ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 5, pp. 986–991. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © E.N. Kablov, D.V. Grashchenkov, N.V. Isaeva, S.St. Solntsev, 2010, published in Rossiiskii Khimicheskii Zhurnal, 2010, Vol. 54, No. 1, pp. 20–24.

Perspective High-Temperature Ceramic Composite Materials

E. N. Kablov, D. V. Grashchenkov, N. V. Isaeva, and S. St. Solntsev

All-Russian Scientific Research Institute of Aviation Materials Federal State Unitary Enterprise, State Research Center of the Russian Federation (RIAM), ul. Radio 17, Moscow, 105005 Russia
e-mail: admin@viam.ru

Received December 1, 2009

Abstract—The high-temperature glass-matrix and ceramic-matrix composites developed by the RIAM are overviewed. The distinctive properties of the developed composites are their high stability at temperatures above 1200°C in an oxidizing medium, high endurance and corrosion resistance, and low density and thermal expansion. Therefore, these composites are unique for production of heat-loaded units and parts of advanced engines. A characteristic feature of the SiC/SiC ceramic-matrix composite is its high resistance (by contrast to traditional monolithic ceramics) to thermocyclic loadings in the medium of fuel combustion products, which is due to its regulated and manageable structure.

DOI: 10.1134/S107036321105029X

The progress of engine building is associated with an increase of the input–output ratio of engines and a decrease of their weight and environmental hazard. One the ways to approach these problems consists in increasing the temperature of gas at the turbine inlet. However, increased gas temperature creates demand for effective cooling of metal components of a hot engine part or development of new thermally stable composite materials. At present no metals or alloys for such thermally loaded components as fire tubes, which would be capable of prolonged operation at temperatures above 1300°C without forced cooling, are available. Thus, the best of known fire-resistant alloys cannot be operated for a long time at temperatures above 1100–1200°C. The high density of metal alloys, sensitivity of their mechanical characteristics to elevated temperatures (600–900°C), as well as limited resources and high cost of such alloy components as Co, Ni, Cr, W, Ti, Mo, Re, etc., much decrease the efficiency and economic profitability of their application.

In this connection special interest is attached to high-temperature composite materials (CMs). Compared with metals, CMs possess a number of unique characteristics and offer such advantages as resistance to oxidation at temperatures above 1200°C, good durability, excellent corrosion properties, low density, and a low heat expansion. This all makes CMs choiceless candidates for application in thermally loaded components of future aircraft and space vehicles, power-, oil- and gas-transfer systems, as well as in new general and special machine-building fields.

Ceramic CMs meet more stringent requirements to the specific material strength and fuel efficiency, noise level, and environmental impact of engines.

Domestic producers scarcely developed the market of structural ceramic composites and articles made of such materials, even though Russia possesses quite favorable technological and scientific prerequisites for that. Raw materials for high-quality powders are easily accessible and inexpensive. Modern powder production, molding, and thickening technologies are rapidly developing. A lot of progress is observed in quality assessment of materials and understanding the nature of their durability.

Analysis of the literature and general trends in high-temperature materials science shows that much research effort is presently directed to ceramic composites. R&D in the field of ceramic composite materials (CCMs) and coatings is in progress at major companies in the USA, France, Germany, Japan, China, etc., and commercialization of research results has already commenced.

Extremely active research is being performed abroad on the performance of fire tubes of composite materials. Fire tubes of SiC/SiC ceramic composites into the annular combustion chambers of Solar Turbines stationary gas turbines. The fire tubes were designed by Honeywell Advanced Composites and B.F. Goodrich Aerospace. The following technologies were involved in the fabrication of composite fire tubes: chemical vapor infiltration (CVI) and melt infiltration (MI). The SiC/SiC composite fire tubes were tested Centaur 50S engines [1].

Of interest are the results of research of General Electric (GE) in the framework of DOE's program for developing a ceramic stationary gas turbine (CSGT). There have been developed and experimentally tested ceramic segments of fire tubes, which allow the temperature of fire tube walls to be raised to 1200°C and above.

Many foreign companies developing structural CCMs for new engines decided in favor of composites with SiC or Si_3N_4 matrices reinforced by SiC or C fibers, or mixtures of these two fibers. The processes of sintering of finished ceramic powders and fibers, as well as sol–gel technologies allowing production of more stable items with lower expenses.

It was noted that the most challenging problems were associated with the choice of fibers and methods to obtain fibers of required purity, since oxide fibers do not provide sufficient mechanical characteristics, whereas oxygen-free fibers like SiC are prone to oxidation during service.

