MAIN AREAS FOR IMPROVING REFRACTORY FIBER-REINFORCED CERAMIC MATRIX COMPOSITE CORROSION AND HEAT RESISTANCE (REVIEW)

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A review and analysis are provided for the state and development rends of contemporary approaches to the problem of improving the corrosion and heat resistance of fiber-reinforced ceramic matrix composite materials. The main approaches are considered for resolving this problem based on modifying the composition, internal structure, and surface of composites, including: use of the best thermodynamically stable corrosion- and heat-resistant reinforcing fibers; application of a protective coating to reinforcing fiber surfaces; matrix modification with micro- and nano-size fillers providing a "self-healing" effect with occurrence of composite microstructure during operation in corrosive media; application of corrosion- and heat-resistant surface layers.

Keywords: ceramic matrix composites (CMC), reinforcing fibers, corrosion- and heat-resistance, refractory ceramic, protective and inter-phase coating, "self-healing" effect.

INTRODUCTION

In planning structures and objects for high-temperature technology considerable attention is devoted to operating reliability in the high and ultra-high temperature ranges. Solution of this scientific and practical task is directly connected with development of new structural materials with a high level of property indices at engineering operating temperatures. Functional objects in these extreme conditions lay down special requirements for reliability of structural materials, which are specified primarily by stability of physicomechanical properties in a prescribed operating temperature range. Recently extensive research has been conducted in the field of material science and technology for new structural materials making it possible to use objects of these materials at high and ultra-high temperatures. Considerable effort has been aimed at improving metallic heat-resistant alloys. However, the reserves for an increase in high-temperature strength and chemical wear resistance for these alloys is almost exhausted, and they cannot subsequently have an operating temperature significantly exceeding 1150°C. For structural applications at high temperature and under conditions under action of oxidizing and corrosive media particular success has been achieved in the direction of preparing high-temperature composite materials (CM) with metal, carbon, or ceramic matrices [1].

It is apparent that with functioning of objects under conditions of actual high-temperature and corrosive media the most promising materials are CM with a matrix based on ultra-high temperature ceramic reinforced with filler particle, i.e., ceramic matric composites (CMC). The good corrosion- and heat-resistance of fiber-reinforced CMC is mainly determined by their ceramic matrix properties. The main properties of various high-temperature ceramics based on oxides, borides, carbides, and nitrides are given below [1 – 4]:

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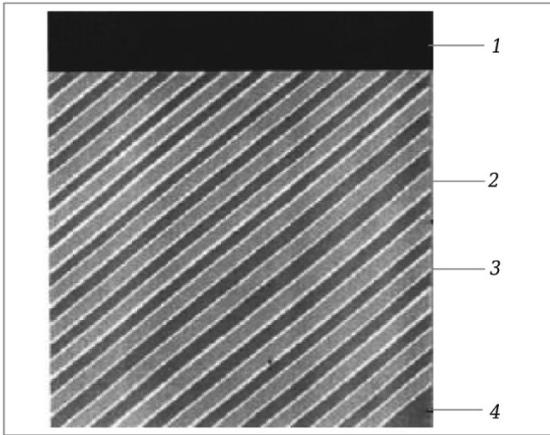| Material	SiO_2	Al_2O_3	BeO	ZrO_2	B_4C	HfB_2	HfC	HfN	ZrB_2	ZrC	ZrN	TiB_2	TiC	TiN	TaB_2	TaC	TaN	SiC	Si_3N_4
Density, g/cm^3	2.65	3.98	3.01	6.10	2.52	11.19	12.76	13.9	6.10	6.56	7.29	4.52	4.94	5.39	12.54	14.50	14.30	3.21	3.44
Melting temperature, °C	1610	2050	2550	2765	2450	3380	3900	3385	3245	3400	2950	3225	3100	2950	3040	3800	2700	2820	1900

Fig. 1. Main CMC components: *1*) outer coating; *2*) reinforcing fibers; *3*) inter-phase coating; 4) matrix.

It is noted that as a rule carbides have a higher melting temperature T_m compared with borides or nitrides of the same metal. From a practical point of view there is most interest in a matrix based on SiC [4]. The melting (sublimation) temperature of SiC is 2820°C with almost the lowest density of the materials provided.

For CMC it is possible to separate the main parameters governing their capacity to operate at high temperature and in corrosive media; thermodynamic stability of composite components in their operating temperature range; heat resistance of composites and the possibility of their operation under conditions of contact with oxidizing media at high temperature. Other general requirements concerning the properties of high-temperature CMC may also be low density, high thermal conductivity coefficient, low linear thermal expansion coefficient (LTEC), cost, and availability of starting components and composite preparation technology.

An overall structural layout of CNC is given in Fig. 1 intended for operation under high-temperature and corrosive media operating conditions [5].

Several basic approaches are used in practice for improving corrosion and heat resistance of CMC, which as a rule are based on modification of their properties, internal structure, and surface:

– use of more thermodynamically stable corrosion- and heat-resistant reinforcing fibers;

– application of a coating to the surface of reinforcing fibers providing improvement of CMC oxidation and heat resistance;

– modification of the matrix of micron and nanosize fillers providing a "self-healing" effect with occurrence of CMC microstructure defects during operation in corrosive media;

– application of corrosion- and heat-resistant surface layers.

