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BEHAVIOR OF DISCRETE AND CONTINUOUS SiC AND C FIBERS IN A SILICON NITRIDE MATRIX UNDER CONDITIONS OF HOT PRESSING

I. Yu. Kelina,[1] N. I. Ershova,[1] L. A. Plyasunkova,[1] E. I. Yakovenko,[1] and A. V. Arakcheev[1]

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Aspects of the problem of creating ceramic-matrix composites (CMC) in Si_3N_4 – SiC_f and Si_3N_4 – C_f systems with high strength and crack resistance under the conditions of hot pressing are considered. Results of an evaluation of physicomechanical properties and a detailed study of the microstructure of CMC by electron and optical microscopy and fractographic analysis are presented. A complex analysis of the microstructure has shown the general rules of its formation in CMC and the behavior of SiC and C fibers of various types under the conditions of the developed technology. The level of the properties of CMC in the studied systems seems to be improvable by the creation of an interphase layer that controls the cohesion between the fibers and the matrix and by optimization of its composition.

Research in the field of creation of ceramic-matrix composites (CMC) reinforced with fiber fillers has intensified in recent years. Silicon carbide whiskers SiC_w and discrete (short) and continuous fibers of silicon carbide SiC_f and carbon C_f, the main properties of which are presented in Table 1 and Fig. 1 [1], are widely used in order to considerably enhance the strength and the crack resistance.

A universal reinforcing filler with properties that are optimum in all respects does not exist in nature. SiC_f fibers are suitable for the reinforcement because of their high resistance to oxidation and good compatibility with most of the matrix materials. C_f fibers have the highest elastic strength parameters of all CMC fillers, which improve with the increase in the temperature to 2000°C. The use of SiC_f is limited by the service temperature, which does not exceed 1000 – 1200°C. The use of carbon fibers is limited by their rapid oxidation at 400 – 500°C and the high anisotropy of the crystal lattice of carbon.

The highest strength and crack resistance have been observed in silicon nitride ceramics obtained by the method of hot pressing. The method is also effective for fabrication of CMC in the Si_3N_4 – SiC_w system.

At the present time, the traditional sintering methods, which include hot pressing, are being replaced by the more complex and laborious technologies of CMC synthesis. However, the classical methods remain effective and available for shaping of layered composites, especially with the use of whiskers or short fibers, and for rapid evaluation of the properties of CMC and the state of their individual components. Taking into account that the process occurs in two isolating media, i.e., nitrogen and the graphite press mold, the fibers will hardly be oxidized in the sintering process.

[1] Tekhnologiya Research and Production Association, Obninsk State Research Center of the Russian Federation, Obninsk, Kaluga Region, Russia.

TABLE 1. Properties* of Reinforcing Elements

Filler	d, μm	ρ, g/cm^3	E, GPa	σ_{tens}, GPa	T_{max}, °C
SiC_w	0.5 – 1	3.2	450 – 650	1.5 – 90	1500 – 1900
SiC_f	10 – 25	2.55	200 – 350	3.0	1000 – 1250
C_f	6 – 14	1.8 – 2.0	100 – 800	3.5	2200

* d is the diameter of the fibers, ρ is the density, E is the modulus of elasticity, σ_{tens} is the ultimate tensile strength, and T_{max} is the maximum service temperature.

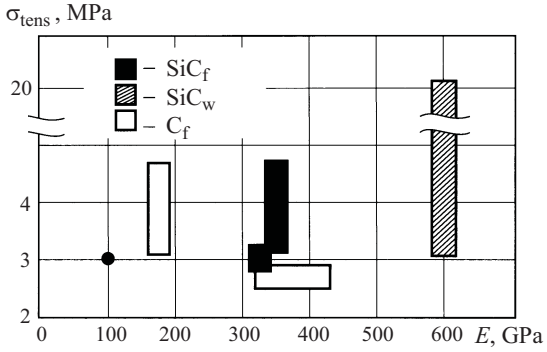

Fig. 1. σ_{tens} and E of ceramic fibers and single crystals.

