

# Sintering oxide ceramics based on $\text{Al}_2\text{O}_3$ and $\text{ZrO}_2$ , activated by $\text{MgO}$ , $\text{TiO}_2$ and $\text{SiO}_2$ additives

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**Abstract.** The positive effect of the addition of  $\text{MgO}$  and  $\text{TiO}_2$  in an amount of no more than 1 wt. % on sintering and physico-mechanical properties of alumina ceramics is established. Addition of 5% of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  provides the mechanism of liquid phase sintering of ceramics, which leads to increase in its density and strength up to 480 MPa. In ceramic system  $\text{Al}_2\text{O}_3$  -  $\text{ZrO}_2$  -  $\text{Y}_2\text{O}_3$  highest level of physical and mechanical properties of the composition had a hypereutectic composition 16.6%  $\text{Al}_2\text{O}_3$  - 76%  $\text{ZrO}_2$  - 7.4%  $\text{Y}_2\text{O}_3$ . In this composition two mechanisms of hardening are realized simultaneously, such as transformational hardening by  $t$ - $m$  -  $\text{ZrO}_2$  transition and dispersion strengthening with high-modulus particles of  $\alpha$ -  $\text{Al}_2\text{O}_3$ .

## 1. Introduction

Strong ceramics based on  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  are very promising structural and functional materials. The most common methods of obtaining solid alumina ceramics are powder technology methods, i.e. various kinds of pressing and sintering, modified as applied to the ceramic. The modification consists in choosing the optimal parameters of ceramics consolidation. These parameters are compacting pressure and methods of its application, the temperature of sintering treatment, the environment and the speed of the process. Nevertheless, wide spread practical solid oxide ceramics prevent complexity and low productivity of hot isostatic pressing and hot technology [1, 2], allowing to obtain materials with high tensile strength [3]. A relatively simple technique of uniaxial compression followed by a free sintering usually cannot produce ceramics with high mechanical properties [4].

The purpose of this work was to study the patterns of consolidation of ceramics based on  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ , activated by the addition of the charged powders  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ .

## 2. Experiment

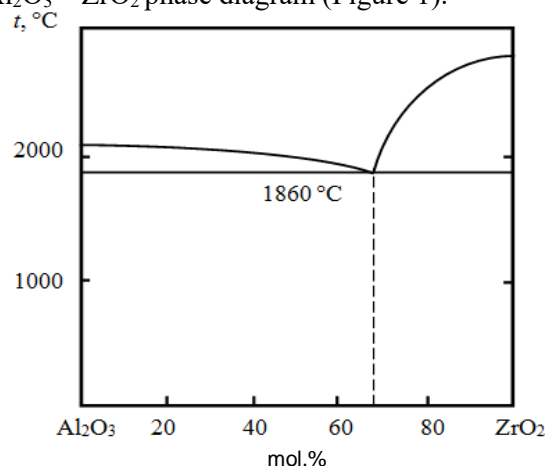
Industrial nanocrystalline oxide powders (NP)  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  -  $\text{ZrO}_2$  -  $\text{Y}_2\text{O}_3$ , obtained by plasma chemical synthesis (PCS) are used. Oxide powders obtained PHS have a characteristic form of hollow spheres consisting of nanocrystallites and amorphized intergranular phase [5]. The size of the spheres varies between 100...1000 nm, the size of nanocrystals which form the sphere, is between 50...100 nm.

Industrial submicron powders  $\text{MgO}$  and  $\text{TiO}_2$  were used as activating additives. Powder  $\text{MgO}$  was added to  $\text{Al}_2\text{O}_3$  with the aim of recrystallization braking during sintering of corundum and preserving fine structure of the sintered ceramic.  $\text{TiO}_2$  was used to reduce the sintering temperature of alumina ceramics. Powder  $\text{SiO}_2$  was prepared in the laboratory by crushing quartz glass and grind in the planetary mill. Fraction was used with a particle size <40 microns.  $\text{SiO}_2$  was added in  $\text{Al}_2\text{O}_3$  powder in order to implement the mechanism of liquid phase sintering and receive mullite-corundum ceramics in accordance with the phase diagram  $\text{SiO}_2$  -  $\text{Al}_2\text{O}_3$ . Powders  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  -  $\text{ZrO}_2$  -  $\text{Y}_2\text{O}_3$  were annealed



in the air atmosphere in a high temperature electric resistance furnace at 1450°C for one hour to convert  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

