**Al$_2$O$_3$–Y$_2$O$_3$–Cr$_2$O$_3$ ceramics based on organochromiumoxane yttriumoxane alumoxanes**

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**Abstract.** Ceramic-forming organochromiumoxane yttriumoxane alumoxanes with various Al:Cr and Al:Y mole ratios have been synthesized by the co-condensation of chelated alkoxyalumoxanes, yttrium acetylacetonate hydrate and chromium acetylacetonate organic solvent. Pyrolysis of the synthesized organochromiumoxane yttriumoxane alumoxanes at 1500°C results in the formation of high-purity multicomponent ceramics of Al$_2$O$_3$–Y$_2$O$_3$–Cr$_2$O$_3$ composition; said ceramics was studied in detail by X-ray analysis.

1. Introduction

Multiphase oxide/oxide ceramic composites with enhanced resistance to oxidation and creep are required for operation under extreme conditions [1,2]. Moreover, the employed oxide components must be chemically compatible and, to prevent mechanical damage, have sufficient heat resistance. Y$_3$Al$_5$O$_{12}$ (YAG)–Al$_2$O$_3$ system is known [3] to be very promising for high temperature use. These two phases are compatible (YAG and $\alpha$-Al$_2$O$_3$) since they have the same coefficients of thermal expansion and high melting points (1940 and 2045°C for YAG and Al$_2$O$_3$ respectively). In addition, YAG retains its flexural strength up to 1400°C and high creep resistance with insignificant Cr$_2$O$_3$ additives improving strength and creep due to the formation of solid solutions, such as Y$_3$(Al$_{1-x}$Cr$_x$)$_5$O$_{12}$ [3].

Ceramics of this composition is promising for use in solid-state lasers, as well as for the manufacture of inorganic luminescent materials and ceramic pigments [4-10].

2. Experimental details

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) [11], ceramic-forming organoyttriumoxane alumoxanes [12], ceramic-forming organochromiumoxane yttriumoxane alumoxanes [13].
Pyrolysis of the ceramic-forming organochromiumoxane yttriumoxane alumoxanes was performed in an upgraded electric resistance furnace SNOL 12/16 at 1500°C in atmospheric air, samples of $x\text{Al}_2\text{O}_3:y\text{Y}_2\text{O}_3:z\text{Cr}_2\text{O}_3$ ceramics were obtained.

The surface morphology and elemental composition of the ceramics samples were 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. Elemental mapping with overlay elements on the same map was carried out on a scanning electron microscope Tescan Mira LMU equipped with an energy dispersive X-ray spectrometer INCA X_MAX-50 Oxford Instruments. Ceramic samples were studied under high vacuum without evaporation, using low values of probe currents and accelerating stresses (up to 5-10 kV).

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 $K_α$-radiation ($λ_{av} = (2λ_{K_{α1}} + λ_{K_{α2}})/3 = 1.54178$. The crystalline phases were identified using ICDD PDF Release 2003 data.

3. Experimental details

We have synthesized ceramic-forming organochromiumoxane yttriumoxane alumoxane oligomers with a molar ratio Al:Cr = 200:1, Al:Y = 200:1 (sample 1) and Al:Cr = 5:1, Al:Y = 1.5:1 (sample 2) according to the scheme

$$[\text{Al(OH)}_3\text{Cr(OH)}_3\text{Al}_2\text{O}_3]_n\text{[R(OH)}_2\text{O]}_d + k\text{[R(\text{OH})}_2\text{Cr]}_d \rightarrow[(\text{R}\text{**O})_b\text{Cr(OH)}_2\text{O]}_d\cdot\text{[Al(OH)}_3\text{Cr(OH)}_3\text{Al}_2\text{O}_3]_n\cdot[(\text{R}\text{**O})_b\text{Y(OH)}_2\text{O]}_d + f\text{ROH}$$

Where: $k, d = 0,1-6; m = 3-12; j + x + 2y + z = 3; s + t + 2r = 3; h + a + 2b = 3$;
$R\text{O}_n\text{H}_{2n+1}; n = 2-4; R^* - \text{C(CH}_3) = \text{CHC}(\text{O})\text{O}_n\text{H}_{2n+1}; R^{**} - \text{C(CH}_3) = \text{CHC(O)CH}_3$

The synthesized oligomers pyrolysis at 1500°C resulted in the following ceramic samples: sample 1 (Al:Cr = 200:1, Al:Y = 200:1) and sample 2 (Al:Cr = 5:1, Al:Y = 1.5:1) that were studied by SEM and X-ray methods.

SEM results (surface morphology and elemental composition) of sample 1 are presented in figure 1a, and those of sample 2 — in figure 1b.

![Figure 1. Electron micrographs and X-ray elemental microanalysis of the ceramic samples: a — sample 1; b — sample 2.](image-url)
X-ray analysis of ceramic sample 1 (figure 3a) showed the presence of corundum phases (α-Al₂O₃) — 99 wt.-% and YAP (YAlO₃) — 1 wt.-%, and ceramic sample 2 (figure 3b) was YAG (Y₃Al₅O₁₂) — 100 wt.-%.

It is known that α-Al₂O₃ and α-Cr₂O₃ oxides crystallize in the structure of corundum (space group R3c, hexagonal syngony). Due to the existence of common faces in pairs of MO₆ octahedrons, there are two sets of M–O distances: 1.89 and 1.93 Å for alumina and for chromium oxide 1.97 and 2.01 Å. Al³⁺ or Cr³⁺ can exist in each particular lattice site, and the probability of their finding depends on the degree of aluminum substitution for chromium. If we consider the structure in general, we can assume that each of them is occupied by an “average” ion, which has some intermediate properties between Al³⁺ and Cr³⁺, that is why there are no diffraction peaks related to α-Cr₂O₃ [14].

All diffraction peaks (figure 3b) are related to Y₃Al₅O₁₂ phase but a detailed consideration of each reflex (figure 4) shows that they are multiplets consisting of two reflexes, less intense one shifted towards smaller angles — phase 2, and more intense one shifted in the direction of large angles — phase 1. This is caused by the presence in the sample of two phases with the same structure (Im3d), but different parameters of the elementary lattice a₂ = 12.136 and a₁ = 12.086 Å. A change in the unit cell parameter of a powder sample can only be caused by a change in the chemical composition, in our case, due to Y₃Al₅O₁₂ Cr³⁺ entering the crystal lattice the ionic radius of which equaling to 0.64 is close to the ionic radius of Al³⁺ 0.57 [14].

Moreover, it is known that “YAG belongs to the cubic space group O¹⁰ (Ia₃d) and contains eight formula units per unit cell. The crystal can be described by the formula C₃A₂D₃O₁₂ where the Y ions sit in dodecahedral C sites and the A1 ions occupy both tetrahedral D sites and trigonally distorted octahedral A cites. When Cr³⁺ is incorporated into the YAG structure, it substitutes for Al in the...
octahedral sites. Cr$^{3+}$ prefers octahedral sites in all compounds due to crystal-chemistry consideration” [4].

Figure 4. Interpretation of the diffraction peaks of each reflex of ceramic sample 2 diffractogram (figure 3b).

4. Conclusion
On the basis of ceramics-forming organochromiumoxane yttriumoxane alunoxanes hydrolytically stable in air we obtained the oxide ceramics samples with specified molar ratio of Al:Cr and Al:Y of the following composition: 1 — YAP modified corundum, and 2 — YAG where aluminum is partially replaced with chromium.

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