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## CREATION OF A THERMAL SHIELD COATING FOR WORK IN EXTREMELY HIGH TEMPERATURES

**Abstract:** *A thermal shield coating (TSC) consisting of carbon fibers, ceramic hollow microspheres and phenol-formaldehyde binder has been created. It is shown that the adding of up to 5% wt of ceramic hollow microspheres makes it possible to obtain a thermal shield coating with a lower density and with the physical and mechanical characteristics at the level of world manufacturers' analogues. The TSC can be applied on metallic and non-metallic (ceramic, carbon-carbon) products to protect them against thermal degradation.*

**Key words:** *polymer composite materials, fibrous press materials, carbon fiber, hollow ceramic microspheres, thermal shield coating, density*

**Introduction.** Reliable operation of solid propellant rocket motor (SPRM) components with preservation of the structure during fuel combustion with the temperatures above 2000° C can be provided by a limited range of high-temperature metal and ceramic materials. Technology for motor parts manufacturing from refractory materials is usually complex, energy-intensive and expensive. Therefore, rocket motor parts are made of heat-resistant steels, which are protected from overheating with special TSC.

Fuel combustion in the SPRM chamber leads to the release of heat, the flow of which is directed to the coating surface and is reflected from the coating surface according to the radiation mechanism into the working space. Part of the heat is absorbed by the layer of thermal shield coating and is spent on heating the coating material to the temperature of evaporation or sublimation. Some heat is transferred due to heat conduction to the metal structural elements of the motor. The less heat is transferred by thermal conductivity, the higher the temperature of the coating surface from the side of the working combustion chamber is, and the longer the heat will dissipate due to radiation, evaporation, and sublimation mechanisms.

In addition to the fact that thermal shield coatings preserve the strength, resistance to erosion and chemical inertness of the combustion chamber walls and rocket structural elements, they further reduce heat loss in the combustion chamber, stabilize the combustion behavior and the rocket motor thrust.

The thermal shielding function is provided by a complex of coating material thermal properties; the heat protective effect of shielding TSCs can be mainly explained by their low thermal conductivity.

Ceramics with low thermal conductivity, pyrolytic graphite, and composite materials with a polymer matrix or a binder are used as coating materials [1].

There are following types of TSC:

– evaporating (sublimating) TSC – a heat-resistant porous matrix impregnated with a low-melting filler [1].

– char-forming TSC – the main type of TSC for SPRMs. In structure, these are plastics or elastomers, the binder in which is phenolic resin or rubber, and the fillers are asbestos, glass, nylon, carbon materials, etc. [1].

The disadvantages of ceramic thermal shield coatings are expensive components and manufacturing technology.

The highest mechanical characteristics are possessed by coatings formed on the basis of carbon fibers, since the fiber strength, as a rule, is 0.5 ... 5 GPa [2], depending on the fiber type.

Since heat resistance is proportional to strength and thermal conductivity and is inversely proportional to the elasticity modulus and thermal expansion coefficient, it is most expedient to use carbon fibers to strengthen polymer materials, which, as a rule, provide a sublimating and radiative component of heat transfer from the coating surface [3].

Composite thermal shield materials, as a rule, consist of a matrix based on polymer binder, and filler in the form of reinforcing fibers.

Thermosetting phenol-formaldehyde matrix with carbon fibers as filler is especially effective in resisting high temperatures, since the matrix evaporates and burns on the surface, creating an additional thermal protective layer. The authors of [4] obtained samples with the following characteristics: bending strength – 247 MPa and tensile modulus – 27.6 GPa. They performed a weight loss test at temperatures above 500° C, resulting in a 40% weight loss of the sample at 600° C in an atmosphere (with the filler to matrix ratio 75/25%).

Since glass fibers have a lower thermal conductivity compared to carbon fibers, Li H. et al. [5] developed a three-dimensional model of thermal calculation using the finite element method to assess the thermal behavior of a glass fiber / phenolic composite exposed to heat flow from one side. The model was built on the equations of heat transfer and energy conservation, in which heat transfer has the form of anisotropic thermal conductivity and absorption during matrix decomposition and gas diffusion. As a result, thermal conductivity 50% lower than on the surface of the samples was obtained (1.9 at the inlet and about 0.80 W \* m<sup>-1</sup> \* K<sup>-1</sup> at the outlet) during 800 seconds.

