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VARIOUS  
TECHNOLOGICAL PROCESSES

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## Ceramic-Forming Compounds Based on Polycarbosilane and Modified Polyorganosilazanes

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**Abstract**—Ceramic-forming compounds based on polycarbosilane and polyorganosilazanes modified with atoms of refractory metals (Ti and Zr) were studied. The curing and pyrolysis of the compounds in an inert medium and the thermal oxidation resistance of ceramic pyrolysis residues were examined by synchronous thermal analysis and extraction. A ceramic matrix composite material was prepared from the compounds studied and a carbon reinforcing filler, and the physicochemical properties and thermal oxidation resistance of this material were evaluated.

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The progress of many branches of industry largely depends on solution of such problems as increasing the efficiency of energy generation and transfer systems and reducing the negative effect on the environment. One of the ways to solve these problems is the development of high-temperature inorganic materials. The use of traditional inorganic materials is restricted to the conditions requiring high mechanical strength in combination with high heat resistance. The structural ceramics generally meet these requirements, i.e., exhibit high chemical stability and mechanical strength at elevated temperatures. However, the use of a ceramic is limited by its brittleness, whereas metals are less resistant to corrosion, and their mechanical properties drastically decrease on approaching the melting point of the metal. Hence, there is high demand for ceramics exhibiting enhanced crack resistance and stability in aggressive media [1–4].

The material capable of reliable operation at elevated temperatures in aggressive media should have definite microstructure (nature of constituent phases, their amount, and distribution throughout the volume). Therefore, new approaches to the development of ceramic materials are required to obtain a ceramic of preset composition with a definite set of useful properties [5].

Efforts of researchers from different countries are focused on the development of scientific and technological principles of methods for preparing ceramic materials of preset microstructure. In most cases, these methods are based on thermochemical transformations of organoelement precursors into inorganic materials. Such transformations of a polymer material into a ceramic include a complex series of chemical and physical processes. The choice of the starting organoelement compound, of procedures for its treatment, and of high-temperature annealing conditions should be based on a rigorous scientific approach to the problem, requiring knowledge from many fields such as organic and inorganic chemistry, mineralogy, materials science, and computer simulation. It is necessary to perform basic interdisciplinary research to develop a procedure for commercial production of ceramic materials of new generation [6–10].

Silicon nitride ( $\text{Si}_3\text{N}_4$ ), silicon carbide (SiC), and their composites prepared from polysilazanes were extensively studied recently in Europe, Japan, and the United States.  $\text{Si}_3\text{N}_4$ /SiC composites show promise for use at high temperatures, e.g., in parts of a gas turbine engine, in cutting devices, and in microelectronics. As compared to the materials prepared from monolithic silicon nitride, the composites exhibit enhanced strength

not only at room temperature, but also at elevated temperatures, even up to 1600°C. However, preparation of such composites by traditional procedures (sintering) is complicated by different physical properties of Si<sub>3</sub>N<sub>4</sub> and SiC at elevated temperatures. One of alternative pathways is using as a starting material silicon carbonitrides of the general formula Si<sub>3+x</sub>N<sub>4</sub>C<sub>x+y</sub>, which form a single-phase material with homogeneous distribution of the silicon, carbon, and nitrogen atoms. Apparently, the ratio of these three elements can be varied and controlled by choosing appropriate Si/C/N precursors [11–13].

Polyorganosilazanes are capable to form an amorphous cross-linked material transforming into amorphous SiCN ceramic at approximately 1000°C. The first crystalline compounds of the Si/C/N system of the compositions SiC<sub>2</sub>N<sub>4</sub> and Si<sub>2</sub>CN<sub>4</sub> were prepared recently. A specific feature of SiCN ceramic prepared from polysilazanes is that the crystallization starts at temperatures higher than 1200°C. The material remains metastable at temperatures lower than 1400°C; further heating leads to the removal of nitrogen, with the composition of the system reaching Si<sub>3+x</sub>C<sub>x</sub>N<sub>4</sub>; by the end of crystallization, the system consists of two phases: Si<sub>3</sub>N<sub>4</sub> and SiC. Hence, the thermal stability of the Si/C/N ceramic prepared from polyorganosilazanes can be considerably enhanced by reducing the nitrogen loss at elevated temperatures, which requires directional formation of the Si<sub>3+x</sub>C<sub>x</sub>N<sub>4</sub> composition. In this case, the carbon content can be controlled by performing the heat treatment of polyorganosilazanes in a mixed NH<sub>3</sub>/Ar atmosphere [14].