TABLE 2. Characteristics of Continuous Fibers of Silicon Carbide

Parameters	SiC fibers produced by			
	UBE Industries, Ltd. (Japan)	Nippon Carbon (Japan)	Nippon Carbon (Japan)	VNIIPV (Russia)
Grade	Tyranno	Nicalon	Nicalon	–
Sort	TM–S1HO8PX	NLM-200	Hi(s)	–
Composition	Si–Ti–C–O	Si–C–O	Si–C=O	Si–C–O
Number of fibers in a bundle	800	500	–	–
σ_{tens}, GPa	2.7 – 2.8	2.5 – 3.0	2.5 – 3.0	2.5 – 3.0
Modulus of elasticity, GPa	170 – 180 (200)	180 – 200	300 – 350	250
Content of O_2, %	12	12	0.5	18
Density, g/cm^3	2.3 – 2.4	2.5	2.5	–
Admixtures	Ti (1.5 – 3.0%)	–	–	–
Diameter, μm	8 – 10	12 – 15	10 – 15	17 – 22
Temperature of long-term service, °C	1200	1000	1500, 1700*	1150, 1250*
Reference	[1, 3]	[1, 3, 4]	[5]	[2]

* The working temperature and the maximum service temperature, respectively, in °C.

We devoted most of our attention to microstructural aspects of the problem of creation of CMC in $Si_3N_4 – SiC_f$ and $Si_4N_4 – C_f$ systems with high strength and crack-resistance parameters under the conditions of hot pressing. The matrices were created from plasmachemical ultrafine powder compositions in $Si_3N_4 – Y_2O_3$ systems, which have proved very efficient in high-strength monolithic materials and as matrices in composites with BN, Al_2O_3 (microspheres), and SiC_f domestic and imported fillers (Tables 2 and 3).

It can be seen from Table 2 that SiC_f fibers produced in Russia have about the same level of properties as Nicalon fibers [2]. However, the fibers of grade Hi(s) contain much less oxygen, which substantially improves their heat resistance. Fibers of grade Tyranno, bearing a modifying additive of titanium, have a much higher heat resistance [1].

TABLE 3. Characteristics of Carbon Fibers

Parameters	Type of C fiber	
	UKN-P/5000	UKN-P/2500
Description	Complex carbon thread	
Rated linear density, tex	410	205
Deviation of the actual linear density from the rated one, %	± 7	± 8
Relative load of thread breaking with breakage of loops, Sn/tex, at most	9.8	5.9
Thread density, g/cm^3	1.730 ± 0.3	
Mass fraction of finishing agent, %	3.5 ± 1.5	
Modulus of elasticity of a thread, GPa	230 ± 20	230 ± 30
Breaking stress of a thread stretched over a microplastic, GPa, at least	2.8	2.0
Fiber diameter, μm	10	10

By the data of [2], SiC_f fibers generally have a dense structure with crystallites 0.7 – 10 nm in size oriented quite randomly. The structure of the Tyranno fibers possesses the finest grains. Studying the morphology of the fibers at a lower resolution, we established that they have a dense structure (Fig. 2*a*). The external surface of the fibers is finished and seems to be covered by a thin (several Angstroms) SiO_2 film easily removable by etching in HF and H_2SO_4. The surface bears densely bonded formations about 1.5 μm in size (Fig. 2*b* and *c*). The surface of the Tyranno fibers is the most resistant to the action of acids among the studied fillers. The number of defects is the greatest in domestic fibers.

The structure of C_f is heterogeneous and is represented by a nucleus and a structurized shell (Fig. 3) the proportion of the thicknesses of which determines the properties of the fibers [6].