USE OF THE MOST THERMODYNAMICALLY STABLE CORROSION- AND HEAT-RESISTANT REINFORCING FIBERS

The main factors governing the properties of fiber-reinforced CMC are: physicomechanical properties of the components themselves; geometric, adhesive, chemical, mechanical, thermophysical indices of fiber and matrix material compatibility. Among a large number of inorganic fibers satisfying these compatibility specifications, in order to reinforce a ceramic matrix it may be possible to use that that withstand the temperatures for preparation and operation of CMC. In order to reinforce high-temperature CMC there has been greatest use of carbon and ceramic fibers based on various nitride, carbide, boride, and oxide compounds. Currently world industry is producing a large of number of carbon and ceramic fibers whose operating properties may differ over very wide ranges (Table 1). Summarized information is provided for grades of fiber that may be used for creating CMC operating under conditions of high temperature and action of corrosive media.

Carbon fibers

Carbon fibers (CF) are used most often and are available for reinforcing CMC, which with respect to a number of indices exhibit unique mechanical and physical properties: good heat resistance, low LTEC, high resistance to atmospheric action and chemical reagents. They are distinguished by good mechanical property indices, whose level increases at

TABLE 1. Inorganic Fiber Composition Used for CMC Reinforcement [6]

Properties	High-modulus carbon fiber	Coreless SiC-fibers	SiC-fiber on tungsten substrate	Coreless Al_2O_3-fiber
Filament diameter, μm	6.7 – 7.5	9 – 15	100 – 140	15 – 25
Ultimate tensile strength, MPa	2.5 – 3.5	1.9 – 3.0	2.5 – 3.7	1.2 – 1.4
Young's modulus, GPa	320 – 390	180 – 200	380 – 420	340 – 400
Density, g/cm³	1.8 – 1.9	2.55 – 2.58	3.4 – 3.5	3.90 – 3.95
LTEC along fiber α, 10^6 1/K	0.2	3.1	4.2 – 4.5	7.0 – 8.6
LTEC across fiber axis α, 10^6 1/K	10 – 15	3.1	4.2 – 5.2	7.0 – 8.6

high temperature up to 3000°C. A serious disadvantage of CF is their high sensitivity towards action of an oxidizing medium, leading to thermochemical degradation of fibers at above 400°C. This significantly complicates use of CF in composites that are intended for operation at high temperature in oxidizing media.

The CF used in CMC are prepared by high-temperature heat treatment of starting organic fibers (cellulose hydrate (CH), polyacrylonitrile (PAN), and pitch), as a result of which volatile products are removed from polymer and a solid residue forms, i.e., a carbon (coke) residue) [7 – 9]. The high-temperature process for CF preparation is normally conducted in two stages, differing in final treatment temperature. The first stage is carbonization and proceeds in the range 900 – 2000°C. The second stage in graphitization performed at up to 3000°C. In selecting CF for CMC intende7d for operation under ultra-high temperature conditions it is necessary give preference to fibers subjected to the graphitization stage at the maximum temperatures. These CF are more thermally stable compared with fibers whose manufacturing process was limited to the carbonization stage. In carbonized fibers at temperatures exceeding the maximum process temperature there may be processes of formation of an original coke structure that was incomplete in the carbon-

ization stage, which leads to composite instability it a high operating temperature (T_{oper}). Physicomechanical properties of some grades of high quality CF are given in Table 2 [7, 10 – 12].

Ceramic fibers

Among continuous ceramic fibers we separate those based on SiO_2 (silica and quartz), SiC, Al_2O_3, B_4C, BN, Si_3N_4, and ZrO_2. For objects operating under ultra-extreme high-temperature conditions and acid-containing media there has been relatively extensive use of CMC with SiC and Al_2O_3 fibers.

Currently coreless SiC fibers are most promising that are mainly prepared by thermal decomposition of starting polymer fibers formed from polycarboxylate. Results of studies in the field of creating SiC fibers of this type have developed three generations of fibers [13], each of which is characterized by its own operating temperature range limits (Table 3). It has been shown that the most thermally stable fibers are the third generation.

The third generation of stoichiometric SiC fibers such as Hi-Niacalon, Tyranno SA, and Sylramic are highly crystalline fibers stable at very high temperature (1600 – 1800°C and above) and exhibit creep resistance up to 1400 – 1500°C

