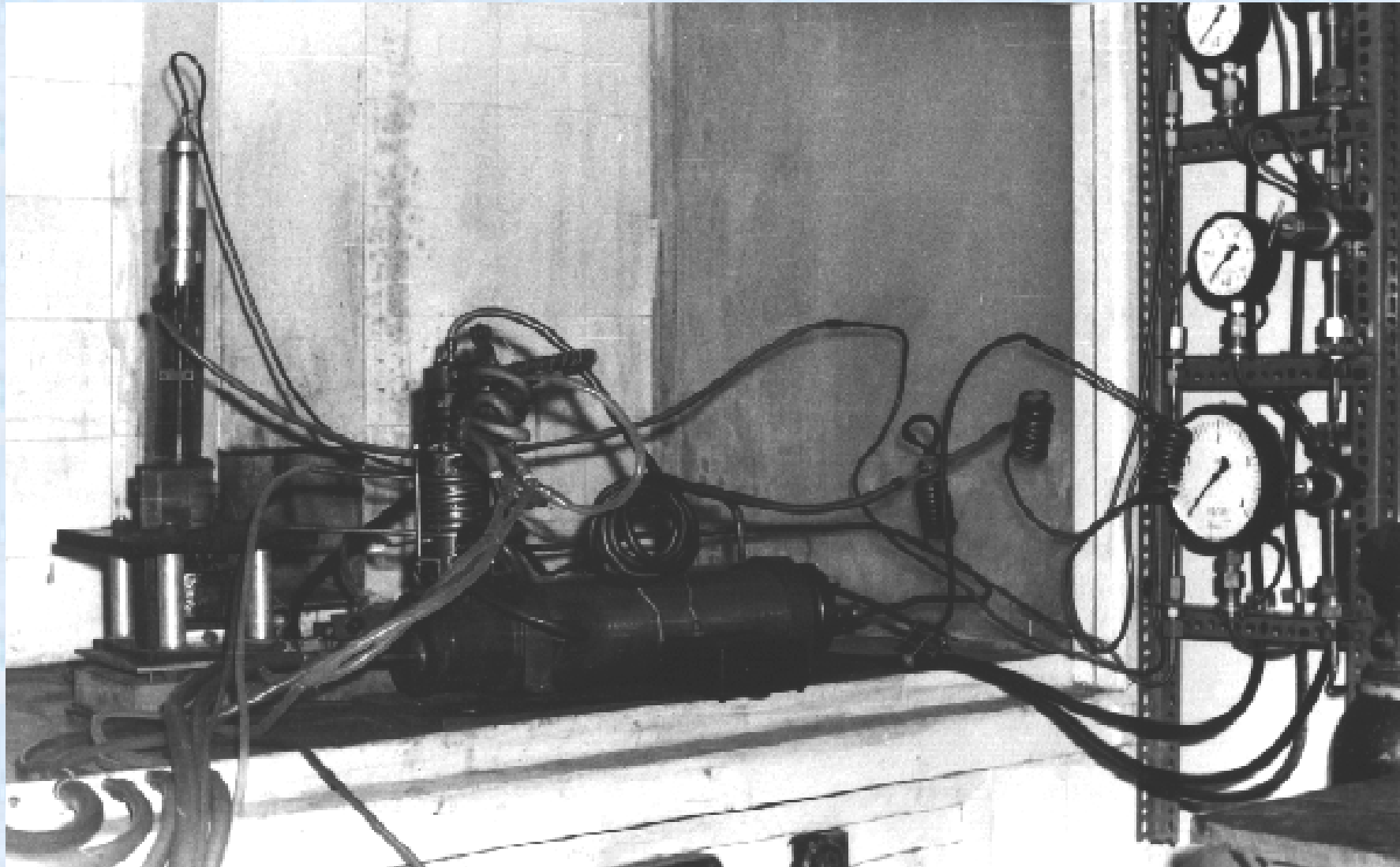


**General view of plasmachemical instalation for preparation of NDP**

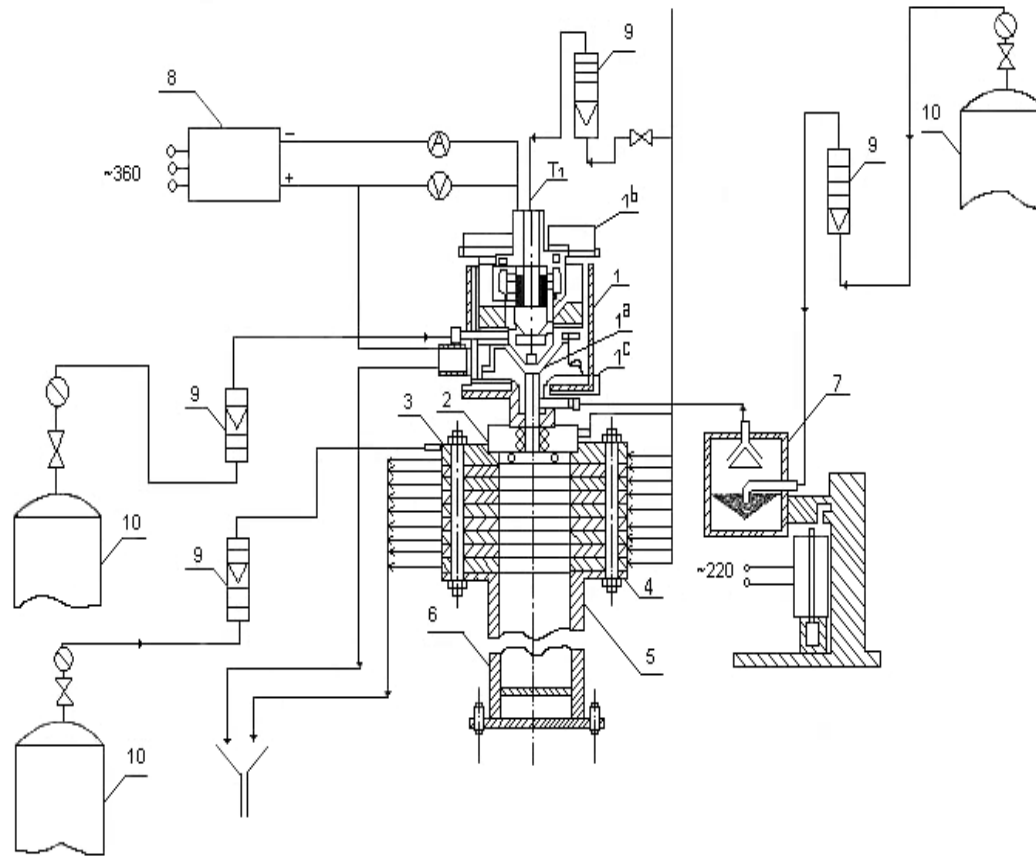


## Schematic of a plasma-chemical installation

**1 - electric-arc plasmatron; 2 - plasmatron's cathode; 3 - plasmatron's anode; 4 - anode nozzle and mixer; 5 - water-cooled copper PCR; 6 - cold gas quenching device; 7 - quenching device and powder-trapping chamber with cold water-cooled walls; 8 - powder-trapping chamber; 9 - filter**



**General view of plasmachemical instalation for preparation of NDP**



**Schematic diagram of plasma-chemical installation for synthesis and/or regeneration of nanodispersed catalysts for ammonia production**

