
**PHYSICOCHEMICAL FUNDAMENTALS
OF CREATING MATERIALS AND TECHNOLOGIES**

High-Temperature Corrosion-Resistant Ceramic Composite Materials Based on (Si–B–C–N) System Compounds (Review)

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Abstract—Systematization of available information on the results achieved in the field of development of promising materials based on two-, three-, and four-component compounds of the (Si–B–C–N) system such as nitrides, carbides, borides, silicon and boron carbonitrides, and silicon borocarbonitride is carried out on the basis of the analysis of domestic and foreign scientific publications. Information about their structure, properties, and methods of obtaining is given. The dependence of the properties of fibers, monoliths, and composite materials on the chemical composition and structure of Si–B–C–N compounds is considered. The results of testing finished products at high temperatures in an oxidizing environment are presented. The prospects of using the materials of the (Si–C–N–B) system in industry and engineering for the manufacture of parts and assemblies designed to work at high temperatures under mechanical loading in aggressive environments are described.

Keywords: silicon carbonitride, boron carbonitride, silicon borocarbonitride, fibers, composite materials

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INTRODUCTION

The development of technology and economics requires the development of new high-temperature materials and coatings with sufficient mechanical strength at high temperatures, chemical and abrasive resistance, and low coefficient of friction at a relatively low cost. Ceramic materials based on carbides, nitrides, and borides of refractory elements are rightfully considered to be the most promising ones for high-temperature applications, since, in comparison with heat-resistant alloys and refractory metals, they have higher temperature resistance, oxidation resistance, low density, low thermal expansion coefficient, wide availability, and relatively low cost [1–7].

Three- and four-component compounds of (Si–C–N–B) systems have new properties compared to crystalline binary compounds: high thermal conductivity, thermal stability (up to 1900°C), oxidation resistance [8], chemical inertness [9], and high hardness [10–12]; this makes them promising wear- and oxidation-resistant materials for use in aggressive environments and at high temperatures [9, 13–18]. It is assumed that the unique physical and mechanical properties are due to the presence of chemical bonds between all atoms in the Si–C–N–B compounds, and it is possible to change their physical, chemical, and

mechanical properties in a wide range by varying their phase and chemical composition.

The high oxidative resistance of such materials is explained by the oxide film of SiO₂, B₂O₃, or B₂O₃·SiO₂ formed on their surface at temperatures above 900°C preventing further penetration of oxygen deep into the material, thereby protecting them from further oxidation and destruction and preserving their high mechanical properties [1, 5, 18]. In addition, the liquid-like oxide film is able to fill cracks formed under high mechanical loads during operation of products at high temperatures and prevent further destruction of the material. Owing to this property, SiBCN ceramic has great potential in aviation and space technology and nuclear power.

The purpose of the article is to analyze publications in the field of development of promising materials based on two-, three-, and four-component compounds of the (Si–B–C–N) system.

STRUCTURE AND PROPERTIES OF MATERIALS OF (Si–C–N–B) SYSTEM

Binary compounds of the (Si–C–N–B) system are well studied [1–6]. Their structure and main properties are given in Table 1. Of greatest interest are three- and four-component compounds, such as silicon car-

Table 1. Structure and properties of (Si–C–N–B) system compounds

Phase	Space group	Density, g/cm ³	Temperatures of melting (decomposition)/beginning of oxidation, °C	Micro-hardness, H _μ , GPa	Elastic modulus, E, GPa	Notes
α-SiC	<i>P6₃/mmc</i>	3.166	–/800	20.9–33.4	290–470	At 1800–2000°C, the phase transition in β-SiC [1–4]
β-SiC	<i>F–43m</i>	3.214	(2300)/800			
α-Si ₃ N ₄	<i>P31c</i>	3.148–3.19	–/900	45.3	120–298	Above 1400°C, phase transition in β-Si ₃ N ₄ [1–3, 5]
β-Si ₃ N ₄	<i>P6₃/m</i>	3.211–3.182	(1600)/900	34.8–35.8		
γ-Si ₃ N ₄	<i>Fd–3m</i> or <i>Fd–3</i>	–	–	–	–	At a pressure of 15 GPa [1–3, 5]
α-C ₃ N ₄	<i>P31c</i>	–	–	–	–	[20, 21]
β-C ₃ N ₄	<i>P6₃/m</i>	3.49	–	–	–	[21, 22]
γ-C ₃ N ₄	<i>P6₃/mmc</i>	–	–	–	–	[23]
<i>c</i> -SiCN	<i>F–43m</i>	2.350		25 21–38*	150 226–360*	*Depending on composition [24]
<i>t</i> -SiCN	<i>P42nm</i>	–	–	41.5	–	Theoretical calculations [25]
α-Si ₂ CN ₄	<i>Aba2</i>	–	–	–	–	Stable up to 1000°C [19, 26]
α-SiC ₂ N ₄	<i>Pn3m</i>	–	–	–	–	Stable up to 900°C [19, 26]
α-BN	<i>P6₃/mmc</i>	2.29	2967**/(700–800)	0.31–0.39	3.123– 7.7854	At 1360°C and a pressure of 6.2 GPa, the phase transition in β-BN [1–3]
β-BN	<i>F–43m</i>	3.51	2927**/(700–800)	62–88.2	909	Up to 2000 °C [1–3]
γ-BN	<i>P6₃mc</i>	3.50	2927**/(700–800)	57.2	–	**Under nitrogen pressure [1–3]
B ₆ Si	<i>Pnnm</i>	2.39	(1850)/500	27.2–29.6	–	[2, 6, 19]
B ₄ Si	<i>R–3m</i>	2.41	(1370)/500	20–25	–	Up to 1370°C [2, 6, 19]
B ₄ C	<i>R–3m</i>	2.52	2350 (2470) / 500	49.5	200–400	[1, 2, 4]
<i>c</i> -BC ₂ N	<i>Fd–3m</i> or <i>F–43m</i>	–	–	76	980	[27, 28]

