Nanometallocarbosilanes and organoelementoxanes as precursors of components of promising ceramic composites

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Abstract. Nanometallocarbosilanes and organoelementoxanes represent a new class of unequaled precursors of components of promising ceramic composites. Ceramic-forming polymers (oligomers) have been synthesized in GNIICHTEOS. They can be used to obtain components of carbide and oxide CCM: nanometallocarbosilanes - precursors of SiC ceramics, modified by mixed carbides (TaₓZrᵧCₑ or TaₓHfᵧCₑ). Organoelementoxane oligomers represent a new class of precursors for components (binders; coatings; fibers, etc.) of corundum (α-Al₂O₃), aluminosilicate (xAl₂O₃·ySiO₂), yttrium aluminum (xY₂O₃·yAl₂O₃), yttrium-aluminosilicate (xY₂O₃·yAl₂O₃·zSiO₂), magnesium aluminum (xMgO·yAl₂O₃), yttrium-aluminum-magnesium (xY₂O₃·yAl₂O₃·zMgO) and high-temperature binary ceramics based on aluminum and yttrium oxides modified by oxides of refractory metals (zirconium, hafnium or chromium) compositions for the preparing high-strength high-temperature and oxidative-resistant ceramic composites.

1. Introduction
The development of new materials with a complex of properties that significantly surpass the physical and mechanical performance of existing materials for operation in extreme conditions becomes the primary task. Ceramic-forming organoelement polymers (oligomers) - nanometallocarbosilanes and organoelementoxanes represent a new class of unequaled precursors for producing components of high-temperature oxidation-resistant high-strength nanostructured ceramic materials: ceramic fibers, matrices, protective coatings, etc. [1, 2].

The active research aimed at the development and investigation of ceramic-forming poly(oligo)carbosilanes (PCS) is in progress in many countries [3-9].

The prospects for the development of modern oxide ceramic materials are determined by the enormous funds that the advanced nations invest in the creation of new highly heat-resistant and chemically inert ceramic materials based on aluminum oxide [9-11].

2. Experimental details
SiC fibers modified with refractory metal compounds were obtained by melt spinning polymer fibers from nanometallocarbosilanes with the following oxidative hardening and carbidization.
The nanometallocarbosilanes and polymer fibers on their basis were pyrolyzed in a Nabertherm 50/500/11 tubular furnace under an argon atmosphere during heating to 1100°C at a rate of 5 °C/min, followed by holding for 1 h and pyrolysis at temperatures up to 1600 °C [12-14].

The organoelementoxanes were heat-treated in a SNOL 12/16 resistance-heated electric furnace at 1300 °C.

The surface morphology and elemental composition of the ceramic samples of the nanometallocarbosilanes and organoelementoxanes were assessed by scanning electron microscopy (SEM) on a Philips SEM 505 equipped with a Sapphire Si(Li) SEM10 energy dispersive detector and a Micro Capture SEM3.0M image capture system and on a Quanta 250.

Phase compositions were determined by X-ray diffraction at room temperature on a Shimadzu XRD-6000 vertical X-ray diffractometer using monochromatized copper radiation with a wavelength of \( \lambda_{K\alpha} = \frac{(2\lambda_{K\alpha 1} + \lambda_{K\alpha 2})}{3} = 1.54178 \ [\text{Å}] \). The crystalline and X-ray amorphous phases present were identified using ICDD PDF Release 2003 data.

Using a previously described procedure, we prepared binders based on organoalumoxanes [15, 16] and organoyttriumoxanealumoxanes [17-19]; film-forming agents and binders based on organoyttriumoxanealumoxanesiloxanes [20-22]; high-purity alumosilicate [23], alumomagnesium [24] ceramics and high-purity ceramics based on oxides of aluminum, yttrium and magnesium [2].

3. Results and discussion

Nanometallocarbosilanes are precursors of SiC ceramics modified with nanoparticles of compounds of refractory metals (Zr, Hf, Ta) [1, 2, 12-14] and SiC ceramics modified by mixed carbides (\( \text{Ta}_x \text{Zr}_y \text{C}_z \) or \( \text{Ta}_x \text{Hf}_y \text{C}_z \)) [2].

Below are micrographs of the SEM and X-ray elemental microanalysis of SiC ceramics modified with mixed carbides (\( \text{Ta}_x \text{Zr}_y \text{C}_z \) or \( \text{Ta}_x \text{Hf}_y \text{C}_z \)) (figure 1).

![Micrographs of SEM and X-ray elemental microanalysis of modified SiC ceramics](image)

**Figure 1.** SEM and X-ray elemental microanalysis of modified SiC ceramics
Samples of SiC ceramics modified with mixed carbides (TaxZryCz or TaxHfyCz) were investigated by powder X-ray diffraction. The phase of nitrogen and carbon carbide was observed in the samples (Table 1). The nitrogen carbide phase was described by the structural Moissanite 3C. The third phase in the studied samples was a system similar to hafnium, tantalum and zirconium carbides. All above carbides have a cubic cell with "NaCl" structural type, the difference between these structures was observed only in the cell parameters. The lowest value of this parameter is inherent to tantalum carbide (4.43Å), in hafnium and zirconium carbides it amounts to 4.64 and 4.70Å, respectively. The “a” parameter of a cubic cell, determined using a refining diffractogram of Rietveld method, is shown in Table 1. In all samples it exceeds this value for tantalum carbide but is lower for hafnium and zirconium carbides. Thus, we can assume that the formation of carbide of a mixed structure takes place in the studied system.

The results are presented in Table 1.