***Electric-arc D.C. plasmatron; 1<sup>a</sup>. Thoriated tungsten cathode; 1<sup>b</sup>. Water-cooled copper anode; 1<sup>c</sup>. Plastic adjusting ring; 2. CW PCR; 3. Quenching device; 4. Water-cooled copper sections of the quenching device; 5. Powder trapping chamber; 6. Filter; 7. Vibration powder-feeding device (if necessary, a piston type vibration powder-feeding device can also be used); 8. Current rectifier; 9. Flow-rate meters; 10. Bottles with plasma-forming, powder-carrying and quenching gases; T<sub>1</sub> - temperature of inlet water; T<sub>2</sub> - temperature of outlet water***



**GENERALIZATIONS ON THE PLASMA-  
CHEMICAL PREPARATION AND  
CHARACTERISTICS OF NANO-  
DISPERSED INORGANIC POWDERS**

# Developed PCPs for preparation of NDP

No.	Main reaction	End product (yield, %)
<b>I. Neutral medium - destruction, re-condensation</b>		
1.	$\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO} \rightarrow \text{Mn}$	Mn
2.	$\text{MoO}_3 \rightarrow \text{MoO}_2 \rightarrow \text{Mo}$	Mo
3.	$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$	$\alpha\text{-Fe}, \gamma\text{-Fe}$
4.	$\text{ZrSiO}_4 = \text{ZrO}_2 + \text{SiO}_2$	$\text{ZrO}_2 + \text{SiO}_2$
5.	$\alpha\text{-Al}_2\text{O}_3 \rightarrow \gamma\text{-}, \delta\text{-Al}_2\text{O}_3$	$\gamma\text{-}, \delta\text{-Al}_2\text{O}_3$

No.	Temperature interval, K	Particles size, nm	Specific surface $\text{m}^2/\text{g}$	Field of application
1.	3500-4000	<100	40-70	powder metallurgy, metal ceramics, pigments
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	

## Developed PCPs for preparation of NDP (continuation)

No	Main reaction	End product (yield, %)
<b>II Reducing medium - reduction</b>		
6.	$(\text{MnO}_2, \text{Mn}_2\text{O}_3, \text{Mn}_3\text{O}_4) + \text{H}_2 \rightarrow \text{Mn} + \text{H}_2\text{O}$	Mn (53 %)
7.	$\text{MoS}_2 + 2\text{H}_2 = \text{Mo} + 2\text{H}_2\text{S}$	Mo (90-93 %)
8.	$\text{MoO}_2 + 2\text{H}_2 = \text{Mo} + 2\text{H}_2\text{O}$	Mo (90-93 %)
9.	$\text{CoO} + \text{H}_2 = \text{Co} + \text{H}_2\text{O}$	Co (100 %)
10.	$\text{ZnO} + \text{H}_2 = \text{Zn} + \text{H}_2\text{O}$	Zn (100 %)
11.	$\text{Fe}_2\text{O}_3 + 3\text{H}_2 = 2\text{Fe} + 3\text{H}_2\text{O}$	$\alpha$ -, , $\gamma$ -Fe (100 %)

No.	Temperature interval, K	Particles size, nm	Specific surface $\text{m}^2/\text{g}$	Field of application
6.	2500-4000	<100	up to 80	powder metallurgy, metal ceramics, chemical industry, microelectronics
7.	2500-4000	<100	20-380	
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	

## Developed PCPs for preparation of NDP (continuation)

No.	Main reaction	End product (yield, %)		
<b>III. Oxidizing medium - oxidation</b>				
12.	$\text{SiCl}_4 + \text{O}_2 = \text{SiO}_2 + 2\text{Cl}_2$	SiO <sub>2</sub> (100 %)		
13.	$\text{SiCl}_4 + 2\text{H}_2\text{O} = \text{SiO}_2 + 4\text{HCl}$	SiO <sub>2</sub> (100 %)		
14.	$\text{Fe} \rightarrow \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$	Fe <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> O <sub>4</sub>		
15.	$4\text{Al} + 3\text{O}_2 = 2\text{Al}_2\text{O}_3$	γ-Al <sub>2</sub> O <sub>3</sub> (100 %)		
16.	$2\text{CoS} + 3\text{O}_2 = 2\text{CoO} + 2\text{SO}_2$	CoO (100 %)		
17.	$(\text{Ni,Al}) + \text{O}_2 \rightarrow \text{NiO} + \text{Al}_2\text{O}_3 + \text{NiAl}_2\text{O}_4$	catalysts for CH <sub>4</sub> reforming		
18.	$(\text{Cu,Zn,Al}) + \text{O}_2 \rightarrow \text{CuO}(\text{Cu}_2\text{O}) + \text{ZnO} + \text{Al}_2\text{O}_3$	catalyst for CO conversion by H <sub>2</sub> O		
19.	$3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4$	synthesized and/or activated (regene-rated) catalysts for ammonia synthesis		
20.	$4\text{Fe} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3$			
21.	$2\text{Fe} + \text{O}_2 = 2\text{FeO}$			
No.	Temperature interval, K	Particles size, nm	Specific surface m <sup>2</sup> /g	Field of application
12.	up to 10000	<100	60-200	chemical, pharmaceutical, rubber industries, metallurgy, pigments, catalysts for CH <sub>4</sub> , CO conversion, ammonia synthesis, industrial catalysis
13.	up to 11000	<100	90-400	
14.	1200-2200	10-50	90-150	
15.	1200-7000	6-45	20-420	
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	

## Developed PCPs for preparation of NDP (continuation)

Main reaction	End product (yield, %)
<b>IV. Nitrogen medium - nitride formation</b>	
22.	$2\text{Al} + \text{N}_2 = 2\text{AlN}$ <b>AlN (100 %)</b>
23.	$3\text{Si} + 2\text{N}_2 = \text{Si}_3\text{N}_4$ <b><math>\alpha</math>-<math>\delta</math>-<math>\text{Si}_3\text{N}_4</math> (48%, 97% after purification)</b>
24.	$3\text{Mg} + \text{N}_2 = \text{Mg}_3\text{N}_2$ <b><math>\text{Mg}_3\text{N}_2</math> (73 %)</b>

No.	Temperature interval, K	Particles size, nm	Specific surface $\text{m}^2/\text{g}$	Field of application
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	

## Developed PCPs for preparation of NDP (continuation)

	Main reaction	End product (yield, %)
<b>V. Reducing-oxidizing medium</b>		
25.	$\text{SiO}_2 + \text{C} = \text{SiO} + \text{CO}$ (I)	SiO <sub>2</sub> (100 %)
26.	$2\text{SiO} + \text{O}_2 = 2\text{SiO}_2$ (II)	
27.	$\text{NiO} + \text{H}_2 = \text{Ni} + \text{H}_2\text{O}$ (I)	synthesized (regenerated) catalyst for CH <sub>4</sub> reforming
28.	$2\text{Ni} + \text{O}_2 = 2\text{NiO}$ (II)	
29.	$(\text{CuO}, \text{ZnO}, \text{Al}_2\text{O}_3) + \text{H}_2 \rightarrow (\text{Cu}, \text{Zn}, \text{Al}) + \text{H}_2\text{O}$ (I)	synthesized (regenerated) catalyst for CO by H <sub>2</sub> O
30.	$(\text{Cu}, \text{Zn}, \text{Al}) + \text{O}_2 \rightarrow \text{CuO}(\text{Cu}_2\text{O}) + \text{ZnO} + \text{Al}_2\text{O}_3$ (II)	
31.	$\text{Fe}_3\text{O}_4 + 4\text{H}_2 = 3\text{Fe} + 4\text{H}_2\text{O}$ (I)	synthesized (regene-rated) catalysts for ammonia synthesis
32.	$3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4$ (II)	

