Organoelementoxanealumoxanes — precursors of ceramic fibers of oxide composition

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Abstract. Researches of ICTOEC have developed efficient methods for the synthesis of ceramic-forming organoelementoxanealumoxane oligomers with fibre-forming properties which are promising precursors of refractory oxide fibers: α-Al₂O₃ modified by Y and Mg oxides, spinel MgAl₂O₄, garnet Y₃Al₅O₁₂ as well as blend composition fibers MgAl₂O₄+Y₃Al₅O₁₂ to produce conceptually new high-temperature ceramic composites for structural purposes.

1. Introduction

For state-of-the art and advanced aviation and space engineering, when developing composite materials, alumina fibers are extremely in demand, they are distinguished by relatively high heat resistance, chemical inertness and low specific gravity [1]. This allows composites reinforced with alumina fibers to work in oxidizing environments under loads and high enough temperatures (~1300°C) [2-4] enabling therewith aircraft weight saving.

It should be kept in mind that α-Al₂O₃ fibers tend to creep [5], to solve the creep problem modifiers are introduced. It has long been known that the introduction of Y₂O₃ into alumina fibers prevents grain-boundary slippage, which reduces creep [6].

Al₂O₃ fibers (or Al₂O₃ fibers modified by Y₂O₃, MgO, Cr₂O₃ and other oxides) are rather difficult to produce by melt spinning the corresponding oxides (their melting point is above 2000°C) [7]. The production of such fibers is based on the processing of sols and gels from the corresponding oxides or compounds containing oxide-forming elements [8-11].

We know the old work of Japanese scientists on the synthesis of fusible poly [(acyloxy)alumoxanes] on which basis aluminum oxide fibers were obtained by melt spinning [12].

The researches of ICTOEC synthesized ceramic-forming organoelementoxanealumoxane oligomers having fiber-forming properties: organoyttriumoxane alumoxanes [13], organomagnesiumoxane alumoxanes [14], organomagnesiumoxane yttriumoxanealumoxanes [15],
organochromiumoxane yttriumoxanealumoxanes [16]. A method of preparing modified alumina fibers was developed on their basis [17].

2. Experimental details
Magnesium acetylacetonates, chromium acetylacetonates and yttrium acetylacetonates hydrates were purchased at joint-stock company “Spectr TT”. Used solvents were purchased at joint-stock company “Component-Reaktiv”.

Using a procedure described previously, we synthesized chelated alkoxyalumoxane oligomers (organoalumoxanes OA) [18], fiber-forming organoyttriumoxane alumoxanes (YA) [13], organomagnesiumoxane alumoxanes (MA) [14], organomagnesiumoxane yttriumoxane alumoxanes (MYA) [15], organochromiumoxane yttriumoxane alumoxanes (CYA) [16].

Polymer fibers were produced from organoelementoxanealumoxanes by melt spinning. The fibers were formed by SmartRheo 20 (SR20) capillary viscometer (CEAST). Curing of the formed polymer fibers was performed in Nabertherm 50/500/11 tube furnace in the air environment at the rate of 1 deg/min up to 500°C. Pyrolysis of the cured fibers was performed in an upgraded electric resistance furnace SNOL 12/16 at 1300-1370°C in atmospheric 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.

X-ray diffraction studies were carried out in a divergent Zeeman-Bolin beam on Shimadzu XRD-6000 vertical X-ray diffractometer at ambient temperature with Cu \( K_\alpha \) radiation \( (\lambda_{av} = (2\lambda_{K_\alpha 1} + \lambda_{K_\alpha 2})/3 = 1.54178) \). The crystalline phases were identified using ICDD PDF Release 2003 data.

The characteristic temperatures — softening point \( (T_1) \), fiberization temperature \( (T_2) \), melting or solidification temperatures \( (T_3) \) were determined by a procedure developed at ICTOEC [13].

3. Results and discussion
We have synthesized ceramic-forming organoelementoxanealumoxane oligomers. Synthesized organoelementoxane alumoxanes (OEA) have fiber-forming properties (Table 1).

| OEA    | Al:Mg(Cr) | Al:Y | \( T_1, °C \) | \( T_2, °C \) | Fiberization area, °C | \( T_3, °C \) |
|--------|-----------|------|--------------|--------------|------------------------|--------------|
| MYA-1  | (50-100):1 | (100-200):1 | 80-82 | 130 | 132-154 | 156-158 |
| MA     | 2:1       | –    | 102-106      | 126 | 130-146 | 158-160 |
| YA     | –         | (1,5-1,8):1 | 100-105 | 130 | 135-150 |
| MYA-2  | 2:1       | 6:1  | 78-80 | 116 | 120-186 |
| CYA    | (100-200):1 | (100-200):1 | 70-80 | 138 | 140-150 |

\( T_1 \) — softening point; 
\( T_2 \) — temperature of fiberization beginning; 
Area of fiberization — fine continuous fiber is formed well; 
\( T_3 \) — melting or solidification points.

