

AT ENTERPRISES AND INSTITUTES

UDC 666.3/.7:629.7

GLASS AND CERAMICS BASED HIGH-TEMPERATURE COMPOSITE MATERIALS FOR USE IN AVIATION TECHNOLOGY

E. N. Kablov,¹ D. V. Grashchenkov,¹ N. V. Isaeva,¹ S. S. Solntsev,¹ and V. G. Sevast'yanov²

Translated from *Steklo i Keramika*, No. 4, pp. 7 – 11, April, 2012.

Promising high-temperature glass-ceramic and ceramic composite materials developed at VIAM, are examined. These materials are distinguished by their capability to retain their properties at high temperatures in an oxidative environment, good durability, excellent corrosion properties, low density, and low thermal expansion. In regards to their performance properties these materials are as good as, and in some respects even surpass, the best foreign analogs, making them the only available materials for use in heat-loaded units and the components of prospective articles.

Key words: ceramic composite material, silicon carbide, high-temperature chemical synthesis, carbon glass-ceramic composite material, oxidative medium, sol-gel technology.

The aviation technology of the future with new-generation engine and ground-based gas-turbine power-generation facilities, having 40 – 60% higher efficiency and 1.5 – 2 times higher operational reliability and longer service life and making it possible to decrease the emission of pollutants, will require higher gas temperature in front of the turbine and, correspondingly, light, strong, tough, corrosion-resistant materials, including for hot-section components that can function at temperatures above 1500°C.

Ceramic materials are distinguished by a complex of properties previously unattainable with other groups of materials and they have a number of advantages over metallic materials: they have the capability to retain their properties in an oxidative medium at temperatures above 1200°C, good durability, excellent corrosion properties, low density and low thermal expansion, which makes them the only available materials for use in heat-loaded units and the components of prospective articles operating under oxidative conditions at high temperatures.

Compared with the best high-temperature metallic alloys, ceramic composite materials SiC_{fiber}/SiC (SiC matrix reinforced with SiC fabric or continuous fibers) have low density (about 30 – 50% of the density of metals) and thermal expansion (about 60% metal CLTE) and, on the basis of the behavior of monolithic SiC, they can potentially function at temperatures to 1600 – 1650°C.

Foreign technologies for manufacturing composite ceramic materials using chemical precipitation from the gas/vapor phase or filtration to obtain SiC-based matrices require complicated, special molding equipment, are expensive because of the high energy-intensiveness of the processes (technological operation time to six months) and use expensive continuous SiC fibers as a reinforcing structural element. Analysis of the working properties of the best foreign ceramic materials, reinforced with Hi-Nicalon or Sylramic silicon carbide fibers has shown that the working temperature levels of SiC–SiC-composites does not exceed 1400 – 1450°C in an oxidative medium.

It is impossible to make a qualitative jump in the development of high-temperature materials engineering without implementing new, unconventional approaches in the development of materials and structures made from them. Such a jump can be made only by developing profitable processes for manufacturing ceramic composite materials, including sol-gel technology, nanotechnology and other cutting edge

¹ Federal State Unitary Enterprise – All-Russia Scientific-Research Institute for Aviation Materials (FGUP VIAM), Moscow, Russia (e-mail: admin@viam.ru).

² N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences (IONKh RAN), Moscow, Russia.

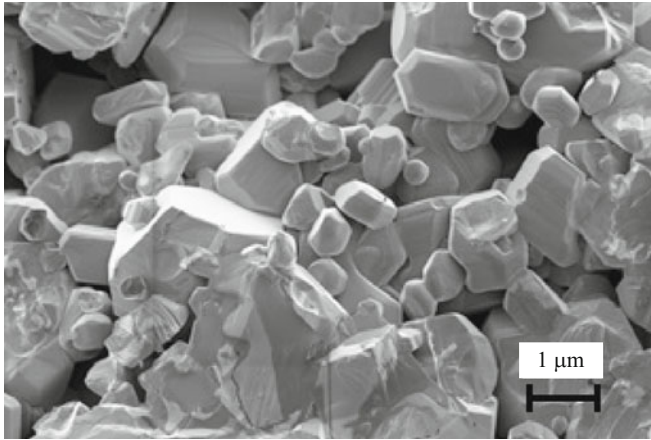


Fig. 1. Microstructure of SiC–SiC ceramic material.

solutions to technological problems based on intensifying the reactivity of structural elements above that of conventional materials, which will make it possible to decrease the energy-intensiveness of the technological operations in high-temperature synthesis of ceramic materials.

The sol-gel method has the following advantages over conventional methods of obtaining materials: it gives initial materials of high purity and a homogenous product, permits regulating the microstructure of the materials at the initial stage of the process and unlike chemical precipitation from the gas/vapor phase or infiltration does not require complicated equipment and is distinguished by low energy-intensiveness of the technological operations [1].