TABLE 2. Carbon Fiber Physicomechanical Properties*

Fiber grade	Starting raw material	d, μm	ρ, kg/m^3	σ_{ten}, MPa	E, GPa	ε, %
			Russian product			
VMN-4	PAN	6 – 7	1710	2210	270	0.80
VMN-5	GTs	—	1750	2750	410	0.70
Kulon M	PAN	7 – 8	1900	3000	600	1.30
Saturn	PAN	—	1700	5000	300	1.70
YKN-P 5000	PAN	7 – 8	1750	2500 – 3000	450 – 500	1.30
GZh-23	PAN	5	1950	2400	450	—
			USA product			
Fortafil 5	PAN	—	1800	2760	330	0.80
Khiteks 46-N	GTs	5.0	1800	5600	322	1.70
Tselion GY-70	PAN	—	1960	1860	520	0.36
Tornel 50	GTs	6.6	1670	2200	400	0.55
Tornel 75	GTs	—	1820	2650	520	0.50
Tornel R55	Pitch	10.0	2000	2100	380	0.55
Tornel R100	Pitch	—	—	2400	690	0.35
Tornel 800	GTs	6.0	1800	5460	273	2.00
			Japanese product			
Toreika T-800	PAN	5.1	1800	5000	250	2.00
Toreika T-1000	PAN	5.1	—	5500 – 7200	300	1.90
Toreika M-40	PAN	6.5	1800	2500	400	0.60
Besfait HM45	PAN	6.4	1900	1800	440	0.35

* d is reinforcing fiber diameter; ρ is density; σ_{ten} is ultimate tensile strength; E is Young's modulus; ε is limiting strain with tension.

and have a high thermal conductivity coefficient ($\lambda = 20 – 65$ W/(m·K) at 25°C). These SiC-fibers exhibit good thermal stability compared with (Si–C–O) fibers of the first and second generations that make it possible to avoid degradation of fiber properties in the course of CMC preparation. Disadvantages of this type of fiber concern the low adaptability and the difficulty in processing into objects of complex shape. Therefore they are used as a rule limited to objects operating at very high temperature.

Of recent achievements in the field of developing technology for producing SiC fibers it is necessary to separate those developed several years ago by Ube Industries Ltd (Japan) SA Turanex fiber, which are currently the most perfect from the point of view of structure and are characterized by the following best properties: they have a thermal conductivity coefficient of 64 W/(m·K) at room temperature and 30 W/(m·K) at 1000°C [14]. These fibers retain strength up to 1600°C.

However, a serious limitation for expansion of the field of application of SiC fibers is their relatively low production volume and high cost. The production volume of SiC fibers reaches tens of tons per year (62 – 70 tons) [14]. On one hand this makes it possible to talk about a change-over from

the stage of research to test work for production and practical use of composites based upon them. On the other hand this volume is incompatibly small with the volume of output of carbon fibers. The cost of third generation SiC fibers reaches 10,000 US$ for 1 kg.

Refractory oxide fibers from the point of view of oxidation resistance may compete with other ceramic fibers and be considered as the best form of CMC filler calculated for a prolonged operating life at high temperature in oxidizing media. Currently among oxide fibers the most well-known fibers based on Al_2O_3. The composition and main physicomechanical properties of different fibers of industrially produced Al_2O_3 materials and some other types of refractory ceramic fibers are given in Table 4 [7, 15].

COATING APPLICATION TO A REINFORCING FIBER SURFACE

It is well known that a weak area of both carbon and SiC fibers is high-temperature oxidation resistance. Carbon fibers start to react actively with oxygen at above 400 – 500°C with formation of gaseous oxides. Similar problems, only at temperatures above 800°C, also arise for SiC fibers when pro-

TABLE 3. Mechanical and Thermophysical Properties of the Main Types of SiC Fibers

Fiber generation	Fiber trade mark	ρ, g/cm^3	d, μm	T_{exp}, °C	σ^*, MPa	E^*, GPa	Thermal conductivity coefficient*, W/(m·K)	α, 10^6 1/K
First	Nicalon 200	2.55	14	1200	3000	200	3.0	3.2
	Tyranno LOX-M	2.48	11	1200	3300	185	1.5	3.1
Second	Hi-Nicalon	2.74	12	1300	2800	270	8.0	3.5
	Tyranno LOX-E	2.39	11	1300	2900	200	No data	No data
	Tyranno ZE	2.55	11	1300	3500	233	No data	No data
Third	Tyranno SA 3	3.10	7.5	>1700	2900	375	65.0	No data
	Sylramic	3.05	10	>1700	3200	400	46.0	5.4
	Hi-Nicalon Type-S	3.05	12	>1500	2500	400 – 420	18.0	No data

* At 20°C.

TABLE 4. Physicomechanical Properties of Refractory Compound Continuous Fibers

Fiber grade	Composition, wt.%	ρ, g/cm^3	d, μm	σ, MPa	E, GPa	ε, %	α, 10^6 1/K	T_{exp}, °C
FP	99.9 Al_2O_3	3920	20	1200	414	0.29	9.6 (900 – 1500°C)	1373
Nextel 610	99 Al_2O_3 / 0.2 – 0.3 SiO_2 / 0.4 – 0.7 Fe_2O_3	3750	10 – 12	1900	370	0.5	8.0 (100 – 1100°C)	No data
PRD-166	80 Al_2O_3 / 20 ZrO_2	4200	20	1460	366	0.4	9.0	No data
Altex	85 Al_2O_3 / 15 SiO_2	3200	15	1800	210	0.8	6.0	1523
Nextel 440	70 Al_2O_3 / 28 SiO_2 / 2 B_2O_3	3.05	10 – 12	2100	190	1.11	5.3	No data
Nextel 720	85 Al_2O_3 / 15 SiO_2	3.4	10 – 12	2100	260	0.81	6.0 (100 – 1100°C)	No data
Fiber BN	99.9 BN	2100	No data	2100	310	0.8	No data	No data
Fiber ZrO_2	99.9 ZrO_2	6270	No data	2600	470	No data	7.7	No data