We studied three types of specimen represented by single-layer or multilayer structures with specified alternation of the layers of the matrix Si_3N_4 powder, a mechanical mixture of the matrix powder and short fibers, and a prepreg based on fibers and a matrix powder (Fig. 4). In order to obtain a mechanical mixture, continuous C_f fibers were cut into 5-mm-long segments and introduced into the matrix in an

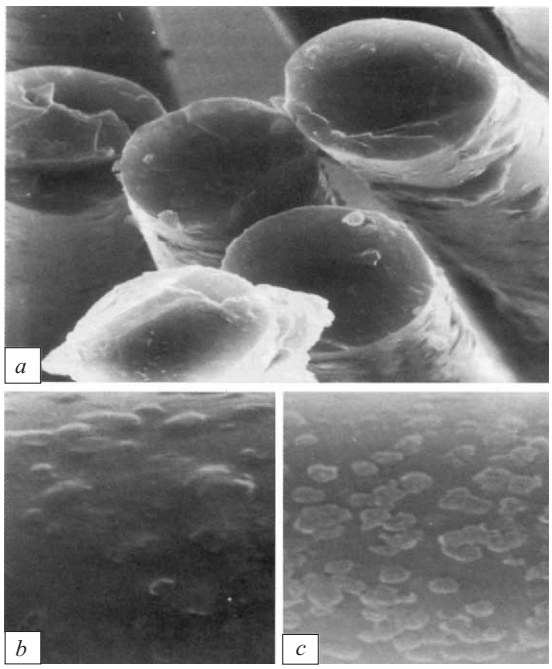

Fig. 2. Morphology (*a*) and surface structure of SiC_f fibers [*b*) initial, *c*) after etching with HF]; *a*) × 2000; *b*, *c*) × 4000.

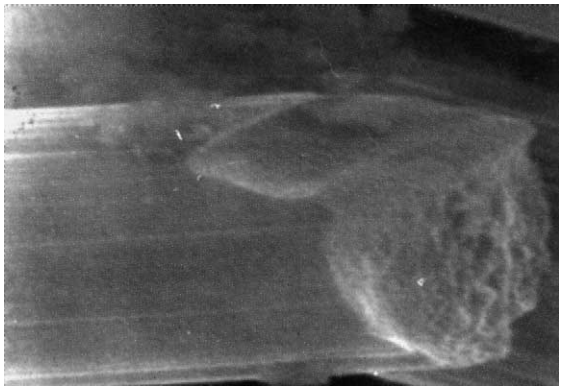

Fig. 3. Morphology of C_f fibers; × 6000.

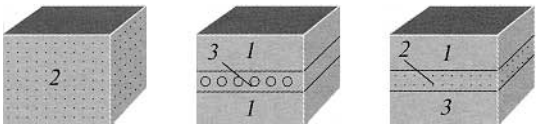

Fig. 4. Standard CMC specimens: *1*) matrix; *2*) short fiber + matrix; *3*) prepreg.

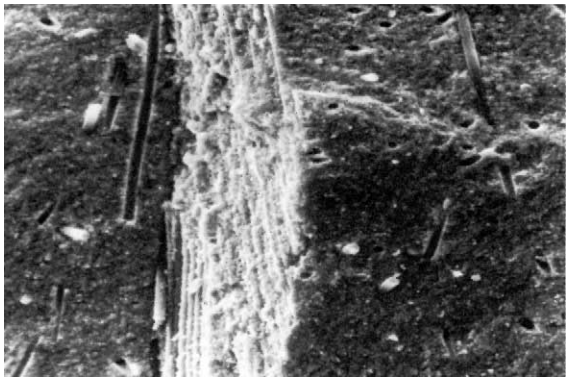

Fig. 5. Structure of a layered CMC reinforced with short and continuous C_f fibers; × 220.

amount of 2 – 5 wt.%. During the mixing the C_f fibers broke (crushed) and their length reduced to 20 – 900 μm depending on their proportion. The length of the majority of short fibers exceeded their diameter by a factor of 5 – 10.

The binder for the prepreg was methylcellulose in an amount of 0.5%. In order to study the behavior of various types of SiC_f and C_f fibers, the thickness of the fiber layer was minimized by rolling it to an 80-μm monolayer in the ready material (Fig. 5).

