Carbide and oxide fibers based on organoelement poly(oligo)mers

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Abstract. The researches of State Research Institute for Chemistry and Technology of Organoelement Compounds (GNIIChTEOS) have developed continuous carbide and oxide fibers based on organoelement poly(oligo)mers synthesized in GNIIChTEOS, which can be used to prepare principally new ceramic composites for structural and functional purposes.

1. Introduction
The current state of the art requires the development of new highly heat-resistant structural and functional ceramic materials. One of the most promising ways to meet this challenge is the development of directed methods for the preparation of ceramic matrices, fibers, coatings based on organoelement poly(oligo)mer precursors of controlled structure and composition. All world’s major economies are intensively searching for new methods of synthesis and studying the properties of a number of organoelement compounds used as raw materials for the above purposes. [1-10].

In Russia, GNIIChTEOS is the main developer and manufacturer of carbide and oxide fibers based on organoelement poly(oligo)mers - ceramic-forming and fiber-forming nanometallocarbosilanes and organoelementoxanearumoxanes [11,12].

In order to prepare metal-modified SiC fibers required for the manufacture of high-temperature ceramic composites, the research team of GNIIChTEOS synthesized nanometallocarbosilanes in the early 2000s [13, 14]. It was shown that the most effective modifiers of polycarbosilanes (PCS) are alkylamide compounds of refractory metals (Zr, Hf, Ta), which do not contain oxygen and chlorine impurities harmful to SiC ceramics. [12,14,15].

Efficient methods for the synthesis of fiber-forming elementoxanearumoxane oligomers - precursors of ceramic alumina fibers modified with yttrium, magnesium, chromium oxides, as well as ceramic fibers of mixed spinel-garnet composition were also developed at GNIIChTEOS [11,12,16-21].

In addition, it is shown that organoelementoxanearumoxanes synthesized at GNIIChTEOS can be used as modifiers of PCS, since they are precursors of oxide ceramics of multicomponent composition: xMgO • yAl2O3, xY2O3 • yAl2O3, xY2O3 • yAl2O3 • zCr2O3, xY2O3 • yAl2O3 • zMgO etc. [22].

It is well known that additives of the oxide composition reduce the sintering temperature of SiC and allow obtaining a dense ceramic material, and the combination of oxides (Al2O3 и Y2O3, Al2O3 and MgO etc.) provides a higher stability of the components of the composite material. [23].
### 2. Experimental details

Polymer fibers were prepared from nanometallocarbosilanes and organoelementoxanealumoxanes by melt spinning. The fibers were produced on Spinning System KS 42 “FOURNE” machine.

Curing of the produced polymer fibers was performed in a box electric furnace “NK 6.6.6/5I4” (with tubular electric heaters) in air at the rate of 1 degree/min up to 200–500 °C.

Carbidization of the cured fibers based on metallocarbosilanes at 1250 °C and further pyrolysis at 1500 °C, 1700 °C and 1900 °C was performed in argon in an electric furnace "Tekhmashservice SVG 4.4.8”

Pyrolysis of the cured fibers based on organoelementoxanealumoxanes, was performed in an upgraded electric resistance furnace SNOL 12/16 at 1200–1300 °C in air.

The surface morphology of the polymer was studied on a Quanta 250 and elemental composition of the polymer fibers and samples of ceramic fibers was studied on a Philips SEM 505 equipped with a Sapphire Si(Li) SEM10 energy dispersive detector and a Micro Capture SEM3.0 M image capture system.

Diffractometric studies were carried out in a divergent Zeeman - Bolin beam on Shimadzu XRD-6000 vertical X-ray diffractometer at ambient temperature with CuKα radiation \( \lambda_{Kα}=\frac{(2\lambda_{Kα1}+\lambda_{Kα2})}{3}=1.54178 \). The crystalline phases were identified using ICDD PDF Release 2003 data.

### 3. Results and discussion

Polymer fibers were prepared from nanometallocarbosilanes and organoelementoxanealumoxanes, the fibers curing and pyrolysis resulted in the formation of modified silicon carbide or corundum fibers, as well as ceramic fibers of spinel and garnet compositions.

Photos of polymer, cured (air) and ceramic (Ar) fibers based on Ta(Zr)PCS (figure 1) are presented below.

![Figure 1. Ta(Zr)PCS based fibers: a – polymeric, b – cured at 200 °C (air), c – after carbidization at 1250 °C (Ar) ](image)

The surface morphology and chemical composition of SiC fibers modified with mixed carbides Ta₄ZrC₅ after carbidization at 1250 °C (Ar) and further pyrolysis at 1500 °C (Ar) are shown in Figure 2.

It should be noted that the crystallite size of modified SiC fibers does not increase with an elevation in the pyrolysis temperature from 1250 °C to 1500 °C and amounts to 16-40 nm (Figure 2).

We found that pyrolysis of SiC fibers carbidized at 1250 °C (Ar) (modified and unmodified), at 1900 °C (Ar) leads to the formation of oxygen-free SiC fibers (Figure 3).

