Components of ceramic composite materials based on organoelement oligomers

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Abstract. Organoelement oligomers represent a new class of unsurpassed precursors for the production of high-temperature, oxidation-resistant, high-strength nanostructured ceramic composites: ceramic fibres, matrices, protective coatings, etc. They allow one to use a fundamentally different “polymeric technology” for the manufacture of ceramics by pyrolysis of ceramic-forming organoelement oligomers. We have synthesized ceramic-forming oligomers, which can be used to obtain components of carbide and oxide CCM: nanometallocarbosilanes - precursors of SiC ceramics, modified by nanoparticles of refractory metals (Zr, Hf, Ta); chelated alkoxyalumoxanes - precursors of high-temperature and chemically inert corundum ceramics; organoalumoxanesiloxanes - precursors of high-purity aluminosilicate ceramics; organoyttriumoxanealumoxanes - precursors of yttrium aluminium ceramics; organoyttriumoxanealumoxanesiloxanes - precursors of glass ceramics based on yttrium, aluminum and silicon oxides; organomagnesiumoxanealumoxanes - precursors of components of high-purity ceramics based on aluminum and magnesium oxides; organomagnesiumoxaneyttriumoxanealumoxanes - precursors of high-purity ceramics based on oxides of aluminum, yttrium and magnesium, in particular Y₃Al₂O₁₂ and Y₃AlO₃ modified by magnesium oxide, MgAl₂O₄ modified by yttrium oxide, as well as α-Al₂O₃ modified by yttrium and magnesium oxides; organometallocoxanealumoxanes are 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).

1. Introduction
Currently, conventional materials, including technical ceramics, traditionally obtained by sintering powders of oxides, carbides, nitrides and silicides, do not meet the higher demand of advanced technology and the technical requirements that are imposed on the development of various products operating under extreme conditions. Therefore, the primary task is to produce new materials that have a set of properties that significantly outperform the physical and mechanical properties of existing materials [1].

Ceramic-forming organoelement oligomers, which have a given chemical composition at the molecular level, allow the use of a fundamentally different “polymeric technology” for ceramics production through pyrolysis of ceramic-forming organoelement oligomers. And this allows us to prepare high-purity materials with unique physical-chemical properties. By intentionally changing their composition, it is possible to control the structure of ceramic compositions and develop components (fibers, coatings, matrices, etc.) of composite ceramic materials (CCM) with preset structural properties. The production of CCM based on ceramic-forming oligomers is related to breakthrough technologies that determine the level of development of advanced and promising technologies [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].

Good prospects for the development of advanced oxide ceramics are determined by the huge investments made by developed countries to the design of new highly thermally stable and chemically inert ceramics based on aluminium oxide [9-11].

2. Experimental details

The main method for the production of oxygen-free silicon carbide fibers modified with Zr, Hf, Ta, and oxide fibers is the method of melt spinning of fiber-forming oligomers to form polymer fibers that have low strength, subsequent thermochemical curing and pyrolysis at temperatures up to 1500 °C [12-14].

Using a procedure described previously, we prepared binders based on organoalumoxanes [15, 16] and organoyttriumoxanealumoxanes [17, 18]; film-forming agents and binders based on organoyttriumoxanealumoxanesiloxanes [19-21]; high-purity alumosilicate [22], alumomagnesium [23] ceramics and high-purity ceramics based on oxides of aluminum, yttrium and magnesium [24].

3. Results and discussion

We have synthesized ceramic-forming oligomers, which can be used to obtain components of carbide CCM: nanometallocarbosilanes - precursors of SiC ceramics, modified by nanoparticles of compounds of refractory metals (Zr, Hf, Ta) [1, 2, 12, 13] and SiC ceramics, modified by mixed carbides (Ta,Zr,C or Ta,Hf,C) [25].

The processes of thermochemical transformation of nanometallocarbosilanes into ceramic phases have been studied (figure 1).

![Thermochemical transformations of nanometallocarbosilanes.](image)

Figure 1. Thermochemical transformations of nanometallocarbosilanes.

The formation of SiC ceramics modified with mixed carbides (Ta,Zr,C or Ta,Hf,C) is confirmed by the results of XRD (table 1).