The studies have shown that the adding graphite flakes can improve the thermo-mechanical properties of composites. Lee et al. [6] used various sizes of graphite particles as well as the extrusion and compression molding process to obtain composite fluorinated ethylene-propylene / graphite parts. The results showed the following: the ultimate strength in bending was about 48 MPa [7].

In order to reduce thermal conductivity, Lee J. et al. investigated the effect of particle size on thermal conductivity in granular mixtures. They used 2 types of mixtures – particles of crushed rubber tyres (200-1100 microns, specific weight 1.05, thermal conductivity 0.25 W\*m<sup>-1</sup>\*K<sup>-1</sup>) and chrome spheres (specific gravity 7.81) with the addition of filler in both mixtures of ceramic solid microspheres (diameter 200...300 microns, specific gravity 2.51, thermal conductivity 1.124 W\*m<sup>-1</sup>\*K<sup>-1</sup>). As a result, thermal conductivity was obtained in the range of 0.025 to 0.25 W\*m<sup>-1</sup>\*K<sup>-1</sup>, depending on the volume fraction of mixtures of solid ceramic microspheres and rubber particles [8].

In the work by Chen et al. [9] on the ignition and combustion properties of fibrous composite materials with a phenolic matrix, glass fibers were used as filler. The tests were carried out on 100x100 mm specimens 3, 5 and 8 mm thick, and the ratio of matrix and filler was 50/50%. The test conditions were as follows: heat flow from 35 to 65 kW\*m, ambient temperature 298 ± 2 K at humidity 50 ±%. With an increase in the external heat flow, it is easier to achieve heat balance for samples 3 mm thick than for 5 and 8 mm thick. The combustion efficiency in the case of 3 mm is greater than that of 5 and 8 mm.

In the work by Wang et al. [10], a composite material of fine dispersed carbon fibers (up to 75 microns long and 1.8 g/cm<sup>3</sup> density), ceramic hollow microspheres (20-85 microns in diameter) and a polyurethane-epoxy matrix was investigated. The composite material was investigated as a damping polymer composite material. The re-

searches added 5...30 % wt of carbon fibers, 1...5 % wt of ceramic hollow microspheres, and 70 % wt of binder. Experimental results have shown that carbon fibers increase the tensile strength index (optimal amount is 5 % wt. Damping is increased due to the adding ceramic hollow microspheres (the optimal amount is 3 % wt); it improves the characteristics of thermal decomposition, but at the same time the impact strength decreases and the brittleness of the composite increases. The composite obtained by the researches has a tensile strength of ~ 40 MPa and impact strength of ~ 15 kJ / m<sup>2</sup> [10].

Thus, the adding carbon and glass fibers as filler for reinforcing polymer composite materials is widely used due to their high tensile strength, Young's modulus. However, carbon fibers have relatively high thermal conductivity characteristics and increase the amount of heat that is transferred through the thermal shield coating. Ceramic hollow microspheres have advantages such as relatively low thermal conductivity, density, high temperature resistance, and sound insulation. They have a larger specific surface area compared to ceramic solid microspheres [10].

For this, the possibility of manufacturing reinforced composite TSCs by compaction under pressure was studied, as well as their physical and technical properties depending on the microstructure, phase composition, and density.

It was assumed that the adding of carbon fibers into the matrix will increase the physical and mechanical characteristics, and the adding of ceramic hollow microspheres will reduce the thermal conductivity of the material created for the TSC. Ceramic hollow microspheres will act as filler for carbon press materials using phenol-formaldehyde matrix.

In addition, the adding of hollow spherical particles from a low-heat-conducting ( $0.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) ceramic material can result in decreasing thermal conductivity, increasing the coating surface temperature, and increasing the heat lost for heating and evaporating, melting and evaporating of the coating material. Considering that polymeric materials have very low values of the elasticity modulus and can compensate for the increase in the tendency to cracking as a result of the adding ceramic particles, the authors studied the possibility of reducing the heat that transferred through the thermal shield coating during the rocket motor operation by adding hollow spherical particles.

