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CATALYTICALLY ACTIVE CERMET MEMBRANE FOR CONVERTING BYPRODUCTS FROM THE PRODUCTION OF COMBUSTIBLES

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The conversion of waste byproducts in water, which are formed stoichiometrically as result of the Fischer–Tropsch process, in obtaining combustibles is examined. Theoretical and experimental studies of the vacuum synthesis of cermet membranes based on the system Al–Ni–Co$_3$O$_4$ are performed. The membranes obtained give 85 – 99% conversion of byproducts into syngas.

Key words: open and closed porosity of materials, microstructure, temperature, combustion, self-propagating high-temperature synthesis (SHS), Fischer–Tropsch process.

A current problem of adopting the Fischer–Tropsch process in the chemical industry is the accumulation of large quantities of water, formed stoichiometrically as a result of the reaction (1), that contains environmentally harmful dissolved organic impurities — alcohols, carbonic acids, ketones (methanol, ethanol, methylethyl ketone, acetic acid, and acetone), methane, and carbon dioxide [1]. The main reaction of the Fischer-Tropsch process is

$$n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O},$$
$$\Delta H = 165 \text{ kJ/mole}. \qquad (1)$$
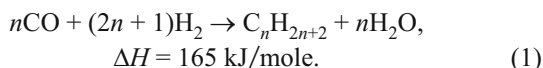
Processing the waste byproducts of the process (organic impurities dissolved in water), returning them into synthesis gas and into the Fischer–Tropsch process, and using the purified water for technical needs are real current problems.

It is well known that on porous membranes synthesized by means of self-propagating high-temperature synthesis (SHS) in vacuum and by modified highly disperse catalytic systems, carbon dioxide reforming of methane (CRM) into syngas, approaching 80% [1 – 4], proceeds intensively at temperatures 200 – 400°C lower than the indices for these processes realized in the conventional continuous-flow reactor with selectivity in syngas formation.

For this reason a promising new approach to solving the problems of reprocessing wastes products of the Fischer–Tropsch process is to use high-porosity cermet membranes comprising an ensemble of microreactors on which the carbon-dioxide-steam conversion reaction of the products occurs.

It is also known that the boiling temperature of metals in vacuum is close to the melting temperature of these metals, and their vaporization rate is two to three orders of magnitude higher than the rate of evaporation of the metal vapors at inert-gas atmosphere pressure of 1 atm. For this reason, the exothermal SHS process in vacuum is favorable for obtaining nanoporous materials for fabricating catalytically active membranes, since in the course of synthesis of the materials a natural increase in porosity occurs as a result of the loosening action of the pressure of the impurity gases and the vapor pressure of the liquid phase of the batch compare with ordinary sintering in a furnace.

The metal in the wave of combustion melts and spreads with liquid interlayers being formed, and in consequence closed pores are formed. The pressure of the impurity gases and vapors of the liquid phase in the closed pores of the material, formed in the SHS process, can reach several atmospheres [5 – 11] and result in opening of the pores with channels being formed (chains of open pores) along which the

impurity gases and liquid-phase vapors filter into the vacuum chamber. In addition, if in the process the pressure of the impurity gases and the pressure of the liquid-phase vapors in the liquid are higher than the external pressure, then very small free bubbles (closed pores), from which open porosity can form during the cavitation, are formed in the liquid.

It is shown in [6, 12] that the pores open at a rate two to three orders of magnitude higher than the linear velocity of combustion. Therefore, the closed porosity is converted into open porosity mainly during the combustion process while a liquid phase exists. The formation of a refractory product only fixes this open porosity, and processes leading to the final formation of the open-porosity structure occur even behind the wave of combustion. This determines the mechanism of the formation of high-porosity materials (membranes) during the SHS process in vacuum. As a result the product obtained possesses a high degree of open channel porosity (> 90%).