## Developed PCPs for preparation of NDP (continuation)

No.	Temperature interval, K	Particles size, nm	Specific surface m <sup>2</sup> /g	Field of application
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.	5000-10000	50-500	50-400	microelectronics, food industry, synthesis of catalysts for CH <sub>4</sub> and CO conversion, catalysts for ammonia synthesis
26.	10000-300			
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			

## Structural, phase and morphological characteristics of plasma-chemically synthesized ND powders of bulk materials

No.	Compound	Chemical content, %	Shape and size of the particles nm	Specific surface, m <sup>2</sup> /g
1.	Silicon nitride I	Si <sub>3</sub> N <sub>4</sub> - 100	bulk	-
	-bulk II	Si <sub>3</sub> N <sub>4</sub> - 100	bulk	-
2.	Silicon Nitride I	Si <sub>3</sub> N <sub>4</sub> - 95.6	spherical and hexagonal	181
	-plasma II	Si <sub>3</sub> N <sub>4</sub> - 94.9	10-60	173
	III	Si <sub>3</sub> N <sub>4</sub> - 95.6	after sintering	
3.	Aluminum nitride-bulk	AlN -100	bulk	-
4.	Aluminum nitride-plasma	AlN - 99	spherical and hexagonal	82
	Aluminum nitride - plasma, sintering	AlN - 99	bulk, after sintering	-
5.	Titanium nitride-bulk	TiN -100	bulk	-
6.	Titanium nitride-plasma *	TiN - 92.4	cubic and tetrahedral 10-80	43
	Titanium nitride-plasma, sintering	TiN - 92.4	bulk, after sintering	-



## Structural, phase and morphological characteristics of plasma-chemically synthesized ND powders of bulk materials (continuation)

No.		Phase	Crystal system	Crystal lattice constants	Relative change of the crystal lattice constants
1.	I	$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hexagonal	$a=0.7818; c=0.5591; c/a=0.7151$	-
	II	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hexagonal	$a=0.7595; c=0.2902; c/a=0.3821$	-
2.	I	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hexagonal	$a=0.7592; c=0.2904; c/a=0.3825$	$a:0.04; c:-0.04$
	I	$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hexagonal	$a=0.7800; c=0.5572; c/a=0.7143$	$a:0.23; c:0.34$
	II	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hexagonal	$a=0.7651; c=0.2877; c/a=0.3760$	$a:-0.74; c:0.86$
	II	$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	hexagonal	$a=0.7822; c=0.5600; c/a=0.7159$	$a:-0.05; c:-0.16$
	III	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	hexagonal	$a=0.7660; c=0.2910; c/a=0.3799$	$a:-0.86; c:-0.27$
3.		AlN	hexagonal	$a=0.3111; c=0.4975; c/a=1.5992$	-
4.		AlN	hexagonal	$a=0.3100; c=0.4950; c/a=1.5968$	$a:0.35; c:0.50$
		AlN	hexagonal	$a=0.3119; c=0.4986; c/a=1.5986$	$a:-0.26; c:-0.22$
5.		TiN	face-centered cubic	$a=0.4243$	-
6.		TiN	face-centered cubic	$a=0.4235$	$a:0.19$
		TiN	face-centered cubic	$a=0.4253$	$a:-0.24$

## Structural, phase and morphological characteristics of plasma-chemically synthesized ND powders of bulk materials

No.	Compound	Chemical content, %	Shape and size of the particles nm	Specific surface, m <sup>2</sup> /g
7.	Di-aluminum trioxide-bulk I	Al <sub>2</sub> O <sub>3</sub> - 100	bulk	-
	Di-aluminum trioxide-bulk II	Al <sub>2</sub> O <sub>3</sub> - 100	bulk	-
8.	Di-aluminum trioxide-plasma	Al <sub>2</sub> O <sub>3</sub> - 100	spherical 5-40	145
9.	Iron-bulk I	Fe - 100	bulk	-
	Iron-bulk II	Fe - 100	bulk	-
10.	Iron-plasma I	Fe - 50	spherical	150
	Iron-plasma II	Fe - 50	10-50	150
11.	Iron oxide-bulk	FeO - 100	bulk	-
12.	Iron oxide-bulk	FeO	spherical 10-50	160
13.	Tri-iron tetraoxide-bulk	Fe <sub>3</sub> O <sub>4</sub> - 100	bulk	-
14.	Tri-iron tetraoxide-plasma	Fe <sub>3</sub> O <sub>4</sub> - 94	spherical 10-50	160
15.	Di-iron trioxide-bulk I	Fe <sub>2</sub> O <sub>3</sub> - 100	bulk	-
	Di-iron trioxide-bulk II	Fe <sub>2</sub> O <sub>3</sub> - 100	bulk	-
16.	Di-iron trioxide-plasma I	Fe <sub>2</sub> O <sub>3</sub> - 100	spherical	190
	Di-iron trioxide-plasmaII	Fe <sub>2</sub> O <sub>3</sub> - 100	5-40	185

## Structural, phase and morphological characteristics of plasma-chemically synthesized ND powders of bulk materials (continuation)