Table 1. Maximum X-ray diffraction of CuK$_\alpha$ radiation on samples of modified SiC ceramics.

| Sample   | HfC-ZrC-TaC wt % | a, Å | C       | SiC     | TaC       |
|----------|------------------|------|---------|---------|-----------|
| SiC(Ta$_a$Zr$_b$C$_c$) | 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$_a$Hf$_b$C$_c$) | 7.1(4)            | 4.495(3) | 1.46(6) | 91(2)   | 0.14(2)%  |
|          |                   |       |         |         | a=4.4734(8)Å, D=46(10)nm |

Phases of silicon carbide and carbon were observed in the samples (Table 1). The third phase in the studied samples was a system similar in structure to carbides of hafnium, tantalum, and zirconium. All the above carbides have a cubic cell; the differences are only in the parameters of the cell. It is the smallest in tantalum carbide (4.43Å), in hafnium and zirconium carbides it is 4.64 and 4.70Å, respectively. In all samples, the parameter "a" of the cubic cell exceeds that of tantalum carbide, but is lower than in hafnium and zirconium carbides. Consequently, it can be assumed that the carbide of the mixed structure is formed in the studied system.
The morphology of the surface of SiC ceramics modified with mixed carbides (Ta_xZr_yC_z or Ta_xHf_yC_z) was studied by SEM method and mapping by the distribution of elements (figure 2).

**Figure 2.** Morphology of the surface of SiC ceramics modified with mixed carbides (Ta_xZr_yC_z or Ta_xHf_yC_z) and mapping by element distribution.

Nanometallocarbosilanes can be used to obtain SiC- fibers modified by compounds of refractory metals (Zr; Hf; Ta) (figure 3).

**Figure 3.** Photographs of nanometallocarbosilanes fibers: (a) polymer, (b) cured, (c) pyrolyzed.
The processes of thermochemical transformation of organoalumoxanes into high-temperature and chemically inert corundum ceramics have been studied (figure 4).

Figure 4. Thermochemical transformations of organoalumoxanes.

This is confirmed by the results of X-ray phase analysis. It was shown diffractometrically that the polymorphic transformation begins with the formation of low-temperature phases of Al$_2$O$_3$ at 900 °C (figure 5, a). Pyrolysis of oligomers results in the formation of $\alpha$-Al$_2$O$_3$ at 1300 °C (Figure 5, b).

Figure 5. Diffractograms of ceramics obtained in the result of organoalumoxane pyrolysis at: a – 900 °C; b –1300 °C.

On the basis of ceramic-forming organoalumoxanes unique technology for the preparation of a high-purity nanostructured silica free organoalumoxane binder of corundum composition $\alpha$-Al$_2$O$_3$ has been developed and patented [2, 15, 16].

The processes of thermochemical transformation of organoalumoxanesiloxanes into high-purity alumosilicate ceramics [22] with a specified molar ratio of Al:Si (in particular, mullite 3Al$_2$O$_3$•2SiO$_2$) was studied (figure 6).

Figure 6. Thermochemical transformations of organoalumoxanesiloxanes.

Figure 7 shows the results of X-ray (a), SEM/EDS (b) for samples of ceramics obtained by pyrolysis of organoalumoxanesiloxanes.

Figure 7. X-ray (a), SEM/EDS (b) for samples of ceramics obtained by pyrolysis of organoalumoxanesiloxanes.
The processes of thermochemical transformation of organoyttriumoxanealumoxanes into yttrium aluminium ceramics with a different molar ratio of Al:Y were investigated (figure 8).

\[
[Y(OR)^{n+}](OH)_n \cdot [Al(OR)_2(OH)_2O]_n \rightarrow mY_2O_3 \cdot nAl_2O_3 \rightarrow Y_3Al_5O_{12} \rightarrow \alpha-Al_2O_3
\]

**Figure 8.** Thermochemical transformations of organoyttriumoxanealumoxanes.

Powder X-ray diffraction study of the yttrium aluminium oxide powders prepared by pyrolysis of organoyttriumoxanealumoxanes demonstrated the obtained yttrium aluminium ceramics consist of yttrium aluminium garnet \( Y_3Al_5O_{12} \) and corundum \( \alpha-Al_2O_3 \) [17] (figure 9).