PRELIMINARY RESULTS

The calculation was performed for SHS in the system Al–Ni–Co_3O_4. The batch used included powders of the following components (mass fraction, %): 42.5 – PNK-UT1 brand Ni with average particle size 5 – 12 μm, 15 – ASD-4 brand aluminum with average particle size 2 – 8 μm, and 42.5 – cobalt oxide with average particle size 15 – 45 nm. The calculation was performed for a reaction with the formation of $(NiCo)_3Al$ and free Ni, Co and Al_2O_3.

A calculation was performed of the influence of a change in the specific volume effect of materials in the presence of a chemical reaction on the formation porosity of the final product by a method published in [13]. The calculations showed that the synthesized material will possess total porosity 5.2% higher than that of the initial material.

The size of the open pores of the synthesized material was determined by means of capillary displacement. The size of the open pores was calculated on the basis of the Laplace relation for the 'cylindrical pore model' and according to GOST 26849–86 (method for determining the pore size) according to typical combustion parameters of the SHS system.

The maximum pore size was calculated using the relation

$$2\pi R\sigma \cos\theta = \pi R^2 (\Delta p - h\gamma g),$$

where R is the capillary radius, cm; σ is the surface tension of the liquid, dynes/cm; θ is the contact angle, °; h is the height of a column of liquid above the surface of the sample, cm; γ is the density of the liquid, g/cm^3; g is the acceleration of gravity, cm/sec^2; $\Delta p = (p_\infty - p_g - p_v)$ is the pressure of the gas phase during pore formation; p_∞ is the pressure in the experimental chamber (vacuum); p_g is the pressure of the impurity gases; and, p_v is the vapor pressure of the liquid phase.

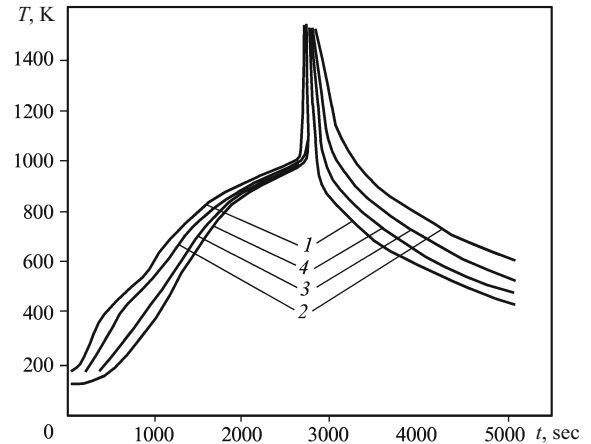The typical combustion parameters of SHS of the system Al–Ni–Co were substituted into the relation for determining

Fig. 1. Variation of the batch temperature in the regime of synthesis of samples from Al–Ni–Co_3O_4: *1 – 4*) indications of thermocouples placed along the height of the sample.

the size of the open pores: $T_g = 1600$ K and the surface tension of aluminum $\sigma = 115.9$ mN/m [15]. The external pressure p_∞ was 0.1 mm Hg (the pressure in the experimental chamber). In the calculations the average pressure p_g of the impurity gases for the system Al–Ni–Co was taken to be 5 atm and the vapor pressure of the liquid phase p_v for aluminum as 0.54 atm [15]. As a result the critical size of the open pores in the synthesized materials was found to be 3.1 μm.

EXPERIMENTAL INVESTIGATIONS

The material, obtained by the SHS method, with open porosity for the system Al–Ni–Co_3O_4 was studied experimentally. Since the main ingredient for obtaining membranes by this method is the presence of through pores (i.e., the absence of closed porosity), it is expedient to conduct synthesis of the porous material not by means of layer-by-layer combustion, characteristic for SHS, but rather in the thermal explosion regime.

The powders were mixed in a ball mill, using Al_2O_3 balls, in 1 h. The ready batch was poured into a demountable graphite compression-mold under pressure 15 MPa, covered, and placed into a vacuum furnace of laboratory stand, and the temperature of the batch was raised to the self-ignition temperature, after which spontaneous combustion of the batch occurred.

The laboratory stand included the following: a high-temperature vacuum setup equipped with a temperature sensor, molybdenum heater, thyristor voltage regulator, and vacuum gauge as well as a setup for precise metering, packing, and pressing of the samples, and other setups.

