Elementoxanealumoxanes – modifiers of silicon carbide ceramic composites components

G I Shcherbakova¹, P A Storozhenko¹, T L Apukhtina¹, M Kh Blokhina¹, D V Zhigalov¹, E A Novokovskaya¹, M S Varfolomeev¹², D D Titov³ and A A Ashmarin³

¹SSC RF “State Research Institute for Chemistry and Technology of Organoelement Compounds” (GNIIChTEOS), 105118, Moscow, Russia
²Moscow Aviation Institute (National Research University), 121552, Moscow, Russia
³Baikov Institute of Metallurgy and Material Science RAS, 119334, Moscow, Russia
E-mail: galina7479@mail.ru

Abstract. Pre-ceramic organoelementoxanealumoxane oligomers whose pyrolysis results in oxide ceramics of multicomponent composition: aluminum yttrium (xY₂O₃·yAl₂O₃), yttrium aluminum silicate (xY₂O₃·yAl₂O₃·zSiO₂), yttrium aluminum magnesium (xY₂O₃·yAl₂O₃·zMgO) ones, are modifiers of silicon carbide based composite materials that increase their resistance to high temperature oxidation.

1. Introduction

One of the most promising approaches to the development of advanced ceramic materials with tailor-made properties (high-strength, high-temperature and oxidation-resistant ceramic composites) is to use pre-ceramic organoelement oligomers and polymers as starting materials [1].

Silicon carbide composites (C/SiC or SiC/SiC) based on pre-ceramic polycarbosilanes (PCS) are priority for science intensive industries [2, 3]. However, such ceramic composites have a relatively low operating temperature (≈1300 °C) in an oxidizing environment, which significantly limits the application area of the material [1, 4].

It is known that the PCS modification with acetylacetonates Y(acac)₃ and Al(acac)₃ has a positive effect on the KD-Y and KD-SY fibers produced from YAIPCS, which have high strength and good thermal stability [5,6].

Oxides Al₂O₃, BeO, Y₂O₃, La₂O₃, CaO, MgO, ZrO₂ are most suitable sintering activators for SiC [7]. The use of additives of oxide composition reduces the sintering temperature of SiC and makes it possible to obtain a dense ceramic material, and the combination of oxides (Al₂O₃ and Y₂O₃, Al₂O₃ and MgO, etc.) provides higher stability of the components of the composite material [8, 9].

We previously showed that preceramic organoelementoxanealumoxanes synthesized at GNIIChTEOS are precursors of multicomponent oxide ceramics: xY₂O₃·yAl₂O₃; xY₂O₃·yAl₂O₃·zSiO₂; xMgO·yAl₂O₃, xY₂O₃·yAl₂O₃·zMgO and other compositions [10, 11].

2. Experimental details

Using a procedure described previously, we synthesized carbosilanes [1], ceramic-forming organoyttriumoxane alumoxanes [12], containing Al and Y polycarbosilanes (AlYPCS) [13], ceramic-forming organoyttriumoxane alumoxanesiloxanes [14], ceramic-forming organomagnesiumoxane alumoxanes [15], ceramic-forming organomagnesiumoxane yttriumoxanealumoxanes [16].

---

[1] A A Ashmarin, et al. Pre-ceramic organoelementoxanealumoxane oligomers whose pyrolysis results in oxide ceramics of multicomponent composition: aluminum yttrium (xY₂O₃·yAl₂O₃), yttrium aluminum silicate (xY₂O₃·yAl₂O₃·zSiO₂), yttrium aluminum magnesium (xY₂O₃·yAl₂O₃·zMgO) ones, are modifiers of silicon carbide based composite materials that increase their resistance to high temperature oxidation. IOP Conf. Series: Materials Science and Engineering 848 (2020) 012081 doi:10.1088/1757-899X/848/1/012081

---

[10] A A Ashmarin, et al. Pre-ceramic organoelementoxanealumoxane oligomers whose pyrolysis results in oxide ceramics of multicomponent composition: aluminum yttrium (xY₂O₃·yAl₂O₃), yttrium aluminum silicate (xY₂O₃·yAl₂O₃·zSiO₂), yttrium aluminum magnesium (xY₂O₃·yAl₂O₃·zMgO) ones, are modifiers of silicon carbide based composite materials that increase their resistance to high temperature oxidation. IOP Conf. Series: Materials Science and Engineering 848 (2020) 012081 doi:10.1088/1757-899X/848/1/012081
The main method for the production of oxygen-free silicon carbide fibers modified with Al, Y is the method of melt spinning of fiber-forming polymers to form polymer fibers that have low strength, subsequent thermochemical curing and pyrolysis at temperatures up to 1700 °C [13, 17].

