MATERIAL POLÍMERO E CERÂMICO PARA A FABRICAÇÃO DA CÂMERA DE DESCARGA DE GÁS DO MOTOR DE FOGUETE ELÉTRICO

THE POLYMER-CERAMIC MATERIAL FOR THE MANUFACTURE OF GAS DISCHARGE CHAMBER FOR THE ELECTRIC ROCKET ENGINE

ПОЛИМЕР-КЕРАМИЧЕСКИЙ МАТЕРИАЛ ДЛЯ ИЗГОТОВЛЕНИЯ ГАЗОРАЗРЯДНОЙ КАМЕРЫ ЭЛЕКТРИЧЕСКОГО РАКЕТНОГО ДВИГАТЕЛЯ

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RESUMO

O artigo discute a criação do material compósito dielétrico resistente ao calor à base de polímeros de organossilício para a fabricação de uma câmara de descarga de gás do motor de foguete elétrico. Foi proposto o aglutinante que atende aos altos requisitos de resistência à vibração e permeabilidade da câmara de descarga de gás na faixa de megahertz de ondas eletromagnéticas. Com base nesse aglutinante preenchido com pó de nitreto de silício, foi produzido a câmara de descarga de gás; este produto foi totalmente testado como parte do motor de foguete elétrico de laboratório de 200 kW. O estudo das transformações estruturais que ocorrem durante o aquecimento dos materiais foi realizado por análise térmica síncrona. O material obtido como resultado do experimento, cuja base foi SiSiB@PVMQ preenchida com Si₃N₄ a 60% em massa, é caracterizado por várias propriedades que são estruturadas e descritas neste artigo. Como resultado do estudo, foi demonstrado que o material estudado é caracterizado por resistência ao calor de até 400°C. Com base nessa pesquisa, os autores produziram a câmara de descarga de gás, que foi testada como parte de um modelo de laboratório. Verificou-se que o aumento da perda de massa acima de 400°C é devido ao início do processo de degradação térmica da principal cadeia polimérica.

Palavras-chave: cerâmica, elastômeros de organossilício, materiais compósitos, motores de foguetes elétricos, câmara de descarga de gás.

ABSTRACT

This study discusses the creation of heat-resistant dielectric composite material based on organosilicon polymers for the manufacture of gas discharge chamber (GDC) for the electric rocket engine (ERE). A binder has been proposed that meets the high requirements for vibration resistance and electromagnetic permeability of GDC in the megahertz range of electromagnetic waves. Based on this binder filled with silicon nitride powder, GRC was designed; this product was fully tested as part of laboratory 200 kW ERE. The research of structural transformations that occur during heating of materials was carried out by synchronous thermal analysis. The material obtained in the result of the experiment, the basis of which was SiSiB@PVMQ filled with Si₃N₄ 60% by mass, is characterized by a number of properties that are structured and described in this study. As a result of the study, it was demonstrated that the studied material is characterized by heat resistance up to 400 °C. On the basis of these materials, the authors produced a GDC, which was tested as part of a laboratory model. It was established that the increase in mass loss over 400 °C is due to the initiation of the process of thermal degradation

of the main polymer chain.

Keywords: *ceramics, organosilicon elastomers, composite materials, electric rocket engines, gas discharge chamber.*

АННОТАЦИЯ

В работе обсуждаются вопросы по созданию термостойкого диэлектрического композиционного материала на основе кремнийорганических полимеров для изготовления газоразрядной камеры (ГРК) электроракетного двигателя (ЭРД). Было предложено связующее, которое соответствовало высоким требованиям к вибростойкости и электромагнитной проницаемости ГРК в мегагерцовом диапазоне электромагнитных волн. На основе данного связующего, наполненного порошком нитрида кремния изготовили ГРК, данное изделие прошло полное испытания в составе лабораторного ЭРД мощностью 200Вт. Исследование структурных превращений, происходящих при нагреве материалов, проводилось методами синхронного термического анализа. Материал, полученный в результате эксперимента, основой которого стал SiSiB@PVMQ наполненный Si₃N₄ 60% масс., характеризуются рядом свойств, которые структурированы и описаны в данной работе. В результате исследования показано, что исследованный материал характеризуется термостойкостью до 400°C. Авторами на основе этого материала была изготовлена ГРК, которая прошла испытания в составе лабораторной модели. Установлено, что рост потери массы свыше 400°C обусловлен инициацией процесса термодеструкции основной полимерной цепи полимера.