**Figure 9.** X-ray for samples of ceramics obtained by pyrolysis of organoyttriumoxanealumoxanes.

The morphology of surface of the obtained yttrium aluminium garnet ceramics was studied by SEM method and mapping was performed by the distribution of elements (figure 10).

**Figure 10.** Morphology of the obtained yttrium aluminium garnet ceramics and mapping by element distribution.

Fiber-forming organoyttriumoxanealumoxanes can be used to obtain yttrium aluminum ceramic fibres [14] (figure 11).

**Figure 11.** SEM images of the surface (a, b, d, e) and elemental composition (c, f) of ceramic fibres according to energy-dispersive X-ray spectroscopy.
The processes of thermochemical transformation of organoyttriumoxanealumoxanesiloxanes (molar ratio of Y:Al:Si = 1:0.8:2.5) into ceramics based on yttrium, aluminum and silicon oxides were studied (figure 12).

Figure 12. Thermochemical transformations of organoyttriumoxanealumoxanesiloxanes.

Powder X-ray diffraction study of the yttrium aluminum and silicon oxide powders prepared by pyrolysis of organoyttriumoxanealumoxanesiloxanes demonstrated that the obtained glass ceramics consisted of keiviyte \( Y_2Si_2O_7 \) and mullite \( 3Al_2O_3 \cdot 2SiO_2 \) [19] (figure 13).

Figure 13. X-ray for samples of ceramics obtained by pyrolysis of organoyttriumoxanealumoxanesiloxanes.

The processes of thermochemical transformation of organoyttriumoxanealumoxanesiloxanes (molar ratio of Y:Al:Si = 1:0.7:0.5) at \( \geq 1400 \, ^\circC \) led to the formation of transparent glass [19] (figure 14).

Figure 14. X-ray (a), SEM/EDS (b) for samples of ceramics obtained by pyrolysis of organoyttriumoxanealumoxanesiloxanes.

So pyrolysis of the organoyttriumoxanealumoxanesiloxanes leads to the formation of amorphous (glass) or glass-ceramic (crystalline) materials with a predetermined Al:Y:Si molar ratio; that is, such oligomers can be used to create chemically stable, durable, transparent and enamel protective coatings and transparent or opaque glass-ceramics from yttrium, aluminum, and silicon oxides at any molar ratio of these components: \( xY_2O_3 \cdot yAl_2O_3 \cdot zSiO_2 \) [19, 20]

It is shown [20] that solutions of organoyttriumoxanealumoxanesiloxanes in organic solvents are effective as binders and film-forming agents for the preparation of protective high-temperature antioxidative \( xY_2O_3 \cdot yAl_2O_3 \cdot zSiO_2 \) coatings on carbon (figure 15) and silicon carbide fibers [21] (figure 16).

Figure 15. SEM photographs of the coatings on C/C composite materials: the end face and lateral surface and the X-ray elemental microanalysis of the lateral surface.
It is found out that the pyrolysis of organomagnesium oxanealumoxanes leads to the formation of MgAl$_2$O$_4$, MgAl$_2$O$_4$, and MgO, or MgAl$_2$O$_4$ and $\alpha$-Al$_2$O$_3$ depending on molar ratio of Al:Mg. That is, the organomagnesium oxanealumoxanes can be used to make a new generation of heat-resistant, optically-transparent, corrosion- and radiation-resistant binary magnesium–aluminum ceramics [23].

The processes of thermochemical transformation of organomagnesium oxanealumoxanes into high-purity ceramics based on aluminum and magnesium oxides (in particular alumomagnesium spinel MgAl$_2$O$_4$) are shown in figure 17.

Diffractometry showed that the pyrolysis of organomagnesium oxanealumoxanes (Al:Mg = 1:2) even at 900 °C results in the formation of magnesium–aluminum spinel MgAl$_2$O$_4$ with the size of the coherent scattering region (CSR) approximately 100 [Å] and lattice parameter 8.076 [Å] (Ref. 8.083 [Å]) [23].

