DOI 10.1007/s11148-019-00351-9
*Refractories and Industrial Ceramics* *Vol. 60, No. 3, September, 2019*

# PERMEABLE CERMET SHS-MATERIALS BASED ON ALLOY-STEEL SCALE AND ILMENITE FOR CLEANING DIESEL ENGINE EXHAUST GASES

**M. S. Kanapinov,**[1] **G. M. Kashkarov,**[1,3] **O. A. Lebedeva,**[1] **T. V. Novoselova,**[2] **N. P. Tubalov,**[1] **and O. V. Yakovleva**[1]

Translated from *Novye Ogneupory*, No. 5, pp. 112 – 116, May, 2019.

*Original article submitted February 4, 2019.*

The possibilities of obtaining porous permeable cermet SHS-materials with catalytic properties are studied. The charge composition consists of powders of alloy steel scale, ilmenite concentrate, aluminum or chromium oxides, the basis of material forming the backbone of cermet ($Al_2O_3$) and reduced iron, and also added metal oxides. The material obtained is intended for the catalytic purification of diesel engine exhaust gases, particularly from nitrous oxide, carbon monoxide and soot.

**Keywords:** porous permeable cermet materials (PPCM), ilmenite (titanium-containing ore), SHS, exhaust gas cleaning.

## INTRODUCTION

Porous permeable cermet materials (PPCM) with catalytic properties are used traditionally as filters for internal combustion engine (ICE) exhaust gas filters. In this case the application sphere is continuously expanding due to a unique combination of good mechanical strength, thermal and chemical stability, and PPCM stability parameters [1 – 5].

The possibility is studied in the present work of preparing PPCM by means of an energy saving process of self-propagating high-temperature synthesis (SHS) [6 – 8] using a plentiful raw material, i.e., alloy steel scale, aluminum or chromium oxides, and natural raw material (ilmenite) concentrates. During SHS of porous materials condensed reaction products enter almost entirely into the composition of the finished product, represented by a composition of metal-like alloy, i.e., aluminum oxide. For the occurrence of SHS the greatest amount of heating effect is proposed, which is typical for the reaction of aluminothermal reduction of metals, and intermetallic formation.

The starting charge used was powders (their preparation is described in an article [9]): alloys steel scale (forging and stamping waste), metals (Cr, Al, Ni), chromium or aluminum (corundum) oxides, and titanium or concentrate, i.e., ilmenite. The ilmenite concentrate ($FeO{\cdot}TiO_2$, or $FeTiO_3$) contains, wt.%: Fe ~37, Ti ~32, and in individual concentrates 42 – 45 wt.% $TiO_2$ is encountered. The value of ilmenite in our case includes the fact that within its composition there are titanium compounds that may emerge as an element strengthening a cermet framework and as a catalyst for oxidation of gases from nitrous oxide, carbon monoxide, soot (solid carbon), and other harmful components. In order to initiate a combustion reaction in the atmosphere (start of the SHS process) a thermite composition or an electric arc was used.

Preparation of cermet materials by thermal synthesis using production waste (steel scale) and natural ores in order to create catalytic filters for ICE exhaust gases is described in publications [9 – 14]. Most often during SHS-processes the reducing agent used is aluminum, and of non-metals it is carbon. For this reason apart from oxides of metal reducing agents, there is preparation of hard alloys, cermets, composite oxides, etc. As subsequent experiments showed, self-supporting combustion of a charge mixture occurs in systems of ilmenite (titanium oxide) – aluminum and chromium oxides aluminum:

$$3TiO_2 + 2Al \rightarrow Al_2O_3 + 3Ti,$$

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3. \qquad (2)$$

[1] FGBOU VO I. I. Polzunov Altai State Technical University, Barnaul, Russia.
[2] Polytechnic Institute, Taganrog, Russia, branch of FGBOU VO Don State Technical University, Rostov-on-Don, Russia.
[3] gennadykashkarov@yandex.ru

These mixtures of compounds were selected as basic. Stoichiometric coefficients of the basic and added mixtures corresponded to the reaction scheme selected. The ilmenite itself has a loose structure and during participation in SHS with aluminum causes an increase in reaction temperature, the rate of reaction occurrence, and more complete combustion of mixture components. As a consequence it facilitates formation of skeletal-like elements of a PPCM framework.

