INVESTIGATIONS OF THE SYNTHESIS PROCESS OF MULTICOMPONENT OXIDE COMPOUNDS IN PLASMA

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ABSTRACT

Theoretical principles of the plasmochemical process calculations of the oxide compounds synthesis have been considered. Some physico-chemical properties of ferrite powders, catalysts and zirconium dioxide have been given.

The increased demands of the quality of the industrial products and tendency of the intensification of technological process have put forward the problem of searching new progressive trend in technology. One of these is plasmochemistry.
The application of low temperature compounds considerably simplifies the technological process; the control of the physico-chemical properties of synthesized products has comparatively become simple due to gas-dynamic and heat influences on starting material and reaction products.
The investigations have been carried out to obtain the bound nitrogen products, simple and complex oxide compounds in a low temperature plasma, the thermodynemic method of metallic surfaces processing being developed.
The present report deals only with the process of obtaining simple and complex oxide compounds, such as ferrites, catalysts and zirconium dioxide.
Our theoretical and experimental researches have the aim of determining the main synthesis process regularities of these products.
Plasmochemical synthesis process of one of the grades of ferrite materials - manganese-zinc ferrite powder - multicomponent oxide compounds has been taken as an example of an investigation approach.
To define the temperature range existence of the given products the thermodynemic examinations of the process by the method of minimizing the complete isobaroisothermic potential at a different gas phase composition have been conducted. The investigation of the system Fe, Mn, Zn, O, N, S at pressure 0,1 MПa, partial pressure of oxygen 0,021 MПa have shown that the range existence of ferrites is in the range 600 - 1400 K.
The gas phase comprises N_2, H_2O, O_2, SO_2 and SO_3 in the temperature range of the final products existence. The maximum of NO_2 and NO corresponds to the temperatures 3000 and 3500 K respectively.
To determine the space-time process characteristics of producing oxide compounds required for the reaction apparatus

calculations, kinetic calculations, including gas - driven dynamo, heat and mass exchange processes have been carried out. As an example, the process of obtaining manganese-zinc ferrite powders from sulfates is considered. The mechanism of chemical reaction process involved and kinetic constants (E, Ko) are the initial data for the mathematical model construction. The data published are insufficient to fulfill the kinetic calculations, therefore the process of the thermal decomposition of the starting material with determination of missing and verification of the existing kinetic constants has been studied by the methods of derivatography, X-ray-phase chemical analysis and iteration. The results of the investigations performed are given in table 1.

Table 1

MECHANISM AND KINETIC DATA OF THE THERMAL DECOMPOSITION PROCESS OF HYDRATED SULFATE IRON, MANGANESE AND ZINC MIXTURE

N^o of reactions	Reaction equations	Ko $\frac{1}{c}$	t $\frac{kkal}{mol}$
1.	$FeSO_4 \cdot 7H_2O \longrightarrow FeSO_4 \cdot 5H_2O + 2H_2O$	$1,3 \cdot 10^6$	15,0
2.	$FeSO_4 \cdot 5H_2O \longrightarrow FeSO_4 \cdot H_2O + 4H_2O$	$1,3 \cdot 10^6$	15,0
3.	$3FeSO_4 \cdot H_2O + 0,5O_2 \longrightarrow 2Fe(OH)SO_4 + FeSO_4 + 2H_2O$	$2,5 \cdot 10^5$	20,0
4.	$2FeSO_4 + 0,5O_2 \longrightarrow Fe_2O(SO_4)_2$	$4,4 \cdot 10^4$	28,0
5.	$2Fe(OH)SO_4 \longrightarrow Fe_2O(SO_4)_2 + H_2O$	$1,5 \cdot 10^4$	34,0
6.	$Fe_2O(SO_4)_2 \longrightarrow Fe_2O_3 + 2SO_3$	$3,1 \cdot 10^4$	41,7
7.	$MnSO_4 \cdot 5H_2O \longrightarrow MnSO_4 \cdot H_2O + 4H_2O$	$1,3 \cdot 10^6$	15,0
8.	$MnSO_4 \cdot H_2O \longrightarrow MnSO_4 + H_2O$	$2,5 \cdot 10^5$	20,0
9.	$3MnSO_4 + 0,5O_2 \longrightarrow Mn_3O_4 + 3SO_3$	$7,3 \cdot 10^6$	55,0
10.	$ZnSO_4 \cdot 7H_2O \longrightarrow ZnSO_4 \cdot H_2O + 6H_2O$	$1,3 \cdot 10^6$	15,0
11.	$ZnSO_4 \cdot H_2O \longrightarrow ZnSO_4 + H_2O$	$2,5 \cdot 10^5$	20,0
12.	$3ZnSO_4 \longrightarrow Zn_3(SO_4)_2O + SO_3$	$3,3 \cdot 10^6$	50,0
13.	$Zn_3(SO_4)_2O \longrightarrow 3ZnO + 2SO_3$	$7,3 \cdot 10^6$	55,0