One of the research directions in the field of the development of ceramics based on ceramic-forming polymers is modification of these polymers by introducing into their structure homogeneously distributed nanoparticles and chemically bound atoms of refractory metals such as Zr, Ti, Mo, etc. In the course of heat treatment, these metals transform into nanoparticles of carbides, silicides, and nitrides, decelerating the crystallite growth and stabilizing the ceramic structure on the nanosized level up to 1600–1700°C. Furthermore, structural disordering of such ceramic leads to an increase in the activation free energy of solid-phase reactions of the Si–N bond with carbon, which enhances the heat resistance of the material [11, 15–17].

This study was aimed at developing polymeric ceramic-forming compounds based on polycarbosilane

and polyorganosilazanes containing as modifying additives atoms of refractory metals (Ti, Zr) and at determining the properties of these compounds and of ceramic matrix composites prepared from them.

## EXPERIMENTAL

The following substances were used for preparing ceramic-forming compounds:

polycarbosilane PKS-M produced by the State Research Institute of Chemical Technology of Organoelement Compounds, a solid substance containing 49.78 wt % Si and 0.70 wt % Si-bonded H; weight gain in the course of heating in air to 200°C 14.6%;

polyorganosilazanes of various structures, produced by the same institute:

Polisil 04M (sample 1): a viscous liquid containing 38.7 wt % Si and 1.0 wt % Si-bonded H;

Polisil 04Ti (sample 2): a viscous liquid containing 33.1 wt % Si, 0.8 wt % Si-bonded H, and 4.0 wt % Ti;

Polisil 04Zr (sample 3): a viscous liquid containing 40.7 wt % Si, 1.2 wt % Si-bonded H, and 0.9 wt % Zr.

Samples of ceramic-forming compounds were prepared by dissolution of the starting components in analytically pure grade hexane at room temperature, followed by solvent removal in a vacuum (1 mmHg) to constant weight.

We prepared compounds based on polycarbosilane and polyorganosilazanes of various structures with the component weight ratio of 2/1, respectively: PKSZ-21M (based on Polisil 04M), PKSZ-21T (based on Polisil 04Ti), and PKSZ-21Ts (based on Polisil 04Zr).

Synchronous thermal analysis (STA) of the initial polyorganosilazanes and their compounds and preparation of the cured and pyrolyzed compound samples were performed under 99.9% argon.

Pyrolysis of the initial polyorganosilazane samples was studied by STA [thermal gravimetric analysis (TGA) combined with differential scanning calorimetry (DSC)] with a Netzsch STA 449 F3 device under the following conditions: temperature interval 30–1200°C, heating rate 10 deg min<sup>-1</sup>, argon flow rate 50 mL min<sup>-1</sup>.

The temperature interval of curing of the compounds was determined by STA on a Netzsch STA 449 F3 device under the following conditions: temperature interval 30–400°C, heating rate 10 deg min<sup>-1</sup>, argon flow rate 50 mL min<sup>-1</sup>.

**Table 1.** Elemental composition of polyorganosilazane samples

Sample	Content, wt %					
	N	Si	C	Si-bonded H	Ti	Zr
Polisil 04M (1)	19.2	38.7	30.2	1.0	–	–
Polisil 04Ti (2)	12.8	33.1	32.0	0.8	4.0	–
Polisil 04Zr (3)	15.6	40.7	27.7	1.2	–	0.9

The cured compound samples were prepared in a Nabertherm N 11H furnace at an argon flow rate of 10 L min<sup>-1</sup>. The temperature interval of curing was 100–350°C.

The yield of the insoluble polymer was determined by extracting the samples with toluene in a Soxhlet apparatus for 40 h.

The temperature interval of pyrolysis of the cured compounds was determined on the basis of the STA data on a Netzsch STA 449 F3 device under the following conditions: temperature interval 30–1400°C, argon flow rate 50 mL min<sup>-1</sup>, heating rate 10 deg min<sup>-1</sup>.

Pyrolysis of the cured samples was performed in a Nabertherm N 11H high-temperature furnace at an argon flow rate of 10 L min<sup>-1</sup>. The temperature interval of pyrolysis was 300–1100°C. The sample was kept for 1 h at each temperature at 100°C intervals.