In order to obtain powder compositions, to improve the processing performance and to enhance their activity, annealed powders were treated in the planetary ball mill for 20 minutes at a rotational speed of the grinding vessel 20 Hz. Grinding bodies were zirconia balls. The content of components in the system Al<sub>2</sub>O<sub>3</sub> - ZrO<sub>2</sub> - Y<sub>2</sub>O<sub>3</sub> varied for obtaining hypoeutectic, eutectic and hypereutectic compositions in accordance with the Al<sub>2</sub>O<sub>3</sub> - ZrO<sub>2</sub> phase diagram (Figure 1).



**Figure 1.** Phase diagram of the Al<sub>2</sub>O<sub>3</sub> - ZrO<sub>2</sub> system [5].

The treated powders were sieved for 10 minutes at vibratory drive to obtain a fraction < 40 micrometers and plasticized with a water-solution of carboxymethylcellulose (CMC). Plasticized powders were formed by uniaxial pressing in a rigid mold, compaction pressure was 300 MPa. The obtained compacts were cylinders with diameter 25±0.01 mm and height of 5±0.01 mm.

Sintering the compacts was carried out in a high temperature resistance furnace at a temperature 1700°C, holding time at this temperature was 1 hour.

Density of sintered specimens  $\rho$  was determined by hydrostatic weighing in an ethanol with an accuracy ±0.001 g. The relative density  $\theta$  of the specimens was also calculated in accordance with equation:

$$\theta = \frac{\rho}{\rho_t} \cdot 100 \%,$$

where  $\rho_t$  is a theoretical density of ceramics.

Indentation was performed using device Nano Indenter G 200. Berkovich pyramid was used as indenter, a load was 500 mN. The device automatically calculates the elastic modulus  $E_{IT}$  and microhardness  $H_{IT}$  in compliance with ISO 14577.

The strength of the sintered ceramics was determined by the «Scratch Testing» method also using the device Nano Indenter G 200. Essence of the method is to apply a scratch on the surface of the sample by linearly increasing load (as a rule from 0 to 40 mN) and determination of the profile depth and width of the scratch. The strength of the samples was calculated according to the formulas

$$\sigma = \frac{F_n}{A_s \sin \alpha} \quad u \quad A_s = \frac{a^2}{2\sqrt{3} \sin \alpha} + \frac{ah}{\cos \alpha},$$

where  $F_n$  – normal load,  $A_s$  – projection print area,  $a$  and  $h$  – profile width and depth of the scratch,  $\alpha=65^\circ$  (for the Berkovich pyramid).

### 3. Results of the experiment

Table 1 shows the density values of samples pressed under a pressure of 300 MPa. It should be noted that all samples have a regular cylindrical shape, exfoliate and shedding edges were not observed.

**Table 1.** The density of compacts.

No.	Composition (wt. %)	$\rho_c$ (g·cm <sup>-3</sup> )	$\rho_t$ (g·cm <sup>-3</sup> )	$\Theta_c$ (%)
1	99.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO	2.13	3.97	53.65
2	98.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 1% TiO <sub>2</sub>	2.18	3.97	54.91
3	97.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 2% TiO <sub>2</sub>	2.19	3.97	55.16
4	95.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 4% TiO <sub>2</sub>	2.24	3.97	56.42
5	94.6 % Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 5% SiO <sub>2</sub>	2.20	3.87	56.85
6	89.6 % Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 10% SiO <sub>2</sub>	2.16	3.78	57.14
7	76.1% Al <sub>2</sub> O <sub>3</sub> – 21.8% ZrO <sub>2</sub> – 2.1% Y <sub>2</sub> O <sub>3</sub>	2.22	4.29	51.75
8	31.7% Al <sub>2</sub> O <sub>3</sub> – 62.2% ZrO <sub>2</sub> – 6.1% Y <sub>2</sub> O <sub>3</sub>	1.96	5.04	38.89
9	16.6% Al <sub>2</sub> O <sub>3</sub> – 76% ZrO <sub>2</sub> – 7.4% Y <sub>2</sub> O <sub>3</sub>	1.31	5.36	24.44
10	92.9% ZrO <sub>2</sub> – 7.1% Y <sub>2</sub> O <sub>3</sub>	2.84	5.78	49.13

Table 2 shows the values of density of the sintered samples.