cesses of their reaction with oxygen commence with formation of SiO_2. This limits use of these fibers in CMC that are intended for operation at high temperature in oxidizing media. An effective method for resolving this problem is fiber protection from oxidation by application at the surface of thin stable mono- and multilayer coatings resistant to oxidation forming a new interphase surface at the fiber-ceramic matrix boundary. The most important tasks in this development of effective protection of reinforcing fibers in CMC are [16]:

– choice of coating materials with good thermal and heat resistant indices ad maximum oxidation resistance;

– selection of material and properties of each layer of a multilayer coating providing minimum strength loss for the fibers themselves;

– provision of those properties of protective coatings that on one hand would good adhesion to a fiber (in order to maintain its oxidation resistance, and on the other hand the possibility of separation and pull-out of fibers from matrix (in order to increase CMC fracture toughness);

– choice of coating thickness that is connected with continuous coexistence and possible reduction in strength;

– provision of similar LTEC values for a coated fiber and matrix.

The protective materials considered most [16] are: carbides SiC, B_4C, ZnC, TiC, TaC, HfC; oxides SiO_2, Al_2O_3, TiO_2, ZrO_2, B_2O_3, HfO_2, CeO_2; borides TiB_2, ZrB_2, HfB_2; nitrides Si_3N_4, TiN, BN, AlN; and also composites of these ceramics. Heat resistance of these materials under operating conditions differs considerably. For example SiC and Si_3N_4 at 1250°C are only stable for a short time [17]. At higher temperature as a result of reaction of these compounds with oxygen formation of SiO_2 is observed ($T_m = 1610$°C) facilitating "healing" of coating defects and masking access for oxygen to a fiber surface.

For carbon fibers and composites that operate at high temperature in oxidizing media there is use of protection from oxidation by application at a fiber surface of this coatings of oxidation resistant ceramic. For example, in [18] methods are given for applying coatings of various ceramic materials (SiC and Si_3N_4). Research has shown that coatings in fibers facilitate and increase in oxidation resistance in oxidizing media although it is possible to fiber mechanical property indices. A composite of silicon carbide and titanium makes it possible to obtain material capable of operating in an oxidizing medium up to 1600°C for 100 h and up to 1850°C for 10 h [19]. At above 1800°C the protective properties of SiC do not develop due to formation of gaseous silicon monoxide by a direct oxidation reaction [20].

Relatively low resistance applies to oxides (especially of lighter metals) entering reaction with carbon at high temperature. In this case reduction of oxides by carbon at different temperatures (SiO_2 at 1200°C, TiO_2 at 1400°C, ZrO_2 at 1730°C, and HfO_2 at 1750°C) with formation of the corresponding carbides [17, 20].
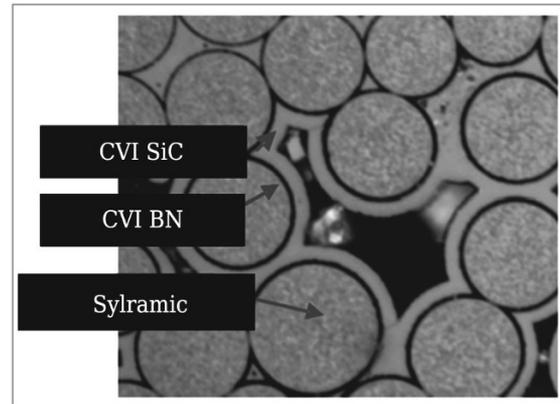

Fig. 2. Structure of CMC with BN coating of fibers and SiC matrix prepared by deposition from the gas phase by CVI technology.

Results are given in [21] for a comprehensive study of features of formation and properties interface coatings on reinforcing carbon and SiC fibers in CMC. Coatings have been prepared by reaction chemical deposition from a gas phase of refractory titanium, zirconium, hafnium, tantalum, vanadium and molybdenum carbides. Problems of synthesis in SiC fibers of nanosize coatings based on refractory oxides of aluminum zirconium and mixtures of them from hydrated gel precursors by a sol-gel method have been considered. It has been shown that application of refractory coatings on carbon and SiC fibers leads to a reduction in roughness and a decrease in adhesion in a ceramic matrix, which may facilitate separation and sliding of modified fibers within CMC. In this case fiber modification by the means developed does not lead to degradation of fiber mechanical properties increasing their oxidation resistance.

Results have been given in [22] for a study of the high-temperature efficiency of CMC of the SiC_f/SiC system with an interphase coating of fibers with BN. A coating and matrix were prepared by deposition from a gas phase by CVI technology (Fig. 2). It has been shown that CMC based on Sylramic fiber with a BN coating provides operating capacity of an object at 1350°B in an air atmosphere for more than 500 h, which is greater by a factor of five compared with CMC based on uncoated fiber.

