

Synthesis and characterization of porous ZrO_2 - Y_2O_3 - TiO_2 ceramics prepared by coprecipitation

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Abstract. Zirconium dioxide (zirconia) ceramics are known by its high strength and toughness and titanium dioxide (titania) ceramics has outstanding surface properties. The ceramic composite formed between the two oxides are expected to have advantages of both ceramics, especially when its surface area is increased by pores. In this work, ceramic composites of ZrO_2 - Y_2O_3 - TiO_2 were synthesized by coprecipitation and rice starch was added as pore former in 10, 20 and 30 wt%. Powders were cold pressed as cylindrical pellets and sintered at 1500 °C for 01 hour and ceramics were characterized by techniques as Archimedes method for density measurements, X-ray diffraction and scanning electron microscopy. Results showed that pores are inhomogeneously distributed through ceramic bodies.

Introduction

Zirconia based ceramic materials are known by their chemical and thermal shock resistance and, when appropriately doped with additives as yttrium, cerium or other rare earth oxides, show outstanding mechanical and/or electrical properties. Indeed, zirconia ceramics, stabilized in tetragonal phase, are recognized as those with higher strength and fracture toughness, among ceramics with one phase⁽¹⁾, and when stabilized in a cubic phase, has been the most employed ceramic for the preparation of solid oxide fuel cells components². As a biomaterial, zirconia is used as structural materials and in contact with living tissue, has bioinert response. This feature implies in a lack of direct bonding with bone tissue besides its excellent mechanical properties³.

By its turn, titanium dioxide (titania) has been extensively investigated for a variety of applications as photocatalysts, photovoltaic cells, treatment of environmental pollutants, electroluminescent devices, biocompatible lining in implant materials, bone treatment and others⁴. Bioceramic applications of titania are due to its ability to induce *In Vitro* formation of apatite⁵, that is consequence of the peculiar photocatalytic properties of titania, and are strongly dependent on surface/volume relation and on its crystalline structure⁶.

Titania can be found in three different crystallographic structures, rutile, anatase and brookite. Brookite transforms to rutile phase in quite low temperatures, and is not commonly studied. Rutile is the most thermodynamically stable phase and some authors suggested that the mixture of rutile/anatase phases can improve titania photocatalytic activities⁷. However, titania has poor mechanical properties and cannot be used directly as structural material.

A common alternative strategy to improve the osteointegration process, to accelerate bone regeneration on a bioinert ceramic and to reach appropriate mechanical properties, is the addition of a bioactive material as calcium phosphate, bioglass or titania on zirconia, for example. Therefore,

ceramic composite as yttria stabilized zirconia (TZP) mixed with titania has been proposed as a way to prepare ceramics that have the better qualities of both system⁸. The most common synthesis processes for these ceramics are the mechanical mixing of oxides, sol-gel methods, coprecipitation of aqueous salts, and combustion synthesis. The drawback of oxides mixing process is the difficulty to prepare chemically homogeneous powders and for the second is the cost of chemicals. The last two processes have low cost for chemicals and operations and yield chemically homogeneous ceramic powders and with small particle size. Both processes have been employed in our laboratory for synthesize ceramic and composite powders as yttria stabilized zirconia⁹, titania-zirconia⁸, zirconia-nickel oxide¹⁰, and others. Moreover ceramic surface relief, including roughness, pores and defects, has been pointed out as a significant factor to improve apatite formation over ceramic surface¹¹. Induction of apatite formation over titania-zirconia ceramic with porous structure was reported recently¹².

Our previous work¹³ demonstrated that the surfaces of samples containing both zirconia and titania - ZrO_2 - Y_2O_3 - TiO_2 ceramics (ZYT) have better cell proliferation results after cell culture in vivo experiments, compared to pure zirconia or titania, and these results are even better for ceramics with porous structure. In this work, ZYT composite ceramics containing up to 30 mol% TiO_2 were synthesized by a coprecipitation process and the effect of the addition of a pore former was evaluated. Based on previous study¹⁴, rice starch was chosen as pore former. The density and porosity of ceramic sintered bodies were determined and pore morphology was observed with scanning electron microscopy.