The thermal explosion regime for an Al–Ni–Co_3O_4 sample is displayed in Fig. 1. A diagram of the thermal explosion process in extended time coordinates (curve *CD*) (thermocouple 2), which is used to calculate the average time and the
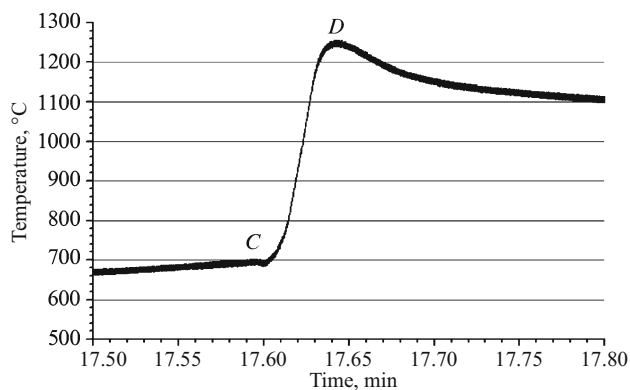
Fig. 2. Diagram of the thermal-explosion process in extended time coordinates.

Fig. 3. Microstructure of the fracture of a synthesized sample.

temperature of the exothermal reaction, is presented in Fig. 2.

The average time and the temperature of the exothermal reaction as well as the mass losses of the experimental sample must be determined in order to calculate the saturated vapor pressure of the liquid phase of the reaction. The calculations are based on kinetic methods of studying the evaporation of matter in a vacuum [16]. In addition, in Langmuir's method it is assumed that evaporation occurs from an open surface in a vacuum. The saturated vapor pressure can be calculated from the equation

$$ p = m \frac{\sqrt{2 \pi R T / M}}{S \tau}, $$

where m is the mass of the material with molar mass M evaporated over time τ with a surface of area S.

Substituting the measured parameters of the process into Langmuir's relation, viz., $m = 9.1$ g, $T = 1580$ K, $S = 4.2$ cm^2, $\tau = 3.6$ sec, and $R = 0.082$ liter $\cdot$ atm/(K $\cdot$ mole), we obtain the saturated vapor pressure of the low-melting component of the liquid phase of the reaction occurring during SHS, which is equal to 0.51 atm. This value of the saturated vapor pressure of the low-melting component of the liquid phase (aluminum) correlates with the published data on the saturated vapor pressure of aluminum (0.44 atm), at which it boils.

The measured values of the combustion parameters of SHS of the system Al–Ni–Co$_3$O$_4$ were substituted into the relation for calculating the size of the open pores in the synthesized material: $T_g = 1580$ K and surface tension of aluminum $\sigma = 111.6$ mN/m [12]. The external pressure p_∞ was 0.1 mm Hg (the pressure in the experimental chamber). The average pressure p_g of the impurity gases for the system Al–Ni–Co$_3$O$_4$ was 5 atm, and the vapor pressure p_v of the liquid phase for aluminum was 0.51 atm. The result was the computed size of the open pores in the synthesized sample, which was 3.12 μm.

Direct measurements of the size of the open pores in the obtained samples of cermet membranes were performed using a mercury porosimeter; the values were 2 – 3.5 μm. The open porosity of the samples, evaluated by the method of hydrostatic weighing, was 48%. Phase analysis of the samples performed in a DRON-Zm diffractometer showed the presence of the main phase (CoNi)$_3$Al and the free phases Ni, Co and Al$_2$O$_3$.

The microstructure and spectrum of the elemental analysis of a fracture of a sample based on Al–Ni–Co$_3$O$_4$ are presented in Fig. 3 and Table 1. The dark spots in the figure indicate roughness of the fracture surface, unevenness, and remains of closed pores. The size of the open pores, which is the equivalent hydraulic diameter of the channel along which the fluid moves (gas or liquid), was measured following GOST 26848–86.

A scheme of a membrane-catalytic module (Fig. 4) was developed on the basis of the synthesized sample and assembled.

Regeneration of the synthesis byproducts of the Fischer–Tropsch process (methane, carbon dioxide gas, and organic impurities dissolved in water) was performed using an assembled module.