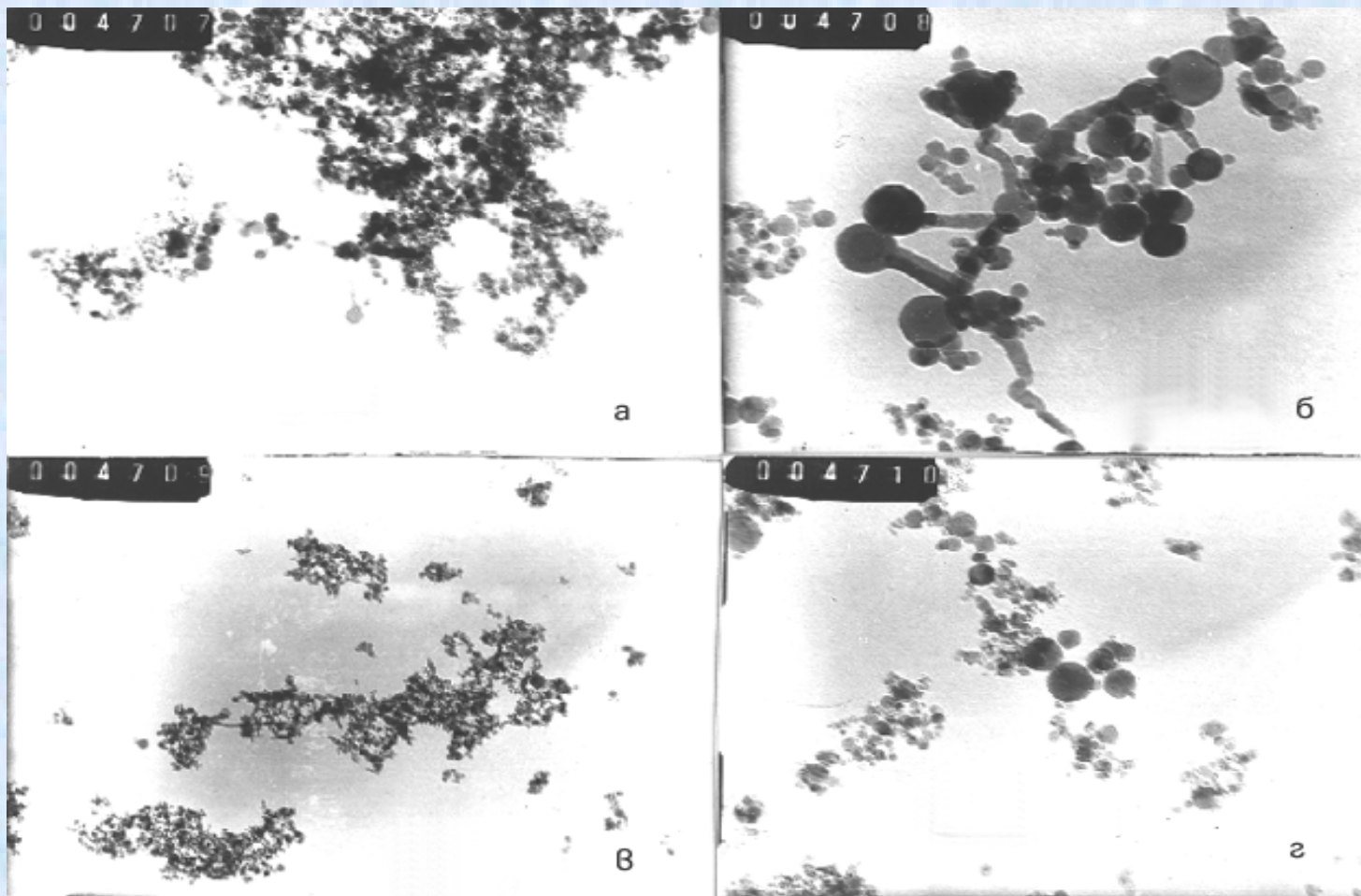
No.		Phase	Crystal system	Crystal lattice constants	Relative change of the crystal lattice constants
7.	I	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	rhombohedral	$a=0.512$ ; $\angle=55.25^\circ$	-
	II	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	tetragonal	$a=0.5620$ ; $c=0.7800$ ; $c/a=1.3879$	-
8.		$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	tetragonal	$a=0.5570$ ; $c=0.7700$ ; $c/a=1.3931$	$a:0.89$ ; $c:0.51$
9.	I	$\alpha$ -Fe	body-centered cubic	$a=0.286645$	-
	II	$\gamma$ -Fe	face-centered cubic	$a=0.3656$	-
10.	I	$\alpha$ -Fe	body-centered cubic	$a=0.2841$	$a:0.89$
	II	$\gamma$ -Fe	face-centered cubic	$a=0.3631$	$a:0.68$
11.		FeO	cubic	$a=0.4357$	-
12.		FeO	cubic	$a=0.4336$	$a:0.48$
13.		Fe <sub>3</sub> O <sub>4</sub>	cubic	$a=0.8390$	-
14.		Fe <sub>3</sub> O <sub>4</sub>	cubic	$a=0.8360$	$a:0.36$
15.	I	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	trigonal	$a=0.5420$ ; $\angle=55.28^\circ$	-
	II	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	cubic	$a=0.8339$	-
16.	I	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	trigonal	$a=0.5400$	$a:0.37$
	II	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	cubic	$a=0.8310$	$a:0.35$

## Structural, phase and morphological characteristics of plasma-chemically synthesized or regenerated type CA-1 catalysts for ammonia synthesis and of a bulk sample.

No.	Type of catalyst for ammonia synthesis	Chemical composition, mass % and Fe <sup>2+</sup> /Fe <sup>3+</sup> ratio	Particles shape and size, nm
1.	CA-1, standard, fraction below 50 μm	FeO- 29; Fe <sub>2</sub> O <sub>3</sub> - 65; Al <sub>2</sub> O <sub>3</sub> - 3.0; K <sub>2</sub> O - 0.8; CaO - 2.0; SiO <sub>2</sub> - 0.2. Fe <sup>2+</sup> /Fe <sup>3+</sup> = 0.44	irregular, below 50 μm
2.	CA-1, regenerated in argon medium	FeO - 27-29; Fe <sub>2</sub> O <sub>3</sub> -64-65; Al <sub>2</sub> O <sub>3</sub> -3.4-3.5; K <sub>2</sub> O- 0.8; CaO- 2.0; SiO <sub>2</sub> - 0.3; α-γ-Fe, Fe <sup>2+</sup> /Fe <sup>3+</sup> = 0.41-0.45	cubic 20-80
3.	CA-1, synthesized in air in CW PCR	(Fe <sub>3</sub> O <sub>4</sub> +Fe <sub>2</sub> O <sub>3</sub> +FeO) - 94; Al <sub>2</sub> O <sub>3</sub> - 3.0; K <sub>2</sub> O - 0.8; CaO - 2.0; SiO <sub>2</sub> - 0.2; Fe <sup>2+</sup> /Fe <sup>3+</sup> = 0.26-0.30	spherical 20-60
4.	CA-1, synthesized in technical grade nitrogen (5% No.O <sub>2</sub> )in CW PCR)	Fe <sub>3</sub> O <sub>4</sub> -75-80; Fe <sub>2</sub> O <sub>3</sub> -13-18; Al <sub>2</sub> O <sub>3</sub> -2.8-3.0; K <sub>2</sub> O-0.8; α-γ-Fe; CaO-2.0; SiO <sub>2</sub> - 0.3; Fe <sup>2+</sup> /Fe <sup>3+</sup> = 0.32-0.41	spherical 20-60
5.	CA-1, synthesized in air in WW PCR	Fe <sub>3</sub> O <sub>4</sub> - 49.6; Fe <sub>2</sub> O <sub>3</sub> - 44; Al <sub>2</sub> O <sub>3</sub> - 3.0; K <sub>2</sub> O- 0.6; CaO- 1.8; SiO <sub>2</sub> - 0.6; MgO - 0.4; Fe <sup>2+</sup> /Fe <sup>3+</sup> = 0.26	spherical 20-45
6.	CA-1, synthesized in technical grade nitrogen (5% O <sub>2</sub> )in WW PCR)	Fe <sub>3</sub> O <sub>4</sub> - 70.5; Fe <sub>2</sub> O <sub>3</sub> - 23; Al <sub>2</sub> O <sub>3</sub> - 3.1; K <sub>2</sub> O- 0.6; CaO- 1.8; SiO <sub>2</sub> - 0.6; MgO- 0.4; Fe <sup>2+</sup> /Fe <sup>3+</sup> =0.32; α-γ-Fe	spherical 20-45