It should be noted that the organomagnesium oxanealumoxanes with a molar ratio Al:Mg = 2:1 and 1:1 have fiber-forming properties, therefore they may be precursors for ceramic oxide fibers of binary composition $x$MgO-$y$Al$_2$O$_3$, spinel MgAl$_2$O$_4$ in particular [23]. Manually formed polymer fibers from organomagnesium oxanealumoxanes were pyrolyzed. Photographs of the SEM of the lateral and of the end face surface of ceramic fibers from organomagnesium oxanealumoxanes, and the X-ray elemental microanalysis of the end face surface are presented in figure 18.

The processes of the pyrolysis of organomagnesium oxaneyttrium oxanealumoxanes into ceramics based on oxides of aluminum, yttrium and magnesium with a different molar ratio of Al:Y:Mg were studied (figure 19).

Powder X-ray diffraction study of the ceramics prepared by pyrolysis of organomagnesium oxaneyttrium oxanealumoxanes demonstrated that the obtained yttrium aluminum ceramics consisted of magnesium–aluminum spinel MgAl$_2$O$_4$, yttrium aluminium garnet Y$_3$Al$_5$O$_{12}$ and corundum $\alpha$-Al$_2$O$_3$ [24] (figure 20).
The surface morphology of the obtained magnesium yttrium aluminium ceramics consisted of magnesium–aluminum spinel MgAl₂O₄, yttrium aluminium garnet Y₃Al₅O₁₂ and corundum α-Al₂O₃ was studied by SEM method and mapping was performed on the distribution of elements (figure 21).

Figure 20. X-ray for samples of ceramics obtained by pyrolysis of organomagnesiumoxane yttriumoxanealumoxanes.

The SiC-composites reinforced with multi-walled carbon nanotubes with a sintering additive based on organomagnesiumoxaneyttriumoxanealumoxane were prepared by spark plasma sintering. In the result 0.5% of the sintering additive increased the strength of the composite by 2.5 times and the fracture toughness resistance was approximately 1.5 times [25].

The processes of thermochemical transformation of organoyttriumoxanealumoxanes modified by compounds of refractory metal (Zr, Hf) were investigated (figure 22).

Figure 21. Morphology of the obtained ceramics consisted of magnesium–aluminum spinel MgAl₂O₄, yttrium aluminium garnet Y₃Al₅O₁₂ and corundum α-Al₂O₃ and mapping by element distribution.

The SiC-composites reinforced with multi-walled carbon nanotubes with a sintering additive based on organomagnesiumoxaneyttriumoxanealumoxane were prepared by spark plasma sintering. In the result 0.5% of the sintering additive increased the strength of the composite by 2.5 times and the fracture toughness resistance was approximately 1.5 times [25].

The processes of thermochemical transformation of organoyttriumoxanealumoxanes modified by compounds of refractory metal (Zr, Hf) were investigated (figure 22).

Figure 22. Thermochemical transformations of organoyttriumoxanealumoxanes modified by compounds of refractory metal (Zr, Hf) compounds

Powder X-ray diffraction study of the ceramics prepared by pyrolysis of organometalloxaneyttriumoxanealumoxanes demonstrated the obtained high-temperature binary ceramics based on aluminum and yttrium oxides modified by oxides of refractory metals (zirconium, hafnium or chromium) [26]. For example for ceramics based on aluminum and yttrium oxides modified by zirconium oxide (figure 23).

Figure 23. X-ray for samples of ceramics based on aluminum and yttrium oxides modified by zirconium oxide: α-Al₂O₃ – 11.11%, Zr₀.₇₂₀.₂₈₀.₃₈ – 30.01%, Y₃Al₅O₁₂ – 58.89%
Figure 24 shows the results SEM/EDS for samples of ceramics obtained by pyrolysis of organozirconiumoxaneyttriumoxanealumoxanes.

**Figure 24.** SEM/EDS for samples of ceramics obtained by pyrolysis of organozirconiumoxaneyttriumoxanealumoxanes

### 4. Conclusions

Effective methods for obtaining components of CCM (fibers, coatings, matrices, etc.) on the basis of ceramic-forming nanometallocarbosilanes 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 Y$_2$O$_3$–Al$_2$O$_3$–SiO$_2$ 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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