**The objective of this paper is to create a new material for thermal shield coating, which has the combined advantages of shielding, sublimating and coking thermal shield coatings.**

**Methodology and discussion.** In order to make a reasonable choice of thermal shield coating components, the chemical and phase composition, microstructure, and physical and mechanical properties of the most common composite materials with a polymer matrix were first investigated. It is shown that the composite material includes as reinforcing fillers carbon or aramid fibers, which are bound by phenol-formaldehyde binder. A small amount of refractory oxides are added as inorganic additives, which increase the integrity of the coating material and decrease the coating thermal conductivity. Hollow oxide particles (in the form of microspheres) have lower thermal conductivity. The possibility of obtaining a polymer reinforced composite material using ceramic hollow microspheres (Fig. 1, a) as filler with a particle diameter (30-150  $\mu\text{m}$ ) (Table 1) was considered.

In order to improve the manufacturability of parts from composite press materials and their transportation, the press mixture was made in the form of tablets in 2 stages (stage 1 – cold pressing, stage 2 – hot pressing). In laboratory conditions tablets can be obtained by pressing them in the form of disks ( $\text{Ø}17 \times 3 \text{ mm}$ ) under a hot press.

Table 1

## Chemical analysis of ceramic hollow microspheres

Element	Atomic percentage, %
B	7,61
O	57,54
Al	9,49
Si	19,63
K	1,27
Mg	1,27
Fe	1,50
Ti	0,40
Na	0,78

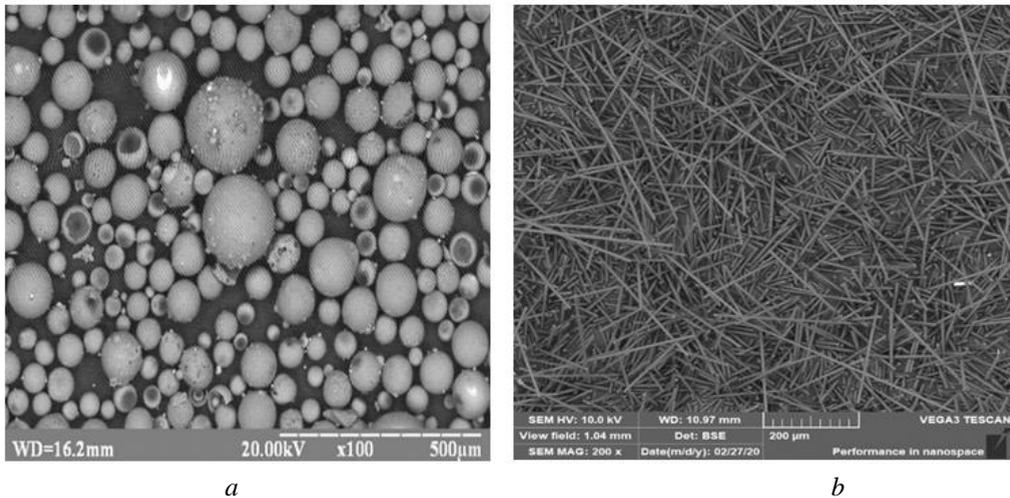


Fig. 1. Initial materials for the development of the TSC model: *a* – ceramic hollow microspheres; *b* – carbon fibers

Carbon fibers (10-600 microns) (Fig. 1, *b*), ceramic hollow microspheres (30-150 microns) and phenol-formaldehyde binder (Table 2) were used to manufacture bulk molding mass. 2 types of mixture were made – with ceramic hollow microspheres and without them. The ratio of the components of the carbon fibers composite, ceramic hollow microspheres and phenol-formaldehyde binder is 50/0/50 and 50/5/45 % wt.

Table 2.

