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HIGH-TEMPERATURE SHS-MATERIALS IN RESOLVING THE PROBLEM OF REPROCESSING TREATMENT AND UTILIZATION OF INDUSTRIAL, DOMESTIC, AND RADIOACTIVE WASTE

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Self-propagating high-temperature synthesis (SHS) is used to prepare materials for lining a pyrolysis reactor shaft and filter material for final cleaning of exhaust gases. The possibility is demonstrated in model mixes of combining an SHS stage for cast fluorophlogopite and binding it with weak radioactive waste. A model is developed for a waste treatment unit, including weakly radioactive (recycling waste), by pyrolysis with simultaneous synthesis of SHS fluorophlogopite for binding and conserving radionuclides.

Keywords: pyrolysis reactor lining, filter material, SHS, cast fluorophlogopite, binding weakly radioactive waste.

INTRODUCTION

High-temperature plasma gasification of waste with liquid slag removal attracts the attention of specialists by its universality, since it provides effective treatment of many wastes of complex morphological condition, such as organic and mineral. High-temperature destruction of organic components is achieved during processing with formation of fuel gases and their subsequent effective combustion [1 – 4].

One of the critical assemblies of the model device for processing waste specifying its efficiency (heat retention) is a reactor for pyrolysis of low calorific raw material and weakly radioactive atomic power station waste. The lining of a reactor shaft should be made from refractory material, radiation-resistant, heat insulating, thermal shock resistant, corrosion resistant, and resistant to molten slag up to 1500°C. The SHS method at high reaction gas, i.e., nitrogen, pressure makes it possible to combine the stages of material synthesis and sintering of an object from it in one stage of direct synthesis of dense refractory corrosion-resistant materials. SHS, performed at low pressure, makes it possible to synthesize highly porous materials with low thermal conductivity.

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Work has been carried out for preparing materials for lining a pyrolysis reactor shaft and filter material for final cleaning of exhaust gases. Model studies have been carried out for treatment of atomic power station weakly radioactive waste, whose morphological and physicomechanical properties are close to those of solid domestic waste. Model experiments have been carried out using SHS-fluorophlogopites for bonding and conserving radionuclides (due to isomorphism (outer layer): homo- and heterogeneous exchange of K^+ ion by ions of alkali and alkaline-earth metals (Na^+, Cs^+, Sr^{2+}, Ba^{2+}). SHS of fluorophlogopites makes it possible to obtain synthesis products in the form of dense cast material with good mechanical strength and chemical resistance, and resistance to long-term action of natural media.

EXPEREMENTAL PROCEDURE

A study of self-propagating high-temperature synthesis of dense refractory materials was carried out in an SHS-gasostat [4, 5], whose dimensions make it possible to prepare objects up to 75 mm in diameter and up to 250 mm thick. Highly porous SHS objects were prepared at low pressure in vacuum furnaces of the SShVÉ-1,2,5/25I2 shaft vacuum electric resistance furnace type.

Refractoriness was determined by a method of 20 min exposure of specimens at 2096 K in a helium atmosphere, and corrosion resistance of specimens was determined by a

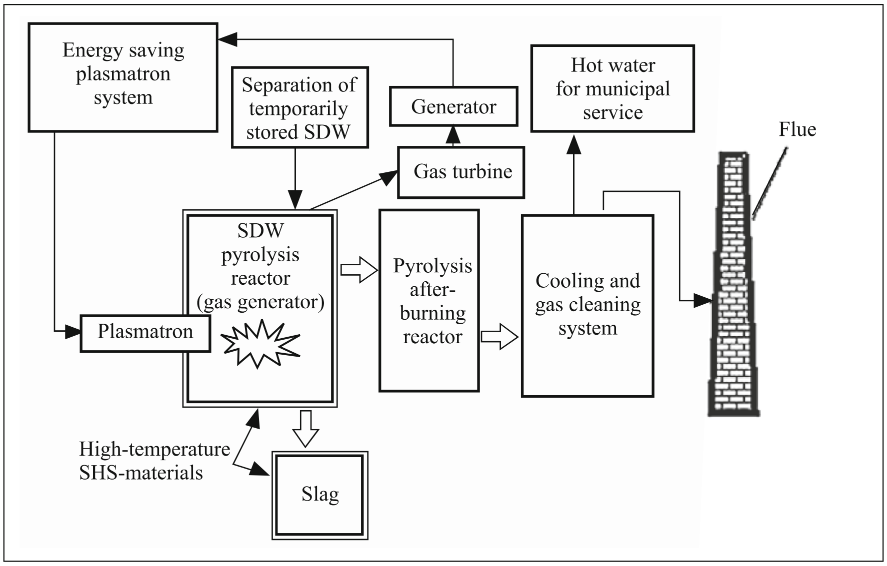

Fig. 1. Diagram of production line for processing sold domestic waste (SDW).