The most resistant coatings are considered to be composites of HfB_2/SiC (80/20 vol.%), $T_m = 2277$°C; ZrB_2/SiC (80/20 vol.%), $T_m = 2017$°C; ZrB_2/C/SiC (54/30/14 vol.%), $T_m = 2110$°C [23]. It is noted that maximum values of operating for the most heat-resistant coatings for example HfB_2/SiC, are markedly lower than the melting temperature of the components of their composition: HfB_2 (3380°C) and SiC (2820°C).

An important problem in creating CMC with barrier coatings is conformity of the base and coating LTEC. A considerable difference between them may serve as a reason for occurrence of internal stresses at interfaces leading to crack
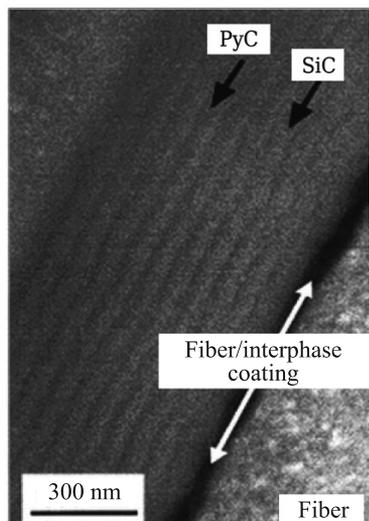
Fig. 3. Microphotograph of interphase layer of Hi-Nicalob fiber/SiC matrix consisting of a multilayer coating (PyC–SiC)n.

development. In this case two approaches are considered for resolving the problem [16]:

– creation of single- or multilayer coatings of compounds with LTEC close to that of a fiber and binder;

– creation of multilayer coatings, including a damping layer, providing conformity for operation of a base and coating.

The best interphase materials for SiC-fibers may be materials with a layered crystal structure or microstructure with layers deposited parallel to a fiber surface, weakly bonded with each other, but securely touching a fiber [24]. Most suitable from a mechanical point of view and often used material contains a thin layer (50 – 200 nm) of anisotropic pyrocarbon deposited by a CVD method from hydrocarbon. However, pyrocarbon is not oxidation resistant. In view of this versions have been proposed of interphase layers with the best oxidation resistance. For example, hexagonal BN is used with a layered crystal structure close to that of graphite, which is also a good mechanical bridge. Its oxidation commences at high temperature (700°C compared with 400°C for carbon), and it forms oxide (B_2O_3) that s retained in a greater temperature range and is well known for its "self-healing" properties. However BN interphase layers prepared by deposition on SiC fibers by a CVD method at relatively low temperature are weakly crystalline and sensitive both to oxidation and to moisture. Its crystallinity may be improved by heat treatment if the fibers are thermally stable, as for example stoichiometric SiC fibers.

Another concept for creating interphase coatings with improved oxidation resistance includes creation of multilayer (n layers) interphases at an interface having an $(X - Y)n$. Here X is a layer of pyrocarbon (PyC) or hexagonal BN, creating a weak interface of fiber — matrix required for providing composite crack resistance; Y is a layer of SiC be-

ing a source of Si for formation of a protective SiO_2 film, increasing interphase oxidation resistance. Therefore, we are talking about creation of (PyC–SiC)n or (BN–SiC)n of multilayer "self-healing" interphase coatings [5, 25, 26]. Normally $n = 10$, the PyC layer thickness is 20 nm, and The SiC layer is 50 nm. A microphotograph is shown in Fig. 3 of an interphase layer of fiber – matrix consisting of a multilayer coating (PyC–SiC)n [27]. This same scheme may be extended to multicomponent interphases $(X–Y–X–Z)n$ in SiC$_f$/SiC composites with a "self-healing" matrix. Here X is as before PyC or BN, and Y and Z are materials forming "healing" oxides and they be B_2O_3 (Y) and Si or B (Z). A C$_f$/SiC composite of this structure withstands 200 h with a nominal stress of 150 MPa (pure bending) at 600°C [14].

MATRIX MODIFICATION WITH MICRO- AND NANO-SIZE FILLERS PROVIDING A "SELF-HEALING" EFFECT

Self-restoring materials (or materials with a "self-healing" effect) are materials capable of partly or entirely restoring damage caused to them, for example crack formation. As applied to CMC is possible to separate both a minimum of two zones with increased damage, i.e., this is ceramic matrix itself and the interphase boundary of a fiber-matrix. With use of CMC with surface coatings (layered materials) damage also arises in coatings. Formation of microcracks increases even more with use of CMC under high-temperature conditions and action of corrosive media. In this case any CMC damage leads to a possibility of the occurrence of corrosive media within the volume of a CMC and development of thermochemical destruction processes for composite components (mainly reinforcing fibers).