Table 1. Maximum X-ray diffraction of CuKα radiation on samples of modified SiC ceramics

| Sample                          | HfC-ZrC-TaC  | C   | SiC | TaC       |
|---------------------------------|--------------|-----|-----|-----------|
| SiC(Ta,Zr,C) 1600 °C N2        | 4.3(6)       | 4.517(5) | 1.34(13) | 94(1)     |
|                                 |              |      |     | 0.42(11)%| a = 4.476(6)Å, D=12(3)nm |
| SiC(Ta,Hf,C) 1500 °C Ar         | 5.2(19)      | 4.522(2) | 0.48(17) | 95 (3)   |
|                                 |              |      |     | 0.09(4)%| a = 4.4839(9)Å, D=50(10)nm |
| SiC(Ta,Hf,C) 1600 °C N2         | 7.1(4)       | 4.495(3) | 1.46(6) | 91(2)    |
|                                 |              |      |     | 0.14(2)%| a = 4.4734(8)Å, D=46(10)nm |
| SiC(Ta,Hf,C) 1600 °C Ar         | 6.8(5)       | 4.501(2) | 1.41(7) | 91(1)    |
|                                 |              |      |     | 0.73(6)%| a = 4.4867(4)Å, D=75(6)nm |

It should be emphasized that nanometallocarbosilanes posses fiber-forming properties. Polymer fibers (figure 2, a) were produced from them by melt processing, after the polymer fibers were subject to oxidative curing (figure 2, b) and carbidization SiC fibers modified with refractory metal compounds (figure 2, c, d) were obtained. Figure 2, d shows the results of the SEM and X-ray elemental microanalysis of SiC fiber modified with Ta and Zr compounds.
Figure 2. Photographs of nanometallocarbosilanes fibers: (a) polymer, (b) cured, (c) pyrolyzed, (d) micrograph of SEM and X-ray elemental microanalysis of SiC(Ta,Zr,C)

We have synthesized organoelementoxane oligomers that can be used to obtain components of the CCM of oxide composition: chelated alkoxy alumoxanes — precursors of highly heat-resistant and chemically inert corundum ceramics [15, 16]; organoalumoxanesiloxanes - precursors of high-purity aluminosilicate ceramics with a given Al:Si molar ratio (in particular, mullite 3Al₂O₃ • 2SiO₂) [23]; organoyttriumoxanealumoxanes – precursors of alumoyttrium ceramics with a given Al:Y molar ratio (in particular, garnet 3Y₂O₃ • 5Al₂O₃) [17-19]; organoyttriumoxanealumoxansiloxanes – precursors of the components for chemically resistant, high-strength, clear or enamel protective coatings, as well as transparent and opaque glass ceramics based on yttrium, aluminum and silicon oxides with any desired molar ratio of xY₂O₃•yAl₂O₃•zSiO₂ [20-22]; organomagnesiumoxanealumoxanes – precursors of high-purity ceramics based on aluminum and magnesium oxides (alumomagnesium spinel MgAl₂O₄, in particular)[24]; organomagnesiumoxaneyttriumoxanealumoxanes – precursors of high-purity ceramics based on aluminum, yttrium and magnesium oxides, in particular, yttrium aluminum garnet (Y₃Al₅O₁₂) and perofskite (YAlO₃) modified by magnesium oxide, spinel (MgAl₂O₄) modified by yttrium oxide, as well as corundum (α-Al₂O₃) modified by yttrium and magnesium oxides [2]; organometalloxaneyttriumoxanealumoxanes – the precursors of high-purity, high-temperature binary ceramics based on aluminum and yttrium oxides modified by oxides of refractory metals (zirconium, hafnium or chromium) [2].

Micrographs of SEM, X-ray elemental microanalysis and diffractograms of oxide ceramics obtained in the result of pyrolysis of elementoxane oligomers at 1300°C follow (Figures 3 - 9)

Figure 3. Micrograph of SEM, X-ray elemental microanalysis and diffractogram of alumina ceramics obtained in the result of organoalumoxane pyrolysis
Figure 4. Micrograph of SEM, X-ray elemental microanalysis and diffractogram of mullite ceramics, obtained in the result of organoalumoxanesiloxanes pyrolysis.

Figure 5. Micrograph of SEM, X-ray elemental microanalysis and diffractogram of aluminum-yttrium ceramics obtained in the result of organoyttriumoxanealumoxanes pyrolysis.

Figure 6. Micrograph of SEM, X-ray elemental microanalysis and diffractogram of aluminum-magnesium ceramics obtained in the result of organomagnesiumoxanealumoxanes pyrolysis.

Figure 7. Micrograph of SEM, X-ray elemental microanalysis and diffractogram of glass obtained in the result of organoyttriumoxanealumoxanesiloxanes pyrolysis.
Figure 8. Micrograph of SEM, X-ray elemental microanalysis and diffractogram of ceramics based on aluminum, yttrium and magnesium oxides obtained in the result of organoyttriumoxanemagnesiumoxanealumoxanes pyrolysis

Figure 9. Micrograph of SEM, X-ray elemental microanalysis and diffractogram of ceramics based on aluminum, yttrium and hafnium oxides obtained in the result of organoyttriumoxanehafniumoxanealumoxanes pyrolysis

Conclusion
Effective methods for obtaining components of CCM (fibers, coatings, matrices, etc.) on the basis of ceramic-forming nanometallocarbolanes and organoelementoxanes have been developed:
- SiC- fibers modified by compounds of refractory metals (Zr; Hf; Ta);
- binders, film-forming and impregnating compositions;
- sintering additives for SiC- composites;
- special and barrier coatings, in particular, glass-ceramic coatings of Y₂O₃–Al₂O₃–SiO₂ composition with a specified molar ratio of components;
- amorphous powders obtained during pyrolysis of organomagnesiumoxaneyttriumoxanealumoxanes as a sintering additive for SiC composite.

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