## Basic physical and mechanical characteristics of the initial components

Parameters	Carbon fibers	Ceramic hallow microspheres	Phenol binder
Size, microns	10-600	30-150	-
Density, g/cm <sup>3</sup>	1,79	0,30-0,45	1,99
Thermal conductivity, W*m <sup>-1</sup> *K <sup>-1</sup>	1,6	0,1	0,36
Elasticity modulus, GPa	262	1,99 [11]	0,0025
Poisson ratio	0,22	0,21	0,27

The choice of the mixing mode for the composite molding mass is one of the most important stages of the technological process for the manufacturing samples. It should be noted that when mixing the molding mass, mechanical loads are created on the carbon fibers. Under the influence of mechanical stress, carbon fibers are crushed into smaller ones, as a result physical and mechanical properties are reduced.

Mixing was carried out for 30 minutes until a homogeneous bulk molding mass of the composite was formed. At the first stage of cold pressing, a laboratory mold Ø16 was used under a pressure from 2 to  $21 \pm 1$  MPa. The second stage of pressing took place in a heated laboratory mold Ø17 at a temperature of  $165 \pm 5^\circ\text{C}$  (the temperature of the phenol-formaldehyde binder polymerization, declared by the manufacturer, is  $+160...170^\circ\text{C}$ ) with a holding time of  $10 \pm 1$  minutes. The mode of hot pressing under pressure from 5 to 25 MPa makes it possible to obtain finished samples without further mechanical machining.

### **Technological scheme for obtaining samples of reinforcing carbon fiber press materials with ceramic hollow microspheres**

#### **1st stage (cold pressing)**

Carbon fibers (size 10-600 microns) - 50 % wt

+

Ceramic hollow microspheres (30-150 microns in diameter) - 5 % wt

+

Phenol-formaldehyde resin - 45 % wt

+

Pressing at room temperature in a Ø16 mold under pressure up to  $21 \pm 1$  MPa

#### **2nd stage (hot pressing)**

Carbon fibers (size 10-600 microns) - 50 % wt

+

Ceramic hollow microspheres (30-150  $\mu\text{m}$  in diameter) - 5 % wt

+

Phenol-formaldehyde resin - 45 % wt

+

Heating the mold up to  $200^\circ\text{C}$

+

Hot pressing in a mold Ø17 under pressure up to  $21 \pm 1$  MPa

It is commonly known that the density of sample material depends on values of molding pressure; therefore, the dependence of the samples density on molding pressure was investigated. To compare and analyze the results of the molding, 6 groups of samples were taken. The samples were molded with cold pressing (Fig. 2) followed by hot pressing with pressure from 2 to  $21 \pm 1$  MPa.

As a result of the work carried out, polymerized samples (17x3 mm) with ceramic hollow microspheres (30...150 microns in diameter) and without ceramic hollow microspheres were obtained. It is known that the raising of molding pressure increases the density and decreases the porosity of materials. The minimum density of samples after hot pressing without adding microspheres at  $\sim 2$  MPa is  $1.462\text{ g/cm}^3$ , and with the addition of ceramic hollow microspheres it is  $1.422\text{ g/cm}^3$  (Fig. 3).

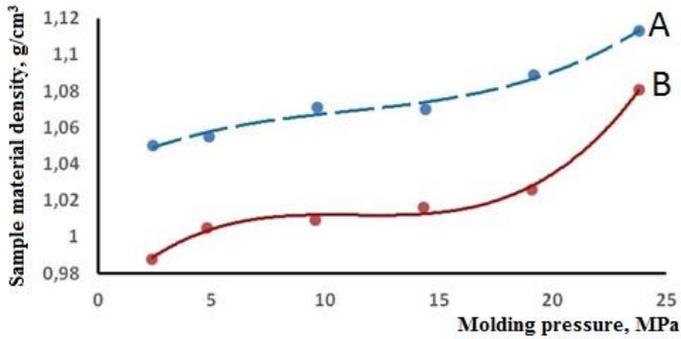


Fig. 2. Dependence of the material density on the value of the molding pressure of samples during cold pressing: A – without ceramic hollow microspheres; B – with ceramic hollow microspheres