The main process having the greatest effect on the structure and properties of the SiC–SiC type ceramic composite materials developed at VIAM is high-temperature synthesis in which occur physical processes (evaporation-condensation, recrystallization via a liquid phase, diffusion-viscous flow and others) and chemical processes, leading to the formation of a matrix and the composite as a whole [4].

High-temperature synthesis results in the directed formation of a continuous silicon-carbide framework at the micro and nano levels in the composite, where the reinforcing particles are incorporated into the structure of the matrix formed from the initial components in the course of the synthesis process. Microstructural analysis revealed an embedded heterogeneous polycrystalline structure with very low closed porosity and crystal grains with predominate size 0.1 – 5 μm [2].

The microstructure of the SiC–SiC ceramic composite material is shown in Fig. 1.

High-temperature chemical synthesis makes it possible to purposefully change the properties of a ceramic material, such as, density, porosity, strength, and others, by regulating the structure.

A distinguishing feature of SiC–SiC composite ceramic materials is their high stability (in contrast to conventional monolithic ceramics) under heat-cycling loads in the combustion products of fuel in the following regime: 1600 –

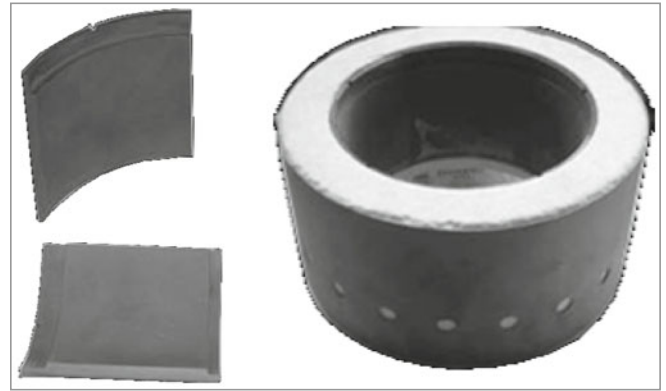


Fig. 2. Model of a prospective combustion chamber.

1650°C ↔ 800 – 850°C more than 7000 cycles (1 cycle = 1 min) without fracture.

The development of an adjustable and controllable structure for this ceramic composite material is one of the main methods for increasing crack resistance and strength.

It should be noted that a ceramic composite material is distinguished by very high resistance to oxidation. The mass of samples increases over a long period of time at temperatures to 1600 – 1650°C. This is due to the formation of a thin amorphous silica film on the surface of silicon carbide grains in an oxidative environment; this film blocks oxygen diffusion into the interior of the material and promotes self-healing of various defects by plugging pores, cracks, and so forth.

Technical Characteristics of SiC–SiC Composite Ceramic Material

Working temperature, °C	1600 – 1650
Medium	Products of fuel combustion
Density, g/cm ³	2.5 – 2.9
Porosity, %	5 – 8
Ultimate strength under 4-point bending, MPa:	
at 20°C	180 – 200
at 1600°C	180 – 200
Thermal conductivity, W/(m · K):	
at 20°C	45 – 50
at 1000°C	30 – 35
CLTE at 20 – 1600°C, K ⁻¹	(4.9 – 5.2) × 10 ⁻⁶

Self-healing of a material in use makes it possible to maintain the mechanical properties at their initial levels and to improve the protective properties at elevated temperatures.

The technology has been perfected experimentally and components (segments) of the combustion chamber for prospective engine facilities made from composite material based on SiC–SiC oxygen-free ceramic have been manufactured.

Figure 2 shows a model of a prospective combustion chamber, whose inner surface is lined with ceramic segments made from a SiC–SiC composite material.

The N. S. Kurnakov Institute of Organic and Inorganic Chemistry and the D. I. Mendeleev Russian Chemical Technology Institute, working jointly, have shown that it is possible to produce a secondary framework-like structure in the interior of a SiC–SiC ceramic composite material for the purpose of structural reinforcement.

Chemical transport reactions make it possible to obtain quite pure compounds with a prescribed morphology, including silicon carbide fibers under relatively mild conditions [3].

The commercial production of single-crystal plates of high-purity silicon carbide is based on the precipitation of volatile precursors of the silicon carbides Si₂C and SiC₂, which are obtained by sublimation of silicon carbide at temperatures of about 2400°C [4].

Gas-phase synthesis of pseudocontinuous SiC nanocrystals in the process of carbon-thermal reduction of silicon dioxide is examined in a number of works, e.g., [5].

The process control in the production of framework-like structures, including the growth of nanofibers, was held back by the lack of reliable experimental data on the saturated vapor pressure of silicon in a wide range of temperatures. Such data are basic for performing thermodynamic calculations of the processes involved.