Research into this issue resulted in the development and commercialization of new fibers with improved characteristics. The first to be mentioned are Nippon Carbon Hi-Nicalon SiC fibers. The traditional Nicalon fiber contains 10–12% of oxygen which induces oxidation of the fiber at high temperatures. The composite material with Hi-Nicalon, where oxygen had been removed by radiation treatment, exhibited much better thermostructural characteristics that superalloys at temperatures above 1200°C. Later Dow Corning under the sponsorship of NASA developed a SiC fiber which was a representative of a new generation of continuous fibers and comprising a stoichiometrically pure SiC and minor boron-containing additives for enhancement of oxidative and high-temperature stability.

Compared with the best high-temperature metal alloys, SiC_f/SiC ceramic composites (SiC matrix reinforced with woven or continuous SiC fibers) have reduced density (by about 30–50%) and thermal expansion coefficient (by about 60%) and are potentially capable of operating at temperatures of up to 1600–1650°C (based on the behavior of SiC monolith). However, whether this potential will be implemented depends to a great extent on success in the improvement of the structure of SiC_f/SiC ceramic composites, especially as relates to the intermediate phase (interphase) for fibers and matrix components.

Nonoxide ceramic materials contain a large fraction of covalent bonds, and, consequently, low diffusion rates, and, therewith, compacting at technological limits by conventional sintering technologies is not infrequently impossible. An alternative technology involves liquid or gas phase-mediated compaction. New composite materials are developed using other technologies: sol–gel technology, CVI, or CVD (chemical vapor deposition), which allow generation of nanodispersions in material compositions.

The best results of high-temperature tests were obtained with SiC_f/SiC ceramic composites including continuous SiC fibers and a SiC matrix.

Specialists of NASA developed 5 base SiC_f/SiC ceramic composites for thermally loaded components of perspective engines [2]. As continuous SiC fibers there were used ATK COI Ceramics Sylramic fibers, with Si-doped BN interphase protective coatings. When the hybrid matrix was formed by the CVI technology, the residual open pores were filled by infiltration of a slurry of SiC particles or liquid-phase impregnation with silicon melt or a SiC-forming polymer. It was found that at 1315°C for 500 h silicon diffuses through grain boundaries of the SiC matrix and interacts with the BN coating and SiC fibers, thereby adversely affecting the composite properties. It was shown that increasing the SiC content in the hybrid matrix allows to slow down this reaction but cannot make the composite stable enough to work at a temperature of 1427°C for more than 100 h. A composite capable of withstanding temperatures of up to 1427°C (even though while having a high residual porosity of 15 vol %) could be obtained by multiple impregnation of the SiC_f/BN/SiC composite with a SiC-forming polymer followed by pyrolysis.

The properties of the SiC_f/SiC material could be improved by using interphase protective coatings on the basis of boron-containing compounds (BN or B_4C) on continuous SiC fibers, which served not only for matrix crack deflection, but also enhanced resistance to oxidation and prevented fiber degradation.

Controlled deposition of SiC, B_xC, Si–B–C, and Si–B–N layers was used to obtain multilayer (hybrid) composite materials. The layered SiC-SiC materials with B_4C and BN interphase protective coatings, obtained in Si–B–C or Si–B–N ternary systems by the CVI technology possess matrix self-healing properties. The oxidation resistance of the SiC_f/BN/SiC composite a BN interphase coating at moderate temperatures is better compared with SiC_f/C/SiC which contains no boron compounds. It was shown that silicon-doped BN favors lower weight losses. A combination of the ability of B_xC and Si–B–C used together with SiC in multilayer matrices to self-healing and the ability of the viscous BN interphase to deflect microcracks from fibers impart to the composite material the ability to preserve its properties in an oxidative medium at temperatures of up to 1450°C.

Gotoh and Tokaji [3] reported a CCM developed for the forebody and leading edges of space shuttles, which makes it possible to increase the working temperatures above 1600°C and ensures resistance of the construction to oxidation under spacecraft re-entry. The material is a mixture of SiC and ZrB_2 particles, prepared by press molding and sintering. The presence of SiC particles favors a higher oxidation resistance, since one of the oxidation products is a borosilicate glass which seals pores and prevents oxygen diffusion to SiC and ZrB_2 grain boundaries. A disadvantage of this material is its fairly short service life (a total of no longer than 100 h), which is associated with cyclic working conditions at space shuttle re-entry.