bonitride SiC_xN_y, boron carbonitride BC_xN_y, and silicon borocarbonitride SiB_xN_yC_z [19].

Silicon carbonitride is a group of compounds of variable composition SiC_xN_y, which is a solid solution of SiN_x and CN_x, where part of the Si atoms are replaced by C atoms or vice versa [29]. Silicon carbonitride is a metastable amorphous (X-ray amorphous) compound up to 1600°C having a short-range order of Si₃N₄ and/or SiC type. Above this temperature, silicon carbonitride crystallizes to form a nanoscale composite consisting of Si₃N₄ and SiC. There is evidence that SiC_xN_y ceramic obtained from polymer consists of micro- or nanocrystalline Si₃N₄ or SiC grains and an amorphous region [30, 31].

The structure of SiC_xN_y is similar to α-Si₃N₄, which is a hexagonal unit cell formed by SiN₄ tetrahedra. The local structure of silicon atoms depends on the ratio of nitrogen and silicon and does not depend

on the amount of carbon. Silicon atoms always have a fourfold or higher coordination and are surrounded by the maximum possible number of nitrogen atoms [8, 13]. The ratio of nitrogen and silicon atoms of about 4/3 leads to the formation of Si₃N₄ structures and, consequently, to separation from the amorphous phase enriched in Si₃N₄. Otherwise, mixed Si(C, N)₄ tetrahedra are preferable [8, 13].

Although the SiC_xN_y compound is mostly amorphous, there is evidence of its crystallization at hot pressing, change in nitrogen pressure, and plasma-enhanced chemical vapor deposition (PE CVD) [32]. This amorphous SiC_xN_y material undergoes a transition to thermodynamically stable crystalline phases accompanied by shrinkage and cracking with preliminary separation of phases onto amorphous domains enriched in C, SiC, and Si₃N₄ [32, 33].

The existence of the stoichiometric *c*-SiCN compound has been experimentally established (space

group $F-43m$), which has a cubic crystal lattice. Theoretical calculations from first principles have shown that the existence of a tetragonal structure of t -SiCN (space group $P42nm$) is possible, which is thermodynamically stable and can be synthesized at atmospheric pressure. The hardness of this material is predicted to be 41.5 GPa [25].

The existence of two more stoichiometric compounds of silicon carbonitride is also described: α -Si₂CN₄ (space group $Aba2$) and α -SiC₂N₄ (space group $Pn3m$) [19, 26]. In α -Si₂CN₄, four carbon atoms are replaced by silicon atoms in four different packing layers, and in α -SiC₂N₄, eight silicon atoms in four different layers are replaced by carbon atoms. These two structures show symmetry identical to the $P31c$ type, when the vectors of the primitive unit cell are the same and the angle between a and b is 120°. These two crystal structures can be called “quasi-hexagonal” with an angle of 119.13° for α -Si₂CN₄ and 120.93° for α -SiC₂N₄. The bond length for C–N is 1.43–1.48 Å, and for Si–N, it is 1.71–1.74 Å [8, 13, 34].

The presence of the C–N covalent bond plays an important role in the hardness and other mechanical properties of the (Si–C–N)-based material. With an increase in the number of C atoms replacing Si atoms, there is a decrease in the bond length and the lattice constant and an increase in the modulus of volume elasticity, which reaches a maximum value in the structure of α -C₃N₄. However, because of the variety of types of bonds between C and N atoms (single, double, triple), it is difficult to experimentally obtain a crystalline C₃N₄ compound, which has the highest hardness, although powders containing graphite-like [23] crystalline carbon nitride have already been obtained [20, 21]. For the same reason, it is difficult to obtain carbon-enriched α -SiCN crystals [33].

The mechanical properties of silicon carbonitride SiC_xN_y strongly depend on its composition, structure, and method of preparation. Depending on the precursor organosilicon compound, the hardness and Young's modulus of SiC_xN_y films can be 7–13 GPa and 50–80 GPa and reach, respectively, values up to 18–36 GPa and 125–190 GPa [14]. For example, at a density of 2350 kg/cm³, the microhardness was 25 GPa, the elastic modulus was ~150 GPa, the bending strength was ~850 MPa, the impact strength was 3.5 MPa m^{1/2}, and the coefficient of thermal expansion was $\sim 3 \times 10^{-6} \text{ K}^{-1}$ [24].