Polymer fibers were prepared from organoelementoxane alumoxanes (MYA-1, MA, YA, MYA-2, CYA) by melt spinning in capillary viscometer. The photos of these fibers, their surface morphology and the results of X-ray elemental microanalysis are presented in Table 2.
Table 2. Photo and electron micrographs and X-ray elemental microanalysis of formed polymer fibers from organoelementoxane alumoxanes (MYA-1, MA, YA, MYA-2, CYA)

| OEA   | Photo | Electron micrographs | X-ray elemental microanalysis |
|-------|-------|----------------------|------------------------------|
| MYA-1 | ![MYA-1 Photo](image1) ![MYA-1 Electron micrograph](image2) ![MYA-1 X-ray analysis](image3) | | |
| MA    | ![MA Photo](image4) ![MA Electron micrograph](image5) ![MA X-ray analysis](image6) | | |
| YA    | ![YA Photo](image7) ![YA Electron micrograph](image8) ![YA X-ray analysis](image9) | | |
| MYA-2 | ![MYA-2 Photo](image10) ![MYA-2 Electron micrograph](image11) ![MYA-2 X-ray analysis](image12) | | |
| CYA   | ![CYA Photo](image13) ![CYA Electron micrograph](image14) ![CYA X-ray analysis](image15) | | |

After spinning, the polymer fiber contains a large amount of organic matter. Therefore, in order to avoid fiber degradation during ceramization, it is necessary to cure (crosslink) polymer fibers. Curing was carried out by slow heat treatment of the fiber (heating rate 1 °C/min) to 200-500°C. Table 3 presents photos of the cured fibers c-MYA-1, c-MA, c-YA, c-MYA-2, c-CYA and SEM results: surface morphology and X-ray elemental microanalysis.
### Table 3. Photo, electron micrographs and X-ray elemental microanalysis of cured formed fibers from organoelementoxane alumoxanes (c-MYA-1, c-MA, c-YA, c-MYA-2, c-CYA)

| c-fibers and $T$ curing, °C | Photo | Electron micrographs | X-ray elemental microanalysis |
|-----------------------------|-------|----------------------|------------------------------|
| MYA-1-500                   | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| MA-200                      | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| YA-500                      | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |
| MYA-2-300                   | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| CYA-500                     | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) |

Ceramization of the cured fibers c-MYA-1, c-MA, c-YA, c-MYA-2, c-CYA was performed at a temperature of 1300-1500°C. Table 4 presents photos, micrographs, elemental composition and diffractograms of ceramic fibers based on OEA.
Table 4. Photo, electron micrographs, elemental microanalysis and diffractograms of ceramic fibers

| Ceramic fibers | Photo | Electron micrographs and X-ray elemental microanalysis | Diffractograms of ceramic fibers |
|----------------|-------|--------------------------------------------------------|----------------------------------|
| MYA-1-1300     | ![Photo](image1) | ![Micrograph](image2) | ![Diffractogram](image3) |
| MA-1500        | ![Photo](image4) | ![Micrograph](image5) | ![Diffractogram](image6) |
| YA-1370        | ![Photo](image7) | ![Micrograph](image8) | ![Diffractogram](image9) |
| MYA-2-1300     | ![Photo](image10) | ![Micrograph](image11) | ![Diffractogram](image12) |
| CYA-1370       | ![Photo](image13) | ![Micrograph](image14) | ![Diffractogram](image15) |

Analyzing the data presented in Table 4, it can be affirmed that to obtain fibers of a more dense structure, the ceramization of the cured c-MYA-1, c-MA, c-YA, c-MYA-2, c-CYA fibers should be carried out at a temperature not higher than 1300°C.
4. Conclusion

Thus fiber-forming organoelementoxanealumoxanes can be used to obtain oxide fibers: $\alpha$-Al$_2$O$_3$ modified by Y and Mg oxides or modified by Cr oxides, spinel MgAl$_2$O$_4$, garnet Y$_3$Al$_5$O$_{12}$ as well as blend composition fibers MgAl$_2$O$_4$+Y$_3$Al$_5$O$_{12}$.

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