REFRACTORY TRIPLE COMPOSITES BASED ON ALUMINA AND ZIRCONIA

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Introduction

Progress of modern techniques requires use new strengthened heat-resistant and corrosion stable ceramic materials. The high dispersity powders and fibers from alumina and stabilized zirconia are used for these materials production. However at temperatures above 1500^{0}C the triple solid solutions of zirconia stabilized by alkali-earth metals have been degraded. These phenomena reduce the strength properties of ceramics. At the same time, at transition from macrostructures to micro-and nanosized structures, kinetic of processes and properties of substances essentially change. Therefore it was logical to assume an increase of physical-mechanical properties of the composite materials prepared from nanostructured refractory oxide powders.

The present work is devoted to research of interaction of oxide nanostructured powders in the triple systems Al_2O_3-ZrO_2-MgO and Al_2O_3-ZrO_2-Y_2O_3, and an influence of composition and production method on structure and properties of composite refractory ceramics.

Experimental

For preparation of composite powders two methods were used. An initial matrix was represented by hydrated cellulose materials: threads, fabrics or unwoven material. In the first way oxide fibers and powders were prepared by impregnation of hydrated cellulose fibers and materials with solutions of salts of aluminium, yttrium, zirconium or aluminium, zirconium, magnesium with the subsequent removal of a moisture and an organic component. The ratio of salts of zirconium and yttrium in impregnating solutions remained constant (in account on zirconia additive Y_2O_3 was 3 mol. %-PSZ), and the ratio of salts (zirconium-yttrium) and aluminium changed from 0 up to 100 wt. % with an interval 20 wt. %. For preparation of three-component fibers Al_2O_3-ZrO_2-MgO polymeric threads became impregnated with solutions of three salts, which ratio in account on metal oxides (mol. %) amounted: 98,5:1:0,5; 93:5:2; and 87,5:10:2,5. Impregnated fibers were dried and heat treated in the air at an assigned temperature over the range 600 - 900^{0}C. As a result, a polymer matrix decomposed, salts dissociated and nano-sized grains of oxide metals are formed. The shape of new inorganic fibrous material was identical to that of the initial polymer fibers, but their sizes (long and diameter) were less in some times [1] (fig. 1).

Prepared three-component oxide fibers were crushed, were graded on fractions. The samples in the form of beams in size of 5x5x50 mm and cylinders in diameter of 10 mm and height 15-20 mm were formed. Then the samples were annealed in an oxidizing atmosphere at the temperatures from 100 up to 1600^{0}C.

On the second way three-component powders were prepared by sedimentation of gel hydroxide of aluminium from a water solution of chloride of

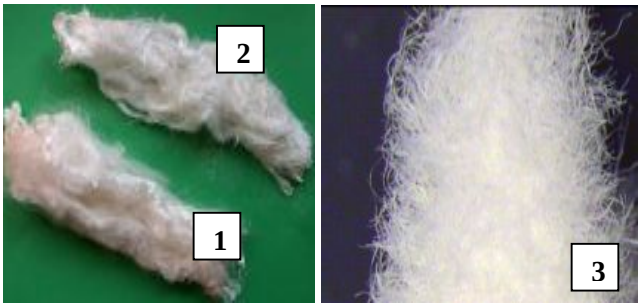

Fig.1 The initial cellulose fibers (1), oxide fibers (2), triple composite fibers Al_2O_3-ZrO_2-Y_2O_3 (3)

aluminium by a solution of ammonia with simultaneous introduction in gel the synthesized fibrous powders partially stabilized zirconia. The quantity of the entered into gel fibers were changed from 5 up to 20 wt. %. The prepared deposits were washed, dried, and samples in the form of cylinders and beams were formed.

Annealing of samples was carried out on air in the foregoing temperature range with an interval 100^{0}C, then structure and physical-chemical properties of ceramic samples were investigated.