The silicon carbonitride films had good mechanical characteristics: high values of hardness and Young's modulus and low coefficient of friction [10–12, 35, 36]. Films with hardness up to 42 GPa were obtained by laser ablation [37]. Silicon carbonitride microcrystals up to 30 μm in size in the form of hexagonal columnar structures were obtained on silicon substrates using plasma-enhanced chemical vapor deposition (PE CVD). The composition of the

crystalline phase varied from Si_{0.08}C_{0.42}N_{0.50} to Si_{0.25}C_{0.42}N_{0.50}. Using scratch tests, it was found that the hardness of this material is comparable to the hardness of a cubic boron nitride [38]. For monoliths obtained from polymers and having an amorphous structure of the formal composition SiC_{0.67}N_{0.80} and SiC_{1.6}N_{1.3}, the microhardness was 13 and 6.1 GPa, and the elastic modulus was 121 and 105 GPa, respectively [16].

It is assumed that high thermal and chemical resistance and mechanical strength of the films are achieved owing to the absence of grain boundaries and oxide phases [13, 14]. Variation of the phase and chemical composition determined by the method of obtaining the material makes it possible to change the physical and chemical properties of silicon carbonitride in a wide range, which opens up wide opportunities for creating materials with desired characteristics that exceed those for materials based on silicon carbides and nitrides and other materials [14, 39].

The resulting boron carbonitrides BC_xN_y can be considered as metastable solid solutions of carbon in boron nitride. Because of the similarity of the crystal structures of α -BN and graphite, the possibility of the existence of solid solutions between both phases was assumed. However, numerous experimental studies have shown that all solid solutions are metastable. The existence of metastable phases of BC₂N and BC₃N has been reported [19].

Ternary compounds of the (Si–B–C) and (Si–B–N) subsystems are little studied [19, 32, 40]. The Si–B–C fibers obtained from polymer precursors have an amorphous structure [16]. Ternary compounds of (Si–B–N) are also amorphous and have a variable SiB_xN_y composition. When heated above 1700°C in a nitrogen atmosphere, a powder of the formal composition Si₃B₃N₇ crystallizes followed by decomposition into Si and BN and the release of N₂. The decomposition process ends at a temperature of 1900°C [40, 41]. Four-component compounds of (Si–B–C–N) are X-ray amorphous like silicon carbonitride [18, 19, 32, 41]. It is assumed that they consist of three-dimensional networks with a homogeneous chemical composition, where atoms are evenly distributed, and strong chemical bonds are formed between them, since, basically, they are obtained by pyrolysis from organic precursor compounds containing atoms of all elements and bonds between them. The high-resolution transmission microscopy (HRTEM) confirmed the homogeneous distribution of elements in the Si–B–C–N compounds without release of any phases or formation of clusters of any atoms. Using nuclear magnetic resonance (NMR), the presence of a short-range order characteristic of Si₃B₃N₇ consisting mainly of SiN₄ tetrahedral units and BN₃ trigonal planar units bound by common nitrogen atoms was determined. The XANES analysis confirmed the formation

Table 2. Maximum temperatures of stability of the $\text{SiB}_x\text{N}_y\text{C}_z$ compounds [32]

Chemical formula of compounds	Maximum temperature of stability, °C
$\text{Si}_{2.3}\text{B}_{0.5}\text{C}_{1.0}\text{N}_{2.9}$	~1500
$\text{Si}_{1.9}\text{B}_{2.6}\text{C}_{4.8}\text{N}_{4.8}$	~1750
$\text{Si}_{3.0}\text{B}_{1.0}\text{C}_{4.3}\text{N}_{2.0}$	~2000
$\text{Si}_{3.0}\text{B}_{1.2}\text{C}_{4.9}\text{N}_{3.1}$	~1980
$\text{Si}_{3.0}\text{B}_{1.1}\text{C}_{5.3}\text{N}_{3.0}$	~1980
$\text{Si}_{3.0}\text{B}_{1.1}\text{C}_{3.0}\text{N}_{4.0}$	~1450
$\text{Si}_{1.0}\text{B}_{0.1}\text{C}_{1.5}\text{N}_{1.0}$	~1650
$\text{Si}_{1.0}\text{B}_{0.2}\text{C}_{1.6}\text{N}_{1.0}$	≥1650
$\text{Si}_{1.0}\text{B}_{0.4}\text{C}_{1.7}\text{N}_{1.0}$	~1900
$\text{Si}_{3.9}\text{B}_{1.0}\text{C}_{11.0}\text{N}_{3.2}$	2000–2200
$\text{Si}_{19.0}\text{B}_{13.0}\text{C}_{49.0}\text{N}_{19.0}$	~1800
$\text{Si}_{15.0}\text{B}_{14.0}\text{C}_{63.0}\text{N}_{8.0}$	2000–2150
$\text{Si}_{2.7}\text{B}_{1.0}\text{C}_{5.1}\text{N}_{2.5}$	~2000
$\text{Si}_{2.3}\text{B}_{1.0}\text{C}_{0.3}\text{N}_{3.6}$	~1600
SiBN_3C	1700–1800