Ключевые слова: *керамика, кремнийорганические эластомеры, композиционные материалы, электроракетные двигатели, газоразрядная камера.*

1. INTRODUCTION

Space exploration is receiving a lot of attention in such economically leading countries as the USA, China, Japan, India, Russia, and countries of the European Community. Success in the development of near-Earth orbit, the lunar surface, interplanetary space is becoming one of the most important drivers for the development of modern technologies in these countries. One of the areas of intensification of space exploration is widespread use and development of electric rocket engines (ERE), which allow for a significant increase in the mass of payload of the spacecraft (SC) via reducing the mass of the working fluid. It should be mentioned that the longest project in the history of astronautics – the flight of Voyager 1 and Voyager 2 spacecraft to the boundaries of the solar system (NASA, USA, since 1977) became possible to some extent due to the use of electro thermal electric propulsion engines – “hydrazine” engines. In modern space technology, ERE is being developed for use in the correction of orbit of the spacecraft, bringing the spacecraft into the geostationary orbit, and also as a mid-flight engine in interplanetary flights (Antropov *et al.*, 2002; Gorshkov *et al.*, 2008; Loeb, 2015; Sitnikov, 2017; Khartov *et al.*, 2013; Rabinsky *et al.*, 2016a).

Among all types of electric propulsion, the greatest achievements have been reached in the use of ion engines (IE). Thus, XIPS-25 ion engines

for orbit reaching and correction has been used for many years on space platforms of Boeing (USA). As sustainer engines, SERT ion engines were used in long interplanetary missions in DEEP SPACE 1 and DAWN missions (ongoing). Japan's Space Agency's Hayabusi 1 mission employed the μ -10 ion engine to fly to and from Itokawa asteroid. The mission of Hayabusi 2 to asteroid 1999 JU3 is currently being successfully performed. Currently, ERE is considered to be the main candidate for use as a sustainer engine in planned missions for the exploration of deep space, including when flying to Mars and other objects of the solar system. Unfortunately, due to some objective and subjective reasons in the development of ion engine technology in the Russian Federation, there was a significant retarding behind the world level, attempts to overcome which have been successful in recent years. At the same time, the technological problems of manufacturing the main structural elements of IE are getting significant.

One of the most effective IEs for use as a sustainer engine for long space flights is usually considered a high-frequency ion engine (HFIE) due to its inherent high efficiency and high resource life. The operation of the engine is based on the generation of plasma of the working matter (for example, xenon) and the acceleration of the ionization products by the electromagnetic field of the HF generator (Figure 1)

The ionization of the HFIE working matter

is carried out in the volume of a thin-walled bowl of a gas-discharge chamber. An increase in HFIE power to a value of 15 kW and above leads to an inevitable increase in the diameter of the gas distribution system (500 mm and more) while maintaining the chamber thickness at the level of 4 ... 7 mm. Currently, GDC chambers are made of ceramics based on aluminum oxide, silicon nitride (Khartov *et al.*, 2013). The diameter of the existing chambers, with a wall thickness of 4 mm, does not exceed 300 mm, because of low vibration resistance of thin-walled ceramic products and technological difficulties in their obtaining. Therefore, there are prerequisites for the search for alternative materials for GDC HFIE. The main requirements for the GDC material are electromagnetic permeability in the megahertz range, vibration resistance, and heat resistance.

Earlier, the authors of the article made attempts to make GDC from polymer-ceramic composites by the method of molding into a closed form (Rabinsky *et al.*, 2016a; Pogodin *et al.*, 2016a; Poliakov *et al.*, 2016; Ripetsky *et al.*, 2016; Rabinsky *et al.*, 2016b; Pogodin *et al.*, 2016b; Lurie *et al.*, 2011; Pogodin *et al.*, 2019; Formalev *et al.*, 2015). The technology of molding large-sized products from organosilicon rubbers obtained by the polycondensation reaction into a metal form was worked out. As a result, an HFIE chamber with a diameter of 100 mm was manufactured and successfully tested. The material for the chamber was polymethylphenylsiloxane rubber modified with terminal vinyl groups and filled with silicon nitride. The main disadvantage of the material used was the insufficiency of heat resistance, up to 370 °C in a vacuum (Lurie *et al.*, 2011; Pogodin *et al.*, 2019; Formalev *et al.*, 2015).

