
Composite ceramics based on nanostructured refractory oxide whiskers

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Abstract: In the present work the influences of thermal-baric effect in the process of nanostructured alumina and zirconia powders consolidation on structure and physical-mechanical properties of the composite ceramics have been investigated. The samples of ceramics have been prepared from nanostructured powders (ZrO_2 -3 mol. % Y_2O_3) and Al_2O_3 in ratio from 100 : 0 to 20 : 80 wt. % in two ways: by static uniaxial pressing and by pulse pressing. Then part blanks were annealed in the temperature region 1560-1670 °C. During pulse process a crystal structure of samples was disordered, and monoclinic ZrO_2 lattice was partially deformed. After a heat treatment of a blank the crystal structure of metal oxides was restored. Ceramics of oxide powders with content 100 - 50 wt. % PSZ synthesized at the 1100 °C possessed a higher level of properties than one of active powders prepared at the 900 °C.

Keywords: Partially Stabilized Zirconia, Alumina, Nanostructured Oxide Whiskers, Structure, Properties

1. Introduction

Nanomaterials on the base of refractory compounds have been intensively investigated recently in connection with the development of nanotechnology [1] The creation of the ZrO_2 based materials with important operation characteristics is based on the alloying of zirconia by oxides of alkaline earth or rare earth metals which allows to get high temperature ZrO_2 tetragonal or cubic form at relatively low temperatures [2] The compounds on its base are used to get both: structural (blades of turbines, cutting tool) materials as well as functional ones (solid body power supply, medical products, targets for emitters) [3]. The proportion between tetragonal and monoclinic phases of zirconia, which can be changed depending not only upon the quantity of incorporated additive but also upon temperature or bar impact on the material [4], has a considerable significance in determining the properties of this ceramics. In connection with the aforesaid, to investigate consolidation processes for nanostructured powders including their moulding, solid

phase reactions at the phase boundary and structure conversions in heat processing, which determine physical and mechanical properties for the ceramics, is an important task. It should be noted that the moulding and sintering processes of ceramic composites from nanostructured refractory oxides powders are not adequately explored. The influence of synthesis temperature of nanostructured fibrous refractory oxides (ZrO_2 - Y_2O_3) - Al_2O_3 powders, their structure and properties as well as moulding and sintering processes on physical-chemical and mechanical characteristics of the obtained ceramic materials have been studied in the present paper.

2. Experiment

The initial oxide whiskers were prepared by biomimetic method when hydrated cellulose fibers have been impregnated with aqueous solution of three chloride salts of yttrium, aluminium and zirconium. The ratio of salt components were calculated in terms of metal oxides: (ZrO_2

with 3 mol. %Y₂O₃ for all samples) as a partially stabilized zirconia (PSZ) : Al₂O₃ = 100: 0, 80 : 20, 60 : 40, 50 : 50, 40 : 60 and 20 : 80 wt.%. The detail procedure of oxide fiber synthesis had been written in papers [5, 6]. Oxide fibers of the specified compositions have been obtained at 900 and 1100 °C, they were distinguished by crystal structure and physical-chemical properties. Crystal structure of aluminium oxide fibers at 900 °C corresponded to θ - or σ -phase and after annealing at 1100 °C, unstable aluminium oxide phases were passed over to α -corundum. Crystal structure of PSZ fibers corresponded to tetragonal and monoclinic ZrO₂ phases. Their ratio was varied depending upon composition of powders and synthesis conditions. To mould blanks, fibers have been ground in ball mill, and prepared oxide whiskers have been graded by fractions. Every whisker had long 0.1–0.5 mm, diameter – 1–5 μ m, and consisted of many nanoparticles with size 5–20 nm. Since high disperse powders of refractory oxides as a rule possess low plasticity and low fluidity, plasticizers are usually used. Granules have been obtained from synthesized powders with added polyvinyl alcohol solution (PVA).

Two ways to mould blanks from nanostructured yttria partially stabilized zirconia (PSZ) and aluminium oxide composition powders have been applied. The blanks from granules have been moulded by two-sided static pressing method with 500 MPa effort. Ceramics samples moulding from nanostructured powders (without PVA) has been performed also by impulse pressing method, which in accordance with paper [7], must improve the strength of blanks and provide the density uniformity of sample volume. Powders have been sprinkled into plastic containers, they have been packed into metal foil and have been subjected to impulse pressing by explosion during which pressure has been developing up to 4.0–4.5 GPa. The fixed detonation wave velocity was about 4000 m/s, and explosion impulse duration constituted 7–10•10⁻⁶ s. Then all moulded blanks have been

sintered within the temperature range 1560–1670 °C.