The thermal oxidation resistance of the pyrolysis products was evaluated from the STA data with a

Netzsch STA 449 F3 device in synthetic air (air flow rate 50 mL min<sup>-1</sup>, protective gas 99.9% nitrogen, 20 mL min<sup>-1</sup>). Experiments were performed in the temperature interval 30–1400°C at a heating rate of 10 deg min<sup>-1</sup>.

The content of carbon, nitrogen, and total hydrogen was determined with a FLASH 2000 elemental analyzer, and the content of silicon and Si-bonded hydrogen was determined gravimetrically.

The viscosity of ceramic-forming suspensions was determined by measuring the time of continuous outflow of a definite suspension volume through a calibrated orifice (4 mm in diameter) of a VZ-246 viscometer.

The density of ceramic-forming suspensions was determined with an AON-5 general-purpose areometer.

The density of composite material samples was determined by hydrostatic weighing.

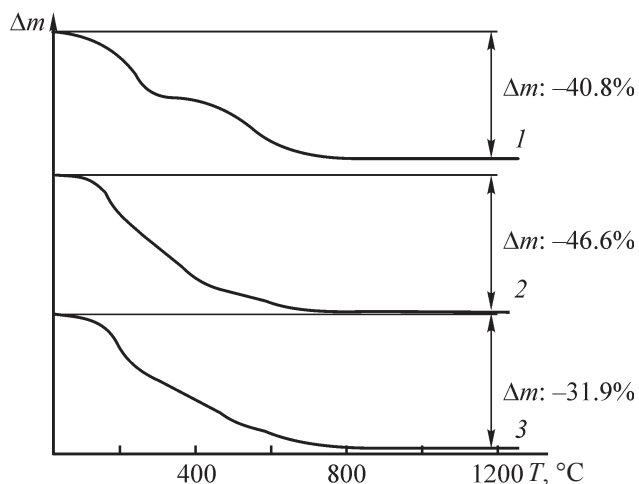
The C heat resistance was determined with a TK-72.1750L3F high-temperature electric furnace with an automatic control system.

The bending,  $\sigma_b$ , and compression,  $\sigma_c$ , strengths of composite materials were determined by measuring the force causing the sample failure at bending or compression.

## RESULTS AND DISCUSSION

**Physicochemical properties of polyorganosilazanes.** We have studied the elemental composition of polyorganosilazane samples: weight fraction of carbon, nitrogen, silicon, and Si-bonded hydrogen (Table 1).

An STA study of the polyorganosilazanes has shown that their TGA curves are, on the whole, similar. Two transitions are manifested in the curves, suggesting the two-step course of pyrolysis. The first step starts at 175–215°C, and the second step, at temperatures from 470 to 700°C. The pyrolysis is complete at 1100–1200°C. The weight loss in the course of pyrolysis is 31.9–46.6 wt %. The smallest weight loss, 31.9%, is



**Fig. 1.** TGA curves recorded in the course of synchronous thermal analysis of polyorganosilazane samples. ( $\Delta m$ ) Weight loss and ( $T$ ) temperature; the same for Figs. 3 and 4. (1) Polisil 04M, (2) Polisil 04Zr, and (3) Polisil 04Ti.

**Table 2.** Characteristics of TGA curves

Samples	Transition steps				Total weight loss, %
	first step		second step		
	$T_{\text{onset}}$ , °C	$T_{\text{end}}$ , °C	$T_{\text{onset}}$ , °C	$T_{\text{end}}$ , °C	
Polisil 04M	209	477	477	1200	40.8
Polisil 04Ti	201	460	460	1200	31.9
Polisil 04Zr	179	596	596	1200	46.6

observed for the polyorganosilazane containing Ti atoms (Polisil 04Ti), and the largest weight loss, 46.6%, for the polyorganosilazane containing Zr (Polisil 04Zr). It should be noted that there is no direct correlation between the temperature intervals of curing and degradation (both first and second steps) of polyorganosilazanes, on the one hand, and amount of the ceramic residue, on the other hand. The temperature intervals of thermochemical transformations of polyorganosilazanes and the ceramic residue are probably determined by the sample history, namely, by the starting components, synthesis conditions, molecular mass of the oligomers, etc.

**Technological and physicochemical properties of ceramic-forming compounds.** We have studied the physicochemical properties of the ceramic-forming compounds based on polycarbosilane and polyorganosilazanes and their thermochemical transformations in the temperature interval 100–1100°C under argon. After removing the solvent in a vacuum, we determined the weight fractions of carbon, nitrogen, silicon, total hydrogen, and Si-bonded hydrogen. The results are given in Table 3.