The material of the chamber – organosilicon polymers, is a high molecular weight compound containing silicon in the main polymer chain bonded to organic substituents in the side frame. Organosilicon polymers are usually classified depending on the heteroatom in the main polymer chain: polyorganosiloxanes (oxygen), polyorganosilazanes (nitrogen), polycarbosilanes (carbon). Materials based on organosilicon compounds can be used in a temperature range from -120 °C to 550 °C, they are good dielectrics transparent to electromagnetic radiation (Andrianov and Sokolov, 1955; Daus and Kharchenko, 2018; Pogodin *et al.*, 2019).

Among organosilicon polymers, polyorganosiloxanes, to the greatest extent, comply with the above requirements for GDC

material. Despite the high heat resistance of polyorganosilazanes and polycarbosilanes, materials based on them do not ensure stability of performance for the HFIE chamber material under conditions of contact with ionized gas at temperatures above 300 °C. Among polyorganosiloxanes, cross-linked polymers have the highest heat resistance; linear polymers, which are characterized by high elongation, have a temperature limit of about 300 °C (Pogodin *et al.*, 2019; Vinogradov *et al.*, 2016). In theory, cross-linked polymers and composite materials based on them have high heat resistance and can withstand repeated heating in an oxidizing environment up to 550 to 600 °C. To achieve such heat resistance, it is necessary to modify organosilicon elastomeric composite materials using MQ resins (Vinogradov *et al.*, 2016), also known in the literature under other names: oligotrimethylsiloxysiloxanes, trimethylsiloxysilicates, or copolymer MQ-siloxanes.

MQ resins are oligomeric organosilicon compounds the molecules of which contain structural fragments of silicon dioxide [$\text{SiO}_{4/2}$] (Q) in the main chain, and trimethylsiloxy [$(\text{CH}_3)_3\text{SiO}_{1/2}$] (M) groups (Molchanov and Kim, 1997; Voronkov *et al.*, 1976; Rabinskiy and Tushavina, 2019a; Rabinsky and Tushavina, 2019b). The above mentioned formula corresponds to the spatial highly branched structure. The lower is the Q / M ratio, the less pronounced is the elasticity. At the same time, the glass transition temperature for the polymer rises. At the ratio of M: Q is less than 0.7, the glass transition temperature rises to 200 °C. So, MQ-siloxanes are characterized by high heat resistance. Co-condensation of MQ Resins with polyorganosiloxanes inhibits the depolymerization of the latter at temperatures above 300 °C. Thermal degradation of MQ resins begins at temperatures above 400 °C, with the formation of amorphous silicon oxide. Therefore, by combining the elasticity of linear polyorganosiloxanes and the heat resistance of MQ-siloxanes, it is possible to increase the heat resistance of composite material for the production of FDC HFIE.

2. MATERIALS AND METHODS

The main efforts in the search for material for GDC were directed to the development of GDC, molded from modified polymer-ceramic composites, based on organosilicon rubber, including ones filled with silicon nitride. The obtained material was developed by polymerization by double bonds of vinyl groups at

silicon atom and polycondensation by the hydrosilylation reaction (Figure 2).

At the first stage of the work on making GDC molded from modified polymer-ceramic composites, the physicochemical fundamentals of producing composite materials with a polymer matrix and ceramic powder were made as a filler to increase the vibration resistance of large-sized thin-walled products. Technology has been developed for forming large-sized products from organosilicon rubbers into a metal form, made by the polycondensation and polymerization reaction. Laboratory plots were made for these alternative methods of forming billets, including those adapted for further use in additive manufacturing.