The content (wt.%) of the dissolved organic impurities, identified by means of chromatographic mass spectrometry, in water was as follows: 2.8 methanol; 18.2 ethanol; 1.3 ace-

TABLE 1. Elemental Analysis Spectrum of the Fracture of a Sample

Points	Content of the elements at the point studied, wt.%				
	O	Al	Co	Ni	Total
1	19.92	6.94	28.06	45.08	100
2	19.33	6.56	28.36	47.78	100
3	18.06	7.21	27.42	47.31	100
4	15.46	6.35	28.24	49.95	100

Fig. 4. Scheme of a membrane-catalytic module: *1*) in-out connecting piece; *2*) fastening nut; *3*) membrane-catalytic reactor; *4*) reactor cover; *5, 6*) graphite foam gasket; *7*) thermocouple pocket.
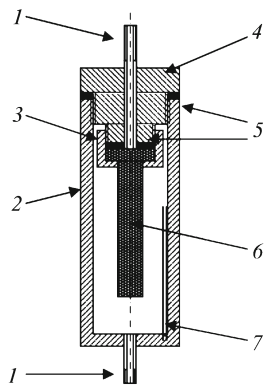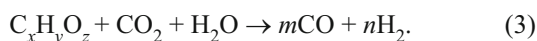
tone; 5.0 acetic acid; 4.0 methylethyl ketone; 0.4 butanol; and, pentanol.

The syngas formed by means of the reactions (2) and (3): carbon-dioxide-vapor conversion reaction of methane into syngas

$$2CH_4 + CO_2 + H_2O \rightarrow 3CO + 5H_2; \qquad (2)$$
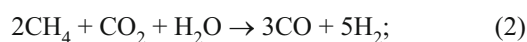
carbon-dioxide vapor conversion reaction of organic substances present in the water

$$C_xH_yO_z + CO_2 + H_2O \rightarrow mCO + nH_2. \qquad (3)$$

The regeneration of the synthesis byproducts of the Fischer–Tropsch process was conducted at temperature 680 – 780°C, pressure 1 – 1.5 atm, and different feed rates of the initial gas mixtures. The process of purifying the water by removing organic impurities occurred with conversion 85 – 99%. The results of regeneration are presented in Table 2.

The choice of elevated temperature of the process was motivated by the fact that at a given temperature methane, being the most stable compound present in the initial mixture, is practically completely converted.

CONCLUSIONS

1. Cermet membranes with open pores of size 3 – 3.5 µm and porosity to 48% were synthesized. The phase analysis of the samples performed with a DRON-3m diffractometer showed the presence of the main phase $(CoNi)_3Al$ and free Ni, Co, and Al_2O_3.

2. A membrane-catalytic module for converting the byproducts of the Fischer–Tropsch process was fabricated.

3. The conversion for the transformation of the byproducts of the Fischer–Tropsch process into syngas on the synthesized membranes was 85 – 99%, which substantially increases the economic gain due to the process as a whole.

4. The water separated after the process and purified meets the sanitary standards for water to be used for technical purposes.

REFERENCES

1. M. V. Tsodikov, A. S. Fedotov, V. V. Teplyakov, et al., "Carbon dioxide reforming of methane on porous membrane-catalytic systems," *Izv. Ross. Akad. Nauk, Ser. Khim.*, No. 1, 54 – 61 (2011).
2. M. V. Tsodikov, A. V. Chistyakov, F. A. Yandieva, et al., "Conversion of the biomass products into energy carriers in the presence of nanosize catalysts and membrane-catalytic systems," *Kataliz v Prom-sti*, No. 5, 155 – 160 (2010).
3. A. Fedotov, V. Zhmakin, M. Tsodikov, and I. Moiseev, "Membrane catalytic systems for dry and steam reforming of bioindustrial products into hydrogen containing gas," in: *Abstracts of Reports at the International Scientific Conference First Workshop of COST Action CM0903 on the Utilization of Biomass for Sustainable Fuels and Chemicals (UBIOCHEM), Cordova, Spain 13 – 15 May 2010*, Cordova (2010), p. 25.
4. V. S. Arutyunov and O. V. Krylov, *Oxidative Transformations of Methane* [in Russian], Nauka, Moscow (1998).
5. A. P. Amosov, A. G. Merzhanov, and I. P. Borovinskaya, *Powder Technology of Self-Propagating High-Temperature Synthesis of Materials* [in Russian], Mashinostroenie-1, Moscow (2007).