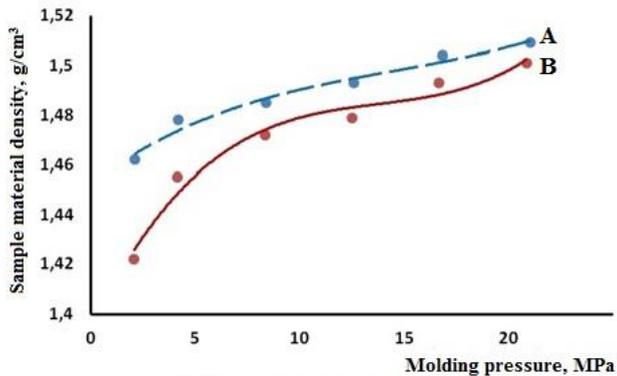


Fig. 3. Dependence of the material density on the value of the molding pressure of samples during hot pressing

After hot pressing of samples (with and without ceramic hollow microspheres) under pressure by scanning electron microscopy, microstructural analysis was performed (Fig. 4).

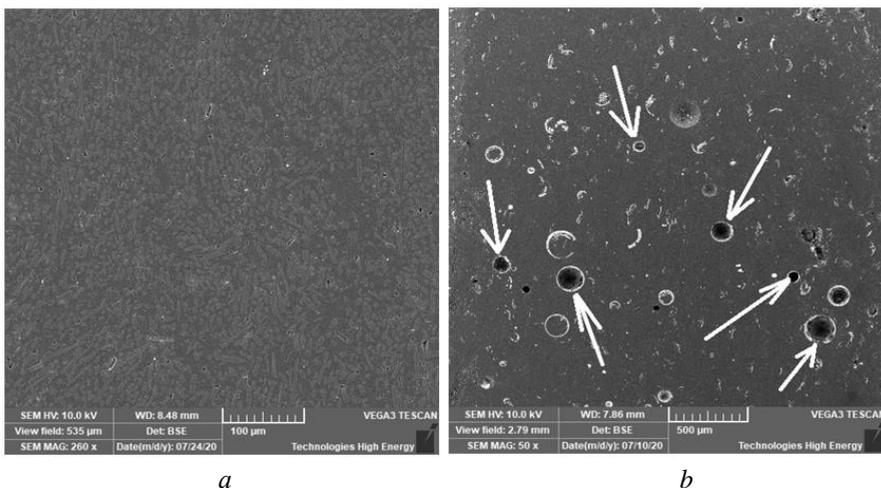


Fig. 4. Microstructure of samples after hot pressing under pressure: a – carbon fibers / ceramic hollow microspheres / phenol-formaldehyde binder (50/0/50 % wt); b – carbon fibers / ceramic hollow microspheres / phenol-formaldehyde binder (50/5/45 % wt)

As a result of the model microstructural analysis of the samples without the addition of ceramic hollow microspheres (Fig. 5), the pores were revealed. The porosity appeared due to the evaporation of phenol-formaldehyde binder gases during hot pressing of samples under pressure. Thus, the porosity of the composite material is an inevitable result of the technological process. The increase in controlled porosity occurs due to the adding ceramic hollow microspheres. Since the pressing mode is not the same (the molding pressure is different for each group of samples), a decrease in porosity occurs with an increase in the molding pressure due to a decrease in voids between the components and due to existing pores in the binder.

The microstructure of samples with the addition of 5% wt ceramic hollow microspheres (Fig. 6) shows the quality of crosslinking between microspheres and binder (phenol formaldehyde).