At the second stage of works, a set of studies was conducted on the properties of the developed polymer-composite materials modified with MQ resins, which made it possible to formulate recommendations on using and adaptation of the obtained materials in space technology. A product under the SiSiB®PVMQ brand with a viscosity of 50,000 cSt and a refractive index $n_D = 1.5490$ from Power Chemical Corporation Limited (China) was used as the starting polymer for making the composite material. The catalyst K-21 was used as a hardener. A composite material was prepared by mixing Si_3N_4 powder with SiSiB®PVMQ in the bead mill for 4 hours. The proportion of silicon nitride was 60% of the mass. The structural transformations occurring during heating of materials were studied by synchronous thermal analysis using STA 449 F3 Jupiter instrument from NETZSCH (Germany) (Figure 3) in the differential scanning calorimetry (DSC) mode and with thermogravimetric analysis (TGA) mode.

The samples were heated to 1100 °C in open melting pots of Al_2O_3 with a volume of 0.085 ml at linearly increasing furnace temperature at a rate of 10 °C/min. The melting pots were placed in cylindrical recesses of the upper part of the DSC / TG sensor made of Pt-Rh alloy. The argon flow rate through the measuring cell (a sample and a reference) during the experiment was 50 ml / min. An empty melting pot was used as a reference. The sample and the reference temperatures were measured using built-in S-type thermocouples made of Pt-Rh alloys. The accuracy of temperature measurement was ± 0.3 °C. The change in mass of the samples was recorded with an accuracy of 1 µg. The isothermal drift of weights in the entire temperature range did not exceed 10 µg / h. Data collection and calculations, as well as device operation control, were performed using NETZSCH Proteus Software (Germany) software

under MS-Windows OS.

For the best assessment of the properties of materials, the following types of tests were used:

- Isothermal annealing of samples with an exposure of 5 hours in a vacuum electric furnace SCHVE 1.2.5 / 25 at a residual pressure of $P = 6 \cdot 10^{-3}$ Pa and measurement of shrinkage after isothermal annealing in a vacuum according to GOST 26433.1-89.
- Measurement of tensile strength at Instron universal testing machine 5960 series for type III samples manufactured in accordance with GOST 269, thickness 2 ± 0.2 mm. The tests were performed at a temperature of 28 °C and loading speed of 500 mm/min.
- Measurement of the hardness of samples before and after isothermal annealing in vacuum at TSHR instrument in accordance with GOST 253-53.
- Performing vibration testing of the obtained prototypes of GDC HFIE with a diameter of 160 mm in accordance with GOST V 24880-81, GOST RV 20.57.305-98, GOST RV 50674-94, GOST B 22589-86.
- Operational tests of prototypes of GDC HFIE with a diameter of 100 mm on a vacuum stand with a volume of 0.4 m³ (Figure 4). In the pumping system of this testing line, oil-free means of obtaining vacuum were used: a two-stage fore-vacuum pump MU-603 from Kashijama (the first stage is a two-rotor five-stage Roots pump, the second stage is a Roots pump) and four turbo molecular pumps with a magnetic suspension of the Tim-2203LM rotor from Shimats. The pump compartment of the vacuum chamber was equipped with a water-cooled target — an aluminum alloy ion stream receiver with ring conical concentric grooves that reduce reverse flows. The pumping system of the testing line provided a dynamic vacuum of 10^{-3} Pa at xenon flow rates of up to 0.65 mg / s.

3. RESULTS AND DISCUSSION:

Figure 5 shows DTA plots of a SiSiB®PVMQ sample and a SiSiB®PVMQ-based material sample filled with Si_3N_4 60 mass% In argon. In the case of SiSiB®PVMQ, the mass loss of the test samples at 400 °C was about 10% of the mass.

The pyrolysis process is accompanied by thermolysis of organic frame: methyl, vinyl, phenyl

substituents at the silicon atom. In the result of pyrolysis, amorphous silicon oxide and silicon carbide are formed. The yield of the pyrolysis residue is about 49%, which is slightly lower than the value obtained based on elemental composition in starting polymer: C – 27.14%; H – 5.55%; Si – 37.00; O – 30.31. The reason for this lies in the occurrence of cyclic depolymerization of linear sections of the polymer chain, loss of silicon and oxygen in the composition of pyrolysis products. The increase in mass loss over 400 °C is due to the initiation of the process of thermal degradation of the polymer chain. Therefore, processes that occur up to 400 °C are mainly associated with the progress of the reaction along unreached functional groups, the telomerization reaction, the intramolecular rearrangement of macromolecules, and removal of low temperature boiling substances. The heat resistance of materials based on SiSiB®PVMQ filled with Si₃N₄ 60 mass%, Slightly higher, according to the schedule of weight loss, 10% corresponds to a temperature of 550 °C. As can be seen from the graph, the proportion of the pyrolysis residue obtained at 1100 °C corresponds to the amount of silicon nitride 60% and 50% of the residue from the polymer part.