Crystal structure of powders and moulded blanks has been investigated with the help of X-ray apparatus Advance 8 and DRON-3, the recording of X-ray grams was carried out in the interval of angles 2 θ from 5 up to 110° with velocity 0.5–1.0 °/min, monochromatic radiation CuK α ($\lambda=1,54$ Å) has been used. The measurement of particles size was made by CSR (coherent scattering region) by physical widening of reflexes for phases under investigation: tetragonal [111] and monoclinic [$\bar{1}11$] for ZrO₂ as well as for α -alumina – [012], [113], the calculation was made by Sherrer formula [8]. The investigation of nanostructure and size of particles for fiber alumina and zirconia has been carried out earlier by atomic-force microscopy, transmission electron microscopy and CSR, the investigation has shown a good similarity of results [9]. Surface microstructure for powders and ceramics has been studied by scanning electron microscopy (LEO Zeiss 1420) in accelerating potential 20 kV. Bulk, pycnometric density for powder material, apparent density and porosity of ceramics have been measured by standard methods. The specific surface of powders has been assessed by nitrogen adsorption-desorption curve (BET method) (Brunauer – Emmett – Teller) [10] using surface and porosity analyzer (ASAP 2020, Micromeritics, USA).

3. Discussion of Results

Synthesized powders have been represented by white highly disperse substances agglomerated into micron size particles, each particle, in its turn, consisted of nanograins with the size from 5–6 up to 50 nm depending upon composition and synthesis temperature. The higher Al₂O₃ content and the lower temperature synthesis are, the lesser the size of metal oxides crystallites is, the specific surface of powder and its reactive activity are higher. Some properties of powders are represented in table 1 and microstructure in figure 1.

Table 1. Characteristics of nanostructured (ZrO₂-Y₂O₃) - Al₂O₃ powders

Chemical Composition, wt. %	Temperature synthesis, °C	Phase ratio, wt. % ZrO ₂ -T : ZrO ₂ -M	Particle size, nm		Specific surface, m ² /g
			ZrO ₂ -T	ZrO ₂ -M	
100 % PSZ	900	84 : 16	6 : 17		47
	1100	87 : 13	20 : 25		28
80 % PSZ + 20 % Al ₂ O ₃	900	73 : 27	9 : 22		60
	1100	68 : 32	18 : 33		34
60 % PSZ + 40 % Al ₂ O ₃	900	83 : 17	10 : 25		65
	1100	72 : 28	25 : 35		30
50 % PSZ + 50 % Al ₂ O ₃	900	63 : 37	6 : 15		90
	1100	75 : 25	17 : 33		45
40 % PSZ + 60 % Al ₂ O ₃	900	66 : 34	9 : 20		85
	1100	72 : 28	18 : 30		38
20 % PSZ + 80 % Al ₂ O ₃	900	76 : 24	11:25		140
	1100	72 : 28	20:35		35

The peculiarity of phase composition of powders, (as we suppose) was the formation the triple solid (ZrO₂-Y₂O₃) – Al₂O₃ solution, based on crystal lattice of ZrO₂ tetragonal phase. The triple solid solution was formed during synthesis of inorganic fibers and was existed in the temperature range 600–1100 °C. When annealing temperature was risen up to

1100–1150 °C the solid solution degraded and powder composition included the following three phases: tetragonal and monoclinic ZrO₂ and α -corund too. In connection with this phenomenon, aluminium oxide reflexes were absented on X-ray grams of powders with ratio 50–100 wt. % PSZ. Low crystal system reflexes γ - or θ -Al₂O₃ were established in

PSZ compositions with great excess for aluminium oxide 60–80 wt. % [11].

