

# Corundum ceramic materials modified with silica nanopowders: structure and mechanical properties

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**Abstract.** Filtering elements are often used in the metallurgy of rare earth metals. Corundum ceramic is one of the most suitable materials for this purpose. The process of formation and the properties of nanomodified ceramic materials, which are proposed as filtering materials with tunable effective porosity, are described. A silica nanopowder is used as a porosity-increasing agent. Vortex layer apparatus is used for mixing of precursor materials. The obtained results show that nanomodification with the vortex layer apparatus using 0.04 wt. % silica nanopowder as a modifying agent leads to an increase in the compression strength of corundum ceramic by the factor of 1.5.

## 1. Introduction.

The production of rare earth metals becomes more important due to rapid industrial development: this development is impossible without new materials, in particular, ceramic filter elements. Various nanosized additives are known to be used to increase the effectiveness of filtering materials. However, one of the main practical difficulties related to the use of nanopowders on the industrial scale is to achieve a homogenous mixture of micro- and nanosized powders [1-5]. This problem leads to the development of new techniques for forming homogenous powder mixtures.

A vortex electromagnetic field is one of the effective solutions to achieve a homogenous nanopowder distribution in the volume of a coarse-grained material [6]. A homogenous particle distribution in the final product can be reached by high-speed rotation of the material to be treated in combination with impact and attrite processes in vortex layer apparatus.

## 2. Experimental

Mullite with particle sizes of 0 – 500  $\mu\text{m}$ , 0.5 – 1.0 mm, and 1 – 3 mm; corundum with a particle size of 100  $\mu\text{m}$ ; and calcium monoaluminate as high-aluminous binding agent were used as precursors. Silica nanoparticles with an average particle size of 15 – 20 nm were used as a modifying agent.

A standard ceramic sample preparation scheme was used; it included weighting, mixing, water addition, drying, and annealing. Standard samples consisted of a mixture having the following proportions: mullite size 0-500  $\mu\text{m}$ , 29 wt. %; 0.5 – 1.0 mm, 12%; 1 – 3 mm, 44%; corundum 10%; and calcium monoaluminate 5%. The standard samples were mixed in a laboratory paddle binder. Modified samples were prepared by the addition of 0.05 wt. % silica nanopowder. This optimal



concentration was investigated. The modified samples were mixed in vortex layer apparatus for 2 min, and 5.5 wt. % water was added after mixing. The samples were first dried at a temperature of 25°C for 24 h and, then, at 110°C. Some samples were annealed at a temperature of 1100°C. Cubic samples with 50-mm edges were then prepared for analysis. The samples were analyzed by compression strength measurements, scanning microprobe spectroscopy, X-ray diffraction, and electron microscopy.

Compression strength tests were carried out on a Zwick Z250 (Germany, Zwick) device. With this device, we performed tensile, compression, and three-point bending tests in the load range from 2 kg to 25 t. The measurement error was at most 1% and the testing rate was 0.0005--600 mm/min. We tested flat, cylindrical, and cubic samples. The frequency of read speed measurement and control electronics was 500 Hz. Compression strength was analyzed at constant loading rate of 2 mm/min.

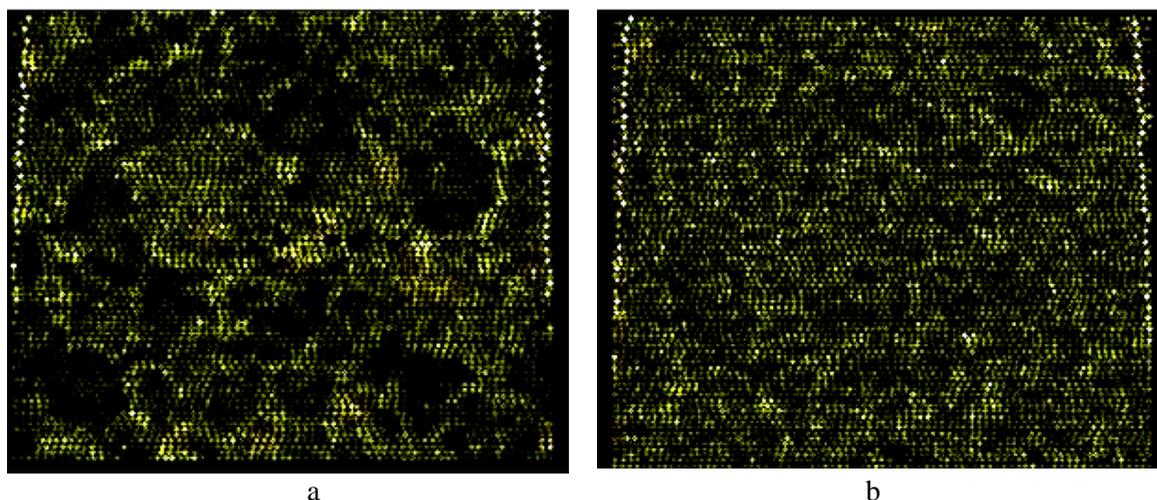
The uniformity of the distribution of nanoscale additives was analyzed by X-ray fluorescence on an RAM-30 (Russia, St. Petersburg, Scientific Instruments) analyzer. We performed elemental mapping of a sample in an area of 50 by 50 mm at a micron range voltage of 15 - 45 kV using Mo- $k\alpha$  radiation. The samples for analysis were prepared in form of tablets compressed in a hydraulic hand press at a pressing force of 5 t. Zirconia nanopowders were used for calibration.