The specimens were prepared by impregnation in a suspension and subsequent hot pressing (SIHP); the main stages of the process are presented in Fig. 6. The layers were compacted in a graphite press mold in a nitrogen medium at 1700°C and a pressure of 20 MPa for 1 h. In order to decrease the sintering temperature (by 100 – 150°C) and the amount of the sintering activator, we used a matrix with a

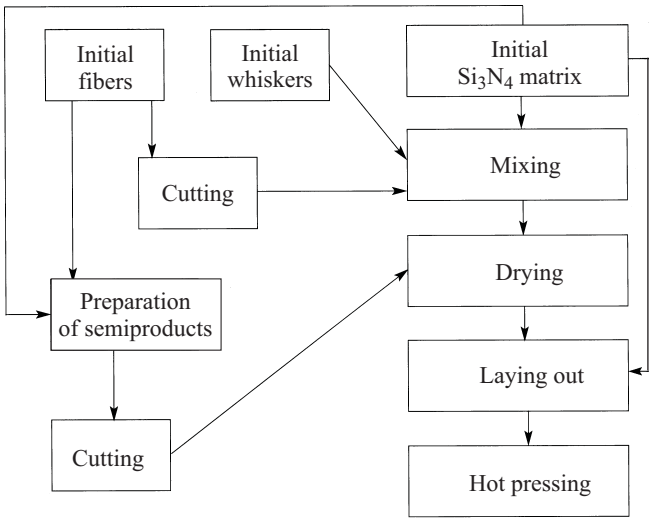

Fig. 6. Diagram of the process of CMC production.

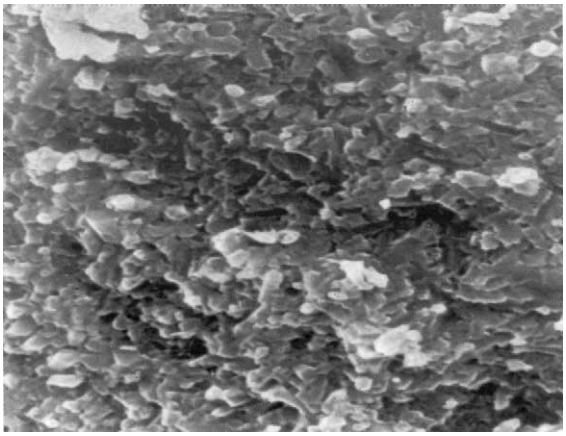

Fig. 7. Microstructure of silicon nitride matrix, × 4000.

Si_3N_4 – MgO composition. We studied the physicochemical properties and the microstructure of the CMC by electron and optical microscopy and fractographic analysis.

On the basis of classical concepts on the creation of CMC, the state of the fibers and the structure of the composite were investigated from the standpoint of formation of a high-density matrix, uniformity of the distribution of the filler at a given content of V_f, degree of orientation of fibers in the matrix, isolation of the fibers by the matrix layer, strength of interaction on the fiber–matrix boundary, minimum mechanical damage to the fibers in the course of sintering, and other factors.

A complex analysis of the microstructure allowed us to determine the general rules of its formation in CMC and the behavior of SiC_f and C_f fibers of various types under the conditions of the developed process, namely,

– in all cases, the formed matrix structure had a density close to the theoretical one (Fig. 7);

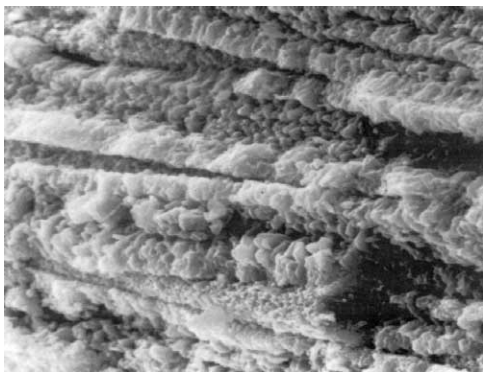

Fig. 8. Illustration of wetting of C_f fibers by the matrix powder, × 2000.