The resulting materials based on SiSiB®PVMQ filled with Si₃N₄ 60 mass%, are characterized by the following properties:

- Hardness according to Shore – 50-60 (scale A).
- Density – 1.20-1.40 g/cm³.
- Elasticity – linear elongation – 35-40% of permanent deformation.
- Elongation at break point – 50 to 60%.
- The tensile strength – 6-8 MPa.
- Volume shrinkage after curing: 3-4%.
- Temperature ratio of linear expansion – 1.0 to 1.5 · 10⁻³ K⁻¹
- Dielectric strength – 15 – 20 kV/mm.
- Dielectric loss tangent: – 0.2 to 0.02.

The confirmation of the electrical properties was performed during the test of gas distribution system made from new material as part of a laboratory model of the engine with a diameter of the ion-optical system 160 mm. For this, a ready-made laboratory model of HF IE was used. For this laboratory model, the dependences of ion beam current on the flow rate and the embedded high-frequency power (HF power) when GDC was previously obtained. A vacuum test bench for testing polymer-ceramic GDCs as part of the laboratory model of HF IE provided a dynamic vacuum of 10⁻³ Pa at xenon consumption

of up to 0.65 mg/s. The objective of these tests was to compare previously obtained integral characteristics of ceramic and polymer-ceramic GDC engines with new ones when the GDC was replaced by a chamber made of polymer-ceramic materials modified with MQ resins.

4. CONCLUSIONS:

As part of the conducted research, promising materials for creating a gas distribution system were studied – polymer-ceramic materials modified with MQ resins, providing the required electro physical and operational characteristics of the HF IE discharge chambers. During the study, the vacuum thermal stability of polymethylphenylsiloxane rubber modified with MQ-siloxane was investigated to create a polymer-ceramic composite that provides required electrical and operational characteristics of GDC of an electric rocket engine (radio transparency, manufacturability, vibration resistance, and so on). It was demonstrated that the studied material is characterized by high heat resistance. Modification with MQ resins partially blocked depolymerization of the linear part of polymer. In the general composition with silicon nitride, the heat resistance of the binder remains at the same level, due to mineral filling, the mass loss is proportionally reduced. Silicon nitride does not affect the process of thermal degradation with the synergistic effect of increasing heat resistance in the system of silicon nitride – a polymer binder was not found.

Methods of obtaining products from complex ceramic materials based on the use of polymer-ceramic materials modified with MQ resins based on silicone rubber filled with silicon nitride were studied. Experimental elements of technological equipment were created for the production of gas distribution systems from the developed polymer-ceramic materials. It was experimentally confirmed that the operating temperature of the gas distribution system made of silicon nitride-filled rubber modified with MQ resins could reach 400 °C without loss of mechanical and electrophysical properties.

Based on this material, GDC was manufactured, which was tested as part of the laboratory model of HF IE. The obtained dependences of the ion beam current on the flow rate of the working fluid and the enclosed HF power were not inferior to the previously obtained values for an engine with a gas discharge chamber based on alumina ceramics. From the obtained results, it follows that mechanical and

electrophysical parameters of the GDC from polymer-ceramic material modified with MQ resins and filled with silicon nitride meet the requirements for gas discharge chambers of HF IE.

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Figure 1. Schematic diagram of the HFIE operation

Figure 2. Forming of test specimens from modified polymer-ceramic composites into a metal mold

Figure 3. STA 449 F3 Jupiter device from NETZSCH company (Germany)

Figure 4 The GDC prototype mounted on the HFIE prototype (left) and the general view of the vacuum testing line for HFIE (right)

Figure 5. Dependence of mass loss on temperature during the DTA of a SiSiB®PVMQ sample and a composite material based on SiSiB®PVMQ filled with Si₃N₄ 60 mass% in argon medium