Experimental Procedure

The synthesis of ZYT powders has been described in our earlier paper¹⁵. Briefly, zirconium oxychloride solution, prepared from zirconium hydroxide (Ipen-Brasil), titanium chloride solution, prepared from a commercial TiO_2 (CAAL –Brasil) and yttrium chloride solution, prepared from yttrium oxide (Aldrich-USA), were mixed to obtain different amounts of TiO_2 in the ZYT composite. The suspensions were filtered, washed with water, ethanol and n-butanol. After azeotropic distillation with n-butanol, the ZYT ceramic powders were dried at 100 °C, calcined (800 °C/1h), and milled in a high energy attritor mill for 24 h using zirconia ball media in ethyl alcohol. Ceramic powders were classified with a series of sieves (60, 150, 270, e 325 Mesh/Tyler). The specific surface area was determined using the N_2 gas adsorption method. Nitrogen gas molecules were adsorbed on the surfaces of the samples and the surface area of the powder calculated by the BET (Brunauer, Emmet and Teller) method.

Sintering and thermal etching procedures were carried out at 1400°C for 01 hour and 1350 °C for 30 minutes, respectively, in a high temperature box furnace (Lindberg, USA). Density and porosity were determined by an immersion method based on Archimedes principle¹⁶. Crystalline phases of ZYT ceramics were identified from X-ray powder diffraction profiles (XRD, Rigaku DMAX 2000 diffractometer, $Cu K\alpha$) and International Centre for Diffraction Data (ICDD) files 037-1484, 081-1545 and 034-0415, corresponding to monoclinic zirconium dioxide (ZrO_2), tetragonal zirconium dioxide (ZrO_2) and zirconium titanate ($ZrTiO_4$) phases, respectively. The morphological features of the powders and ceramics were examined in two scanning electron microscopes (Philips – XL30 and Hitachi-TM 3000 Table Top microscope).

Obtained powders were mixed with 10, 20 and 30 wt% of rice starch (Lineco-USA) in a high energy attrition mill with zirconia ball media in ethyl alcohol during 04 hours. After drying and deagglomeration in an agate mortar, powders were formed in an uniaxial press as cylindrical pellets of 10 mm diameter and 10mm height. Sample codification is presented in table 01.

Table 01. Sample codifications

Titanium content (mol%)	Rice starch content (wt%)		
	10	20	30
10	ZYT10-10	ZYT20-10	ZYT30-10
20	ZYT10-20	ZYT20-20	ZYT30-20
30	ZYT10-30	ZYT20-30	ZYT30-30

Results and Discussion

Surface area of ZYT ceramic powders and densities of ceramic pellets without pore formers, sintered at 1350 °C for 01 hour, and compared to calculated theoretical densities, are presented in table 02. X-ray diffraction patterns of samples are plotted in figure 01 and peaks found agree with tetragonal zirconia. Zirconium titanate pattern are still not much visible, indicating the formation of a solid solution.

Table 02. Surface area of ZYT powders and density of ceramics sintered at 1350 °C for 1 hour.

Sample code	Surface area (m ² .g ⁻¹)	Measured density (g.cm ⁻³)	Relative density* (%)
ZYT10	87.6	4.78±0.03	80.8
ZYT20	98.6	5.37±0.62	93.6
ZYT30	95.6	5.18±0.01	93.3

* Theoretical densities of 5.92, 5.74 and 5.55 for ZYT10, 20 and 30.

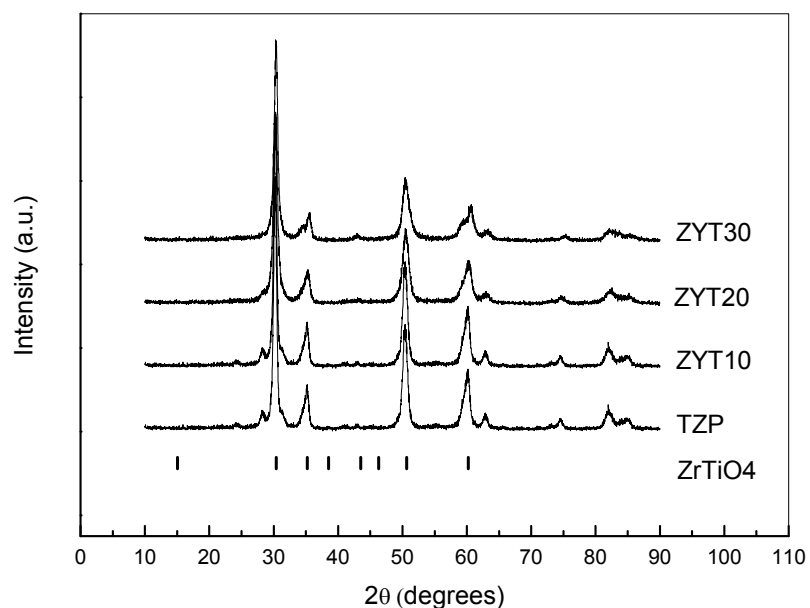


Fig. 01. X-ray diffraction patterns of ceramic samples after sintering at 1350 °C for 01 hour.