Igawa and Taguchi [4] reported successful testing of discharge jet flaps manufactured from the SiC_f/SiC composite obtained by the sol–gel and infiltration technologies. The sol–gel technology was also used to obtain the SiC_f/SiC composite with Hi-Nicalon S fibers coated with SiO_2–MgO or SiO_2–Mg_xSi_yO interphase layers amorphous up to 1200°C and 1400°C, respectively [5].

Silicon–nitride–carbide fibers and matrices $Si_3BC_4N_2$, whose high thermal stability (up to 1500°C) is associated with a positive effect of boron on the stability of metastable amorphous phases of a SiO_2 material [6].

The chemical purity of the materials and coatings obtained by chemical vapor deposition (CVD technology) is much higher than those obtained by the sol–gel technology. On the other hand, the sol–gel method makes it possible to prepare volume-doped samples, whereas on attempted preparation of such samples by gas infiltration (CVI procedure) serious problems arise, associated primarily with the necessity to ensure a uniform volume distribution of the disperse component.

The sol–gel technology forms highly dispersed and active oxides [7], whereas CVD is capable of producing, along with oxides, binary compounds directly. However, the CVD process not infrequently forms toxic or explosive by-products: hydrogen, gaseous and hot HCl and other hydrogen halides, hydrocarbons, etc.

Comparative assessment of the levels of technological development showed that the foreign technology of the production of SiC-matrix CCMs by chemical vapor deposition uses a complex special equipment, is expensive due to high energy consumption (some technological operations take up to half a year) and use costly continuous SiC fibers as a reinforcing structural element (up to 6000 USD/kg). Analysis of performance characteristics of the best foreign CCMs reinforced with SiC fibers (Hi-Nicalon, Sylramic) showed that the working temperatures of such SiC–SiC composites in oxidative media are no higher than 1400–1450°C.

In Russia until present no analogs of continuous SiC fibers used in foreign countries as the basic CCM reinforcing material have been developed. The need in independent R&D on high-temperature CCMs is motivated by economic and technological safety reasons.

The basic process which predetermines the structure and properties of the SiC–SiC-type CCM developed at the RIAM is high-temperature synthesis involving physical (evaporation–condensation, liquid phase–mediated recrystallization, diffusive viscous flow, etc.) and chemical processes forming matrices and whole composites [8].

The high-temperature synthesis involves directed formation, at the micro and nano levels, of a continuous SiC carcass, where reinforcing particles are incorporated in the structure of the matrix formed by high-temperature synthesis from the starting components. Microstructural analysis revealed an embedded heterogeneous polycrystalline structure with an inconsiderable closed porosity and the prevailing crystal size of 0.1–5 μm. Figure 1 shows the microstructure of a SiC–SiC-type CCM.

High-temperature chemical synthesis allows one to control the structure of CCMs and vary purposely such their properties as density, porosity, strength, etc.

It is known that materials with a coarsely dispersed unordered structure and appreciable pore volume exhibit worsened properties. However, as shown in

Fig. 2, the same structural features can pose barrier for and localize microcracks.

The SiC–SiC-type CCM characteristically exhibits a high resistance (unlike traditional monolithic ceramics) to thermocyclic loadings (1550°C ↔ 800–850°C) in an oxidative medium (fuel combustion products). The material withstands more than 5000 cycles without damage (1 cycle/min).

Controlling the structure of this CCM is one of the principal ways to enhancing its crack resistance and strength.

It should be noted that this material features quite a high oxidation resistance. At 1500–1550°C, no weight loss was detected for a long time (up to 500 h); vice versa, weight gain is observed. Such behavior is obviously explained by the formation on the surface of silicon carbide grains in the oxidative media of a thin amorphous silica film which blocks oxygen diffusion into material bulk and favors defect self-healing by closing pores, cracks, etc. Figure 3 shows the surface microstructure of the CCM with a self-healed microcrack.

The self-healing process favors maintaining initial mechanical characteristics and improving protective characteristics at high temperatures.

The SiC–SiC-type CCM has the following technical characteristics: working temperature 1500–1550°C in an oxidative medium (fuel combustion products); density 2.5–2.9 g cm^{-3}; porosity 5–8%; 4-point flexural bend strength 180–200 MPa at 20°C and 1550°C; thermal conductivity 45–50 W m^{-1} K^{-1} at 20°C and 30–35 W m^{-1} K^{-1} at 1000°C; thermal linear expansion coefficient (TLEC) 4.9–5.2×10^{-6} 1/°C (20–1550°C).

At present experimental technology tuning and fabrication of segments of the combustion chamber for perspective engine assemblies made of CMs on the basis of SiC–SiC-type oxygen-free ceramics. Figure 4 shows some SiC–SiC ceramic segments and a model of the combustion chamber lined with these segments.