The question of limiting concentrations of aluminum and ilmenite in a charge is resolved taking account of the PPCM obtained [15, 16]. On one hand, it is necessary to provide "skeletal-forming" components ($Al_2O_3$, $Cr_2O_3$, Fe) in a charge, and also alloying and catalytic additives (Cr, Ni, Ti), creating complex and strong intermetallic compounds, and on the other hand a composition required in order to provide combustion in an SHS process (Al, $Fe_2O_3$). Exceeding the amount of one or another component leads to deterioration of material physicomechanical properties due to incomplete combustion, which is undesirable under conditions of vibration, impact, and corrosion.

In the Altai State Technical University and Taganrog Polytechnic Institute research has been conducted and the possibility has been confirmed of using titanium ore ilmenite mineral in order to prepare PPCM with catalytic properties under SGS conditions, The aim of this work is development and preparation by the SHS method of PPCM with addition of titanium-containing (based on $TiO_2$) mineral, i.e., ilmenite. This additive makes it possible to provide optimum material quality for filtration of diesel exhaust gases (pore size, porosity, mechanical strength, catalytic properties for neutralizing nitrous oxide, carbon monoxide, and solid carbon. i.e., soot).

## PROCEDURE

The microstructure, elemental composition, and pore size were determined using a metallographic universal microscopes Axio Observer Z1m (×1000, Carl Zeiss) and EVOSO (Carl Zeiss) with an EDS

X-act (Oxford Instruments) attachment, and x-ray analysis of PPCM was conducted in a DRON-6 diffractometer. The efficiency of cleaning ICE exhaust gases on the filters obtained made from PPCM was evaluated in a research complex including a 8Ch12/12 diesel, gas analyzer MEXA-321E, RS 325L, and a smoke meter EFAW65A BOSH. In order to obtain an identical nature for exhaust gas composition tests were performed under identical conditions (fuel supply, loading characteristics, crankshaft rotation rate, normal atmospheric pressure and temperature and moisture content of 50%).

## PPCM USING TITANIUM ORE ILMENITE MINERAL

A charge for preparing PPCM was prepared on the basis of alloyed steel scale, aluminum, ilmenite, and aluminum or chromium oxides (Table 1). A feature of the SHS process is interaction and formation of a cermet framework made of crystalline aluminum oxide, and iron and chromium oxides [8 – 10]. In addition, in our case (with use of ilmenite) titanium and titanium oxide are added. Formation of porosity, pore size, their extent (through and blind pores) and anisotropy were determined by SHS process at 1500 – 2000 K, and in fact: melting of steel scale and reduction of iron by aluminum in a liquid condition (with intense gas liberation, pore formation), its alloying with metal components (Cr, Ji. Ti); joining into iron, iron oxide, aluminum, titanium, and other metal conglomerates during subsequent metal base crystallization; a change in reaction rate (with addition of metal oxides into a charge).

The PPCM microstructure and phase composition based on charges 1 and 2 are shown in Figs. 1 and 2. In Fig. 1*a* the lightest inclusions have been identified as intermetallic compounds $Cr_3Al$, darkened compounds NiAl, dark compounds Fe, and black areas are pores; light inclusions shown in Fig. 2*a* are Fe, shade are Ni, dark, $Al_2O_3$, and black are pores. In diffraction patterns (see Fig. 1*b* and 2b) it follows that a framework of SHS-material comprises cermet based on $Al_2O_3$, Fe, $Fe_3O_4$, $NiO_2$, Ti, $Cr_5Al_8$, and NiAl. The physicomechanical and functional properties of PPCM prepared using titanium ore and charge 1 basic composition (see Table 1) give an idea about changes in their relationships due to ilmenite concentration as a starting component (Table 1). It is seen from Table 2 that an increase in charge ilmenite content from 15 to 18 wt.% increases PPCM porosity by a factor of 1.34 and reduces mechanical strength by about a factor of 1.5 due to a reduction in completeness of transformation of the original components and appearance is looseness in finished material due presence of $TiO_2$. The increase in pore size by 12 – 36% should be noted, and specific sur-