**Table 2.** Density of sintered samples.

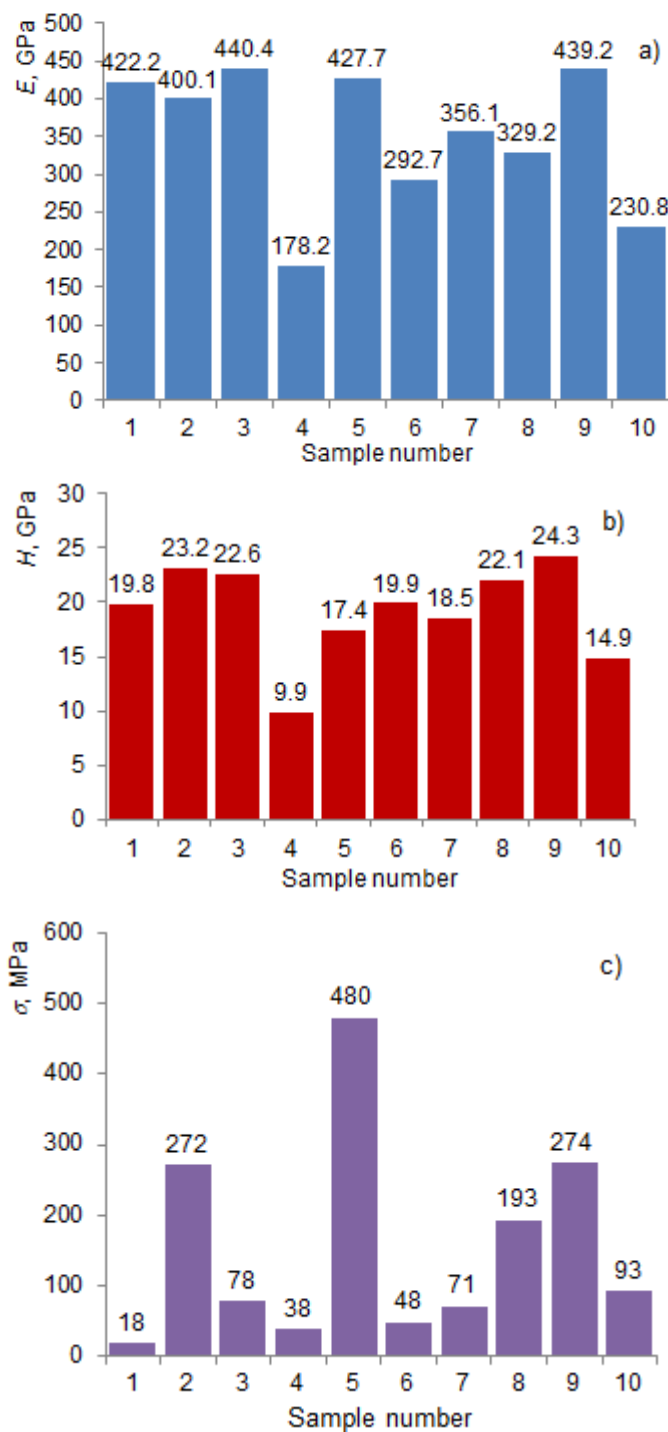
No.	Composition (wt. %)	$\rho_s$ (g·cm <sup>-3</sup> )	$\rho_t$ (g·cm <sup>-3</sup> )	$\Theta_s$ (%)
1	99.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO	3.60	3.97	90.68
2	98.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 1% TiO <sub>2</sub>	3.66	3.97	92.07
3	97.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 2% TiO <sub>2</sub>	3.57	3.97	89.92
4	95.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 4% TiO <sub>2</sub>	3.67	3.97	92.44
5	94.6 % Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 5% SiO <sub>2</sub>	3.44	3.87	88.89
6	89.6 % Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 10% SiO <sub>2</sub>	3.02	3.78	79.89
7	76.1% Al <sub>2</sub> O <sub>3</sub> – 21.8% ZrO <sub>2</sub> – 2.1% Y <sub>2</sub> O <sub>3</sub>	3.25	4.29	75.76
8	31.7% Al <sub>2</sub> O <sub>3</sub> – 62.2% ZrO <sub>2</sub> – 6.1% Y <sub>2</sub> O <sub>3</sub>	3.39	5.04	67.26
9	16.6% Al <sub>2</sub> O <sub>3</sub> – 76% ZrO <sub>2</sub> – 7.4% Y <sub>2</sub> O <sub>3</sub>	3.07	5.36	57.28
10	92.9% ZrO <sub>2</sub> – 7.1% Y <sub>2</sub> O <sub>3</sub>	5.16	5.78	89.27