The polymer fibers from them 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 in an electric furnace "Tekhmashservice SVG 4.4.8" at temperatures up to 1700 °C[13, 17].

The organoelementoxane alumoxanes were heat-treated in a SNOL 12/16 resistance-heated electric furnace at 1500 °C.

The surface morphology and elemental composition of the polymer and ceramic fibers from the AlYPCS and the ceramics samples of organoelementoxane alumoxanes 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.

The thermal analysis of organoyttriumoxane alumoxane siloxanes was carried out in the temperature range from room temperature to 1500 °C in an argon atmosphere in the DSC/TG mode on a NETZSCH STA 409 Luxx.

The ceramics produced from the organoyttriumoxane alumoxane siloxanes were characterized by XRD at room temperature on a Bruker D8 Advance diffractometer with monochromatized CuKα1 radiation in reflection geometry. XRD intensities were measured by a Lynx eye position sensitive detector. The phases present were identified using ICDD PDF-2 and Inorganic Crystal Structure Data base (ICSD). Phase compositions were determined by the Rietveld profile analysis method.

Phase compositions (xY2O3·yAl2O3·zMgO) 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 $\lambda = 1.54178 \text{Å}$. The crystalline and X-ray amorphous phases present were identified using ICDD PDF Release 2003 data.

Using a procedure described previously, we prepared film-forming agents and binders based on AlYPCS [13], organoyttriumoxane alumoxane siloxanes [18] and high-purity ceramics based on oxides of aluminum, yttrium and magnesium [19].

3. Results and discussion

The researches of GNIIChTEOS synthesized AlYPCS with the desired Al:Y molar ratio by cocondensation of raw PCS and organoyttriumoxane alumoxane oligomers, they are the base for polymer fibers [13].

It is demonstrated that the introduction of only 0.5 wt. % of organoyttriumoxane aluminoxane oligomers leads to the production of AlYPCS with good fiber-forming properties: softening temperature $T_1 = 210 \text{ °C}$, fiberization temperature $T_2 = 230 \text{ °C}$ and dropping point $T_3 = 320 \text{ °C}$.

The pictures of AlYPCS fibers (figure 1: a – polymer, b – after curing and pyrolysis at 1100 °C, c – after pyrolysis at 1700 °C) and X-ray elemental microanalysis obtained by electron microscopy are presented below (figure 1).

![Figure 1. AlYPCS fibers](image)

Figure 1. AlYPCS fibers (a – polymeric, b – after curing and pyrolysis at 1100 °C, c – after pyrolysis at 1700 °C) and X-ray elemental microanalysis.
Moreover, a solution of AlYP in toluene (concentration of 50 wt. %) was used as a binder, imparting plasticity and moldability to the ceramic paste. In addition, in the production of ceramics by cold molding from micropowders of silicon carbide SiC, it increases its oxidative stability. Ceramic samples after high-temperature sintering at 1500 °C in air, where: a – SiC sample (AlYP binder - 10 wt. % of yttriumoxanealumoxane), b – SiC sample (AlYP – 0.5 wt. % of yttriumoxanealumoxane), c – SiC sample (PCS binder) are presented below (figure 2).

![Figure 2](image2.jpg)

**Figure 2.** Ceramic SiC samples on binders: a – AlYPCS - 10 wt % of yttriumoxanealumoxane, b – AlYPCS – 0.5 wt. % of yttriumoxanealumoxane, c – PCS.

Film-forming compositions based on organoyttriumoxane alumoxanesiloxanes were used to prepare protective high-temperature antioxidant coatings of $\text{Y}_2\text{O}_3$–$\text{Al}_2\text{O}_3$–$\text{SiO}_2$ composition on silicon carbide SiC fibers (figure 3) [1, 18].