Fig. 9. Isolation of $Si_3N_4 - SiC_f$ fibers by a matrix layer, × 6000.

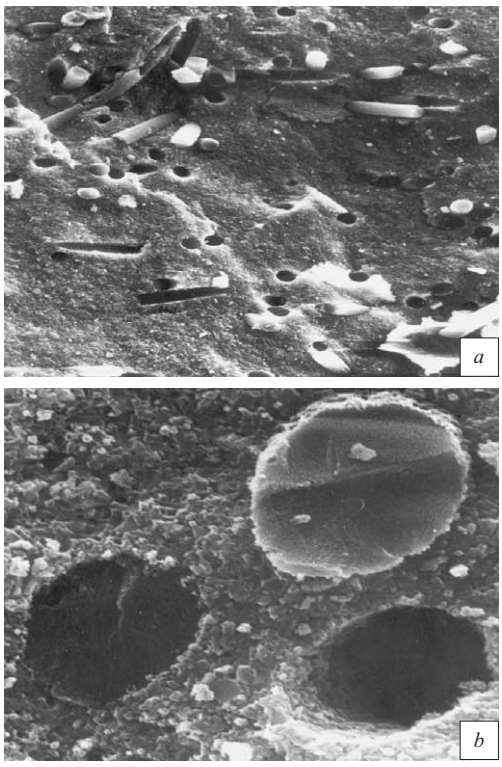

Fig. 10. Distribution of short C_f fibers in silicon nitride matrix, *a*) × 400; *b*) × 4000.

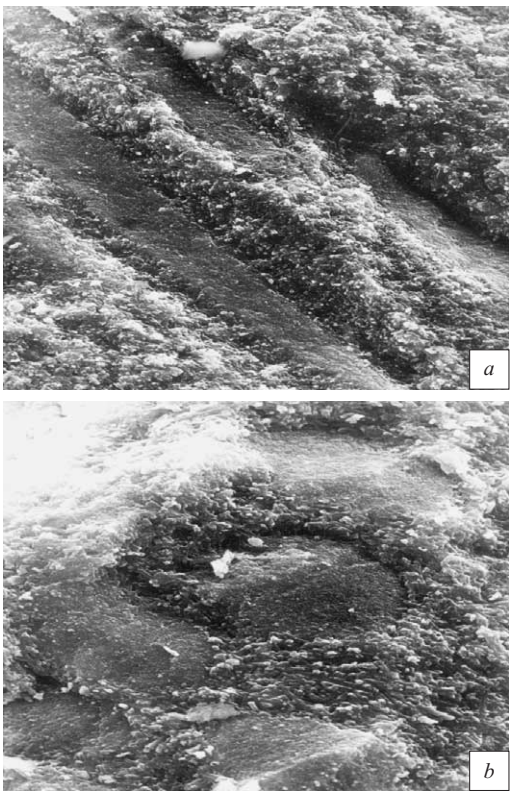

Fig. 11. Orientation of SiC_f fibers in silicon nitride matrix: *a*) normal to the hot pressing force, × 1000; *b*) parallel to the hot pressing force, × 2000.

– in all cases, the fibers were fully wetted by the matrix powder (Fig. 8);

– the fibers in the monolayer of $Si_3N_4 - SiC_f$ and $Si_3N_4 - C_f$ systems had a diameter ranging from 6 to 22 μm and were isolated by a layer of the matrix material (Fig. 9);

– the short fibers were uniformly distributed in the matrix of the $Si_3N_4 - (10 - 20$ vol.%) C_f system without forming bundles or clusters (Fig. 10*a*); there is an opinion that unidirectional fibers in a continuous matrix should be positioned in vertices of an equilateral triangle (Fig. 10*b*) [7];

– in all cases, the SiC_f and C_f fibers were oriented in the matrix; as in SiC_w, their crystallographic axis *c* was perpendicular to the hot pressing force (Figs. 11 and 12);