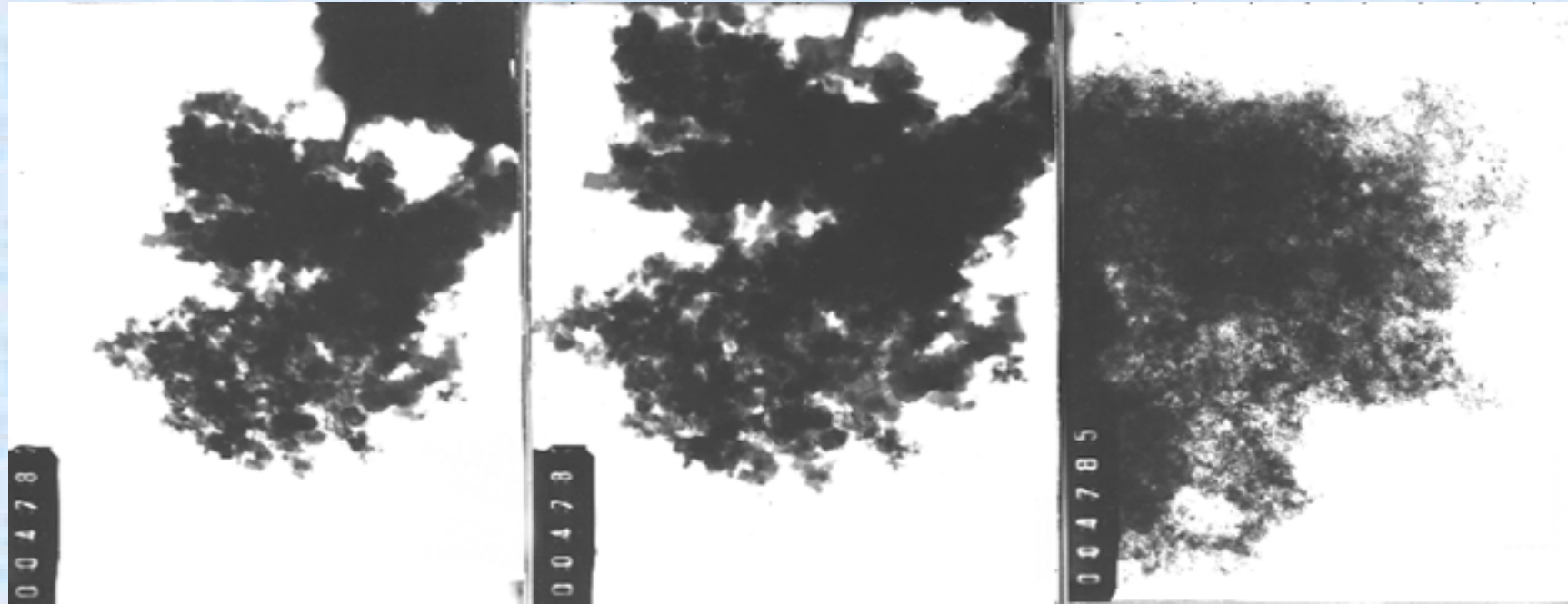
**Structural, phase and morphological characteristics of plasma-chemically synthesized or regenerated type CA-1 catalysts for ammonia synthesis and of a bulk sample (continuation)**

	Specific surface, m <sup>2</sup> /g	Main phases and crystal system	Crystal lattice constant of some of the main phases, nm	Relative change of the lattice constant: $a = (a_b - a_p)/a_b \cdot 100, \%$
1.	1,6	Fe <sub>3</sub> O <sub>4</sub> - cubic	Fe <sub>3</sub> O <sub>4</sub> - a = 0.840	a <sub>Fe<sub>3</sub>O<sub>4</sub></sub> : 0.12
2.	14-22	Fe <sub>3</sub> O <sub>4</sub> - cubic	Fe <sub>3</sub> O <sub>4</sub> - a = 0.83788	a <sub>Fe<sub>3</sub>O<sub>4</sub></sub> : 0.13
		α-Fe - body-centered cubic	α-Fe - a = 0.28657	a <sub>α-Fe</sub> : 0.03
		γ-Fe - face-centered cubic		
		FeO - cubic		
3.	21-33	Fe <sub>3</sub> O <sub>4</sub> - cubic	Fe <sub>3</sub> O <sub>4</sub> - a = 0.83761	a <sub>Fe<sub>3</sub>O<sub>4</sub></sub> : 0.17
		γ-Fe <sub>2</sub> O <sub>3</sub> cubic		
		FeO - cubic		
4.	20-30	Fe <sub>3</sub> O <sub>4</sub> - cubic	Fe <sub>3</sub> O <sub>4</sub> - a = 0.8369	a <sub>Fe<sub>3</sub>O<sub>4</sub></sub> : 0.25
		α-Fe - body-centered cubic	α-Fe - a = 0.28664	a <sub>α-Fe</sub> : 0.00
		γ-Fe - face-centered cubic		
		FeO		
5.	45	Fe <sub>3</sub> O <sub>4</sub> - cubic	Fe <sub>3</sub> O <sub>4</sub> - a = 8373	a <sub>Fe<sub>3</sub>O<sub>4</sub></sub> : 0.20
		γ-Fe <sub>2</sub> O <sub>3</sub> cubic		
		FeO - cubic		
6.	50	Fe <sub>3</sub> O <sub>4</sub> - cubic	Fe <sub>3</sub> O <sub>4</sub> - a = 8390	a <sub>Fe<sub>2</sub>O<sub>4</sub></sub> : 0.00
		α-Fe - body-centered cubic	α-Fe - a = 0.28655	a <sub>α-Fe</sub> : 0.03
		γ-Fe - face-centered cubic		
		Fe <sub>2</sub> O <sub>3</sub> - cubic		
		FeO - cubic		



**Electron-microscope photographs of plasma-chemically synthesized ND AlN.**

- a - magnification 43 000, 1 mm = 22 nm;*
- b - magnification 98 000, 1 mm = 10.2 nm;*
- c - magnification 43 000, 1 mm = 22 nm;*
- d - magnification 98 000, 1 mm = 10.2 nm*