High-temperature mass-spectrometry was used to study evaporation processes and determine the partial saturated vapor pressure of gaseous silicon above its melt in the interval 1739 – 2326 K. These values, obtained with silicon evaporation from Knudsen effusion chambers, made of molybdenum, tungsten, and siliconized molybdenum and graphite, which were siliconized by the gas-phase method, were compared [6]. It was found that among the materials listed for effusion chambers siliconized graphite is most inert during silicon evaporation, and the silicon partial pressures obtained in this case are close to the corresponding values recommended in handbooks and in the review [7].

The temperature dependence of the partial vapor pressure of atomic silicon above its melt, measured in the temperature interval 1770–2035 K, is represented by the equation

$$\log p(\text{Si, Pa}) = (26580 \pm 602)/T + (14.25 \pm 0.31).$$

The experimentally determined partial vapor pressure of monatomic silicon at 1850 K was 0.644 Pa.

In the course of the work a choice was substantiated for the starting reagents on the basis of the experimental-theoretical data. Synthesis was performed by a hybrid method combining sol-gel technology and high-temperature chemistry in a gaseous medium (carbon-thermal synthesis), nanosize SiC in the form of 20–50 nm particles, whiskers and fibers < 50 nm in diameter and 200–400 nm long ($l/d = 5–60$) in the pores of the ceramic material.

Figure 3 shows the microstructure of SiC–SiC ceramic composite material after the pores are filled with nano-size SiC.

We note that at 1850 K not only carbon monoxide but also carbon dioxide (carbon precursors) as well as, besides

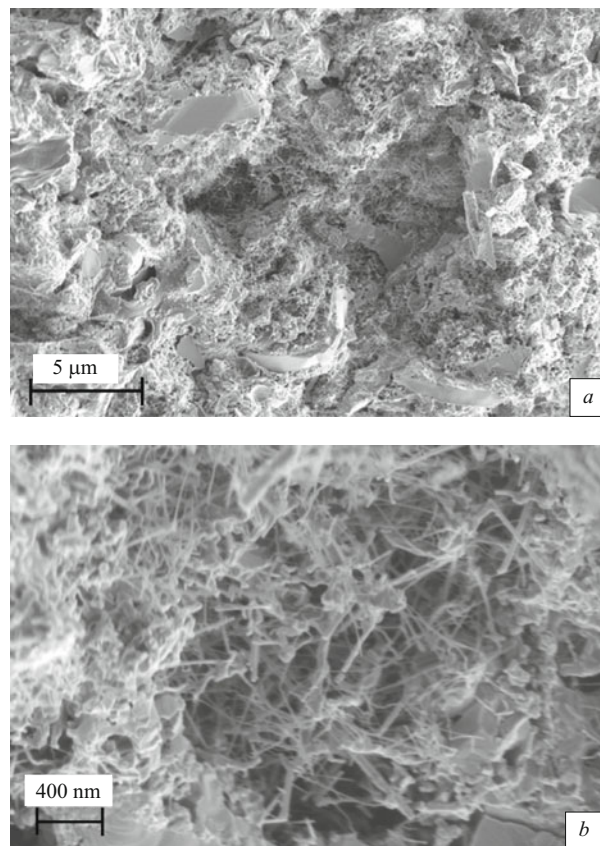


Fig. 3. Microstructure of SiC–SiC ceramic material: *a, b*) after nanosize SiC fills pores.

silicon, silicon monoxide (silicon precursor) are present in the system. This presupposes the possibility of a number particle, whisker, and fiber growth processes occurring. Further studies are needed to control these processes and to discover the reactions determining the synthesis of fibrous silicon carbide.

Compositions and methods of obtaining carbon glass-ceramic composite material (CGCCM) based on carbon reinforcing fillers and a glass matrix for working temperature 700–800°C with strength to 800 MPa and density < 2 g/cm³ have been developed. Two of the most important advantages of composite materials with a glass or glass-crystal matrix are the low cost of the raw material used to prepare the matrix (oxides of silicon, calcium, sodium, and so on) and the relative simplicity of the preparation methods. The unique technology developed on the basis of the sol-gel method in combination with the use of fine and ultrafine glass-forming particles and active technological additives makes it possible to form a glass matrix and secure protection by a reinforcing phase without resorting to high temperatures and pressure, as in the case of the production of conventional ceramics [8].

Figure 4 shows the microstructure of carbon-glass-ceramic composite material.