On the base of this mechanism the system of equations based on this mechanism has been worked out.

$$\frac{dn_1}{d\tau} = -K_1 n_1 \qquad (1)$$

$$\frac{dn_3}{d\tau} = K_2 n_2 - K_3 n_3 \qquad (3)$$

$$\frac{dn_2}{d\tau} = K_1 n_1 - K_2 n_2 \qquad (2)$$

$$\frac{dn_4}{d\tau} = \frac{1}{3} K_3 n_3 - K_4 n_4 \qquad (4)$$

$$\frac{dn_5}{d\tau}=\frac{2}{3}K_3n_3-K_4n_4 \qquad (5)$$

$$\frac{dn_6}{d\tau}=\frac{1}{2}K_4n_4+\frac{1}{2}K_5n_5-K_6n_6 \qquad (6)$$

$$\frac{dn_7}{d\tau}=-K_7n_7 \qquad (7)$$

$$\frac{dn_8}{d\tau}=K_7n_7-K_8n_8 \qquad (8)$$

$$\frac{dn_9}{d\tau}=K_8n_8-K_9n_9 \qquad (9)$$

$$\frac{dn_{10}}{d\tau}=-K_{10}n_{10} \qquad (10)$$

$$\frac{dn_{11}}{d\tau}=K_{10}n_{10}-K_{11}n_{11} \qquad (11)$$

$$\frac{dn_{12}}{d\tau}=K_{11}n_{11}-K_{12}n_{12} \qquad (12)$$

$$\frac{dn_{13}}{d\tau}=\frac{1}{3}K_{12}n_{12}-K_{13}n_{13} \qquad (13)$$

$$n_{14}=0{,}5(n_1^0-n_1-n_2-n_3-n_4-n_5-2n_6); \qquad (14)$$

$$n_{15}=\frac{1}{3}(n_7^0-n_7-n_8-n_9) \qquad (15)$$

$$n_{16}=n_{10}^0-n_{10}-n_{11}-n_{12}-3n_{13} \qquad (16)$$

$$n_{17}=0{,}5(14n_1^0-14n_1-10n_2-2n_3-n_5+10n_7^0-10n_7-2n_8+ \\ +14n_{10}^0-14n_{10}-2n_{11}) \qquad (17)$$

$$n_{18}=n_1^0-n_1-n_2-n_3-n_4-n_5-2n_6+n_7^0-n_7-n_8- \\ -n_9+n_{10}^0-n_{10}-n_{11}-n_{12}-2n_{13} \qquad (18)$$

Temperature of gas and condensed phases, motion speed of gas and condensed phases, volatility of a condensed phase and pressure in the reactor have been determined according to the equations /2/:

$$T=\left\{[m(1+z_nW)+0{,}018n_{17}+0{,}08n_{18}]\sum_{i=1}^{i=K}b_ix_i\right\}^{-1}\left\{E_0-[m(1+z_nW)+0{,}018n_{17}+ \right. \\ \left. +0{,}08n_{18}]\left(\sum_{i=1}^{i=K}a_ix_i+\frac{\omega^2}{2}\right)-[Wm(1-z_n)-0{,}018n_{17}-0{,}08n_{18}]\left(c_sT_s+\frac{\omega_s}{2}\right)\right\}; \qquad (19)$$

$$\frac{dT_s}{d\tau}=\varphi_2(T-T_s); \quad (20) \qquad \omega=\frac{[m(1+z_nW)+0{,}018n_{17}+0{,}08n_{18}]\vartheta}{0{,}785\mathcal{D}_p^2}; \quad (21)$$

$$\frac{d\omega_s}{d\tau}=\varphi_1(\omega-\omega_s); \quad (22) \qquad z_n=1-\left(\frac{d}{d_0}\right)^3\frac{\rho_s}{\rho_{s0}}; \quad (23) \qquad P=\frac{RT}{\vartheta} \quad (24)$$

$$\frac{dd}{d\tau}=-\frac{1}{2}\cdot\frac{\theta}{d}\left(1+0{,}3\varphi\sqrt{Re\,P_r}\right); \quad (25) \qquad \varphi_1=18f(x)\frac{\eta}{d^2\rho_s}; \quad \varphi_2=\frac{Nu\,\varphi_1\,C_p}{3P_rf(x)C_s};$$