a

b

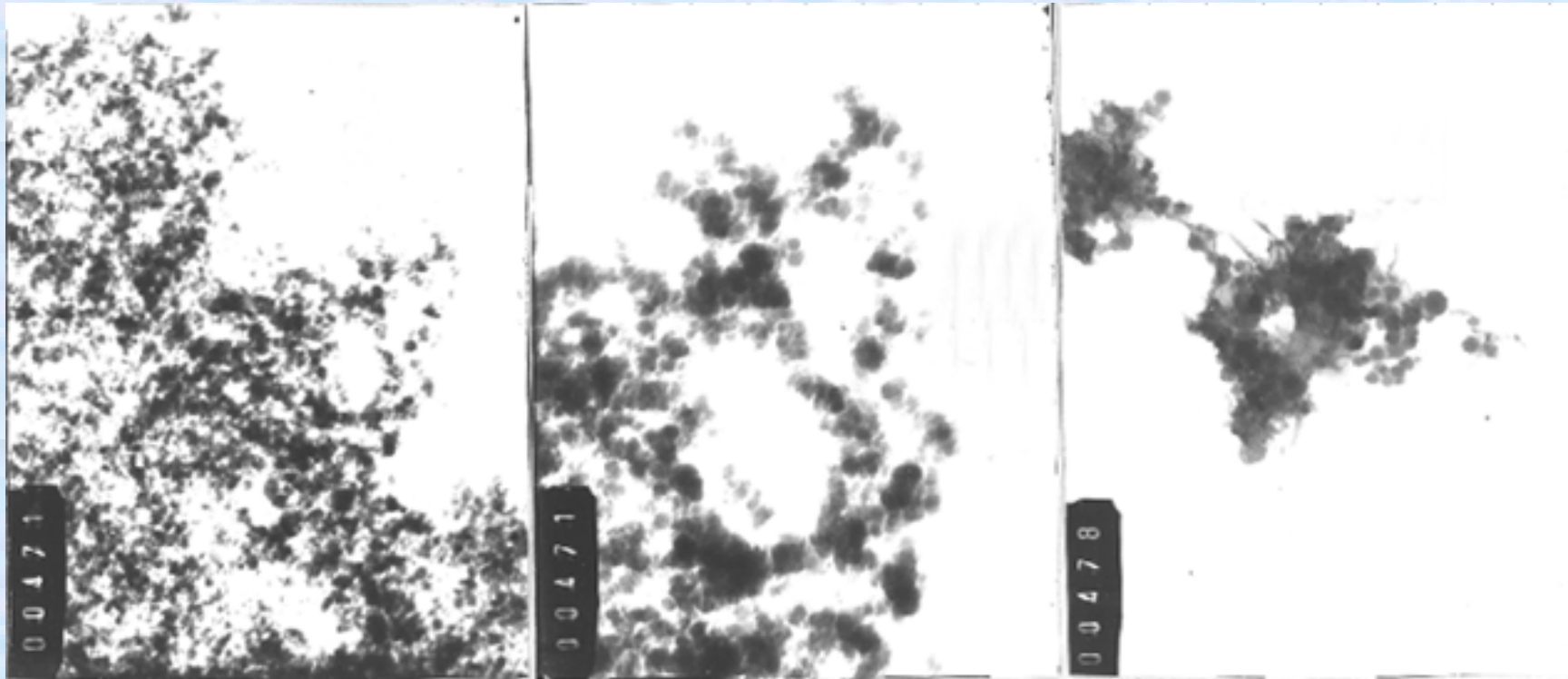
c

**Electron-microscope photographs of plasma-chemically synthesized  
ND  $Mg_3N_2$ .**

*a - magnification 28 000, 1 mm = 38 nm;*

*b - magnification 36 000, 1 mm = 28 nm;*

*c - magnification 36 000, 1 mm = 28 nm*



**a**

**b**

**c**

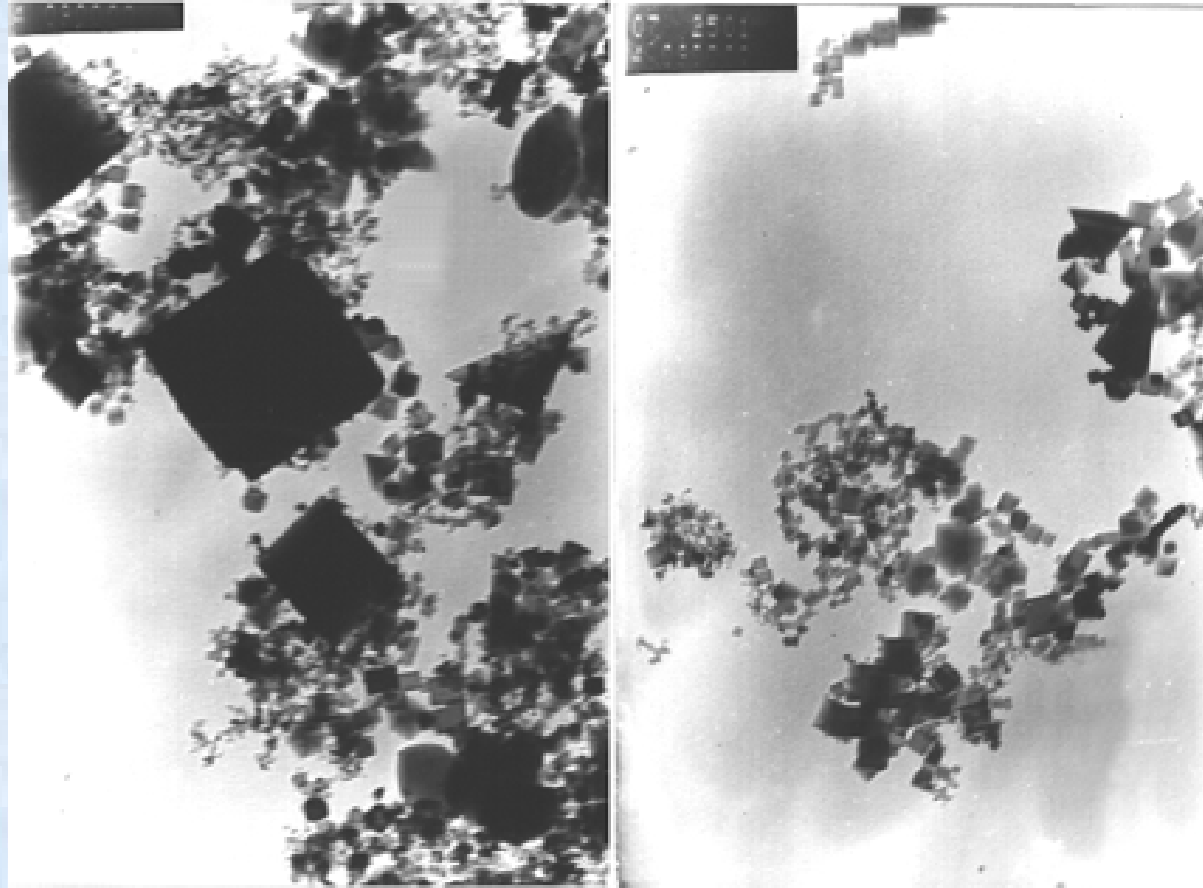
**Electron-microscope photographs of ND Si<sub>3</sub>N<sub>4</sub> plasma-chemically synthesized in a WW PCR**

*a - magnification 36 000, 1 mm = 28 nm;*

*b - magnification 98 000, 1 mm = 10.2 nm;*

*c - magnification 43 000, 1 mm = 22 nm*





a

b

**Electron microscope photographs of PCS ND TiN**

*a - magnification 90 000; 1 mm = 10 nm; S = 32 m<sup>2</sup>/g;*

*b - magnification 90 000; 1 mm = 10 nm; S = 80 m<sup>2</sup>/g*

$$T \geq \frac{E}{2R \ln \frac{A^{1/2} \Delta H m^{2/3} \gamma^{1/3}}{K \lambda \rho d \tau^{1/2}}}$$

**T** - the self-ignition temperature; the activation, K;

**E** – the energy of oxidation, J/mol;

**$\lambda$**  - the ND powder heat conduction, J/mK;

**$\rho$**  - the density, g/m<sup>3</sup> of the ND particles;

**d** - the diameter of the ND particles, m;

**$\tau$**  - the heating duration, s;

in inversely proportional to pre-exponential factor;

**$\Delta H$**  - the thermal effect of oxidation, J/g;

**m** - the sample's mass, g;

**$\gamma$**  - the bulk mass of the powder, g/m<sup>3</sup>

## Some technological characteristics and physico-chemical properties of chemically active and/or pyrophoric ND powders synthesized in electric-arc low-temperature plasma\*