rotating electrode method at 1873 K. Ultimate strength in compression was measured for materials by a standard procedure. Features of the microstructure and phase composition of materials were studied by means of a Neophot-30 microscope and a DRON-2 x-ray diffractometer. Chemical analysis of products was carried out by standard procedures. Measurement accuracy of thermal conductivity corresponded to GOST 8.140.

The starting components used in experiments were powders of amorphous black boron grade B-99A, boron nitride SHS-powder, aluminum powders grade ASD-1 or ASD-4, magnesium powder grade MPF-3 and magnesium oxide, carbon black, Na_3AlF_6 cryolite powder, titanium powder grade PTOM, aluminum nitride and titanium boride SHS-powders, silicon powder of different grades, SHS-silicon nitride, silicon oxide powder, and quartz sand. Mixture starting components were mixed in ball mills. Starting billets with a diameter of 30 – 80 mm, height of 20 – 300 mm, were prepared by uniaxial compression in steel dies and isostatic compaction in rubber shells (gasostatic or hydrostatic). The overall porosity of the original specimens was 40 – 50%. Experiments were carried out in an SHS-gasostat. Synthesis was performed in a nitrogen atmosphere at pressure of 10 – 300 MPa. Fluorophlogopites were synthesized in air.

EXPERIMENTAL STUDIES

The scheme proposed for modifying a production line (Fig. 1) for processing and utilization of industrial, domestic, and weakly radioactive waste, including atomic power station waste, makes it possible to use pyrogas by two methods:

– with supply to a gas turbine and generator with development of electric power for feeding a plasmatron;

– with supply to a heating furnace, then to a cooling system for heating water for the communal economy, gas cleaning, discharge through a flue.

Studies were carried out on SHS-materials for lining a solid domestic waste pyrolysis reactor and for a filter in a gas cleaning system. It is suggested to use a pyrolysis reactor three-layer lining for low-calorie raw material and atomic power station weakly radioactive waste made from SHS-ceramic: (first (inner) layer of slag-resistant composite SHS-material SiAlON–SiC–BN, second layer of radiation-resistant SHS-ceramic based on boron nitride BN–MgO–B, and third (outer) layer of highly porous heat insulation material based on SHS-silicon carbide.

Objects for the first layer were prepared as follows. 6% B and 47% SiC were added to an original charge of xAl + ySiO$_2$ + zSi, calculated for synthesis of $Si_4Al_2O_2N_6$. Objects of the required shape were prepared from the charge by isostatic pressing with an overall porosity of about 35%. A billet was placed in an SHS-gasostat [5], and combustion reaction was initiated under a nitrogen pressure of 100 MPa. The combustion product is material of apparent porosity of about 10% with phase composition, %: 57% $Si_4Al_2O_2N_6$, 38 SiC, 5 BN. A study of physicomechanical properties of this material showed that its ultimate strength in bending is 250 – 300 MPa at room temperature, and 100 MPa at 1673 K. A study of material refractoriness established that with heating to 1813 K for 4 h in argon the weight loss was ≤1%. Results of testing material for corrosion resistance in a corrosive metallurgical slag are given in Fig. 2. Corrosion resistance was determined by an immersion method and rotation of test specimens in molten steel and slag. Specimens dimensions 12.5 × 12.5 × 150 mm Slag composition, %: SO_2 35, CaO 38, Al_2O_3 3, Na_2O 4, F_2 11, MnO 5, Fe_2O_3 3. Test duration 48 min, temperature 1873 K.