The methods of investigations

The processes of forming oxide fibers were studied on the Paulic-Paulic-Erdei thermograph by the differential thermal analysis. The material was heated in air with a velocity of 5^0/min, the weighed portion constituted 0.5 g, and high-pure Al_2O_3 served as a standard substance of comparison. The fiber structure was investigated by the X-ray methods, IR spectroscopy, and scanning electron microscopy. The change in the phase composition of fiber samples thermally by treated at given temperatures was studied by the quantitative X-ray phase analysis. The phase content in these samples was determined through the integral reflex intensities: γ - Al_2O_3 - [400], θ - Al_2O_3 - [200], α - Al_2O_3 - [012], MgO - [220] and $MgAl_2O_4$ - [440], and of phases: ZrO_2 tetragonal [111] and monoclinic [$\bar{1}$11]. A high-pure magnesium oxide powder was used as an external standard. The BET method was adopted to estimate the specific surface and sorption ability of fibrous oxides through adsorption of nitrogen and benzene vapor. Surface microstructure of powders and fibers was examined on the scanning electron microscope (SEM) – JSM-35 (JEOL) with x 10000-15000. A shape and size of particles were examined on the transmission electron microscope (TEM) – JSM 200A with x 100000-120000. Crystallite sizes were determined by the X-ray analysis in terms of the physical broadening of the reflex contours of test phases [2].

Results and Discussion

The research of crystal structure of prepared three-component powders had shown that in the field of temperatures 550-600^{0}C from metal oxides the triple solid solution was formed which existed up to 1200^{0}C.

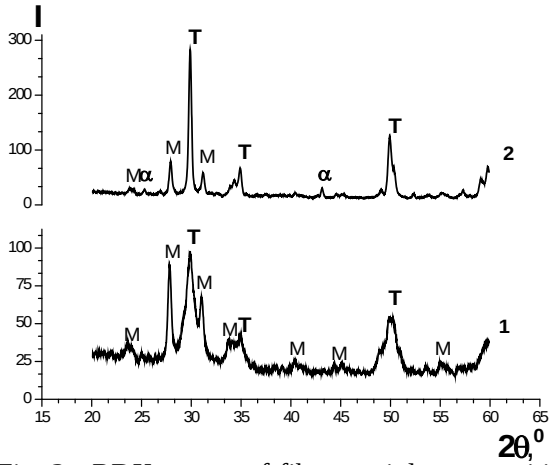

Fig. 2 RDX–grams of fibrous triple composition of $ZrO_2(Y_2O_3)$ - Al_2O_3 (wt.%): 60:40 annealed at temperatures: 900 – **1**, 1200^{o}C – **2; T** – ZrO_2 tetragonal, **M** – ZrO_2 monoclinic, α – α-Al_2O_3

Above this temperature it was broken up to three phases: zirconia of tetragonal and monoclinic structures, and α-Al_2O_3. The content of monoclinic ZrO_2 did not exceed 5-10 %, and oxide fibers became strong and rigid.

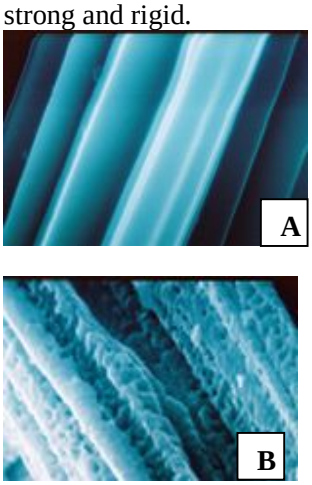

Fig. 3 Microstructure of triple oxide fibers (wt.% 60:40) annealed at the temperature: 700 – **A**, 1500^{0}C - **B**; and the variations of crystallite sizes of tetragonal (T) and monoclinic (M) ZrO_2 of this fibers - **C**

During sedimentation of gel aluminium hydroxide with the reactive fibrous dispersions possessed high dispersed surface energy, chemical adsorption of gel particles at the filler surface occurred. Then aqua complexes were formed. At the heat treatment in the field of 500-600^{0}C they lost the adsorbed and chemically associated water, compounds were dissociated and nanograins of metal oxides were formed. Usually solid reactions in such systems proceed above 1000-1200^{0}C. Density annealed at the 1600^{0}C ceramic samples of partially stabilized zirconia and composite powder of 80 % PSZ: 20 % Al_2O_3 amounted 5,96 and 5,54 g/cm^3, it's value went down up to 4,2 g/cm^3 with increasing in content Al_2O_3 to 80 wt. %.%. The open porosity did not exceed 0,2 – 0,4 %. The bending strength of ceramic samples from nanostructured powders was equaled 540-560 МПа, and compression strength - 1550 МПа. Where as, the ceramics from the nanograins mixtures of alumina gel with fibrous filler had these characteristics 480 and 1630 МПа, accordingly. The fibrous oxide three-component powders can be used as fillers for composites and dense ceramics.

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References

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