It is seen that the highest density after sintering had a sample of the composition No.4 of 95.6% Al<sub>2</sub>O<sub>3</sub> – 0.4% MgO – 4% TiO<sub>2</sub>. This is due to the formation of a solid solution of subtraction TiO<sub>2</sub> in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, grill of which has a high diffusivity and activates the sintering process. Addition of SiO<sub>2</sub> in alumina ceramics in an amount more than 10% improves the sinterability of the ceramic. Samples of ceramic system Al<sub>2</sub>O<sub>3</sub>– ZrO<sub>2</sub> – Y<sub>2</sub>O<sub>3</sub> investigated compositions also had a low level of relative density after sintering. Table 3 and diagrams (Figure 2) show the physical and mechanical properties of sintered samples determined by nanoindentation technique.

**Table 3.** Physical and mechanical properties of sintered ceramics.

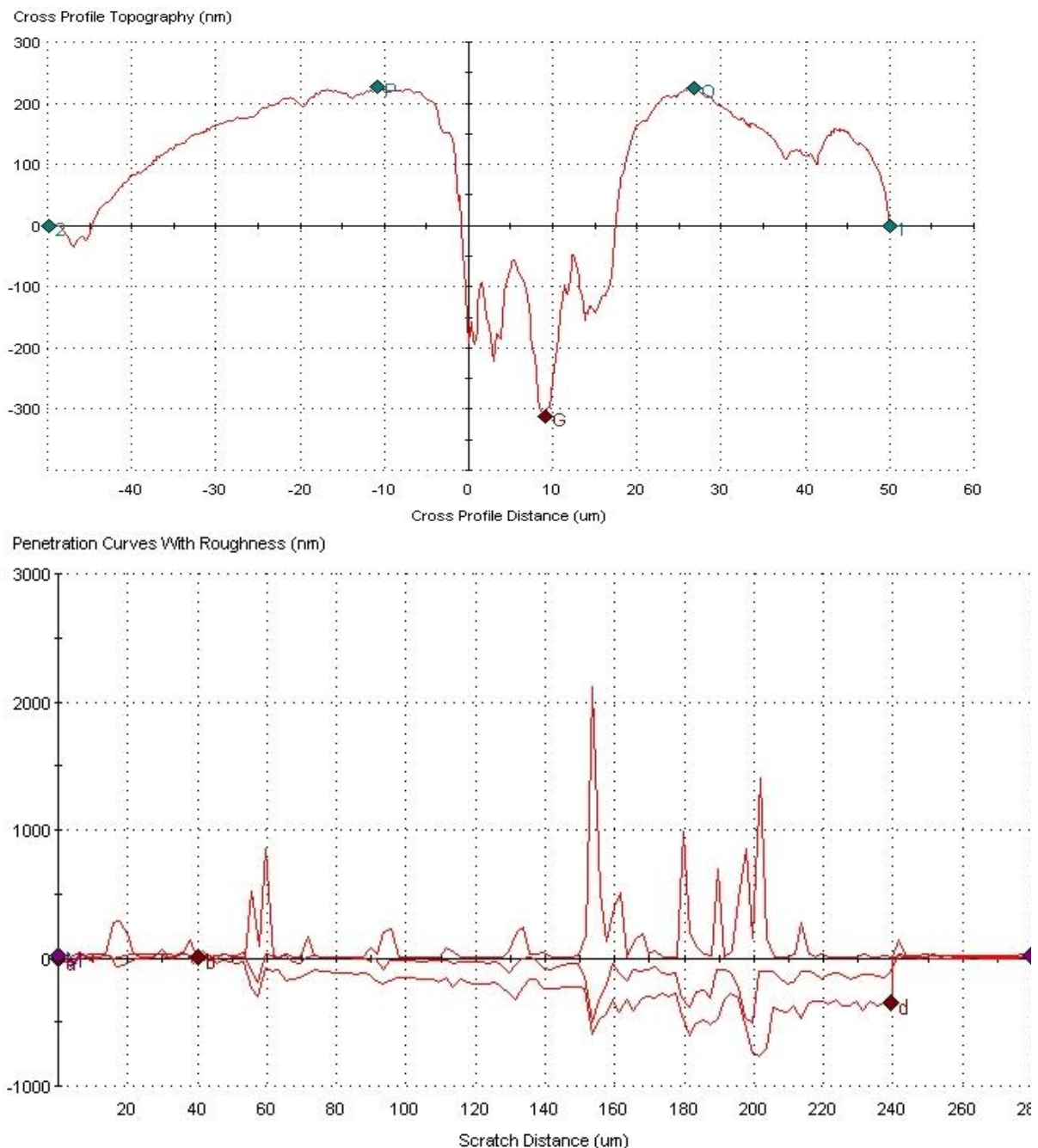
No.	Composition (wt. %)	$E_{IT}$ (GPa)	$H_{IT}$ (GPa)	$\sigma$ (MPa)
1	99.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO	422.2	19.8	18
2	98.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 1% TiO <sub>2</sub>	400.1	23.2	272
3	97.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 2% TiO <sub>2</sub>	440.4	22.6	78