XRD analysis of samples was performed using an Ultima IV (Japan, Rigaku) X-ray diffractometer and copper radiation. The X-ray tube current was 40 mA and the voltage was 40 kV. X-ray diffraction patterns were recorded in the angular range  $2\theta = 0-100^\circ$  at a step of  $0.1^\circ$  and an exposure time of 2 s. The Bragg-Brentano focusing scheme with two Soller slits was used.

Micrographs were taken with a JSM-6700F (Japan, JEOL) field emission scanning electron microscope.

### 3. Results and discussion

We used scanning X-ray fluorescence to compare the samples treated in the vortex layer apparatus and traditionally prepared samples (figure 1). As is seen in figure 1, the vortex layer apparatus produces a more homogenous zirconia nanopowder mixture as compared to a standard laboratory binder.



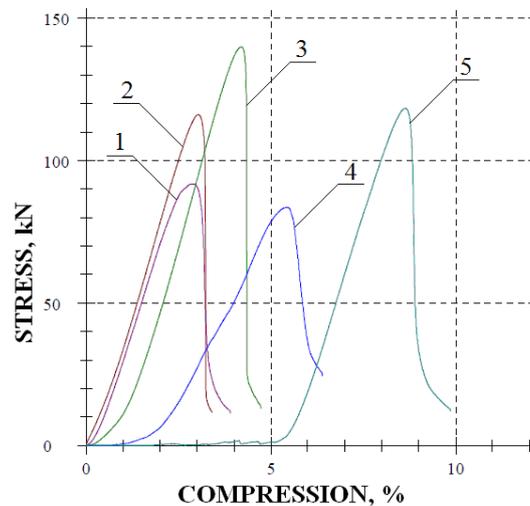
**Figure 1.** Distribution of zirconia nanoparticles: a – standard laboratory binder mixing, b – vortex layer apparatus.

According to the experimental data, the optimal silica concentration is 0.05 wt. % (figure 2). The compression strength of the sample with 0.05 wt. %  $\text{SiO}_2$  increased by 52 % as compared to the sample with no  $\text{SiO}_2$  modifier. It is possible that the material strength increases due to both mechanical activation process and chemical modification at the stage of hydration.

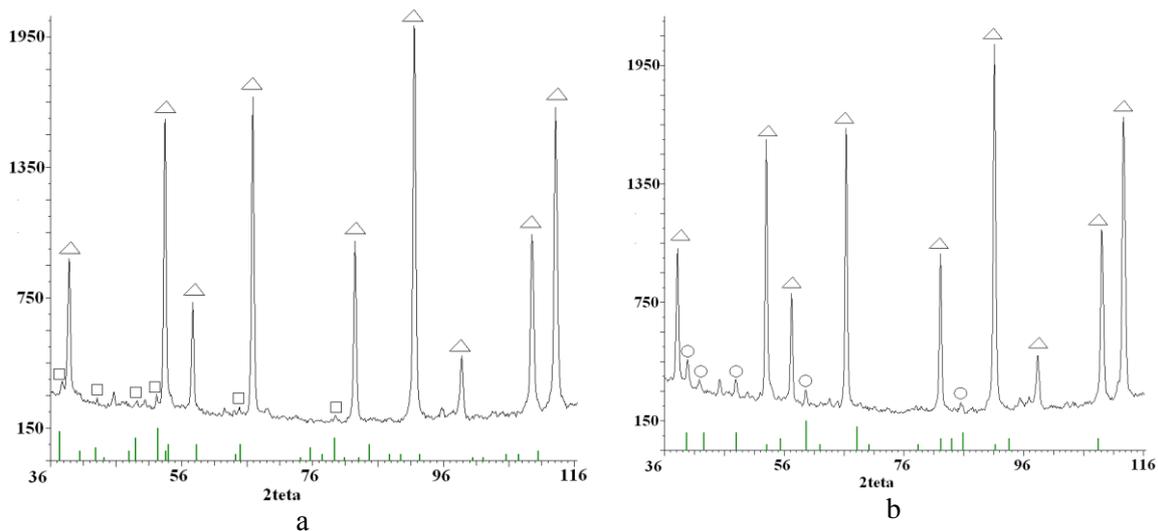
The XRD results (figures 3 – 4) of studying the modified samples show the formation of metastable calcium hydroaluminate  $\text{CaAl}_2\text{O}_4 \cdot 8\text{H}_2\text{O}$  at room temperature. The XRD data obtained for a reference