The research resulted in the development of formulations and production technologies for a carbon glass ceramic composite material (CGCCM) on the basis of carbon reinforcing fillers and a glass matrix, having the working temperature 750–800°C, strength up to 800 MPa, and density lower 2 g cm^{-3}. One of the key advantages of CMs with glass and crystalline glass matrices is a low cost raw materials (silicon, calcium,

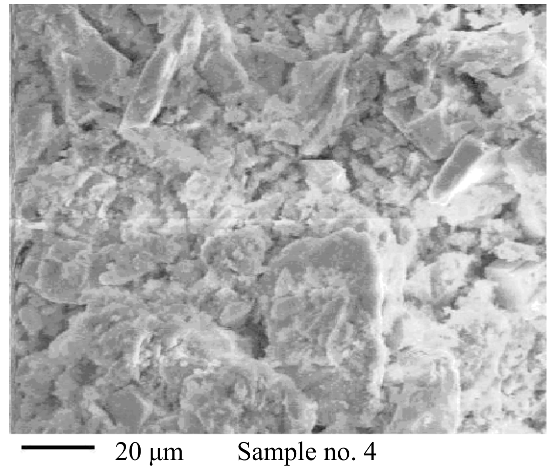

Fig. 1. Microstructure of a SiC–SiC-type CCM.

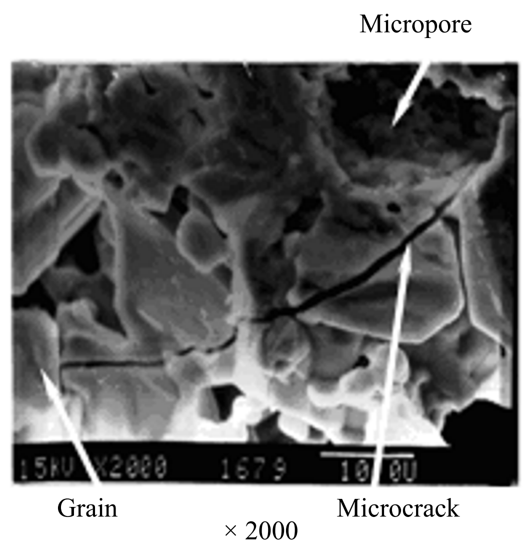

Fig. 2. Localization of microcrack in CCM.

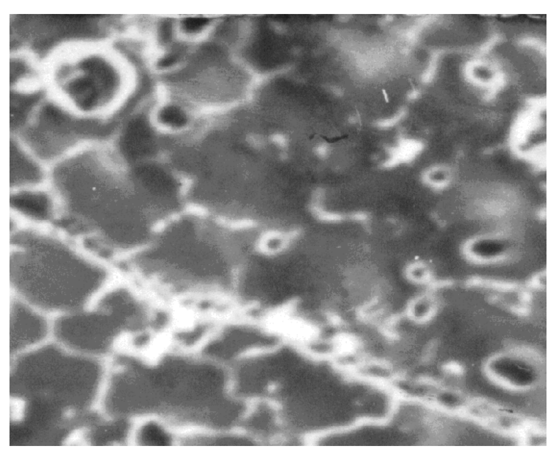

Fig. 3. Effect of microcrack self-healing on CCM surface.

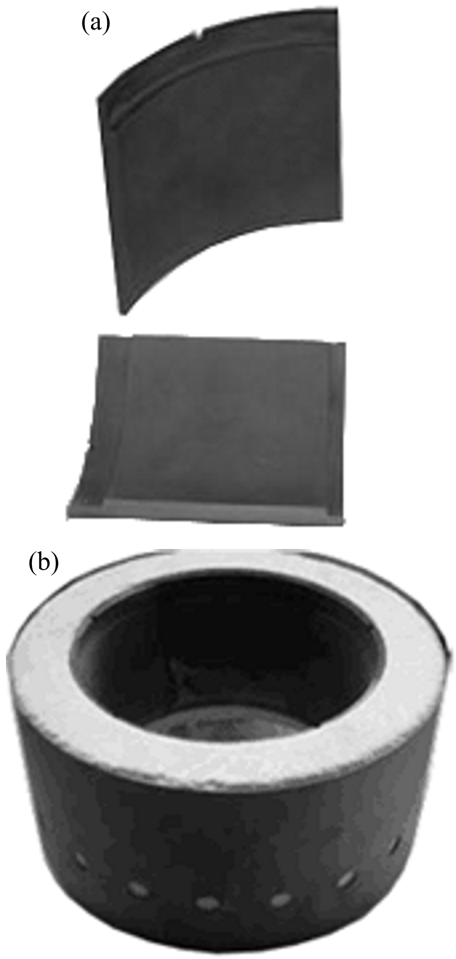

Fig. 4. (a) Ceramic lining segments and (b) model of a perspective combustion chamber.