![Figure 3](image3.jpg)

**Figure 3.** Protective coatings of $\text{Y}_2\text{O}_3$–$\text{Al}_2\text{O}_3$–$\text{SiO}_2$ composition on SiC fibers.

Protective coatings consist of crystalline phases with high melting points ($\text{Y}_2\text{Si}_2\text{O}_7$ – 1790 °C, $3\text{Al}_2\text{O}_3$·$2\text{SiO}_2$ – 1870 °C) (figure 4), low heat conduction; temperature factor of linear expansion close to that of silicon carbide (38–45·10⁻⁷ К⁻¹); oxidation resistance at temperatures up to 1700 °C [18].

![Figure 4](image4.jpg)

**Figure 4.** Diffractogram of organoyttriumoxane aluminosiloxane after pyrolysis at 1300 °C.
Organoyttriumoxane alumoxanesiloxanes up to 1500 °C (figure 5a) and the oligomer pyrolyzed at 700 °C to 1600 °C (figure 5b) were analyzed by DSC. The DSC results of pyrolyzed yttriumoxane alumoxanesiloxane at 700 °C show (figure 5b) that the composition crystallizes first at a temperature of 1101 °C, then at 1365.7 and at 1403.8 °C. Melting of all crystalline phases is observed at 1418.3 °C, that is, glass formation occurs at this temperature, which confirms the possibility of the formation of a dense non-porous oxide coating.

**Figure 5.** A thermogram of organoyttriumoxane alumoxanesiloxane (a) and DSC results of yttriumoxanealumoxanesiloxane pyrolyzed at 700 °C (b).

The organomagnesiumoxane yttriumoxanealumoxanes have been synthesized at GNIICHTEOS [16], which are the organoelement precursors of oxide nanoceramics of the composition: MgO-Al₂O₃-Y₂O₃ (actual SiC sintering additives [8, 9]). This result opens up new prospects for the development of high-density modified ceramics based on silicon carbide [19].

The pyrolysis of organomagnesiumoxane yttriumoxanealumoxanes with a molar ratio of Al: Mg≈2 and Al: Y≈6 leads to the formation of ceramics of MgAl₂O₄ and Y₃Al₅O₁₂ composition according to the scheme:

20-750°C

\[
\text{[Mg(OR^*)O]_x[Al(OR^*)O]_y[O]_z:[OH]_w[OH]_x[T[OR^*]O]_y[OH]_z}_n \rightarrow \text{K}_m\text{Mg}_{n}\text{O}_{m}\text{Al}_{m}\text{O}_{n}\text{Y}_n\rightarrow \text{MgAl}_2\text{O}_4 \rightarrow \text{Y}_3\text{Al}_5\text{O}_{12}
\]

The diffractogram, surface morphology and elemental composition of the ceramic sample follow (figure 6).

**Figure 6.** Diffractogram, surface morphology and elemental composition of the ceramic sample after pyrolysis of organomagnesiumoxane yttriumoxanealumoxane.

Dense SiC ceramics modified with magnesium, yttrium and aluminum oxides from micropowders of silicon carbide and a mixture of magnesium, yttrium and aluminum oxides (=10 wt. %) with the addition of organomagnesiumoxane yttriumoxanealumoxane binder imparting plasticity and
moldability to the ceramic paste was produced by high-temperature sintering of samples prepared by cold molding. Samples of ceramics with low porosity and high density, presented below were prepared. They are shown below (figure 7).

![Figure 7. High density ceramic samples of mixed carbide-oxide composition: SiC + MgO + Y_2O_3 + Al_2O_3 based on organomagnesium oxane yttriumoxane alumoxane.](image)

Samples of the SiC composite with an oxide additive of eutectic composition prepared from organomagnesiumoxane yttriumoxanealumoxane (OMYA) and with the addition of multilayer carbon nanotubes (CNTs) were produced by spark plasma sintering. It is found that the combined introduction of an oxide additive and CNTs significantly increases the fracture resistance and strength of the composite [19]. Table 1 presents the test results of the samples for mechanical properties.