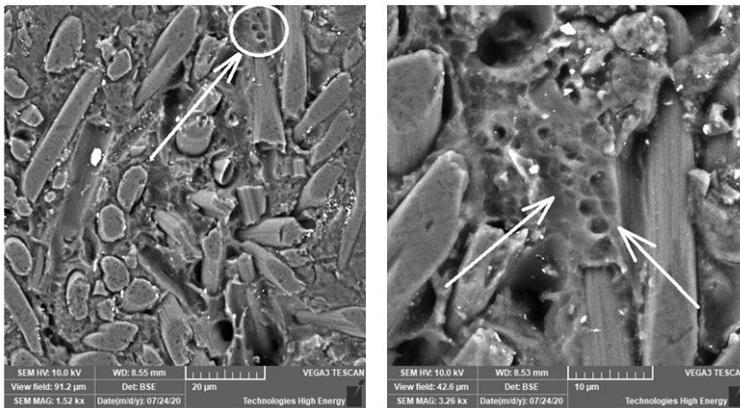


Fig. 5. Microstructure of a sample with carbon fibers and phenol-formaldehyde matrix shows the presence of pores

It was revealed that when pressing the samples (Fig. 6, *a*) under pressure (2 MPa), the crosslinking of the composite with ceramic hollow microspheres is minimal. This fact reduces the adhesion between the components significantly. On the other hand, the adhesion of ceramic microspheres (Fig. 6, *b*) increased significantly at pressing under pressure ( $21 \pm 1$  MPa).

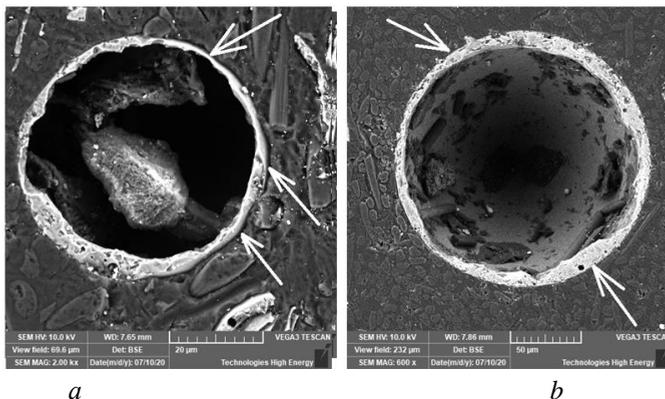


Fig. 6. Model microstructure of the of samples with the addition of ceramic hollow microspheres: *a* – microsphere with low adhesion (molding pressure  $\sim 2$  MPa); *b* – ceramic hollow microspheres with high adhesion (molding pressure  $\sim 21 \pm 1$  MPa).

## Conclusions

Based on the results obtained on the mixture compaction of carbon fibers up to 600 microns in length, up to 7 microns in diameter with phenol-formaldehyde binder, the possibility of forming a practically nonporous material of a composite thermal shield coating, which has a density lower than traditional world analogues, is shown.

The factors influencing the occurrence of porosity, methods of reducing the density due to the controlled porosity of the composite material are studied.

It has been established that the adding of spherical hollow ceramic particles does not impair the compaction process under pressure, but it makes it possible to regulate the porosity of the composite thermal shield coating, which can remain up to temperatures above 2000° C or the melting temperatures of the ceramic material. This opens up the possibility of controlling the thermal conductivity of the thermal shield coating material in a wide temperature range.

Since the amount of ceramic hollow particles will affect not only the thermal conductivity, but also the strength of the thermal shield coating material, in the future, it is important to study the properties of the coatings depending on the concentration of hollow ceramic particles in them.

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### **СТВОРЕННЯ ТЕПЛОЗАХИСНОГО ПОКРИТТЯ ДЛЯ РОБОТИ В УМОВАХ ЕКСТРЕМАЛЬНО ВИСОКИХ ТЕМПЕРАТУР**

Створений матеріал теплозахисного покриття (ТЗП), що складається з вуглецевих волокон, керамічних порожнистих мікросфер і фенолформальдегідного зв'язуючого. Показано, що введення до 5 мас. керамічних порожнистих мікросфер дозволяє отримувати теплозахисне покриття з меншою щільністю і фізико-механічними характеристиками на рівні аналогів світових виробників. ТЗП можна наносити на металеві і неметалічні (керамічні, вуглець-вуглецеві) вироби для захисту від теплової деградації.

**Ключові слова:** полімерні композиційні матеріали, волокнисті пресс-матеріали, вуглецеве волокно, порожнисті керамічні мікросфери, теплозахисне покриття

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