Depending on the mechanism realized for initiation and nature of self-healing there are two different classes of self-healing materials, i.e., autonomous, and non-autonomous. For non-autonomous self-restoring materials external initiation is required for example high temperature or light. In the case of autonomous self recovery the damage itself is a pulse for material recovery [27]. In addition, initiation of self-recovery may be considered as "external", i.e., a process of recovery is based on some external restoring micro- or nano-components, especially introduced into the material matrix, and as "internal ", i.e., there is no consideration of presence of any separate restoring composition. An example of a non-autonomous self-recovering material with "internal" initiation is that obtained as a result of self-recovery of SiC oxidation. During CMC oxidation with an SiC matrix above 800°C reaction of SiC with oxygen commences with formation of SiO_2 that fills cracks in the material thereby preventing occurrence of oxygen penetration into the depth of material [28].

A more effective method for CMC protection from oxidizing media is introduction into the matrix of nano- and micro-powders realizing a mechanism of "external" initiation

of self-recovery. The materials used most extensively for implementing this approach are boron and boron-containing compounds. Boron and many of its compounds from B_2O_3 oxide that melts at 470°C and remains in a condensed state up to 1100°C, thereby facilitating healing of microcracks and cavities in CMC and a protective coating [28]. With introduction into a matrix of B_4C powder at above 950°C it oxidizes to B_2O_3 also providing material self-healing.

An effective way of resolving the problem is modification with amorphous boron powder of a polymer binder used for preparing CMC by polymer pyrolysis technology (PIP). This approach combined with formation of an external protective coating with boron-containing powder has shown the best results of CMC protection from high-temperature oxidation [28].

In CMC with and SiC matrix with introduction of boron-containing powder a combined form of self-healing is realized for cracks arising in a material, caused by oxidation of SiC to SiO_2 and boron compounds to B_2O_3. As a consequence of this reaction there is formation of glass phase of the composition SiO_2–B_2O_3 arising at above 500°C and protecting a fiber and interphase from oxidation at higher temperatures. However, a weakness in this scheme is the increased sensitivity of this structure to water vapor. It is possible to compensate this disadvantage by adding Al to a matrix with the aim of forming aluminum borates that make it possible to retain structure stability under a load up to 800°C [14].

In [29] as an "external" mechanism for initiating the "self-healing" process it is proposed to introduce into the ceramic matrix structure finely dispersed Si capsules. At above 1420°C the capsules melt and the Si vapor phase entering into reaction with oxygen of an oxidizing medium forms SiO_2 that heals defects, increases crack resistance, and creates additional protection from CMC oxidation at elevated temperature.

It should be noted that the protective and healing properties of SiO_2 formed as a result of oxidation of an SiC matrix or Si as a rule are limited to a temperature not exceeding 1650 – 1700°C. At higher operating temperatures it is necessary to use other approaches for improving CMC oxidation resistance In particular, this problem may be resolved due to introducing into a matrix new powder components that are capable of operating at higher temperature and during oxidation from oxides with a higher melting temperature. Consideration has been given to TaC, ZrO_2, ZrB_2, and HfB_2 [30 – 32] as such components. Microparticles of ceramic powders were introduced into a preform during CMC preparation of the C_f/SiC system. For example, during oxidation of TaC there is formation of oxide Ta_2O_5 that at above 1870°C is transformed into a liquid state providing a sealing mechanism of filling cracks and pores in a matrix and improving CMC stability at ultra-high temperature (above 2000°C) [31]. In [30, 32] CMC of the C_f/SiC system have been studied with introduction into the matric ZrB_2 particles increasing oxidation resistance provided by formation during matrix oxidation of SiO_2, ZrO_2, and B_2O_3 oxides and borosilicate.

APPLICATION OF CORROSION-
AND HEAT-RESISTANT LAYERS
ON A CMC OUTER SURFACE

One of the main approaches to resolving the problem of high-temperature oxidation is application to a composite surface of functional protective coatings that may fulfil different functions [33]:
– to improve substrate mechanical properties with action of a temperature gradient;
– to limit chemical processes of composite oxidation and corrosion;
– to regulate heat transfer at high operating temperature for an object by changing material thermal conductivity. Generally this may be a complex multilayer system of CMC protection. Each of the layers should fulfil its own function, and altogether they should exhibit certain specifications and answer the requirements [34]: be compatible with each other and with the CMC; to retain good adhesion to a composite during a certain time; to protect CMC effectively from oxidation; to have a high melting temperature; to withstand thermal shock and mechanical loading; to have low thermal conductivity; to resists erosion, vibration, wear, and gas or liquid flow.

There is most extensive use of anti-oxidation coatings of various compositions containing refractory compounds, i.e., silicides, carbides, borides, oxides of a number of metals (Si, Zr., Hf, Ti, Ta, etc.) and nonmetallic structural components in the form of refractory silicates, glasses (often borosilicate), etc. [35]. There is quite extensive use for carbon-containing CMC of coatings based on SiC. They are capable of providing short-term protection from oxidation at a temperature not exceeding 1600 – 170°C.