| No | Material          | Load P, g | Vickers hardness (HV), HPa | Fracture toughness coefficient C_{1C}, MPa·m^{1/2} | Flexing strength σ_0, MPa |
|----|-------------------|-----------|---------------------------|-----------------------------------------------|----------------------------|
| 1  | SiC               | 300       | 12.5                      | 3.77                                          | 100                        |
| 2  | SiC + 10% CNTs    | 300       | 23.7                      | 4.26                                          | 137                        |
| 3  | SiC + 0.5% OMYA   | 300       | 30.3                      | 4.84                                          | 220                        |

**Conclusion**

It is found that pre-ceramic organoelementoxanealumoxane oligomers, whose pyrolysis results in multicomponent oxide ceramics, are precursors for obtaining modified components (fibers, binders, coatings, powders) of silicon carbide ceramic composites with increased resistance to high-temperature oxidation, in particular:

- organoyttriumoxanealumoxanes – PCS modifiers; ceramic fibers AlYSiC were prepared on the base of AlYPCS, and AlYPCS binder was produced for press molding silicon carbide SiC micropowders;
- organoyttriumoxane alumoxanesiloxanes – precursors for film-forming compositions to prepare protective high-temperature antioxidant glass-ceramic (Y_2Si_2O_7 + 3Al_2O_3·2SiO_2) coatings on SiC-fibers;
- organomagnesiumoxane yttriumoxanealumoxanes – precursors of binding compositions xY_2O_3·yAl_2O_3·zMgO to prepare high density ceramic samples of combined carbide-oxide composition and precursors of amorphous powder s – sintering additives of SiC-composite with higher fracture toughness and strength.

**Acknowledgements**

The work was financially supported by RFFI. Project 17-03-00331 A.

The work was financially supported by the Grant of President of the Russian Federation. Project MK-39.2019.3
References

[1] Abakumov G A et al 2018 Russ. Chem. Rev. 87 (5) 393–507
[2] Joo Y J, Khishigbayar K-E, Cho KY and Kim C J 2018 Fibers and Polymers 19 (9) 1806–12
[3] Mera G, Gallei M, Bernard S and Ionescu E 2015 Nanomaterials. 5 468–540
[4] Flores O, Bordia R K, Nestler D, Krenkel W and Motz G 2014 Adv. Eng. Mater. 16 (6) 621–36
[5] Yang D, Song Y 2008 Key Eng. Mater. 368–372 827–30
[6] Bai W, Jian K 2019 IOP Conf. Ser.: Mater. Sci. Eng. 2019 – 490 022057
[7] Ortiz A L, Cumbera F L, Sánchez-Bajo F, Guiberteau F, Xu H, Padture N P 2000 J. Am. Ceram. Soc. 83 (9) 2282–6
[8] Johari M I A, Mustapha M, Mamat O, Kakooei S, Ginta T L, Ismadi M Z P 2016 J. Eng. Appl. Sci. 11 13300–4
[9] Zharikov E V, Kapustin V V, Faikov P P, Popova N A, Barmin A A, Ivanov A V 2017 IOP Conf. Ser.: Mater. Sci. Eng. 2017 – 175. 012065
[10] Shcherbakova G I et al. 2018 FNM2018. IOP Conf. Ser.: Journal of Physics: Conf. Series 2018 – 1134 012054
[11] Shcherbakova G I, Storozhenko P A, Apukhtina T L, Zhigalov D V, Varfolomeev M S, Drachev A I, Ashmarin A A 2019 NMPT-4. IOP Conf. Ser.: Mater. Sci. Eng. 2019 – 525 012057
[12] Shcherbakova G I et al 2012 Inorg. Mater. 48 (10) 1058–63
[13] Shcherbakova G I et al 2019 RF Patent Application 2019115647
[14] Shcherbakova G I et al 2014 Inorg. Mater. 50 (3) 306–13
[15] Shcherbakova G I, Storozhenko P A, Apukhtina T L, Varfolomeev M S, Kuznetsova M G, Drachev A I and Ashmarin A A 2017 Polyhedron 135 144–52
[16] Shcherbakova G I et al 2019 Inorg. Mater. 55 (10) 1068–78
[17] Shcherbakova G I et al 2014 Inorg. Mater. 50 (4) 423–30
[18] Shcherbakova G I et al 2014 Inorg. Mater. 50 (6) 686–91
[19] Zabelina A A, Shcherbakova G I, Faikov P P, Zharikov E V 2019 Ceramics International (In Press CERI-D-19-06846)