**TABLE 1.** Charge Composition for PPCM

| Component | Component content, wt.% |
|---|---|
| *Charge 1* | |
| Alloy-steel scale | 46 |
| Chromium oxide | 13 |
| Chromium | 5 |
| Nickel | 6 |
| Aluminum | 15 |
| Ilmenite | 15 |
| *Charge 2* | |
| Alloy-steel scale | 46 |
| Aluminum oxide | 18 |
| Aluminum | 18 |
| Ilmenite | 18 |

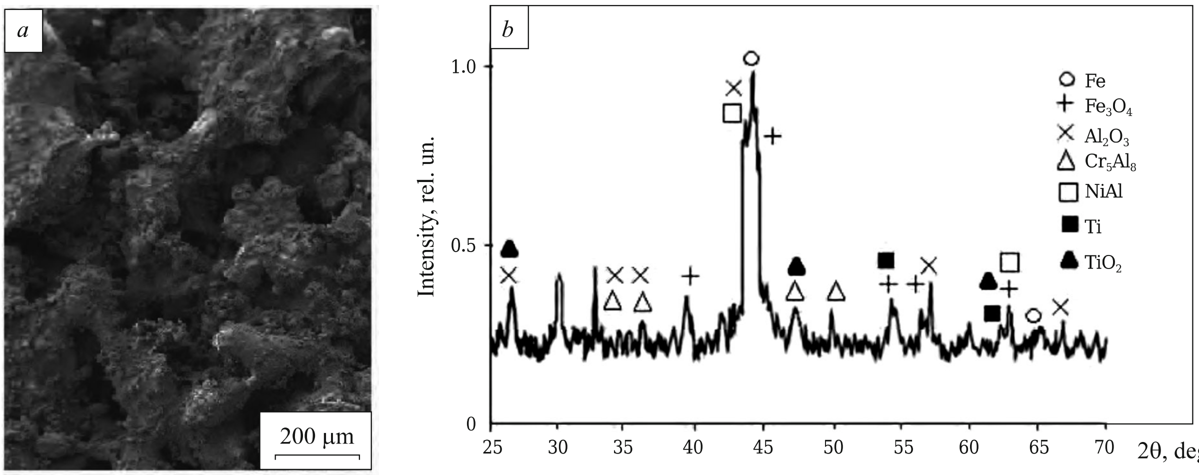


**Fig. 1.** Microstructure (*a*) and diffraction pattern (*b*) of SHS-material of basic composition + $Al_2O_3$ + ilmenite (charge 1, see Table 1).