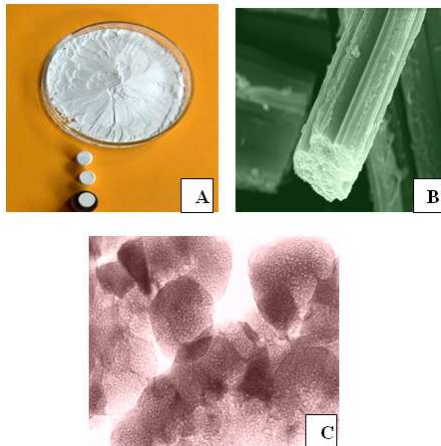


Fig. 1. Nanostructured 80% PSZ – 20% Al₂O₃ powder: overview – A, microstructure of oxide monofiber – B (SEM x10000), nanostructure of powder particle – C (TEM x100000)

During the moulding of blanks by static and impulse pressing, the particles of powders have passed through loads different by their nature. In case with static pressing, temporary bonding for better fluidity and plasticity of powders has been used since particles have experienced

friction relative each other and with the walls of die mould and punch. That is why, the ratio between height and cross section did not exceed from 3 : 1 to 5 : 1 for uniform blank density. Besides, the powders were sprinkled into die mould before pressing and they were subject to vibration for better granular laying. During loading, air and adsorbed moisture were partially removed and temporary binder fixed particles between each other. At the same time, crystal structure of powders did not change.

In case with impulse pressing, temporary binder was not used since tangential shock wave was formed in explosion during very short time period and local temperature 600–1100 °C is developing by calculation [12]. As a result, disordering for crystal monoclinic zirconia lattice occurred what is marked by inversion of its reflexes on x-ray grams, the widening for contours of all reflexes occurred too. Besides, solid (ZrO₂–Y₂O₃) PSZ solution partially degraded, monoclinic phase content increased and substance amorphization was observed. After heat treatment of blanks at 1300 °C, the crystal structure of metal oxides restored and did not change with annealing temperature increase up to 1600 °C (Fig. 2). Tetragonal zirconia phase content was increased up to 94-96%, porosity was decreased up to 0.1–0.5 % what improved strength of ceramic material.

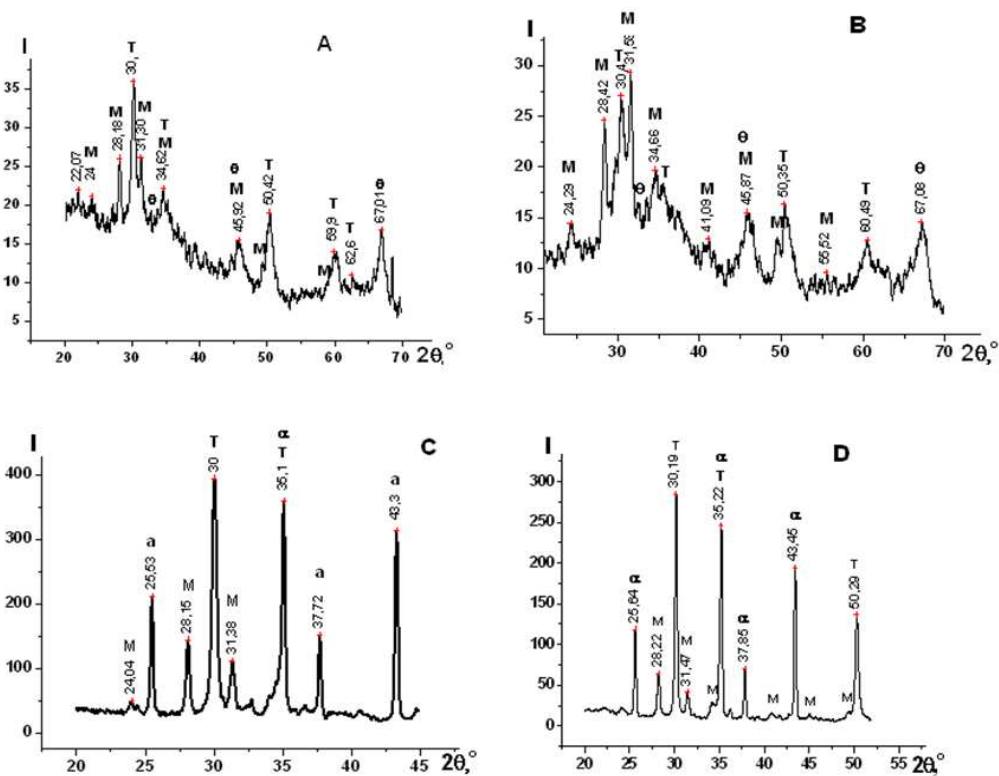


Fig. 2. X-ray grams of 20 % PSZ + 80 % Al₂O₃ powder, synthesized at the 900 °C – A, blank after pulse pressing – B, ceramics annealed at the 1300 °C – C, ceramics annealed at the 1600 °C – D; M – monoclinic phase ZrO₂, T – tetragonal phase ZrO₂, θ – Al₂O₃, a – Al₂O₃

The changes of samples microstructure after their pressing by pulse method and sintering are presented on figure 3.