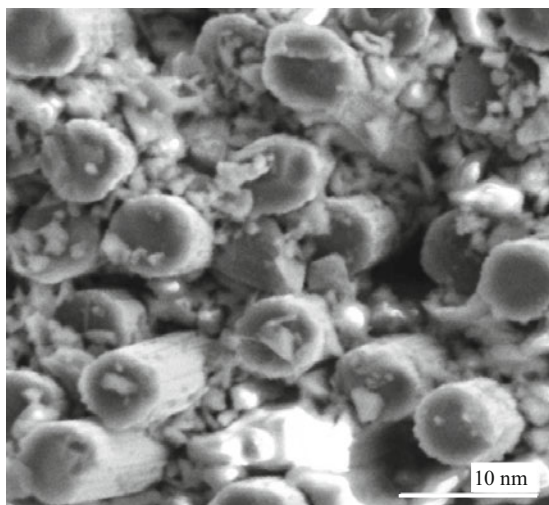


Fig. 4. Microstructure of glass-matrix CGCCM; $\times 1000$.

Technical Characteristics of Carbon Glass-Ceramic Composite Material

Working temperature, °C	700 – 800
Density, g/cm ³	< 2.0
Ultimate strength under 4-point bending, MPa	800
Heat tolerance (800°C \leftrightarrow 20°C, 1 cycle – 1.5 min)	> 1000 cycles
CLTE at 20 – 800°C, K ⁻¹	(0.8 – 1.15) $\times 10^{-6}$

In the course of developing a technology for producing a composite material for fabricating structural components, such as the thrust rings of the working wheel of a high-pressure compressor of prospective engines, matrix organohydride suspensions, synthesized by the sol-gel method together with functional technological surfactant additives, as well as a technology for impregnating the suspension into the reinforcing elements in the form of unidirectional carbon ribbons, cords and fabric fillers of the volume structure, were developed. This made it possible to obtain the prescribed degree of filling and directed anisotropy, which secure the required structural and functional properties of heat-loaded elements made of ceramic materials [9].

The use of carbon fibers for reinforcing glass makes it possible to obtain a wide diversity of fiber – glass systems. For such a system the type and structure of the carbon filler have a large effect on the properties of the ceramic materials. The studies showed that there is an advantage to using composites obtained on the basis of high-modulus carbon fibers

over high-strength fibers with respect to the mechanical properties and operating temperature.

The high-temperature glass-ceramic and ceramic composite materials, developed at VIAM, with density 2 – 4 times lower than that of metallic alloys are intended to be used as structural and functional elements in the prospective aviation, space and machine engineering articles as well as in other fields.

Aviation and machine engineering enterprises together with academic, educational and other institutes are developing technologies for manufacturing heat-loaded structural elements to be used in the prospective technology from glass-ceramic and ceramic materials.

The high-temperature composites now under development, distinguished by unique operating properties and possessing a number of technological advantages, are good as and with respect to some characteristics surpass foreign analogs.

REFERENCES

1. N. A. Shabanova and P. D. Sarkisov, *Principles of Sol-Gel Technology of Nano-Silica* [in Russian], Akademkniga, Moscow (2004).
2. S. S. Solntsev, D. V. Grashchenkov, and N. V. Isaeva, “High-temperature composite materials for advance parts for aviation and machine engineering,” *Konversiya v Mashinostroenii*, No. 4, 60 – 64 (2004).
3. H. Schefer, *Chemical Transport Reactions (Gas-Phase Transport of Inorganic Substances and Its Application)* [Russian translation], Mir, Moscow (1964).
4. W. Wesch, “Silicon carbide: synthesis and processing,” *Nucl. Instrum. Methods Phys. Rev. B*, **116**, 305 – 321 (1996).
5. J. J. Biernacki and G. P. Wotzak, “Stoichiometry of the C + SiO Reaction,” *J. Am. Ceram. Soc.*, **12**(1), 122 – 129 (1989).
6. S. I. Lopatin, V. L. Stolyarova, V. G. Sevast’yanov, et al., “Determination of the saturated vapor pressure of silicon by the spectrometric Knudsen effusion method,” *Zh. Neorg. Khim.*, No. 2, 262 – 269 (2012).
7. V. G. Sevast’yanov, N. T. Kuznetsov, Yu. S. Ezhov, et al., “Experimental and theoretical determination of the saturation vapor pressure of silicon in a wide range of temperatures,” *Russian J. Inorg. Chem.*, **55**(13), 1 – 16 (2010).
8. E. N. Kablov, S. S. Solntsev, and D. V. Grashchenkov, “Properties of carbon-glass-ceramic composites,” in: *Proc. 10th Intern. Ceramics Congress, CIMTEC-2002 and 3rd Forum on New Materials*, Florence (2002), pp. 176 – 182.
9. E. Kablov, S. Solntsev, and D. Grashchenkov, “Investigation of carbon-glass-ceramics composites,” in: *HTCMC 5: 5th Intern. Conf. on High-Temperature Ceramic Matrix Composites*, American Ceramic Society, September 12 – 16, 2004, Seattle, Washington, pp. 223 – 227.