Material of the second lining layer should exhibit radiation resistance. For this a layer of material was developed based on boron nitride with addition of magnesium oxide, whose boron concentration was 1g/cm^3. Objects of the second layer were synthesized as follows. An original mixture was prepared of 40% B + 7% MgO + 53% BN, and then a billet was pressed isostatically from it with a total porosity of about 40%, which was placed in an SHS-gasostat, then the combustion reaction was initiated under a nitrogen pressure of 100 MPa. The combustion product is material of apparent porosity of about 10% with phase composition BN + MgO + B. The free boron content within this material may reach 15%, and this corresponds to boron concentration

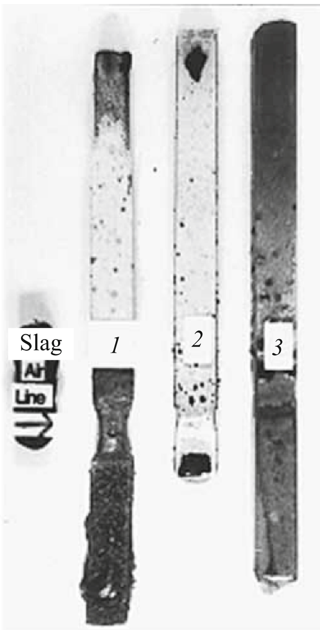

Fig. 2. SHS-material corrosion resistance in slag: *1*) ZrO_2–C; *2*) BN–SiO_2; *3*) SiAlON–SiC–BN. Resistance 3 > 2 >>> 1 (ZrO_2–C — standard).

in a unit volume of ≥1 g/cm^3. Material thermal conductivity is 30 W/(m·K) at 3373 K and 10 W/(m·K) at 873 K.

Material of the third lining layer objects should exhibit low thermal conductivity, and therefore porous silicon carbide was selected for this layer. In preparing objects from this by the SHS method β-SiC powder was synthesized, from which billets were pressed. Billet sintering was carried out in SShVÉ-1,2,5/25I2 shaft vacuum electric resistance furnace at 1573 K. Sintered object porosity was ≤60%, thermal conductivity 2.5 W/(m·K), and ultimate strength in compression greater than 100 MPa. Objects are shown in Fig. 3.

For final cleaning of exhaust gases of installations, SHS-filters were prepared with high ion-exchange capacity, retaining positively charged ions with efficiency $E = 99.99$. SHS-filters were developed and manufactured on the basis of a Ti–C system. The Ti powder used was Ti grade PTOM with particle size of 45 – 60 μm, and graphite with a particle size of 35 – 50 μm in a stoichiometric ratio. Powders were mixed in a ball mill with balls made of Al_2O_3 for 1 h. The prepared charge was poured into a graphite mold and placed in a vacuum furnace. Then the charge was brought to the self-ignition temperature, and there was arbitrary charge combustion. Prepared filter properties: working temperature up to 1273 K, apparent porosity >60%, of which 98% is open porosity, pore size depending on production scheme and regimes from 0.1 to 20 μm, gas ultrafiltration productivity with a pressure drop in a filter of 2 kPa is 40 liter/cm^2 per h.

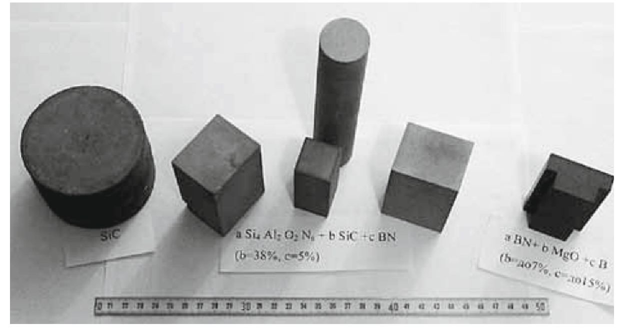

Fig. 3. SHS-objects for reactor shaft lining.

The average open pore size (equivalent hydraulic channel diameter, through gas or liquid moves), measured according to GOST 13523, was, μm: for volume 16.73; for surface 15.4; average pore size ($4V/A$, where V is mercury volume extruded into a test specimen pore; A is test specimen outer surface, covered with mercury) 16.2. Specimen apparent porosity, estimated by hydrostatic weighing, was 62%, and of it 95% was open porosity. The considerable specific surface of a specimen, measured by low-temperature nitrogen absorption (BET method), which specifies specimen absorption properties, was 31 m^2/g.