– the geometry and size of the fibers in the structure of the $Si_3N_4 - C_f$ material were preserved in hot pressing (see Fig. 11), though they were transformed into polycrystalline β-SiC;

– in the $Si_3N_4 - C_f$ system, the fibers preserved their physical and chemical integrity both in discrete and continuous forms (see Fig. 5);

– a close contact was observed between the matrix and the fibers at the level of chemical interaction of components in the $Si_3N_4 - SiC_f$ system without the formation of an intermediate interphase layer (Fig. 13);

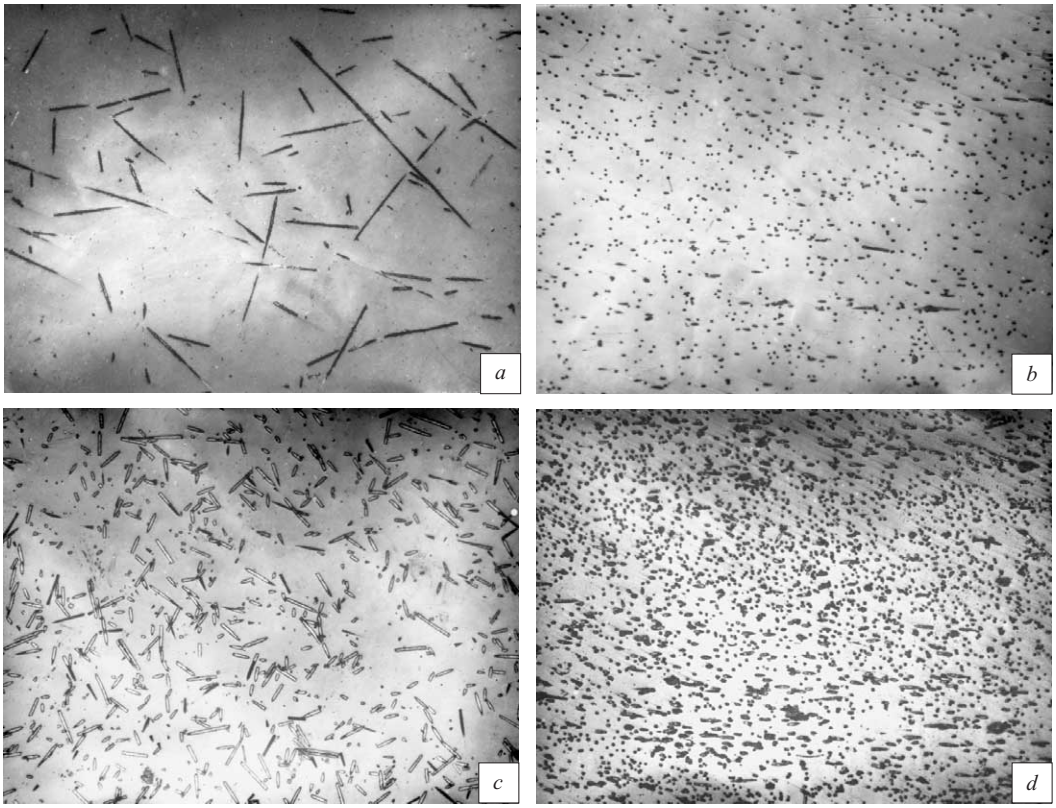

Fig. 12. Orientation and distribution of short C_f fibers in silicon nitride matrices with different contents of the filler (*a*, *b*) 10 vol.% C_f; *c*, *d*) 20 vol.% C_f): *a*, *c*) normal to the hot pressing force, × 100; *b*, *d*) parallel to the hot pressing force, × 100.

– in the $Si_3N_4 – C_f$ system, on the contrary, the matrix and the fibers were virtually not bonded to each other and the mechanical cohesion seemed to be provided by the roughness of the surface (Fig. 14).