We have studied curing of ceramic-forming compounds based on polycarbosilane and polyorganosilazanes containing Ti and Zr as modifying additives.

The temperature interval of curing of the compounds was determined by synchronous thermal analysis. The results are shown in Fig. 2. Curing of the compound containing Polisil 04M occurs in the temperature interval 100–350°C. Sample of PKSZ-21M exhibits a strong maximum at 300°C.

The DSC curves of the compounds containing polyorganosilazanes with Ti and Zr modifying additives are similar in shape but have certain specific features. The main difference is a shift of the curing interval toward lower temperatures. For example, the PKSZ-21T system containing polyorganosilazane with the modifying Ti additive undergoes curing in two steps

in the temperature interval 80–300°C with a strong maximum at 235°C.

For PKSZ-21Ts containing polyorganosilazane with the modifying Zr additive, curing occurs at still lower temperatures in the interval 80–250°C. A strong maximum is observed at 123°C.

Taking the data obtained into account, we performed curing of the compounds in the temperature interval 150–350°C under argon. The curing completeness was determined from the yield of the insoluble polymer (gel fraction) after extraction of the cured compound samples with toluene in a Soxhlet apparatus for 24 h. Data on the gel fraction yield are given in Table 4.

As can be seen, the degree of curing of the PKSZ-21M compound is the lowest, 67.0 wt %.

The compound containing polyorganosilazane with the modifying Zr additive is cured virtually completely, whereas the degree of curing of the PKSZ-21T compound is 73.3%.

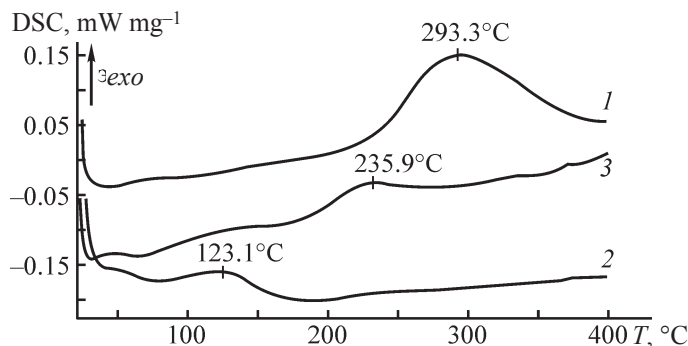
The pyrolysis of the cured compounds was studied by thermal gravimetric analysis (Fig. 3, Table 4).

The copolymer degradation occurs in the interval 300–800°C and is accompanied by the weight loss determined by the compound composition. For example, for the PKSZ-21M compound the weight loss in this temperature interval was 15.8%; for the PKSZ-21T

**Table 3.** Physicochemical properties of ceramic-forming compounds

Compound	Content, wt %				
	N	C	H	Si	Si-H
PKSZ-21M	6.27	35.88	7.75	45.25	0.85
PKSZ-21T	3.60	37.00	7.90	42.63	0.66
PKSZ-21Ts	4.63	33.78	7.71	44.93	0.91





**Fig. 2.** DSC curves recorded in the course of synchronous thermal analysis of samples of ceramic-forming compounds, (*T*) Temperature. (1) PKSZ-21M, (2) PKSZ-21Ts, and (3) PKSZ-21T.

compound, 13.0%; and for the PKSZ-21Ts compound, 15.2 wt %. In the second step, from 750 to 1400°C, the ceramic residue undergoes densification, and the weight loss does not exceed 5%.

Taking the TGA data for the cured compounds into account, we performed their pyrolysis under argon in the temperature interval 300–1100°C and determined the yield of the ceramic residue (Table 4).

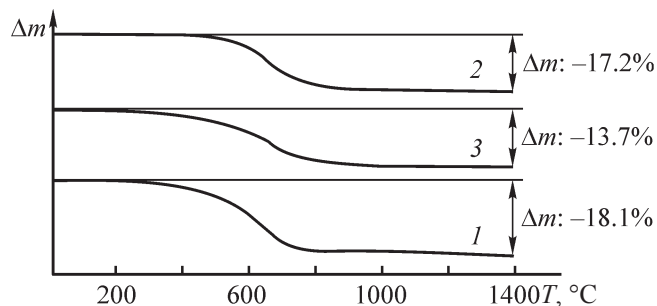
The thermal oxidation resistance of the ceramic residues of PKSZ-21M, PKSZ-21T, and PKDZ-21Ts was studied by STA.