The system of equations (1-24) has been solved by Rung-Kut numerical method with automatic selection of integration step with the electronic digital computer.
Such theoretical investigations have allowed us to define a profile and volume of the reactor required for the treatment of the sulfate mixture in a plasma with given initial and final process parameters.
The limiting stage of the process concerned has been determined to be chemical kinetics of the thermal sulfate decomposition process.
Different grades of ferrite powders have been synthesized in the calculator reactor. Electromagnetic characteristics are illustrated in table 2.

Table 2

ELECTROMAGNETIC CHARACTERISTICS OF THE CONTROLLED CYCLIC CORES

Name	Mn gs/e	tg δ/Mn		Ky
		H=1Oe	H=10Oe	
Samples produced in plasma	1814	10,9	24,5	1,11
	1798	7,9	22,1	1,16
	1789	8,0	22,3	1,16
Demands	1700-2500	15	45	1,08-1,17

Similar investigations have been performed for a number of other plasmochemical processes.
Experimental comparative data of low temperature conversion CO catalysts and some physicochemical zirconium dioxide properties plasmochemically produced are given in table 3 and 4.

Table 3

ACTIVITY OF THE CONVERSION CO CATALYSTS

	Activity, residual content of CO %		
	1 day	3 days	5 days
LTC-4 industrial	0,21-0,26	0,37-0,47	0,78-1,00
LTC-4 plasma	0,19-0,2	0,32-0,42	0,65-0,89
LTC-8 industrial	0,18-0,23	0,31-0,36	0,60-0,81
LTC-8 plasma	0,16-0,22	0,28-0,34	0,51-0,72

Table 4

SOME PHYSICOCHEMICAL ZIRCONIUM DIOXIDE PROPERTIES PRODUCED FROM DIFFERENT RAW MATERIALS

N°	Characteristic names	From nitric and zirconyl	From basic carbonate zirconium	From dihydrosulfate zirconium
1.	Main substance content	99,7	99,5	98,5
2.	Specific surface (on BET) mg/g	10	6	26
3.	Particle size	0,1-0,5	0,5-1	0,05-0,1
4.	Phase composition	monoclinic+ tetragonal	monoclinic+ tetragonal	monoclinic+ tetragonal

Thus theoretical and experimental investigations of ferrite powder synthesis processes, zirconium dioxide catalysts and other chemical products show that it is possible to synthesize oxide compounds with necessary physicochemical properties in the plasmochemical reactors.

Accepted symbols:

$FeSO_4$, $7H_2O$, $FeSO_4 \cdot 5H_2O$, $FeSO_4 \cdot H_2O$, $FeSO_4$, $FeOHSO_4$, $Fe_2O(SO_4)_2$, $MnSO_4 \cdot 5H_2O$, $MnSO_4 \cdot H_2O$, $MnSO_4$, $ZnSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot H_2O$, $ZnSO_4$, $Zn_3(SO_4)_2O$, Fe_2O_3, Mn_3O_4, ZnO, H_2O, O_3 respectively Π_1, Π_2, Π_3, Π_4, Π_5, Π_6, Π_7, Π_8, Π_9, Π_{10}, Π_{11}, Π_{12}, Π_{13}, Π_{14}, Π_{15}, Π_{16}, Π_{17}, Π_{18}.

T - gas phase temperature, T_s - condensed phase temperature, W - gas phase speed, W_s - condensed phase speed, m - mass of plasmoforming gas, W - initial relation of condensed and gas phase mass expenditure, Aibi - coefficients of approximated equation. $Ii = \sum (ai + biT)$, Ii - gas phase component entalpia, K - component number, Xi - mas portion of gas phase component, Eo - system energy in the initial section, Cp -Cs - gas and condensed phase heat capacity respectively, Dp - reactor diameter, V - specific volume of gas phase, P - pressure in the reactor, R - gas constant, dgd - initial and variable diameter of condensed phase, f(x) - relationship function of condensed and gas phase, ξ - dynamic coefficient of gas phase viscosity, Nu, Re, Pr - Nusselt, Reinold and Prandl criterions, Θ - static evaporation coefficient.

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