A model was assembled on the basis of a PrestigePlasma 34 plasmatron of mobile modulus for ecological cleanliness of processing and utilization of industrial, domestic, and radioactive waste. Experimental specimens were pressed from

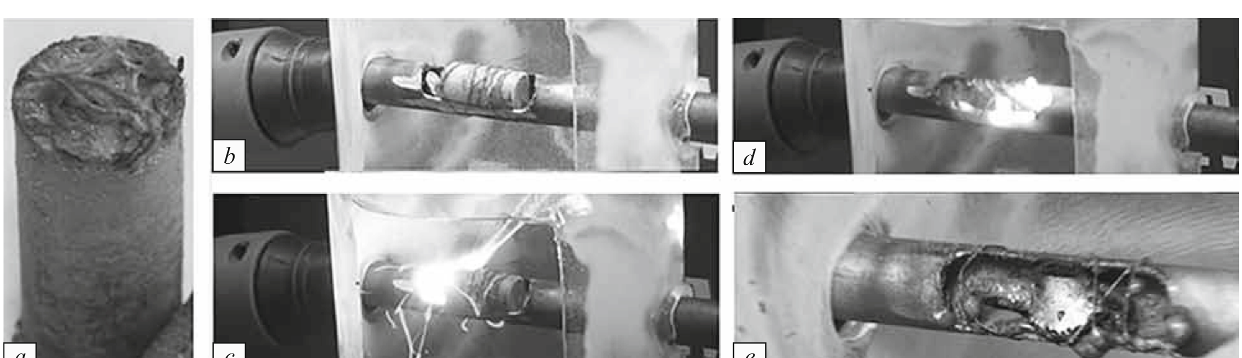

Fig. 4. Stages of plasma reprocessing of experimental specimens.

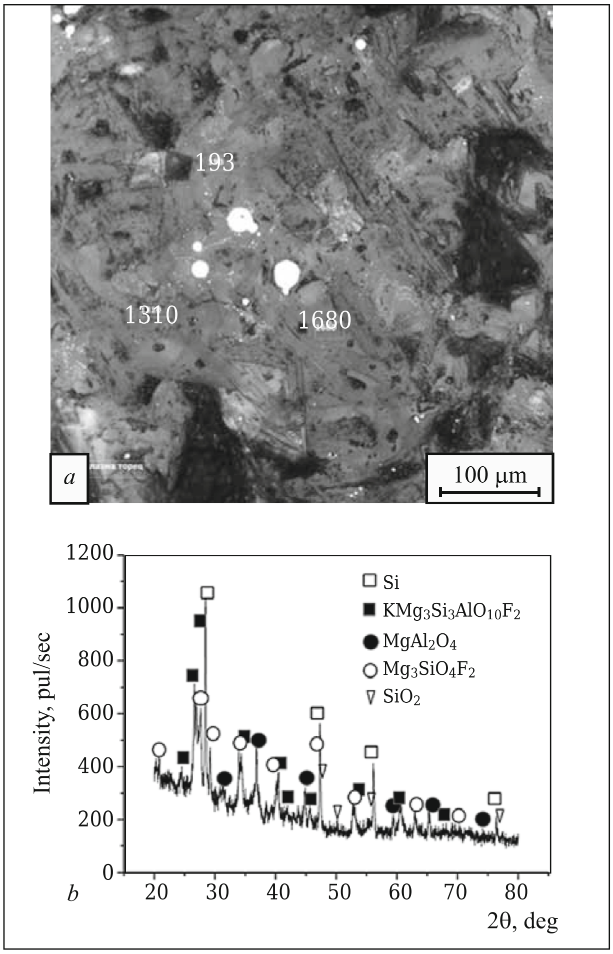

Fig. 5. Droplet microstructure and x-ray patter: *a*) droplet microstructure, fluorophlogopite specimen, experiment performed using plasmatron, end view of specimen shown, phase microhardness indicated, kg/mm^2; *b*) droplet material x-ray pattern.

a charge for synthesizing SHS-phlogopites, containing fragments of cotton cloth, simulating weakly radioactive waste of atomic power station servicing personnel working clothing. Fragments of cloth inclusions are seen in a pressed specimen, given in Fig. 4*a*. In Fig. 4*b* – *d* stages are shown in the process of plasma reprocessing of experimental specimens. In the concluding stage (Fig. 4*e*) the final product of the process of utilization is seen in the form of congealed molten droplets. A droplet microstructure is shown in Fig. 5*a*, and phase microhardness indices are provided. It is seen that in the course of SHS there was processing of starting materials with a change in aggregate substance composition in a combustion front with subsequent crystallization of combustion products into densely cast material in the form of droplets. X-ray phase analysis of this material is presented in Fig. 5*b*.