of SiN_4 , SiN_xC_y , BN_3 , NSi_xB_y , and (C=C) structural units. A comprehensive study using NMR spectroscopy, Raman scattering, and electron paramagnetic resonance (EPR) showed the presence of structures of hexagonal (*h*-BN) and turbostratic BN(*t*-BN) and BN_2C . However, not all Si–B–C–N compounds after pyrolysis demonstrate a completely amorphous structure because of the difference in the initial precursor, chemical composition, synthesis technology, and pyrolysis process. For example, Si–B–C–N ceramic based on poly(propenylsilazane) exhibits weak SiC diffraction peaks, while HRTEM patterns show SiC crystallites with the size of 2–4 nm and regions of graphite-like turbostratic BNC [16].

The X-ray diffraction showed that, at temperatures above 1600°C in a nitrogen atmosphere, amorphous Si–B–C–N compounds crystallize with the release of crystalline phases of SiC, Si_3N_4 , and turbostratic BNC. The change in the structure of the fibers is associated with a decrease in their strength characteristics at temperatures above 1600°C. The transition temperature from the amorphous state to the crystalline state for Si–B–C–N compounds is determined by their chemical composition [16, 32, 41, 42]. The temperatures of stability for various ratios of the components of the compounds of the (Si–B–C–N) system [32] are shown in Table 2. The amorphous structure of the SiBN_3C composition is retained up to a temperature of 1800°C in a nitrogen atmosphere. In an argon atmosphere, the crystallization process starts at a slightly lower temperature of 1700°C. In this regard,

Table 3. Mechanical properties of $\text{SiB}_x\text{N}_y\text{C}_z$ monoliths [16]

Composition	Microhardness, GPa	Elastic modulus, GPa
$\text{Si}_3\text{B}_3\text{C}_5\text{N}_7$	8.5 ± 0.2	91 ± 2
$\text{Si}_3\text{B}_3\text{C}_7\text{N}_5$	14.4 ± 0.2	123 ± 8
$\text{Si}_3\text{B}_3\text{C}_4\text{N}_7$	11.4 ± 0.8	107 ± 8
$\text{Si}_3\text{B}_3\text{C}_5\text{N}_5$	14.5 ± 0.6	127 ± 8

the inorganic fibers of the SiBN_3C composition lack pronounced boundaries and the growth of crystallite grains up to a temperature of 1800°C. The stability of amorphous microstructure of fibers of $\text{SiB}_x\text{N}_y\text{C}_z$ composition explains their excellent creep resistance at high temperatures [42].

The composition of the precursor compound affects the structure and mechanical properties of the resulting compound. The values of microhardness and modulus of elasticity for some compounds are given in Table 3 [16].

The Si–B–C–N compounds demonstrate higher oxidation resistance than their analogs from SiC and Si_3N_4 at temperatures above 1000°C. The oxidation activation energy for Si–B–C–N powders with an average particle size of about 200 nm is about 350 kJ/mol, which is higher than that of SiC powders (80 kJ/mol) with the same particle size [42].

METHODS FOR OBTAINING (Si–C–N–B) SYSTEM COMPOUNDS AND MATERIALS BASED ON THEM

Obtaining binary compounds of the (Si–C–N–B) system and materials from them is not particularly difficult [1–6] except for carbon nitride [22–24, 43, 44].

There are several ways to get ternary and quaternary compounds. Basically, these are methods for obtaining using chemical synthesis from organic precursor compounds that have the necessary molecules (Si–C–N–B) and the bonds between them. The process of obtaining can be divided into five stages: synthesis of an organic precursor compound by standard Schlenk methods; crosslinking or curing the polymer; hot-pressing molding at 200–400°C of the obtained precursor powders of (Si–B–C–N); pyrolysis at 1000–1400°C to obtain amorphous Si–B–C–N; and annealing at temperatures up to 2000°C of amorphous ceramic to obtain nanocrystalline composites. The chemical composition, microstructure, and properties of the Si–B–C–N ceramic obtained from polymers are controlled by the choice of the initial structures of the reagents, the chemical reactions, and the parameters of further processing. This method ensures the production of chemically pure Si–B–C–N ceramic. This method produces fibers, as well as films and monolithic and composite ceramics during subse-

quent pressing of the Si–B–C–N powders obtained by hot isostatic pressing, hot pressing, spark plasma sintering or pressure sintering, etc. [16, 45–47]. However, the considered method has a number of disadvantages that limit mass production. The use of harmful and flammable solvents makes production hazardous. Expensive raw materials, a small yield of the finished product, and the complexity of the technological process greatly increase the commercial cost of such materials. The pyrolysis process, in which mass loss occurs owing to gas evolution and shrinkage, requires special control in the manufacture of monolithic products, since pores and microcracks may arise, reducing the mechanical properties and oxidative resistance of the final product [16, 48].