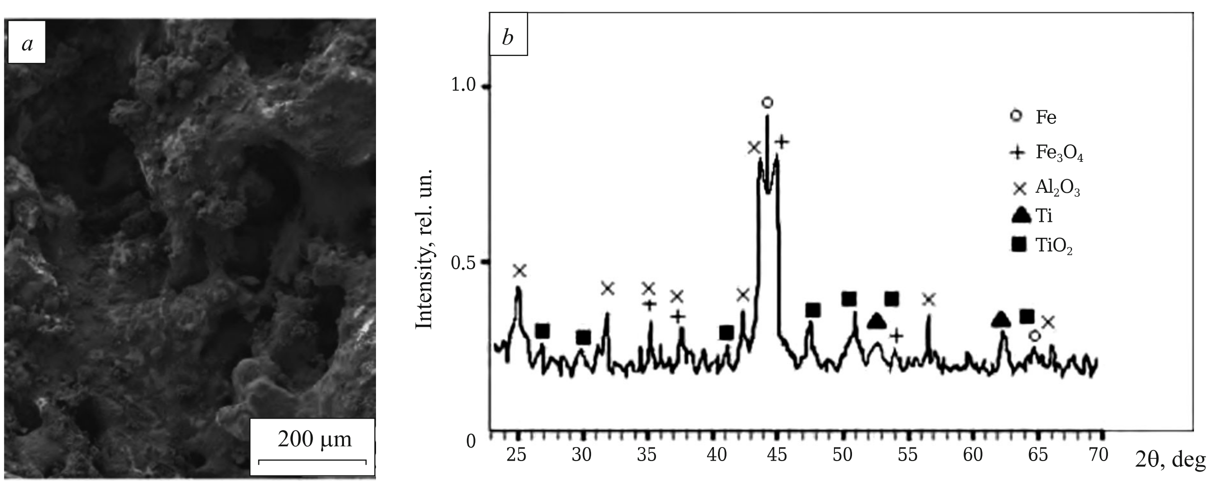


**Fig. 2.** Microstructure (*a*) and diffraction pattern (*b*) of SHS-material of basic composition + $Al_2O_3$ + ilmenite (charge 2, see Table 1).

face by 9 – 38%, porosity by 14 – 34% are important indices for the efficiency of PPCM for an exhaust gas catalytic filter, which is explained by introduction of metals oxides ($TiO_2$, $Cr_2O_3$) and as a consequence a change in thermal synthesis reaction. An increase in permeability of the SHS material obtained with an increase in ilmenite concentration (and correspondingly $TiO_2$) is connected with appearance of cavities due to incomplete reaction of $TiO_2$ in iron solid phase. The ultimate strengths in compression $\sigma_{co}$ and bending $\sigma_{ben}$ for the materials obtained decrease with an increase in ilmenite content within them (see Table 2). A reduction in $\sigma_{co}$ from 10.2 to 4.8 MPa and $\sigma_{ben}$ from 8 to 5 MPa point to an increase in the proportion of $TiO_2$ in final product due to incomplete reaction of ilmenite during synthesis. An increase in the amount of oxides at boundaries of the PPCM framework metal component provides conditions of creation of stress concentrators. The material structure obtained consists of pearlite and ferrite with a small cementite content. On the other hand, a reduction in $\sigma_{co}$ and $\sigma_{ben}$ is connected with an increase in pores and porosity. With increase in ilmenite ($TiO_2$) concentration more than 17 wt.% there is a marked reduction in material impact strength. This is also explained by the fact that during SHS there is a reduction in completeness of transformation of the original components (incomplete occurrence of thermal synthesis reaction).

The efficiency of PPCM as filters for diesel exhaust gases has been evaluated in experimental units at 400 – 723 K and in trucks for a reduction in the amount of carbon monoxide, nitrous oxide, hydrocarbons, and solid particles.

## CONCLUSION

The following have been established as a result of these studies:

– an increase in ilmenite concentration in a charge from 15 to 18 wt.% increases pore diameter by 12 – 36%, porosity by 14 – 34%, specific surface by 9 – 38% and reduces mate-

**TABLE 2.** Charge Composition, PPCM Physicomechanical and Operating Properties

| PPCM Composition and individual properties | PPCM charge version | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Charge composition, wt.%: | | | | |
| alloy steel 18Kh2N4MA | 46 | 46 | 46 | 46 |
| chromium oxide | 13 | 12 | 11 | 10 |
| chromium | 5 | 5 | 5 | 5 |
| nickel | 6 | 6 | 6 | 6 |
| aluminum | 15 | 15 | 15 | 15 |
| ilmenite $FeO \cdot TiO_2$ | 15 | 16 | 17 | 18 |
| PPCM properties | | | | |
| average pore diameter, μm | 125 | 140 | 156 | 170 |
| pore sinuosity with $h_{st} = 10$ mm | 1.20 | 1.27 | 1.30 | 1.35 |
| specific surface, $m^2/g$ | 86 | 94 | 108 | 119 |
| porosity, % | 50 | 57 | 63 | 67 |
| air permeability, $10^{-12}$ $m^2$ | 1.40 | 1.50 | 1.65 | 2.15 |
| ultimate strength, MPa: | | | | |
| in compression | 10.7 | 9.2 | 7.3 | 6.5 |
| in bending | 8.0 | 7.1 | 6.0 | 5.0 |
| strength, $J/m^2$ | 0.285 | 0.281 | 0.272 | 0.250 |
| Degree of exhaust gas cleaning (concentration reduction), %: | | | | |
| CO | 40 | 45 | 50 | 65 |
| $NO_x$ | 37 | 40 | 45 | 57 |
| $C_xN_y$ | 48 | 57 | 64 | 72 |
| solid particles | 82 | 90 | 94 | 96 |

rial ultimate strength in compression by 14.0 – 39.2% and in bending by 11.2 – 37.5%;