SEM results show that unmodified SiC fibers stick together, crystallites grow from 1.5 μm to 12.1μm on the side surface of the fiber, while modified SiC fibers do not stick together, and the crystallite size on the side surface of the fiber is from 116 nm up to 550 nm (Figure 3).
Figure 2. Surface morphology and chemical composition of samples of SiC ceramic fibers modified with mixed carbides Ta$_4$ZrC$_5$: a – 1250 °C; b – 1500 °C.

Figure 3. Surface morphology and chemical composition of SiC fiber samples pyrolyzed at 1900°C: a - unmodified; b - modified.
AlY(Zr)PCS was synthesized at GNIICHTEOS by co-condensation of oligocarbosilane and zirconium-containing organoyttriumoxane alumoxane, weight percent was found according to elemental analysis data: С 44.2; Н 7.4; Si 46.5; Al 0.98; Y 0.36; Zr ≈ 0.0001 [24].

Photomicrographs and X-ray elemental microanalysis, obtained by SEM, of ceramic fibers based on AlYPCS are presented below (Figure 4).

It is shown that the pyrolysis of AlYPCS-based fibers carbidized at 1100 °C (Ar) 1700 °C and 1900°C (Ar) results in oxygen-free Al(Y)SiC fibers, and the crystallite size with an elevation in the pyrolysis temperature from 1700 °C up to 1900 °C does not increase and amounts to 80-200 nm (Figure 4).

![Surface morphology and chemical composition of AlYPCS-based SiC fiber samples: a – pyrolysis at 1100 °C, b – pyrolysis at 1700 °C, c – pyrolysis at 1900 °C.](image)

Polymers fibers - precursors of ceramic alumina fibers modified with oxides of yttrium, magnesium, chromium, as well as ceramic fibers of spinel-garnet composition were prepared by melt spinning of fiber-forming elementoxanealumoxane oligomers [12, 16-21].

Below are photographs, photomicrographs and X-ray elemental microanalysis, obtained by SEM, of polymer fibers based on organomagnesiumoxane yttriumoxanealumoxanes with the following molar ratios: Al:Mg≈40, Al:Y≈80 (a) and Al:Mg≈3.5, Al:Y≈5 (c); organoyttriumoxanealumoxane with Al:Y≈6 (b); organochromiumoxane yttriumoxanealumoxanes with Al:Cr≈90 and Al:Y≈2.5 (d) (Figure 5).
Figure 5. Photos, micrographs and SEM elemental microanalysis of polymer fibers based on: a – organomagnesiumoxane yttriumoxanealumoxanes with Al:Mg≈40 and Al:Y≈80; b - organoyttriumoxanealumoxanes with Al:Y≈6; c – organomagnesiumoxane yttriumoxanealumoxanes with Al:Mg≈3.5 and Al:Y≈5; d – organochromiumoxane yttriumoxanealumoxanes with Al:Cr≈90 and Al:Y≈2.5

Polymer fibers were cured by slow heat treatment of the fiber (heating rate 1 degree/min.) to 200−500 °C in air.

Ceramization of the cured fibers was carried out in an oxidizing atmosphere at a temperature of 1200−1300 °C.

Samples of modified alumina fibers were prepared [12, 18-21]:

a – of corundum composition (α-Al₂O₃ ≈ 99.6 wt %) modified with MgAl₂O₄ spinel (MAS ≈ 0.2 wt%) and yttrium aluminum garnet Y₃Al₅O₁₂ (YAG ≈ 0.2 wt %);

b – of aluminum-yttrium composition: corundum and Y₃Al₅O₁₂ (α-Al₂O₃ ≈ 70 wt % and YAG ≈ 30 wt %);

c – of magnesium-aluminum-yttrium composition: MgAl₂O₄, Al₂Y₄O₉, Y₃Al₅O₁₂ and Al₃Y₅ traces (MAS ≈ 79 wt %, YAM ≈ 17 wt %, YAG ≈ 4 wt %, Al₃Y₅ traces);

d – of chromium-containing yttrium aluminum garnet (Y₃[Cr₃Al₅₋₃]O₁₂ = 100 wt %).

Photos, micrographs, elemental microanalysis of SEM and diffraction patterns of samples of modified alumina fibers based on ceramic-forming and fiber-forming organoelementoxanealumoxanes are shown in Figure 6.
Figure 6. Photos, micrographs, SEM elemental microanalysis and diffraction patterns of modified alumina fiber samples based on:

- a – $\alpha$-$\text{Al}_2\text{O}_3 \approx 99.6$ wt %, MAS $\approx 0.2$ wt %, YAG $\approx 0.2$ wt %
- b – $\alpha$-$\text{Al}_2\text{O}_3 \approx 70$ wt %, YAG $\approx 30$ wt %
- c – MAS $\approx 79$ wt %, YAM $\approx 17$ wt %, YAG $\approx 4$ wt %, Al$_3$Y$_5$ traces
- d – Y$_3$(Cr$_x$Al$_{5-x}$)O$_{12}$ $= 100$ wt %

4. Conclusion

GNIIChTEOS is closely involved in the development of carbide and oxide fibers based on organoelement poly(oligo)mers - ceramic-forming and fiber-forming nanometallocarbosilanes and organoelementoxanealumoxanes.

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