Obtaining three- or four-component compounds of the (Si–B–C–N) system is possible using mechanical activation from powders of pure elements or binary compounds [16, 49]. This method allows obtaining powders with a homogeneous amorphous structure. From these powders, monolithic or composite ceramics are made using various pressing methods. Crystallization of amorphous ceramics at high temperatures occurring during sintering or additional heat treatment leads to the production of nanostructures with a higher uniformity, which favorably affects the mechanical properties of the resulting material. The microstructure and properties of the resulting material can be controlled by the chemical composition and ratio of the initial powders. This method has several advantages that make this technology possible on an industrial scale. The process is relatively environmentally friendly, since it uses readily available and relatively inexpensive inorganic starting powders and does not form harmful by-products. With additional high-temperature processing of products, there is no significant reduction in mass and geometric dimensions, which are noted when processing products obtained with the use of organic precursors [16, 47].

The $\text{SiB}_x\text{N}_y\text{C}_z$ films and coatings, as well as films of carbonitrides up to 1 μm thick, are obtained by physical or chemical vapor deposition [16, 29, 50–53]. The disadvantage of chemical synthesis methods is the use of substances with increased toxicity and explosiveness. Therefore, in order to increase the safety of the synthesis, new starting materials are being sought [14, 17]. For example, in [54], a method was proposed for plasma-chemical vapor deposition from vapors of compounds of the class of silanes (precursors of silicon carbonitride) in a scheme with remote plasma (RP CVD), which is modification of the method of PE CVD (Plasma Enhanced Chemical Vapor Deposition). The method is based on the transformation of vapors of molecular precursors during their interaction with excited atoms of carrier gases (He , H_2) and their subsequent deposition on the surface of a solid substrate with the formation of $\text{SiB}_x\text{N}_y\text{C}_z$ nanocomposite layers. Also, the methods of chemical deposi-

tion from the gas phase include the activation of the gas phase by ultraviolet radiation of a certain wavelength (Ultraviolet-activated Chemical Vapor Deposition—UV CVD) and thermal activation (Low Pressure Chemical Vapor Deposition—LP CVD), including deposition on hot wire (Hot Wire Chemical Vapor Deposition—HW CVD). Magnetron sputtering and laser ablation belong to physical vapor deposition (PVD) methods and are also used to obtain thin films [11, 50, 51, 55, 56]. The PVD methods make it possible to deposit uniform films only on smooth surfaces; it is difficult to obtain uniform films on surfaces of complex shape. The manufacture of massive products by methods of physical or chemical deposition is difficult because of the low productivity of the processes and mechanical stresses arising during the deposition of thick layers.

The CVD method makes it possible to deposit silicon carbonitride on the surface of a porous reinforcing frame made of carbon or silicon carbide fibers or fabrics, thereby forming a high-quality ceramic-matrix composite material [14, 17]. Currently, a method is being developed for obtaining silicon carbide and silicon carbonitride ceramic composite material combining infiltration with a pre-ceramic polymer of the reinforcing frame and subsequent pyrolysis of the pre-ceramic polymer to obtain a matrix of nitride, carbide, carbonitride, or silicon borocarbonitride or silicides of refractory compounds [57]. This method is called Polymer Infiltration and Pyrolysis (PIP) [17]. This approach makes it possible to obtain materials with porosity close to theoretical. In the volume of a porous reinforcing frame made of carbon fabrics or fibers in the form of filaments, bundles, and layered filaments of a continuous or discrete structure, a ceramic matrix is formed from the Si–B–C–N compound using various combinations and sequences of the chemical vapor deposition (CVD) and multiple cyclic infiltration of the frame with a pre-ceramic polymer followed by polymerization and pyrolysis. Usually, chemical deposition is carried out in gas-vacuum furnaces at a temperature from 500 to 900°C and a pressure from 50 to 500 Pa, and multiple cyclic infiltration of the frame with a pre-ceramic polymer followed by polymerization and pyrolysis is implemented in vacuum-compression furnaces at temperatures up to 1600°C and pressures up to 20 MPa [58].

Traditional methods of consolidation of powder compositions (reaction sintering, hot isostatic pressing, slip casting) make it possible to obtain massive products of complex forms, but with high porosity and not very high mechanical characteristics. The use of various activating oxide or nanoscale additives and sintering using microwave electromagnetic radiation [3] or spark plasma sintering (SPS) makes it possible to obtain high-density ceramic materials (up to 99% of the theoretical density) [59, 60].

The use of 3D printing technology in the manufacture of complex-shaped products from durable, high-temperature, and oxidation-resistant SiBCN/Si₃N_{4w} composites expands the possibilities of application of materials of the (Si–B–C–N) system. For example, in [61], a method of manufacturing complex-shaped products from composite material with a density of 2.10 g/cm³ based on a matrix of Si–B–N–C and whiskers of Si₃N₄ was proposed using 3D printing by DLP technology (Digital Light Processing—digital LED projection). A suspension made from pre-ceramic poly(borosilazane) polymer and 60% of Si₃N₄ whiskers was used to create the product. Studies have shown that, when sintering printed semifinished products at 1200°C, the shrinkage during pyrolysis is only 18%, and the bending strength of the resulting SiBCN/Si₃N_{4w} composite is 183 MPa, which is higher than that of SiBCN monoliths and SiCN obtained by DLP technology. The values of microhardness of 3.4 GPa and elastic modulus of 54.1 GPa of this composite are lower than those of monolithic SiBCN ceramic—7.8 and 54.7 GPa, respectively.