As we found (Fig. 4), the ceramic residues undergo no weight loss at temperatures of up to 1100°C, and in the interval 1100–1450°C the weight loss for the PKSZ-21M residue is 0.32 wt %. Introduction of titanium and zirconium into polyorganosilazanes enhances the resistance of the ceramic pyrolysis products to thermal oxidation: The weight loss in the interval 1100–1450°C is 0.1 and 0.2 wt %, respectively.

**Technological and operation properties of ceramic matrix materials based on compounds with polyorganosilazanes containing modifying Ti and Zr additives.** The following characteristics were determined:

- viscosity and density of impregnating ceramic-forming suspensions,
- ultimate compression strength,
- ultimate bending strength,
- heat resistance.

We prepared samples of ceramic matrix composite materials (CMs) from UKN-5000 reinforcing carbon fibers, PKSZ-21T and PKSZ-21Ts ceramic-forming compounds, amorphous boron, and cobalt sulfate.



**Fig. 3.** TGA curves recorded in the course of synchronous thermal analysis of cured samples of ceramic-forming compounds. (1) PKSZ-21M, (2) PKSZ-21Ts, and (3) PKSZ-21T.

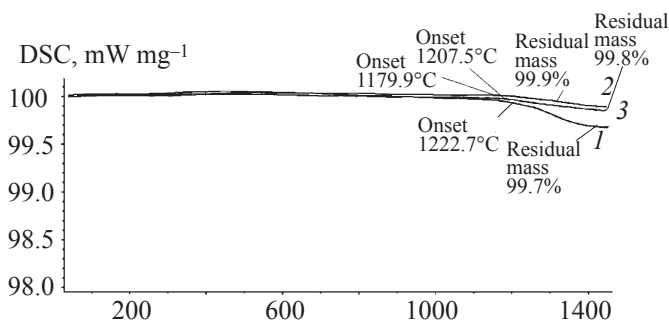
The CM fabrication process involved the following operations: preparation of reinforcing components, preparation of impregnating suspensions, fabrication of prepreg (fiber laying and impregnation), drying of the prepreg in air, heat treatment (curing and pyrolysis in a vacuum), and determination of the properties of the material.

The characteristics of impregnating suspensions are given in Table 5.

As the impregnating solution concentration is decreased from 40 to 10 wt %, the conventional viscosity decreases from 22 to 19 s for PKSZ-21Ts and from 18 to 16 s for PKSZ-21T, and the density, from 780 to 620 kg m<sup>-3</sup> for PKSZ-21Ts and from 670 to 578 kg m<sup>-3</sup> for PKSZ-21T, respectively.

For determining the operation characteristics, the CM samples were prepared by hot pressing.

In the course of CM fabrication, we studied how the number of impregnation–pyrolysis cycles influences the sample density. The results are given in Table 6.



**Fig. 4.** TGA curves of thermal oxidative degradation of ceramic products obtained by pyrolysis of the cured compounds. (1) PKSZ-21M, (2) PKSZ-21T, and (3) PKSZ-21Ts.

**Table 4.** Yield of the gel fraction and ceramic residue of the cured compounds

Compound	Gel fraction yield (average), wt %	Yield of ceramic residue in pyrolysis, wt %	
		TGA in Ar to 1200°C	stepwise heating to 1100°C
PKSZ-21M	67.0	84.2	79.0
PKSZ-21T	73.3	87.0	83.8
PKSZ-21Ts	82.7	84.8	83.3

**Table 5.** Technological properties of impregnating suspensions

Suspension no.	Suspension composition	Conventional viscosity, s	Suspension density, kg m <sup>-3</sup>
1	40%. solution of PKSΖ-21	22	780
2	20% solution PKSΖ-21	20	680
3	10% solution PKSΖ-21Ts	19	620
4	40% solution PKSΖ-21T	18	670
5	20% solution PKSΖ-21T	17	600
6	10% solution PKSΖ-21T	16	578

**Table 6.** Density of composite materials

CM no.	Material composition	CM density, kg m <sup>-3</sup> after indicated number of impregnation–pyrolysis cycles				
		1	2	3	4	5
1	C <sub>f</sub> /(SiC–ZrC) <sub>m</sub>	1300	1450	1520	1750	1950
2	C <sub>f</sub> /(SiC–TiC) <sub>m</sub>	1280	1390	1500	1680	1820

The maximal sample density, 1950 kg m<sup>-3</sup>, was obtained with zirconium-modified polyorganosilazane.