TABLE 2. Carbon Dioxide Steam Conversion of the Waste Byproducts of the Fischer–Tropsch Process at 780°C

Experiment	Q, h^{-1}	X_{CH4}, %	B_{H2}, liter/(h · dm$^3_{membrane}$)	B_{CO}, liter/(h · dm$^3_{membrane}$)	B_{s-g}, liter/(h · dm$^3_{membrane}$)	H_2/CO
1	16,000	89	3100	3900	7000	0.8
2	32,000	92	6100	6900	13,000	0.9
3	64,000	95	11,800	11,200	23,000	1.1
4	32,000	99	6400	7000	13,400	0.9
5	64,000	98	14,000	12,500	26,500	1.1
6	96,000	99	21,500	17,500	39,000	1.2
7	6400	30	500	800	1300	0.6
8	9600	83	750	950	1700	0.8
9	16,000	91	3100	3400	7500	0.8

Notations: Q) feed rate of waste products from the Fischer–Tropsch process under normal conditions; X_{CH4}) conversion on methane; B_{H2}) productivity on hydrogen; B_{CO}) productivity on CO; B_{s-g}) productivity on syngas.

6. V. N. Bloshenko, V. A. Bokii, V. I. Boyarchenko, et al., "Porous Materials Based on Titanium Carbide, Obtained in the combustion regime," in: *Abstracts of Reports at the All-Union Symposium on Advanced Metallic Materials, May 12 – 17, 1991* [in Russian], Moscow (1991), p. 29.

7. A. G. Merzhanov, A. S. Rogachev, A. S. Mukas'yan, et al., "Macrokinetics of structural transformations in gas-free combustion of mixtures of titanium and carbon powders," *Fiz. Goreniya Vzryva*, **26**(1), 104 (1990).

8. V. A. Shcherbakov, A. E. Sychev, and A. S. Shteinberg, "Macrokinetics of degassing in SHS process," *Fiz. Goreniya Vzryva*, **22**(4), 55 (1986).

9. V. N. Bloshenko, V. A. Bokiy, I. P. Borovinskaya, et. al., "Adsorption-diffusion theory of impurity oxygen evolution from solid flames," in: *3rd Int. Seminar on Flame Structure, 18 – 23 Sept. 1989*, Alma-Ata (1989), p. 100.

10. V. I. Moskvitin, I. V. Nikolaev, and B. A. Fomin, *Metallurgy of Light Metals* [in Russian], Intermet Inzhiniring, Moscow (2005).

11. M. M. Martynyuk, P. A. Tamanga, and N. Yu. Kravchenko, "Phase diagram of titanium near a liquid – vapor phase transition," *Vestn. RUDN*, *Ser. Fiz.*, **10**(1), pp. 121 – 125 (2002).

12. A. N. Ivanov, *Hydrodynamics of Develop Cavitation Flows* [Russian translation], Mir, Moscow (1980).

13. V. I. Uvarov, I. P. Borovinskaya, and E. S. Lukin, "Formation of materials with open porosity based on nickel, aluminum and cobalt in SHS processes in vacuum," *Steklo Keram.*, No. 12, 28 (2012).

14. V. S. Bakunov, V. L. Balkevich, A. Ya. Guzman, et al., *Study with Experimental Work in the Technology of Ceramics and Refractories* [in Russian], Stroiizdat, Moscow (1972).

15. A. P. Babichev, N. A. Babushkin, and A. M. Bratkovskii, *Handbook of Physical* Quantities [in Russian], Énergoatomizdat, Moscow (1991).

16. A. N. Nesmeyanov, *Vapor Pressure of Chemical Elements* [in Russian], Moscow (1961).