EXAMPLES OF APPLICATION OF MATERIALS OF (Si–C–N–B) SYSTEM

Silicon carbide and silicon nitride have high thermal and chemical resistance, mechanical strength, and wear resistance; they are traditionally used as a lining for high-temperature furnaces, electrodes, electric heaters, nozzles, heat-resistant dishes, bearings, and rotor and nozzle blades in gas and gas-turbine engines [1–5].

Owing to their unique properties, composite materials of the (Si–B–N–C) system are used as structural materials for heat-loaded parts of equipment; for example, in aviation and rocket technology operating in an oxidizing environment at high temperatures and high mechanical loads. The use of such materials reduces the weight of structures by 3–4 times and increases the flight performance of aircraft. The main contribution to the strength and crack resistance of such materials is made by the reinforcing fibers used in their manufacture [42].

Many foreign developments of structural ceramic materials for new propulsion systems are based on composite materials with matrices of SiC or Si₃N₄ reinforced with SiC or C fibers or both together [62–64]. For example, flame tubes installed in the annular combustion chambers of stationary gas turbines of the Centaur 50S engine are made of ceramic SiC/SiC composite materials (CMs) [62]. And at the All-Russian Scientific Research Institute of Aviation Materials (VIAM), a model of a promising combustion chamber was developed, the inner surface of which is lined with ceramic segments from CM based on SiC/SiC having an operating temperature in the oxidizing environment of combustion products from 1600 to 1650°C

[65]. The use of heat-resistant CMs in heat-loaded assemblies and parts of propulsion systems is determined by an increase of the operating temperature in fuel combustion chambers, flame tubes, and gas turbines in order to increase the efficiency and reduce the level of harmful emissions owing to an increase in the temperature of combustion gases [62, 66].

Composite materials based on SiC–Si₃N₄ containing particular particles of the nanoscale range have higher strength properties [67, 68]. According to [3, 69], the reinforcement of ceramics based on Si₃N₄ with SiC nanoparticles leads to an increase in strength from 700 to 1300 MPa and crack resistance from 5.3 to 7 MPa m⁻². Composite materials may have a more complex structure. For example, they may contain SiC particles with the size from 200 to 300 nm and Si₃N₄ particles with the size from 0.8 to 1.5 μm with an intergrain boundary up to 50 nm, which have a significant effect on their properties [68].

Fibers from the materials of the (Si–C–N–B) system are actively used in high-temperature composite materials. The most common SiC fibers are used as a highly heat-resistant reinforcing material in polymer composite materials (PCMs) and in CMs with a ceramic matrix (CCMs). Felt based on SiC fibers is used in powder diesel filters for automobiles, and polymer CMs reinforced with SiC fibers are used in aircraft structures, such as elements of the fuselage and wings, and CCMs containing SiC fibers are used in heat-loaded parts of the new GE LEAP jet engine for passenger aircraft [42]. Table 4 shows the physical and mechanical properties of the most common fibers. Boron fibers coated with a thin film of silicon carbide called Borsic have proven themselves well. To improve the oxidative resistance of SiC fibers, they are coated with interphase protective coatings based on boron-containing compounds of boron nitride BN or boron carbide B₄C [1]. The most promising is the use of Si–B–N–C fibers.

The wide scatter of mechanical properties observed for Si–B–N–C fibers is probably due to different conditions for their production and, accordingly, chemical composition. For example, an amorphous SiBCN₃ fiber with an oxygen content of less than 1% and diameter from 8 to 14 μm has a density of 1.8–2.0 g/cm³. The strength of such a fiber at room temperature is 3.0–4.0 GPa. Such fibers retain their properties in an inert atmosphere of helium or argon up to a temperature of 1750°C. But in an oxidizing environment, the strength decreases; for example, at 1400°C, the strength is about 3 GPa. For a SiBC_{0.8}N_{2.3} fiber obtained in a similar way but subjected to additional heat treatment at 1300°C, the strength characteristics are lower than those of a fiber not subjected to an additional short exposure at 1300°C. The length of the resulting fibers can reach 200 m [16, 32, 41, 70].

Currently commercially available fibers based on poly(silazanes) are absent, with the exception of

Table 4. Physical and mechanical characteristics of the (Si–C–N–B) fibers [1, 12, 16, 42]

Fiber material	Density, g/cm ³	Diameter, μm	Tensile strength, GPa	Elastic modulus, GPa
Boron	2.6	101.6	3.5	420
Silicon carbide	4.05	100	2.8	480
SiC Sylramic (COI Ceramics)	3.1	10	3.0	400
SiC Tyranno SA (Ube Industries)	3.1	10	2.4	380
Si–N (Tonen)	2.5	10	2.5	180
Boron coated with Borsic silicon carbide	2.8	105.4	2.8	450
Si–B–N–C	–	–	2–4	180–360
SiBN ₃ C (Fraunhofer Institute)	1.8	8–14	2.0–4.0	180–350
SiC/BN (Sylramic iBN) (COI Ceramics)	3.1	10	3.0	400
SiNC–1400X (MATECH)	2.48	12–14	2.8	200
Boron carbide	2.53	–	2.31	490
Boron nitride	1.9	103	1.4	90
Si–B–C	3.1	8–10	3.4–4.8	430

SiBN₃C type fibers, which are produced in a pilot plant in Germany. These fibers retain their amorphous structure up to 1800°C, have high creep resistance, and are expected to be commercially available in the near future [42].