sample demonstrate the formation of cubic calcium hydroaluminate  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ . This difference can be explained by good ability of hydrophilic silica nanoparticles to retain moisture in ceramic; as a result, the hydration of aluminate is longer than that of the reference sample. The longer hydration time leads to a decrease in the heat release per unit time, decreasing the probability of self-heating to the temperature of transformation of metastable  $\text{CaAl}_2\text{O}_4\cdot 8\text{H}_2\text{O}$  into stable  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ .

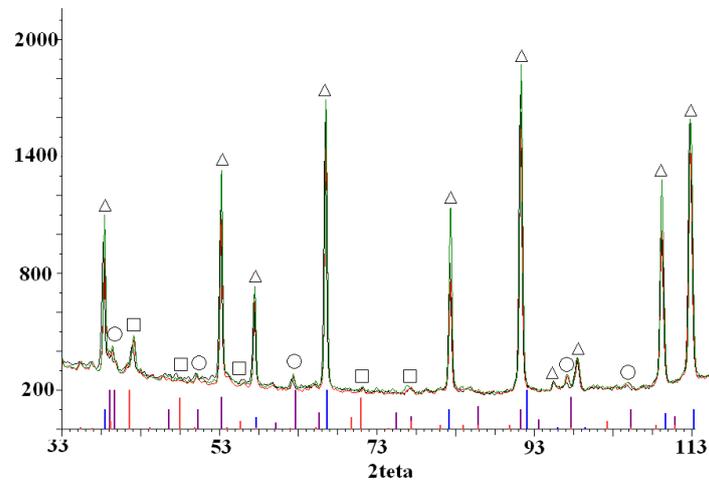
Based on the XRD data, we can conclude that the formation of the metastable  $\text{CaAl}_2\text{O}_4\cdot 8\text{H}_2\text{O}$  phase with a less steep hydration process improves the structure of the material. The XRD data of the sintered samples show that their phase composition is the same, namely,  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{SiO}_5$ , and  $\text{CaSiO}_3$ , and the measured patterns are quite similar.



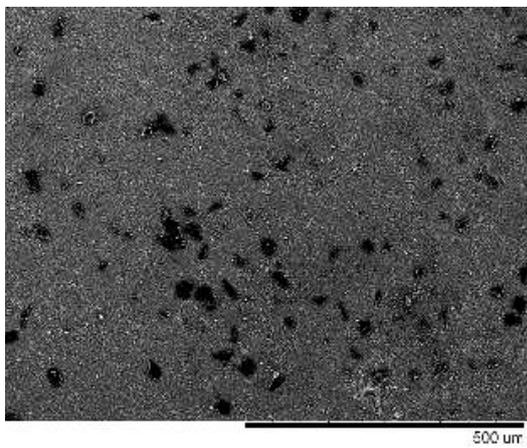
**Figure 2.** Loading curves of mullite-corrundum samples: 1 – 0%  $\text{SiO}_2$ ; 2 – 0.01%  $\text{SiO}_2$ ; 3 – 0.05%  $\text{SiO}_2$ ; 4 – 0.1%  $\text{SiO}_2$ ; 5 – 0.2%  $\text{SiO}_2$



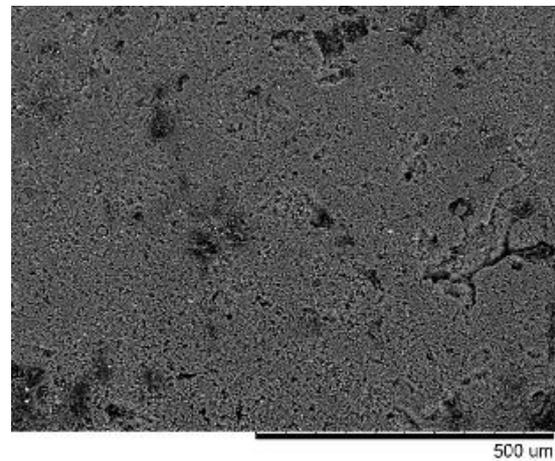
**Figure 3.** XRD data of mullite-corrundum mixture at the first drying stage: a – reference; b –  $\text{SiO}_2$  0.04 wt. %;  $\Delta$  -  $\text{Al}_2\text{O}_3$ ;  $\square$  -  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ ;  $\circ$  -  $\text{CaAl}_2\text{O}_4\cdot 8.5\text{H}_2\text{O}$