4	95.6% Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 4% TiO <sub>2</sub>	178.2	99.1	38
5	94.6 % Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 5% SiO <sub>2</sub>	427.2	17.4	480
6	89.6 % Al <sub>2</sub> O <sub>3</sub> – 0.4% MgO – 10% SiO <sub>2</sub>	292.7	19.9	48
7	76.1% Al <sub>2</sub> O <sub>3</sub> – 21.8% ZrO <sub>2</sub> – 2.1% Y <sub>2</sub> O <sub>3</sub>	356.1	18.5	71
8	31.7% Al <sub>2</sub> O <sub>3</sub> – 62.2% ZrO <sub>2</sub> – 6.1% Y <sub>2</sub> O <sub>3</sub>	329.2	22.1	193
9	16.6% Al <sub>2</sub> O <sub>3</sub> – 76% ZrO <sub>2</sub> – 7.4% Y <sub>2</sub> O <sub>3</sub>	439.2	24.3	274
10	92.9% ZrO <sub>2</sub> – 7.1% Y <sub>2</sub> O <sub>3</sub>	230.2	14.9	93



**Figure 2.** a) Elasticity modulus, b) microhardness, c) strength of sintered ceramics.

It is seen that the elasticity modulus and hardness of ceramics based on the corundum generally correspond tabular (19...21 GPa), while the scatter of strength values determined by the method of scratching is significant. This is due to feature Scratch method: scratching distance of 200 microns, the depth varied between 100...800 nm, the indenter often was stopped on the softening of the grain boundaries (Figure 2). In general, it should be noted that Scratch testing technique requires a very high quality surface preparation of the samples. However, they should have minimal residual porosity.



**Figure 3.** The profile and length of the scratch on the surface of the sample No. 10.

#### 4. Conclusion

The positive effect of the addition of MgO and TiO<sub>2</sub> in an amount of no more than 1 wt. % on sintering and physico-mechanical properties of alumina is established.

Addition of 5 percent by weight of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> provides a mechanism of liquid phase sintering of ceramics, which leads to increase of its density and strength up to 480 MPa (table value of flexural strength high density alumina is not more than 400 MPa).

Introduction to the corundum powder additives TiO<sub>2</sub> submicron powder leads to the formation of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> subtraction solid during sintering, which has a high diffusivity and activates the sintering process.

From the investigated compounds ceramic system Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> highest level of physical and mechanical properties had a hypereutectic composition 16.6% Al<sub>2</sub>O<sub>3</sub> - 76% ZrO<sub>2</sub> - 7.4% Y<sub>2</sub>O<sub>3</sub>. In this composition two mechanisms of hardening are realized simultaneously, such as transformational hardening by *t-m* - ZrO<sub>2</sub> transition and dispersion strengthening with high-modulus particles of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

#### References

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