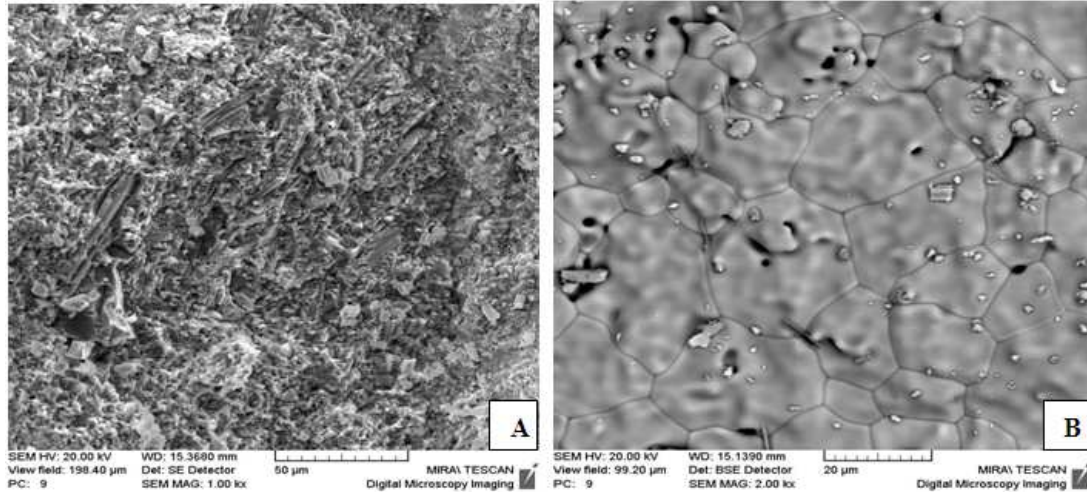


Fig. 3. Microstructure of 60% PSZ + 40% Al_2O_3 sample, formed by pulse pressing - (A), and after annealing at the 1600 °C - (B)

The study of physical - mechanical properties of sintered blanks has shown that the use of different moulding methods of blanks from nanostructured powders leads to ambiguous results. Ceramics powders moulded by static pressing from powders with synthesis temperature 900 °C are characterized by higher density and low porosity than from powders obtained at 1100 °C. Probably, this is stipulated by higher plasticity and reaction activity of powders with synthesis temperature 900 °C. The curve course – the dependence of density upon composition is regular since with the increased aluminium oxide content, the true density value decreases from 6.0 g/cm³ in PSZ up to 4.0 g/cm³ in α -corundum.

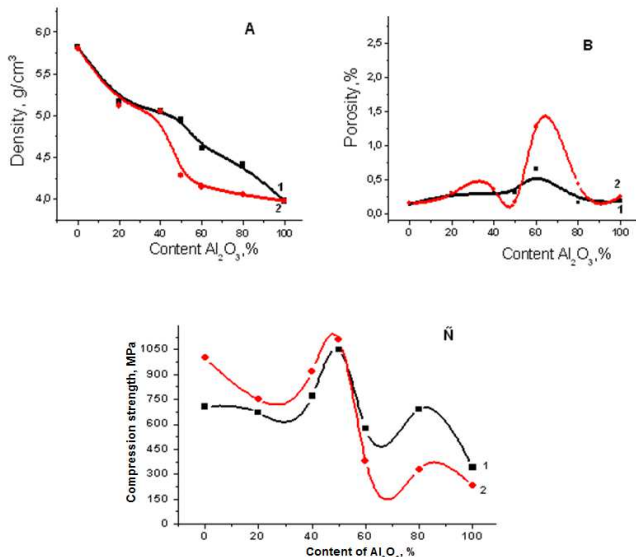


Fig. 4. Dependences of density – A, porosity – B and compression strength – C of ceramics samples, formed by static pressure from powders synthesized at the 900 °C -1, –at the 1100 °C, -2 and annealed at the temperatures: 1580+1670 °C vs. composition