Results are provided in [36] for a study of a combined anti-oxidation coating based on ZrB_2 ad SiC for C_f/SiC composites prepared by PIP technology. A suspension of a mixture of ZrB_2 and SiC powders is applied to a composite surface and then SiC is compacted, deposited at the surface in a gas phase by CVD technology. It was detected that this composite coating provides prolonged protection of CMC at 1700°C and improves ablation resistance by forming ZrO_2 and SiO_2 during oxidation of ZrB_2 and SiC.

As a rule coatings based on other refractory compounds have a temperature limit for their protective action towards oxygen-containing flows not exceeding 1650 – 1750°C. Effective coatings for surface and volumetric protection of CMC with an SiC matrix are those based on silicates and aluminates: mullite, cordierite, celsian, strontium anorthite, rare earth element silicates, and also those based on high-temperature compounds: titanates, zirconates and hafnates of aluminum, scandium, and rare-earth elements [37 – 43].

An alternative CMC based on an SiC matrix for functioning in air at high temperature is CMC of an oxide/oxide system. Here most success has been achieved in creating CMC based on Al_2O_3 fibers and an Al_2O_3 matrix. However, for use with a very long duration (>100 h) at above 1100°C an additional heat protective coating (HPC) is required. Vari-
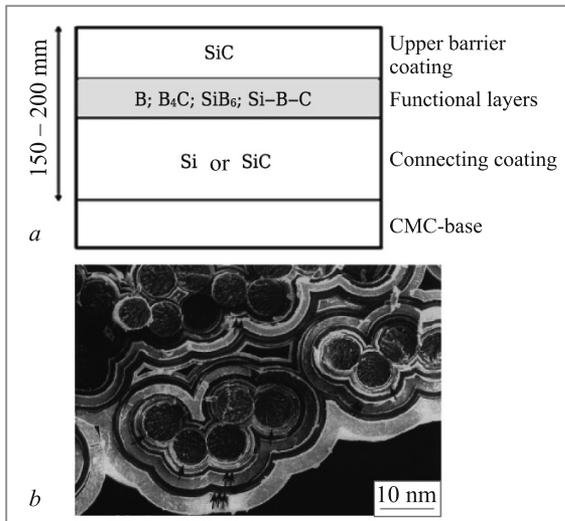
Fig. 4. CMC with multilayer coating (*a*) and multilayer self-healing matrix (*b*).

ous versions of HPC for CMC are considered in [44] of porous Al_2O_3, strengthened with Al_2O_3 fibers of the Nextel 720 type. Alumina and mullite are selected as a base for HCP. In order to prepare a coating for these, material plasma deposition and immersion in a suspension followed by sintering were used. In addition, in order to apply a coating of Al_2O_3 another method was used, i.e., reaction bonding, based on oxidation of a mixture of $Al–Al_2O_3$ powders. This method leads to preparation of porous Al_2O_3 with better mechanical strength compared with normal sintering. The main coating quality index for these CMC is their thermal conductivity. It has been established that the least thermal conductivity is achieved with use a mullite coating prepared by natural sintering of sub-micron powder applied by immersion (0.7 W/(m·K)), and reaction-bonded Al_2O_3 (0.3 W/(m·K)). Research has shown that HCP is sintered mullite with porosity of 40% and thickness of 2 mm does not separate from a base after withstanding 100 h at 1200°C, since the LTEC is closer to the composite LTEC (difference less than 1×10^{-6} 1/K). it should be noted that single-layer protective coatings are developed primarily for uncooled structures of CMC operating at relatively low temperature, and should be permeable (dense without cracks) and have LTEC corresponding to the composite LTEC to a maximum [45]. With development of new types of CMC for use at significantly higher temperature (1600°C) it was necessary to develop new composites for creating multilayer protective coatings

Recently protective structures of a second generation have been developed and used in practice with two-layer chemically resistant barrier coatings. In choosing compounds capable of fulfilling the function of barrier layer it is necessary to consider a number of conditions [33]:

– compounds should be thermodynamically stable and chemically resistant over the whole object operating temperature range;

– a barrier layer should conform with the physico-mechanical properties of the substrate and coating and also provide a reduction in chemical and diffusion process rates in a transition layer between a substrate and coating.

In addition, the problem should be considered of thermal expansion of a substrate and coating, which is part of the problem of adhesion of a substrate with a coating. Different substrate and coating LTEC may lead to occurrence of stresses. It is known from the practice of applying coatings that the most resistant coatings are those with different LTEC for coating and substrate not exceeding 10% [43]. One way of resolving this problem is based on creating special multilayer coatings (for example the ZrB_2–SiC system) making it possible to compensate the difference in LTEC for the base and coating.

Even greater efficiency is demonstrated by barrier coatings of a third generation that concern coatings consisting of three layers each of which has its own functional purpose [46, 47]. For example a lower (primer) layer of silica provides good adhesion with a substrate; and intermediate layer, i.e., mullite or a composite of mullite and barium and strontium aluminosilicates; an upper layer of barium and strontium aluminosilicates providing heat protective properties as a result of low thermal conductivity. All of the layers are applied by modified plasma deposition. This coating provides operating capacity for CMC of the SiC/SiC system at 1250°C for 14 – 17 thousand hours [48].