No.	Nano-dispersed substance	Main plasma-chemical reactions of synthesis	Temperature interval in the plasma-chemical reactor, K	Particles size, nm	Specific surface, m <sup>2</sup> /g	Passivating agent	Protective layer composition
1.	Mn	$Mn_xO_y + yH_2 \rightarrow xMn + yH_2O$	2000-4000	<100	up to 80	N <sub>2</sub>	Mn <sub>3</sub> N <sub>2</sub> , Mn <sub>4</sub> N, Mn <sub>2</sub> N
2.	Mo	$MoS_2 + 2H_2 \rightarrow Mo + 2H_2S$	2000-4000	<100	20-380	CO	Mo(CO) <sub>6</sub>
3.	α-Fe, γ-Fe	$Fe_xO_y + yH_2 \rightarrow xFe + yH_2O$	2000-3000	10-100	up to 160	N <sub>2</sub> (0.5% O <sub>2</sub> ), CO	Fe <sub>x</sub> O <sub>y</sub> Fe(CO) <sub>5</sub>
4.	Catalyst for NH <sub>3</sub> synthesis, type CA-1	$3Fe + 2O_2 \rightarrow Fe_3O_4$	1100-3500	20-60	10-40	N <sub>2</sub> (0.5-2% O <sub>2</sub> ) CO <sub>2</sub> (2% O <sub>2</sub> )	Fe <sub>x</sub> O <sub>y</sub> Fe <sub>x</sub> O <sub>y</sub>

**Some technological characteristics and physico-chemical properties of chemically active and/or pyrophoric ND powders synthesized in electric-arc low-temperature plasma\* (continuation)**

No.	Nano-dispersed substance	Main plasma-chemical reactions of synthesis	Temperature interval in the plasma-chemical reactor, K	Particles size, nm	Specific surface, m <sup>2</sup> /g	Passivating agent	Protective layer composition
5.	Catalyst for LTC of CO with H <sub>2</sub> O	$(\text{Cu,Zn,Al})+\text{O}_2 \rightarrow \text{CuO}(\text{Cu}_2\text{O})+\text{ZnO}+\text{Al}_2\text{O}_3$	up to 5100	10-40	45-51	N <sub>2</sub> (1% O <sub>2</sub> )	CuO, Cu <sub>2</sub> O
6.	Catalyst for CH <sub>4</sub> reforming	$(\text{NiAl})+\text{O}_2 \rightarrow \text{NiO}+\text{Al}_2\text{O}_3$	2000-3000	10-30	Up to 110	N <sub>2</sub> (1-2% O <sub>2</sub> )	NiO
7.	AlN	$2\text{Al}+\text{N}_2 \rightarrow 2\text{AlN}$	3300-3800	50-70	60-100	annealing up to 1000 K	-
8.	Ng <sub>3</sub> N <sub>2</sub>	$3\text{Mg}+\text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$	2000-2500	10-60	Up to 180	annealing up to 900 K	-

\* The Table is compiled on the basis of G. Vissokov's scientific publications.

# SPECIFIC ENERGY OF SOME PLASMACHEMICAL PROCESSES

## I. PLASMACHEMICAL THERMAL DESTRUCTION

No	Basic reaction	MJ/kg	kW.h/kg
1.	$\text{ZrSiO}_4 \Rightarrow \text{ZrO}_2 + \text{SiO}_2$	7.92	2.2
1 <sup>a</sup>	for conventional	10.8 ÷ 33	12
2.	$\text{MoS}_2 \Rightarrow \text{Mo} + \text{S}_2$ (B = 48 ÷ 58 %)	36 ÷ 43,2	10 ÷ 12
3.	$\text{Al}_2\text{O}_3 \Rightarrow 2\text{Al} + 1.5\text{O}_2$	24.7	6.9
4.	$\text{TlO}_2 \Rightarrow \text{Tl} + 2\text{O}$	5.0	1.4
5.	$\text{NiO} \Rightarrow \text{Ni} + \text{O}$	9.0	2.5
6.	$\text{CuO} \Rightarrow \text{Cu} + \text{O}$	4.7	1.3
7.	$\text{Ca}_3(\text{PO}_4)_2 \Rightarrow 3\text{CaO} + 2\text{PO} + 3\text{O}$	20.68	5.74

## II. REDUCTION PLASMACHEMICAL PROCESSES

No	Basic reaction	MJ/kg	kW.h/kg
1.	$\text{Fe}_x\text{O}_y + y\text{H}_2 \Rightarrow x\text{Fe} + y\text{H}_2\text{O}$ (Theor.)	7.92	2.2
1a.	(when W = 100 kW)	17.4÷21.4	4.8÷5.9
1b.	(when W = 1000 kW)	15 ÷ 19	4.2÷5.3
1c.	(when $\text{H}_2 : \text{CH}_4 = 2 : 1$ )	9.5	2.6
1d.	(ref.)	10 ÷ 37	2.8÷10.3
2.	$\text{W}_x\text{O}_y + y\text{H}_2 \Rightarrow x\text{W} + y\text{H}_2\text{O}$	~ 50	~13.9
3.	$\text{MoO}_x + x\text{H}_2 \Rightarrow \text{Mo} + x\text{H}_2\text{O}$	72	20
4.	$\text{V}_2\text{O}_3 + \text{C}(\text{H}_2) \Rightarrow \text{V} + \text{CO}_2(\text{H}_2\text{O})$	22.4	6.2
5.	$\text{Nb}_2\text{O}_5 + 5\text{H}_2 \Rightarrow 2\text{Nb} + 5\text{H}_2\text{O}$	34.2÷41.8	9.5÷11.6
6.	$\text{Fe}_x\text{O}_y + z\text{V}_2\text{O}_5 + 5z\text{H}_2 \Rightarrow x\text{Fe} + 2z\text{V} + 5z\text{H}_2\text{O}$	22.4	6.2
7.	Iron-based alloys	14.4	4
8.	$\text{SnO}_2 + 2\text{H}_2 \Rightarrow \text{Sn} + 2\text{H}_2\text{O}$	9.83	2.7
9.	$\text{Fe}_x\text{O}_y + z\text{Cr}_2\text{O}_3 + 3z\text{H}_2 \Rightarrow x\text{Fe} + 2z\text{Cr} + 3z\text{H}_2\text{O}$	43.2	12
10.	$\text{NiO} + \text{H}_2 \Rightarrow \text{Ni} + \text{H}_2\text{O}$	14.4	4
11.	$\text{Co}_3\text{O}_4 + 4\text{C} \Rightarrow 3\text{Co} + 4\text{CO}$	10.8÷12.6	3÷3.5
12.	$\text{Co}_3\text{O}_4 + 4\text{H}_2 \Rightarrow 3\text{Co} + 4\text{H}_2\text{O}$	7.2÷9.0	2÷2.5
13.	$\text{MgO} + \text{C} \Rightarrow \text{Mg} + \text{CO}$	64.8	18

## II. REDUCTION PLASMACHEMICAL PROCESSES (EXTENSION)

No.	Basic reaction	MJ/kg	kW.h/kg
14.	$\text{FeO} \cdot \text{TiO}_2 + \text{CH}_4 \Rightarrow \text{Fe} + \text{TiO}_2 + \text{CO} + 2\text{H}_2$	4	1.1
15.	$\text{BCl}_3 + 1.5\text{H}_2 \Rightarrow \text{B} + 3\text{HCl}$	~ 20	~ 5.6
16.	$\text{TiCl}_4 + 2\text{H}_2 \Rightarrow \text{Ti} + 4\text{HCl}$	31	8.6
17.	$\text{SiCl}_4 + 2\text{H}_2 \Rightarrow \text{Si} + 4\text{HCl}$	~ 20	~ 5.6
18.	$\text{AlCl}_3 + 1.5\text{H}_2 \Rightarrow \text{Al} + 3\text{HCl}$	45.36	12.6
19.	$\text{ZrCl}_4 + 2\text{H}_2 \Rightarrow \text{Zr} + 4\text{HCl}$	~ 25	~ 6.9