The physical and mechanical characteristics of monolithic and composite materials with the Si–C–N–B matrix obtained by hot pressing and spark plasma sintering in a nitrogen atmosphere are shown in Table 5. Aluminum, aluminum nitride, zirconium, zirconium dioxide, zirconium diboride, graphene, multiwalled carbon nanotubes (MWCNTs), and carbon (C_f) and silicon carbide (SiC_f) fibers were used as fillers [16].

The resulting composite materials exhibit improved mechanical properties and high-temperature properties compared to monolithic Si–B–C–N ceramics. The use of short carbon (C_{sf}) or silicon carbide (SiC_{sf}) fibers provides improved resistance to thermal shock and gas flow ablation (entrainment of material by high-temperature gas flow) compared to pure Si–B–C–N materials. It was found that the C_{sf}/(Si–B–C–N) material retains 67.3% of the bending strength after thermal shock with a temperature difference of 1100°C. Carbon fibers oxidize heavily near surfaces, while internal fibers show only minor damage and yet effectively reinforce and strengthen the matrix. The addition of short carbon fiber (C_{sf}) or SiC fiber (SiC_{sf}) can improve the rupture performance and even change the way the material breaks from brittle to pseudoplastic, as well as increase the thermal shock resistance [16].

Composite SiC/(Si–B–C–N) materials show good oxidation resistance at temperatures up to 1500°C in accordance with typical parabolic kinetics. The calculated oxidation rate constants for SiC/(Si–

B–C–N) at 1200–1300°C are almost an order of magnitude greater than for hot-pressed pure SiC and Si₃N₄. As the oxidation time or temperature increases, SiC/(Si–B–C–N) CM shows better oxidation resistance than SiC owing to the formation of a B₂O₃·SiO₂ oxide film, which prevents further oxidation [16].

In recent years, composite materials with the Si–B–C–N matrix have been of great interest for use in heat-loaded parts of spacecraft such as the leading edge of the wing, the nose cone of the rocket, and the turbine blade and the nozzle in the propulsion systems, since these materials are able to withstand temperatures up to 1600°C in an oxidizing environment and up to 1900°C in an inert atmosphere [15, 16]. The presence of boron-containing compounds in the matrix ensures reliable operation of products in the temperature range from 1100 to 1500°C, since, at these temperatures, boron increases the viscosity of the SiO₂ oxide film and does not allow oxygen to penetrate through it into the material, and thereby it preserves the reinforcing frame and, accordingly, the high mechanical properties of the composite [15, 17]. For example, samples of the nose cone and the combustion chamber of the engine made of CM based on the Si–B–C–N matrix and short carbon and/or silicon carbide fibers have successfully passed simulation tests on the ground stand, which indicates the applicability of these composites under severe conditions of high-temperature oxidation, thermal shock, and ablation gas flow [16]. Thermal shock resistance tests were carried out on nose cone models made of SiBCN monolith and SiC_f/C_f/SiBCN and SiC_f/SiBCN ceramic composites. Samples of the nose cone made of ceramic composites were not destroyed under the influence of a heat flow of 12 MW/m² (the flame temperature on the sample surface reached about 3000°C)

Table 5. Physical and mechanical characteristics of the Si–C–N–B ceramic materials [16]

Material	Density, g/cm ³	Bending strength, MPa	Elastic modulus, GPa	Crack resistance, MPa m ^{1/2}	Vickers hardness, GPa
SiBCN//40 ^{1,2}	–	313 ± 5	136 ± 18	3.31 ± 0.02	4.2 ± 0.5
SiBCN ³	–	511 ± 18	157 ± 15	5.64 ± 0.32	5.9 ± 0.7
SiBCN	2.52	331 ± 41	139 ± 16	2.81 ± 0.89	5.7 ± 0.4
SiBCN–Al//50/Ar	2.77	422 ± 27	174 ± 10	3.40 ± 0.15	12.7 ± 0.3
SiBCN–Al//50/N ₂	2.90	527 ± 10	222 ± 28	5.25 ± 0.20	11.6 ± 0.5
SiBCN–AlN	2.74	416 ± 147	148 ± 8	4.08 ± 1.18	6.4 ± 1.2
SiBCN–Zr	4.11	400	252	3.16	9.6
SiBCN–ZrO ₂	2.83	575 ± 74	159 ± 22	3.67 ± 0.01	6.7 ± 0.7
SiBCN–ZrB ₂ ⁴	3.12	338 ± 15	160 ± 5	4.60 ± 0.30	6.5 ± 0.1
SiBCN–graphene ⁵	2.44	135 ± 8	150 ± 3	5.40 ± 0.63	2.4 ± 0.1
SiBCN–MWCNT ⁶	2.58	462 ± 50	115 ± 2	5.54 ± 0.6	5.1 ± 0.2
SiBCN–C _f //2000//60	2.18	71 ± 3	42 ± 11	2.37 ± 0.05	3.0
SiBCN–C _f –ZrO ₂ //60	2.39	112 ± 12	111 ± 23	2.94 ± 0.25	–
SiBCN–SiC _f //60	2.57	284 ± 18	184 ± 11	2.78 ± 0.14	–
SiBCN–SiC _f /BN//60	2.67	193 ± 4	154 ± 25	3.92 ± 0.45	–