**Figure 4.** XRD data of sintered samples:  $\Delta$  -  $\text{Al}_2\text{O}_3$ ;  $\circ$  -  $\text{Al}_2\text{SiO}_5$  and  $\square$  -  $\text{CaSiO}_3$

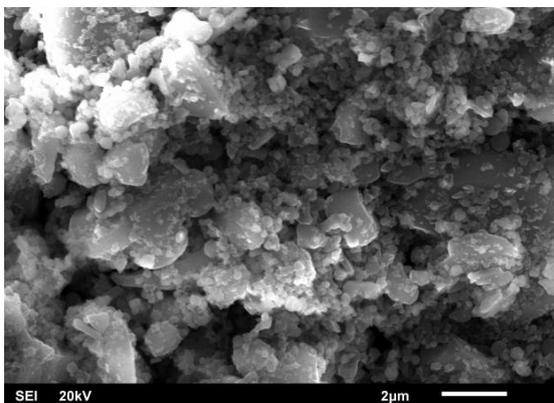


a

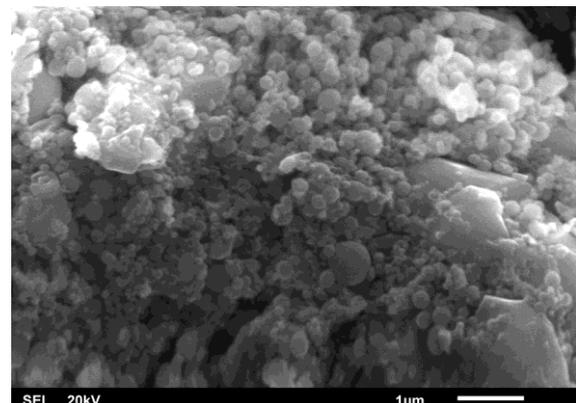


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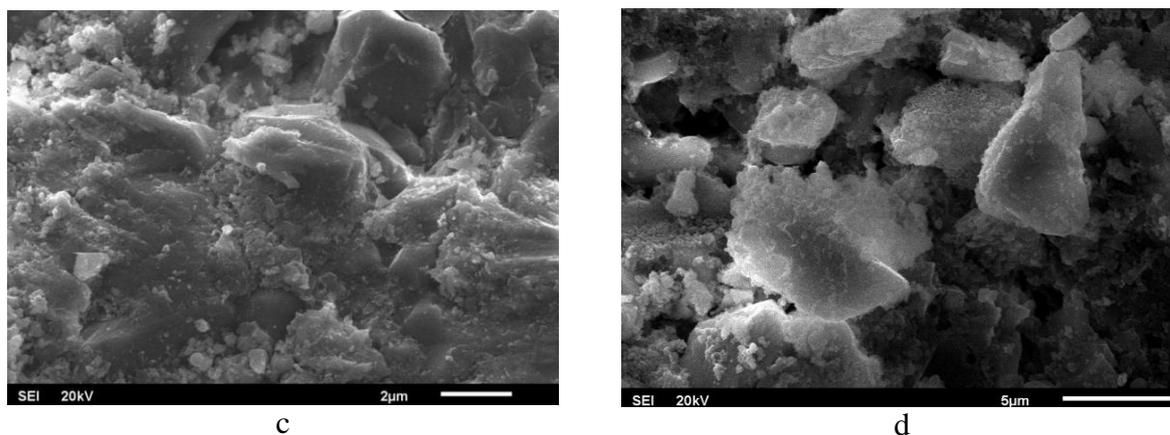
**Figure 5.** SEM images of mullite-corundum ceramics: a – reference; b –  $\text{SiO}_2$  0.04%



a



b



**Figure 6.** SEM images of mullite-corundum ceramic samples: a, b – reference; c, d –SiO<sub>2</sub> 0.04 wt. %

Scanning electron microscopy showed that the samples containing nanostructured silica are less porous as compared to the reference sample, which is due to an inhibited hydration process and high water-binding properties at the first stages of drying. The reference sample has a much more porous structure.

Before annealing, the structure of the reference samples mostly consists of calcium hydroxide nanoparticles filling the pores between corundum particles. The binding phase has an average particle size of 50 – 150 nm. The silica-modified samples have a coarser structure due to a longer hydration time, when the particle growth rate is higher than the nucleation rate.

#### 4. Conclusions

The obtained results show that the addition of 0.05 wt % nanostructured silica increases the compression strength of ceramic by 52%. Treatment in vortex layer apparatus results in the formation of a more homogenous mixture as compared to standard mechanical mixing methods. The addition of 0.1 wt. % silica nanopowder increases the hydration period, which results in the formation of metastable high-strength calcium hydroaluminate.

#### Acknowledgements

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