– addition to a charge of up to 18 wt.% of ilmenite leads to a reduction in harmful exhaust gas discharges additionally by 5 – 15%

## REFERENCES


1. B. A. Adamovich, “Catalytic neutralizers for exhaust gases and ecological security of a transport system,” *Avtomobil. Prom.*, No. 1, 9 – 11 (2005).
2. I. L. Varshavskii and R. V. Malov, *How to Render Automobile Exhaust Gases Harmless*. [in Russia], Transport, Moscow (1968).
3. L. A. Novikov, “Development of TsNIDI work in the area of reducing harmful substances and smoke content of diesel exhaust gases,” *Dvigatel’*, No. 3, 4 – 6 (2004).
4. A. L. Novoselov, V. I. Prolubnikov, and N. P. Tubalov, (V. V. Evstigneev, editor) *Improvement of Diesel Exhaust Gas Cleaning Based on SHS-Materials: Monograph* [in Russian], Nauka, Novosibirsk (2001).
5. A. A. Mel’bert and A. L. Novoselov, *Catalytic Cleaning of Piston Engine Exhaust Gases* [in Russian], AltGTU, Barnaul (2017).
6. A. G. Merzhanov, *Self-Propagating High-Temperature Synthesis: Twenty Years of Searches and Findings* [in Russian], ISMAN, Chernogolovka (1989).
7. V. E. Ovcharenko, O. P. Solonenko, A. E. Chesnokov, and V. M. Fomin, “Effect of high-energy action on the microstructure of synthesized cermet,” *Pis’ma ZhTF*, **39**(21), 77 – 94 (2012).
8. E. A. Leveshov, A. S. Rogachev, V. I. Yukhvid, and I. P. Borovitskaya, *Physicochemical and Technological Bases of Self--Propagating High-Temperature Synthesis* [in Russian], BINOM, Moscow (2000).
9. M. S. Kanapinov, A. V. Maetskii, A. A. Sitnikov, et al., “Porous permeable cermet materials based on iron oxides with additions of ground polymetal ores,” *Refract. Ind. Ceram.*, **59**(4), 378 – 385 (2018).
10. M. A. Kolomeets, A. V. Maetskii, T. V. Novoselova, et al. “Porous SHS-materials based on iron oxide and aluminum with additions of alloying elements,” *Refract. Ind. Ceram.*, **58**(3), 293 – 298 (2017).
11. A. E. Baklanov, M. S. Kanapinov, S. A. Malashina, et al., “Preparation of porous permeable materials using polymetal ore instead of rare-earth elements,” *Polzunov Vestn.*, No. 2, 205 – 212 (2016)
12. V. V. Evstigneev, A. A. Geineman, V. I. Prolubnikov, and N. P. Tubalov, “Porous permeable materials in the iron oxide – silicon oxide – aluminum system,” *Perspekt. Materialy*, No. 1, 69 – 72 (2007).
13. A. E. Baklanov, O. E. Baklanova, M. S. Kanapinov, et al., *SHS Materials for Cleaning Diesel Exhaust Gases: Monograph* [in Russian], VKGTU Ust’ Kamenogorsk (2016).
14. T. V. Novoselova, M. A. Kolomets, A. A. Sitnikov, et al., *Vibration-Resistant Porous Permeable Cermet Materials* [in Russian], DGTU, Nevinnomyssk (2017).
15. N. L. Chun and L. C. Shyan, “Combustion synthesis of aluminum nitride powder using additives,” *J. Mater. Res.*, **16**, 2200 – 2208 (2001).
16. L. C. Shyan and H. L. Chun, “Combustion synthesis of aluminum nitride,” *Key Eng. Mater.*, **521**, 101 – 111 (2012).