The curves, showing the change in strength depending upon composition, have extreme points in the following ratio of PSZ : Al_2O_3 – 60 : 40 and 50 : 50 wt. %, what is stipulated by their crystal structure. Monoclinic zirconia content did not

exceed 5 wt. %. Besides, aluminium oxide was partially included into triple solid solution in connection with which the growth of crystallites became slower and after heat treatment at 1560–1600 °, the granular tetragonal phase ZrO_2 size constituted 30–35 nm, as for monoclinic one, it constituted 17–27 nm, they were consolidated in ceramics blocks. In general, ceramics strength in samples moulded from powders synthesized at 1100 °C is higher for compositions of PSZ : Al_2O_3 – 100: 0 up to 50 : 50 and becomes lower with the increase in aluminium oxide content in composition powders. In the latter case, the samples from powders synthesized at 900 °C had higher physical-mechanical characteristics (Fig. 4).

As for ceramic samples from nanostructured aluminium oxide powder, strength in compression was also increasing with their synthesis temperature increase from 750 up to 1500 °C.

In samples, moulded from powders with different synthesis temperature by explosion, the density values were closer, porosity was lower and compression strength was higher in samples the powders of which were synthesized at 1100 °C. The study of heat treatment mode of moulded samples has shown that single annealing at 1670 °C allows to obtain ceramics with higher strength characteristics in comparison with temperature mode: 1560+1670 °C in case powders with synthesis temperature 1100 °C are used in impulse moulding method. Maximal ceramics strength value was observed in samples with ratio: PSZ : Al_2O_3 – 50 : 50 (Fig. 5) in case with static pressing of blanks and in using explosion method.

After heat treatment of blanks at the 1670 °C the content of tetragonal component ZrO_2 was increased. The size of crystalline particles of a tetragonal phase increased to 45–50 nm, and of monoclinic phase – to 55–65 nm. Microhardness of ceramic samples PSZ made 13.9–14.2 GPa and ones of composite (80% PSZ + 20% Al_2O_3) was equal 19.0–20.5 GPa.

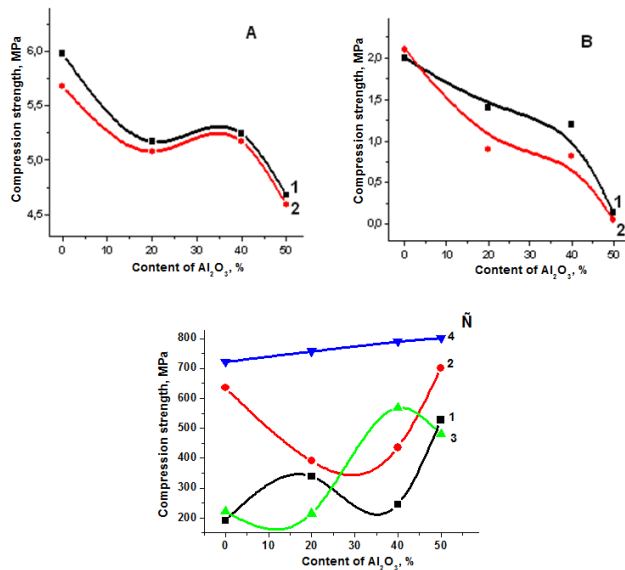


Fig. 5. Dependences of density – A, porosity – B and compression strength – C of ceramics samples, obtained by explosion method and annealed at the temperatures: 1580+1670 °C – 1, 2 and – at the 1670 °C – 3, 4, vs. composition; the samples: 1, 3 were prepared from powders synthesized at the 900 °C and 2, 4 – were prepared from powders synthesized at the 1100 °C

4. Conclusion

Porous as well as high density ceramics with high engineering characteristics can be obtained from nanostructured powders of refractory (ZrO₂-Y₂O₃) – Al₂O₃ oxides in observing definite technology conditions.

Substance amorphization, partial deformation and disordering for crystal oxides lattice occur during the moulding of blanks from nanopowders by explosion method, the crystal lattice is restored in further heat treatment. To get dense ceramics from composition powders having compositions from 100 up to 50 wt. % PSZ, it is advisable to use powders with annealing temperature higher than 1000 °C. Annealing temperature of powders, enriched with aluminium oxide, must not exceed 900 °C. In general, to get small one type parts from nanostructured powders of refractory oxides, one can use one axial static pressing method. To get large blanks, it is expedient to use impulse moulding method with further single annealing at a given temperature.

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