Currently for heat protection of silicon-containing CMC there are usually multilayer coatings in which the number of layers reaches 6 – 8. In particular, a multilayer coating s well known including a layer based on silicates and refractory oxides of hafnium and zirconium (melting temperatures 2758 and 2755°C respectively) that provides an increased operating temperature to 1650°C [40].

A promising and intensely developed approach to resolving the problem of protecting CMC is application of an outer glass-forming or metal coating subjected to chemical transformation during heat treatment or during object operation. As already noted above, this type of materials concerns Si, SiC, B, and boron-containing compounds forming oxides on heating facilitating microcrack healing [28].

This strategy has been implemented and multilayer coatings have been created. A three-layer coating was described in [49] in which each layer fulfils its own function (Fig. 4*a*): the first is a binder layer, for example a dense layer of SiC (for SiC-matrices prepared by gas phase technology) or a layer of silicon (for an SiC matrix prepared by liquid-phase siliciding technology) that is deposited on the outer surface of a composite at the end of compaction of a fiber workpiece; the second is a functional layer containing for example B, B_4C, SiB_6, or an Si–B–C mixture that may form liquid oxides (B_2O_3 or B_2O_3–SiO_2) on reaction with an oxidizing atmosphere in a prescribed temperature range; the third is an upper barrier layer that may be a dense SiC layer. The overall coating thickness is of the order of 150 – 200 μm. When under action of cyclic loading in a coating microcracks arise

they are filled with liquid oxide that slows down or stops diffusion of oxygen into a CMC.

An even more effective strategy for CMC protection involves replacing a uniform SiC matrix by a multilayer matrix created on the basis of a similar principle [49]. This self-restoring matrix may be prepared by technology of pulsating gas-phase compaction of a fiber framework. Here the matrix is deposited in the form of a repeated sequence of layers containing a thin X, acting as a mechanical protection (X may be C, C (B), BN, BN (Si) or any other suitable material for mechanical protection), and a layer Y of materials forming liquid oxides (Fig. 4*b*). This organization of the matrix provides functioning of CMC for 1000 h with cyclic loading in air up to 1100°C.

Recently information has appeared about development of protective coatings of a new class based on complexly alloyed silicide systems, for example a coating of the system Si–Ti–Mo–alloying element (B, Y, Al, Zr, Hf, Nb, V, W, Cr, Fe, Mn, etc.) [35, 50]. These coatings are capable of providing effective protection in high temperatures gas streams from erosion over a wide temperature range, i.e., 300 – 2100 K. a coating is a multilayer nanostructure with the thickness of individual layers of 10 – 1000 nm. Rapid self-healing is provided for micro- and macro-defects of a coating and effective formation of an oxide at the surface.

Another promising way of creating a new generation of heat protection and anti-oxidation coatings includes development of compositions based on oxygen-free compounds, i.e., borides and carbides. Technology is described in [33] for producing multilayer coatings based on HfC/SiC. Results of tests showed that CM specimens with coatings withstand quite prolonged (for 140 min) high temperature action (~2300°C). As a result of the low thermal conductivity temperature gradient at a coating surface and a layer of carbon-containing substrate reached 480°C. With short-term heating of a coating protection of a composite was provided at 2837°C for 60 sec.

New possibilities for providing CMC protection from high-temperature oxidation open up an approach based on creating functional graded materials within which the protective materials created as part of a surface volume of CMC in contrast to layered material with special protective coating. Graded material has been prepared [51] based on porous ceramic CM using sol-gel technology. Porous SiC material is impregnated with a solution of Zr, Hf, and Y alkoxyacetyl acetonates. After conducting some sol-gel process cycle in the surface layer of a composite there was formation of a refractory oxide matrix ZrO_2–HfO_2–Y_2O_3. A study of the thermal behavior of CM of the $SiC/(ZrO_2$–HfO_2–$Y_2O_3)$ system in the range up to 1400°C has shown a marked improvement in oxidation resistance of the material obtained compared with an original SiC composite. A study of CM microstructure confirmed formation of a surface layer with a thickness of 1 – 1.5 mm considerably denser than the volumetric part of the material with almost no open porosity (of the order of 0.04%).

CONCLUSION

This analysis has shown that currently there are, and are being developed, several main approaches to the problem of improving the corrosion and heat resistance of refractory fiber reinforced CMC based on modifying their composition, internal structure, and surface. Four areas for resolving this problem have been separated:

– use of the most thermodynamically stable corrosion- and heat-resistant reinforcing fibers;

– application of protective coatings to the surface of reinforcing fibers;

– modification of the matrix with micro- and nano-size fillers providing a "self-healing" effect with occurrence of composite microstructure defects during operation is corrosive media;

– application of corrosion- and heat-resistant surface layers.

The contemporary state of the main trends in developing these approaches has been analyzed, which has shown that their implementation, including in combination, opens up extensive possibilities for creating effective CMC for use in high-temperature technology objects operating is fields of high and ultra-high temperature and under conditions of the action of oxidizing and corrosive media.

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