¹SiBCN//40: processing parameter 1900°C/40 MPa/N₂. All processing parameters without notes refer to hot pressing at 1900°C/80 MPa/N₂.

²The bending strength of the SiBCN//40 sample at 1100 and 1400°C is 287.2 ± 15.5 and 225.3 ± 15.1 MPa, respectively.

³Chemical composition Si : BN : C = 3 : 1 : 4. Obtained by SPS at 1800°C/40 MPa/N₂. Chemical composition of all others without notes is Si : BN : C = 2 : 1 : 3.

⁴The 15 wt % of ZrB₂ was introduced into the SiBCN system using the sol-gel method. The material was sintered using SPS at 2000°C/40 MPa/5 min in N₂.

⁵The SiBCN ceramic with 5 vol % of graphene was prepared using SPS at 1800°C/40 MPa/5 min in N₂.

⁶The SiBCN ceramic with 1 vol % of MWCNT was prepared using SPS at 1900°C/40 MPa/5 min in N₂.

for 10 s during bench tests of the engine using liquid oxygen and kerosene as fuel. However, monolithic SiBCN samples containing no fibers broke down when heated in just 4 s because of poor heat resistance [16].

Multilayer (hybrid) composite materials are manufactured by controlled deposition of SiC, B_xC, Si–B–C, and Si–B–N layers. Layered materials based on SiC–SiC with protective interphase boron-containing B₄C and BN coatings obtained using CVI in the ternary (Si–B–C) and (Si–B–N) subsystems also have the ability to self-heal the CM matrix. The resistance of CM of SiC_f/BN/SiC type with BN interphase coating to oxidation at moderate temperatures is improved compared to SiC_f/C/SiC, which does not contain boron compounds. It has been found that the presence of a silicon additive in BN contributes to a lower weight loss. And the combination of the ability of B_xC and Si–B–C to self-heal at different temperatures and the ability of the viscous intermediate BN phase to deflect microcracks from fibers ensures the preservation of CM properties in an oxidizing environment at temperatures up to 1450°C [62].

A technology of formation of a ceramic matrix from silicon carbonitride using chemical vapor deposition on a carbon-carbon frame has been developed at JSC Kompozit. The resulting CM (C–C)/(Si–C–N) withstood two test cycles without destruction in a free subsonic dissociated flow according to the regime corresponding to the entry of a reusable spacecraft into the atmosphere. The total duration of the tests was 1320 s, and the temperature on the surface of the material was 1600°C. Using this technology, a model bushing was manufactured, which passed three cycles of testing in a supersonic high-temperature oxidizing flow at a temperature of 1780°C. The total duration of the tests was 30 s. According to the test results, no cracks, chips, burnouts, or other defects of the matrix material were found. There is no change in the cut diameter of the bushing. Between tests, a visual inspection of the bushing was carried out; only a change in the color of the inner and outer surfaces due to the oxidation of the matrix material was noted [24].

CONCLUSIONS

An analysis of domestic and foreign scientific publications of the materials of the (Si–B–C–N) system was carried out. The structure and properties of new compounds of this system, C_3N_4 , SiC_xN_y , BC_xSi_y , and $SiB_xN_yC_z$, were described. Four-component compounds of silicon borocarbonitride $SiB_xN_yC_z$ with high temperature (up to 1800°C and above) and oxidative resistance (up to 900°C) are the most promising materials of this system for the manufacture of parts and assemblies designed to operate in an oxidizing environment under mechanical loading at temperatures above 1400°C. They retain their high mechanical characteristics at temperatures of 1100–1400°C and have the effect of self-healing of cracks at temperatures above 900°C due to the formation of a liquid oxide film that prevents further oxidation of the material.

Composite materials with the $SiB_xN_yC_z$ matrix have higher strength and mechanical characteristics than monolithic ceramics, since the cracks are retarded on the filler particles. This makes them the most promising for the manufacture of parts subjected to high thermal and mechanical loads, thermal shock, or ablation by gas flow.

Work on the study of the dependence of the properties of four-component $SiB_xN_yC_z$ materials on the composition and method of their preparation and the search for the possibilities of application in engineering continues. For example, they can be used as firm (up to 22 GPa), wear-, temperature-, and corrosion-resistant protective coatings.

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