A more detailed analysis of the state of SiC_f fibers of various grades in CMC showed considerable differences in their structure. For example, Hi(s) fibers have a dense granular structure with grains 0.1 – 0.25 μm in size (see Fig. 13b), whereas domestic fibers have a looser structure in which individual coarser grains have a round shape and the same size but are not bonded to each other (Fig. 15). This softening of the fibers is caused by recrystallization of SiC above 1200°C, which is accompanied by growth of the crystal sizes. Simultaneously, the interaction with oxygen at the same temperature by the reaction $SiC + O_2 = SiO + CO$ intensifies and yields unstable silicon monoxide, which causes fracture of the fibers [8]. Fibers of grades TM and NLM (see Table 2) occupy an intermediate position and have a structure closer to Hi(s). In order to suppress the high-temperature structural changes, recrystallization in the first place, the composition of the Tyranno fibers is enriched with 4 wt.% Ti [1].

The transition from a matrix with a $Si_3N_4 – Y_2O_3$ composition to a $Si_3N_4 – MgO$ composition influences the number of defects in the fiber layer considerably; cavities, voids, and glass-phase clusters that have emerged at higher

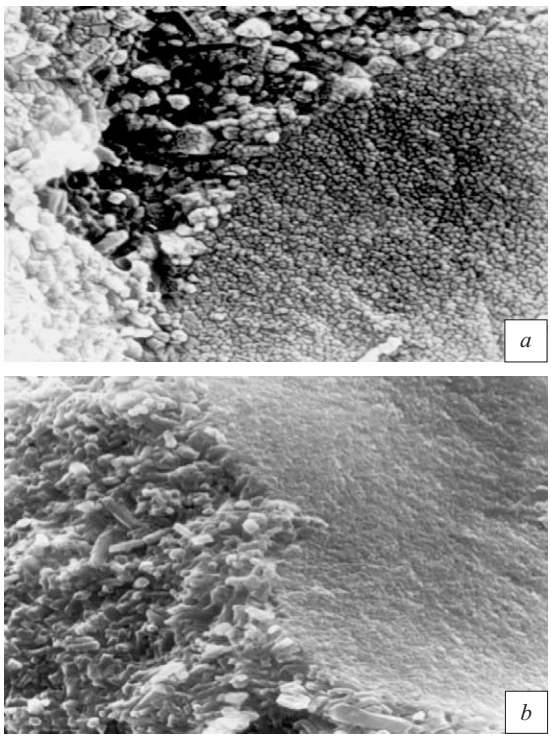

Fig. 13. SiC_f fiber/matrix interface: *a*) domestic fibers, × 6000; *b*) Hi(s) fibers, × 4000.

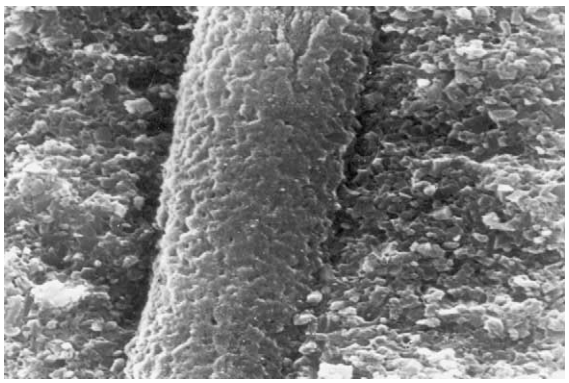

Fig. 14. C_f fiber/matrix interface, × 4000.

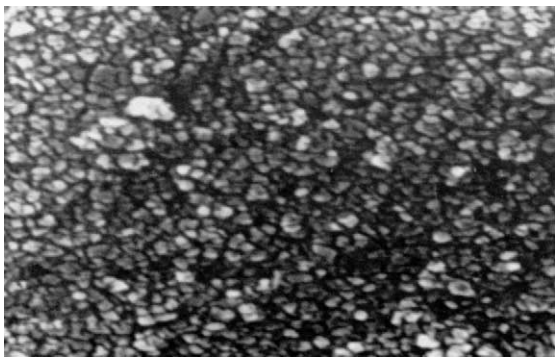

Fig. 15. Recrystallization of silicon carbide fiber in hot pressing, × 10,000.