TABLE 1. Comparative Properties of Ceramic membrane Filters from Leading Firms

Properties	ISMAN, Russia	Millipore, USA	Sartorius, FRG	Seitz, FRG	Whatman, England
Pore size, μm	0.1	0.22	0.45	0.2	0.19
K, 10^{-6}	1	5	5	1	5
Δp, mm wat. col.	100	160	100	125	184
γ	0.061	0.033	0.053	0.048	0.029

The calorific value of pyrolysis gases was 1200 $kcal/m^3$, which makes it possible to use them for preparing heat for domestic needs or generation of electric power. For example, it is possible to use fuel gases in a gas turbine, connected with an electric generator.

DISCUSSION OF RESULTS

Waste processing by high-temperature plasma gasification with liquid slag removal dictates determination of a requirement for pyrolysis reactor lining material properties: it should exhibit specific refractoriness, thermal stability, slag resistance, radiation resistance, and heat insulating properties. Three materials have been developed for a three-layer pyrolysis reactor lining. Each of the layers has some required properties. As demonstrated in this work, material of the first layer is thermally stable, slag-resistant refractory, the second layer is radiation resistant material, and the third layer is highly porous heat insulation material.

For treating weakly radioactive waste SHS-phlogopite was proposed in the work with simultaneous conservation of radionuclides. It has been shown in [6] in preparing phlogopites as a result of isomorphism (outside a layer) homo- and heterovalent exchange of K^+ by alkali and alkaline earth metal ions (Na^+, Cs^+, Sr^{2+}, Ba^{2+}), it is possible to introduce radionuclides into a fluorophlogopite structure. It has been shown in [7] that during synthesis of SHS-phlogopites it is possible to obtain both porous and cast materials with good mechanical strength, resistant to prolonged action of natural media. As experiments on model mixtures have shown, in this work it was possible to combine into one stage synthesis of material, whose basis is cast fluorophlogopite, its compaction, and bonding within it of substances simulating radioactive waste.

In order to specify contemporary filters for fine cleaning of air and production gases from dispersed micro-impurities and radioactive aerosols, apart from changing pore size and their distribution, they are used for testing model aerosol particles. Normally in selecting a membrane it is necessary to know efficiency of porous material E, resistance to gas flow (pressure drop on a membrane) Δp under standard conditions. The value of Δp is expressed in mm of a water column[3] with a gas flow rate through a membrane of v = 1 cm/sec.

Material porous quality is specified by a filtration index $\gamma = -\frac{\log K}{\Delta p}$, which depends on material thickness and is de-

[3] 1 mm of a water column ≈ 9.8 Pa.

termined by perfection of the organization of pore space structure. K is a particle passage coefficient, i.e., ratio of concentration of model particles after filter N and ahead of it N_0. Porous material efficiency $E = (1 - N/N_0) \times 100\%$. As a result of preliminary studies for a ceramic SHS-filter based on SiC values have been obtained $E = 99.99\%$, $\Delta p = 100$ Pa, $\gamma = 0.061$. Comparative characteristics are provided in Table 1 for ceramic membrane filters of known leading firms for filtering liquids and gases. It is seen that representative filters obtained in the work have properties that are at the level of indices of the best ceramic membranes.

CONCLUSION

A model has been developed for a waste processing unit, including weakly radioactive (waste recycling) by pyrolysis with simultaneous synthesis of SHS-fluorophlogopite for bonding and conserving radionuclides. The possibility is demonstrated in model mixtures of combining the SHS stage for cast fluorophlogopite and binding weakly radioactive waste within it.

The SHS method for a waste pyrolysis reactor lining has been used to prepare dense and highly porous heat insulation, corrosion resistant materials: high porosity silicon carbide β-SiC, dense corrosion-resistant material SiAlON + SiC + BN, and dense radiation-resistant material based on hexagonal boron nitride BN + MgO + B.

SHS-filters have been prepared based on TiC with good ion-exchange capacity, retaining positively charged ions and with efficiency for a model aerosol $E = 99.99\%$.

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