The thermal oxidation resistance of CM samples was evaluated in the temperature interval 1000–1300°C, and the influence of the CM composition on this characteristic was studied. The tests were performed for up to 10 h. The thermal oxidation resistance was evaluated by the change in the sample weight after heating at 1000–1300°C. For high-temperature tests, a two-layer SiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub>–MeS<sub>x</sub> protective coating was additionally applied onto the sample surface. The results are given in Table 7.

The material was found to be resistant to thermal oxidation irrespective of the composition of the initial ceramic-forming compound. The sample weight did not change significantly after 10-h heating at 1000 and even at 1300°C. Slight weight gain of the samples after 8-h heating at 1300°C is caused by chemical processes (oxidation of metal silicides) that occur in the protective layer of the coating and are required for ensuring reliable protection of the material from oxidation.

The mechanical properties of the ceramic matrix material were evaluated from the results of tests to determine the ultimate three-point bending strength and the ultimate compression strength (test temperatures 20, 1000, and 1300°C). The test results are given in Table 8.

The mechanical properties of the CMs at 1000 and 1300°C are virtually identical:  $\sigma_b = 155\text{--}150$  MPa,  $\sigma_c = 75$  MPa upon impregnation with PKSΖ-21Ts compound;  $\sigma_b = 163\text{--}160$  MPa,  $\sigma_c = 98\text{--}97$  MPa upon impregnation with PKSΖ-21T compound.

Thus, CM samples prepared by hot pressing with impregnation using PKSΖ-21T have the highest strength at test temperatures of 1000 and 1300°C.

## CONCLUSIONS

(1) Physicochemical properties of samples of ceramic-forming compounds based on polycarbosilane and polyorganosilazanes containing titanium and zirconium modifying additives were studied.

**Table 7.** Oxidation resistance of CM samples

CM no.	Material composition	CM weight change after heat treatment, wt %										
		1000°C					1300°C					
		2 h	4 h	6 h	8 h	10 h	2 h	4 h	6 h	8 h	10 h	
1	$C_f/(SiC-ZrC)_m$	0	0	0	0	0	0	0	0	0	+0.1	+0.15
2	$C_f/(SiC-TiC)_m$	0	0	0	0	0	0	0	0	0	+0.09	+0.11

**Table 8.** Mechanical properties of CMs

CM no.	Material composition	Ultimate bending strength $\sigma_b$ , MPa			Ultimate compression strength $\sigma_c$ , MPa		
		20°C	1000°C	1300°C	20°C	1000°C	1300°C
1	$C_f/(SiC-ZrC)_m$	180	155	150	92	75	75
2	$C_f/(SiC-TiC)_m$	185	163	160	100	98	97

(2) Curing of the ceramic-forming compounds was studied by synchronous thermal analysis and extraction. Introduction of titanium and zirconium modifying additives into polyorganosilazane shifts the curing interval toward lower temperatures. The gel fraction yield was 73.3 wt % for PKSZ-21T and 82.7 wt % for PKSZ-21Ts.

(3) The pyrolysis of the ceramic-forming compounds in an inert medium was studied by synchronous thermal analysis. The pyrolysis occurs in the temperature interval 350–1100°C irrespective of the compound composition. The yield of the ceramic residue was 79.0 wt % for PKSZ-21M, 83.8 wt % for PKSZ-21T, and 83.3 wt % for PKSZ-21TS under the conditions of stepwise heating to 1100°C.

(4) The thermal oxidation resistance of the ceramic pyrolysis residues was studied by synchronous thermal analysis in an oxidizing medium (air). No weight loss was observed on heating the samples to 1400°C in air.

(5) The density of the composite material samples increases by a factor of 1.5 with increasing number of impregnation cycles. The maximal density, 1950 kg m<sup>-3</sup>, is reached after five impregnations using zirconium-modified polyorganosilazane.

(6) The composite material is resistant to 10-h heat treatment at 1000–1300°C, irrespective of the composition of the initial ceramic-forming compounds.

(7) The composite material preserves the mechanical properties at 1000–1300°C [ $\sigma_b$  150 MPa,  $\sigma_c$  75 MPa (PKSZ-21Ts);  $\sigma_b$  160 MPa,  $\sigma_c$  97 MPa (PKSZ-21T)].

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