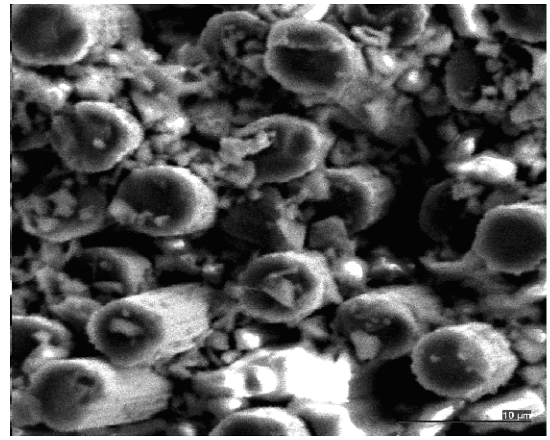

Fig. 5. Microstructure of a CGCCM sample with a glass matrix.

sodium, and other oxides) and relatively simple matrix production technologies. The developed unique sol–gel technology using fine or ultradispersed particles and active technological additives allows forming a glass matrix and protected reinforcing phase without high temperatures and pressures, like with traditional ceramics. Figure 5 shows the microstructure of a CGCCM sample.

During development of the production technology for CMs for such structural elements as strong rings for high-pressure compressor rotor wheels for perspective engines, matrix organic hydro suspensions were also developed. They are synthesized by the sol–gel technology by introducing functional surfactant additives. A technology for impregnation of suspensions into reinforcing elements, specifically carbon unidirectional tapes, bundles, and 3D fabric fillers, which provided preset filling degrees and directed anisotropy, thereby providing the required structural and functional characteristics of thermally loaded CM elements [9].

The technical characteristics of the CGCCMs are as follows: working temperature 800°C; density lower 2.0 g cm^{-3}; 4-point flexural bend strength 800 MPa; thermal stability (800°C↔20°C, 1cycle/1.5 min) more than 1000 cycles without damage; TLEC (0.8–1.15)× 10^{-6} 1/°C (20–800°C).

The use of carbon fibers for reinforcing glass opens the way to a wide variety of fiber–glass systems. In such systems, the type and structure of the carbon filler strongly affect the properties of the CM. Composites on the basis of high-modulus carbon fibers excel those on the basis of high-strength carbon fibers in mechanical characteristics and working temperatures.

The RIAM developed perspective high-temperature glass ceramic and ceramic composite materials for structural and functional elements of aviation and space technics, engine- and machine-building, and other applications, whose specific weight is 2–4 times lower compared with metal alloys. The RIAM together with academic, higher education, and other institutions, as well as aircraft- and machine-building enterprises is presently developing production technologies for thermally loaded structural elements made of glass ceramic and ceramic composite materials which compare with foreign analogs in performance characteristics or even excel them in certain parameters.

REFERENCES

1. Andrees, G., Filsinger, D., Miinz, S., Schulz, A., and Wittig, S., *J. Eng. Gas Turbines Power*, 2001, vol. 123, pp. 271–274.
2. DiCarlo, J.A., *J. Am. Ceram. Soc*., 2005, vol. 87, pp. 104–112.
3. Gotoh, J. and Tokaji, K., *J. Ceram. Soc. Jpn.,* 2002, vol. 110, no. 1285, pp. 852–858.
4. Igawa, N. and Taguchi, T., *J. Nucl. Mater*., 2004, pp. 329–333.
5. Ravi Kumar, N.V., Mager, R., and Zimmermann, A., *Scr. Mater*., 2004, vol. 51, no. 1, pp. 65–69.
6. Shabanova, N.A. and Sarkisov, P.D., *Osnovy zol'-gel' tehnologii nanodispersnogo kremnezema* (Fundamentals of the Zol–Gel Technology of Nanodospersed Silica), Moscow: Akademkniga, 2004.
7. Solntsev, S.S., Grashchenkov, D.V., and Isaeva, N.V., *Konversiya v mashinostroenii* (Conversion in Machine Building), Moscow: Informkonversiya, 2004, no. 4, pp. 60–64.
8. Kablov, E.N., Solntsev, S.S., and Grashchenkov, D.V., *Proc. 5th Int. Conf. on High-temperature Ceramomatrix materials (HTCMC5)*, Seattle, WA: ACS, 2004, pp. 223–227.