### III. NITRIDING PLASMACHEMICAL PROCESSES

No.	Basic reaction	MJ/kg	kW.h/kg
1.	$2P + N_2 \Rightarrow 2PN$	11.6	3.23
2.	$6P + 5N_2 \Rightarrow 2P_3N_5$	11.7	3.26
3.	$TiCl_4 + NH_3 + H_2 \Rightarrow TiN + 4HCl$	35	9.7



## CARBIDE PLASMACHEMICAL PROCESSES

No.	Basic reaction	MJ/kg	kW.h/kg
1.	$\text{TiCl}_4 + \text{CH}_4 + \text{H}_2 \Rightarrow \text{TiC} + 4\text{HCl}$	20 ÷ 60	5.6 ÷ 16.7
2.	$\text{MoCl}_5 + \text{CH}_4 + \text{H}_2 \Rightarrow \text{Mo}_2\text{C} + \text{HCl}$	~ 15	~ 4.2
3.	$\text{WCl}_6 + \text{CH}_4 + \text{H}_2 \Rightarrow \text{WC} + \text{W}_2\text{C} + \text{HCl}$	5 ÷ 10	1.4 ÷ 2.8

## OXIDIZING PLASMACHEMICAL PROCESSES

No.	Basic reaction	MJ/kg	kW.h/kg
1.	$\text{TiCl}_4 + \text{O}_2 \Rightarrow \text{TiO}_2 + 2\text{Cl}_2$	1.8	0.5
2.	$\text{SiCl}_4 + \text{O}_2 \Rightarrow \text{SiO}_2 + 2\text{Cl}_2$	~ 2.0	~ 0.56

# REDOXI PLASMACHEMICAL PROCESSES

No.	Basic reaction	MJ/kg	kW.h/kg
1 <sup>a</sup> .	$\text{SiO}_2 + \text{C} \Rightarrow \text{SiO} + \text{CO}$		
2 <sup>b</sup> .	$\text{SiO} + \text{O} \Rightarrow \text{SiO}_2$	~ 36	~ 10

## **CONCLUSIONS**

**1. For the first time we:**

- **proposed and developed a technique for plasma-chemical regeneration (and, in certain cases, synthesis) of spent deactivated catalysts used in the production of ammonia, such as catalysts for natural gas reforming (steam conversion of methane), for low-temperature conversion of carbon monoxide with water vapour and for synthesis of ammonia; in a number of cases, these catalysts exhibit catalytic activity and thermal stability higher than those of the conventional analogs;**

- **implemented a process for production of nano-dispersed silicon dioxide through hydrolysis of silicon tetrachloride in electric-arc low-temperature plasma;**

- **synthesized aluminium, silicon, and magnesium nitride, in high-frequency induction electrode-less cold plasma, achieving degree of nitride formation of 73 % (for magnesium nitride);**

- proposed and developed a technique for preparation of ND metal powders (manganese, molybdenum, cobalt) by means of reduction of the respective concentrates (manganese-oxide, molybdenite and cobalt cake) in electric-arc low-temperature plasma with gas-phase reducing agents (hydrogen, butane, ammonia);
- proposed a technique for plasma-chemical preparation of nano-dispersed  $\gamma$ -iron with specific surface reaching 160 m<sup>2</sup>/g by means of reducing iron oxides by hydrogen in electric-arc low-temperature plasma, with the possibility to control the ratio between the  $\alpha$ - and  $\gamma$ -iron via the rate of quenching;

**2. Furthermore, we performed a thorough physicochemical study of plasma-chemically synthesized and/or regenerated catalysts, using X-ray diffraction pattern analysis, electron microscopy, derivatography, Moessbauer spectroscopy, as well as chemical, thermo-magnetic etc. analyses; we also explored the dynamics and kinetics of the formation via reduction of the active surface (the “plasma” catalysts are reduced at a rate 2 - 5 times as high as that of the respective industrial analogs); The following was also established:**

- for a catalyst for natural gas reforming: degree of methane conversion, efficiency, output;**
- for catalysts for synthesis of ammonia (in the case of a stoichiometric nitrogen-hydrogen mixture, volume velocity of 30 000 h<sup>-1</sup> and pressures of 0.1 and 30 MPa): activity (15 to 20 % higher than that of the SA-1 catalyst, relative degree of conversion, rate constants, activation energies, relative activity, degree of conversion during deactivation.**

**3. We analysed the characteristics of the quasi-equilibrium and non-equilibrium plasma-chemical processes employed in the technologies for production of nano-dispersed inorganic powders. From a technological and, to some extent, design point of view, we discussed the main component of the plasma-chemical installation, namely, the plasmatron (plasma generator) - electric-arc and induction, the plasma-chemical mixer and reactor, the quenching device.**

**4. We developed and built installations for plasma-chemical preparation of ultra-dispersed inorganic powders (metals, oxides, nitrides, pigments, catalysts, etc.) by processing ingredients with given purity (metals, oxides, salts) and/or raw materials or wastes of inorganic (metallurgical origin), such as mineral salts, deactivated (spent) catalysts, pyrite burnt, various concentrates and cakes, etc.**

**5. We designed and built different variants of various devices: high-frequency induction (quartz) plasmatrons and inductors, plasma-chemical mixers and reactors (cylindrical, conical, with “cold” or “warm” walls), power feeding devices (with boiling layer, piston, with pneumatic transport) power traps (chamber, with partitions, with settler, with filters - mechanical and electrical, cyclones), etc.**

**6. The plasma-chemical techniques are very promising, especially when there are no alternative methods for production of ultra-dispersed powders with specific properties.**



**7. The nano-dispersed powders have found extensive applications in various industrial branches as:**

- reagents, fillers and catalysts - in the chemical industry;**

- intensifying agents in the sintering processing, for production of materials with zero porosity and specific properties, for hardening of metals and alloys - in the powder metallurgy (metal ceramics);**

- for production of artificial dielectrics with high dielectric constant, for production of ferrites, for production of materials with specific semiconducting characteristics, for production of high-temperature superconductors, for manufacture of cathodes for electro-vacuum devices - in the electronic industry;**

- for alloying (modification) of metals and alloys - in the metallurgy, and many others.**

**8. The experimental results obtained on the technological parameters of the plasma-chemical processes for production of nano-dispersed powders can be applied to the design of experimental semi-industrial installations, when the modelling criteria are taken into account; in some cases (e.g., production of nano-dispersed silicon dioxide through vaporization of quartz sands, synthesis of nano-dispersed nitrides of silicon, aluminium titanium), these criteria can be used for the design of industrial equipment. The practical utilization of the techniques necessitates adjustment of some of the processes under industrial conditions.**

**This can be carried out in any chemical or metallurgical industrial enterprise that shows interest in the production of nano-dispersed powders with unique properties.**

**THANK YOU FOR YOUR  
ATTENTION !**