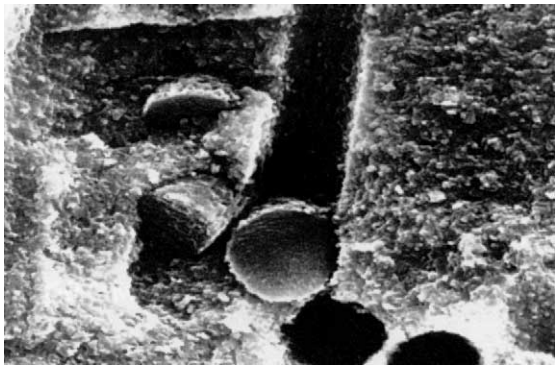

Fig. 16. Fracture in $Si_3N_4 - C_f$ CMC, × 2000.

sintering temperatures disappear. An estimation of the physicomechanical properties of CMC showed that the maximum value of crack resistance in the $Si_3N_4 - SiC_f$ system is 8.2 MPa · $m^{1/2}$ and that in the $Si_3N_4 - C_f$ system is 9.8 MPa · $m^{1/2}$ relative to a matrix level of 6.6 MPa · $m^{1/2}$. Simultaneously, the ultimate bending strength decreases by 10 – 20%, amounting to 600 MPa. We obtained these results for pure fibers, which can be treated as a reference point. A microstructural study showed that the crack resistance of $Si_3N_4 - SiC_f$ and $Si_3N_4 - C_f$ could be improved further by optimizing the strength of the fiber–matrix bonding by the use of barrier coatings or modification of the surface. Maximum values of the properties are typical for combined layered specimens with short and continuous fibers (see Fig. 12).

An analysis of fracture surfaces showed that defects typical for monolithic ceramics, i.e., cleavage facets, inclusions, and pores in the fiber layer, initiate fracture in layered specimens with a fiber monolayer also. When the size of the fiber layer exceeds the critical value, fracture in composite ceramics is initiated in the layer of SiC_f and C_f fibers, because the stresses in the region of the layer exceed the stresses caused by the applied load (double-front crack and zone of final breaking).

Figures 10*b* and 16 present the types of fracture in CMC depending on the type of interaction between the fibers and the matrix, i.e., a cavity in the matrix due to stretching of the fibers and fracture of a fiber over the end face. The fracture surfaces bear microregions of tough fracture with lamination over the fiber/matrix interface and microregions of brittle fracture with mirror cleavage and without lamination. We can also discern outcrops of fibers up to 10 μm long (Fig. 10*a*).

The level of properties of CMC in the considered systems seems to be further improvable by creating an interphase layer controlling the cohesion between the fibers and the matrix and by optimizing its composition. The strength of the cohesion between the fibers and the matrix in CMC should be optimum, because when it is insufficiently high the distribution of stresses among neighbor fibers is impeded, and when it is too high the fracture mechanism of the CMC changes [8, 9]. For example, for the $Si_3N_4 - SiC_f$ system this cohesion is quite strong and turns the composite into a monolithic brittle body, which decreases its strength. In the $Si_3N_4 - C_f$ system, on the contrary, the fiber–matrix bonding is weakened, the fibers are easily withdrawable, and do not hamper fracture of the material.

Control of the fiber–matrix cohesion characteristics is a difficult problem. One way of solving it consists of creating an intermediate barrier layer or protective coatings on the SiC_f fibers, for example, C and BN coatings that serve as barriers for the diffusion interaction and create zones of relative weakening of the structure on phase boundaries. In the $Si_3N_4 - C_f$ system it is necessary to intensify the adhesion interaction between the fibers and the matrix to make it sufficient for transfer of the stresses from fiber to fiber. Since the surface of C_f is characterized by weak adhesion to the silicon nitride matrix, it should be treated in order to deepen the relief and increase the polarity and the content of the functional groups [9, 10].

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