SEM micrographs of fractured surface and polished and thermally etched surfaces are shown in figure 02. Grain size of all three samples is estimated to be about 1 micrometer.

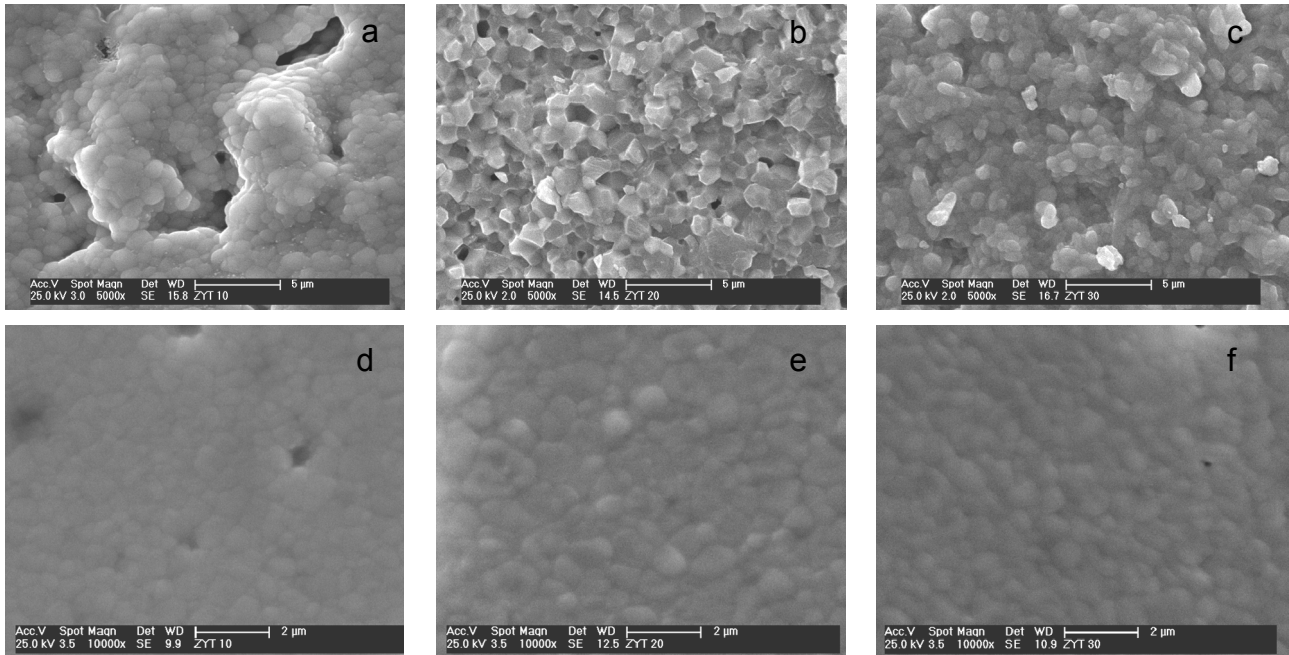


Fig. 02. SEM micrographs of fractured (a, b and c) and polished and thermally etched surface (d, e, and f) of samples ZYT10, ZYT20 and ZYT30, respectively.

Density and porosity of ceramic samples are shown in table 03. Among the series of samples, density decrease with higher titanium and pore former content and porosity increases for the same conditions.

Table 03. Density and porosity of ceramic samples with pore former after sintering at 1350 °C for 01 hour.

Sample code	Density (g.cm ⁻³)	Porosity (%)
ZYT10-10	5.52 ± 0.01	0.67 ± 0.12
ZYT10-20	5.19 ± 0.01	9.89 ± 0.21
ZYT10-30	4.77 ± 0.01	18.13 ± 0.14
ZYT20-10	5.45 ± 0.01	1,17 ± 0,17
ZYT20-20	5.12 ± 0.01	9,97 ± 0,16
ZYT20-30	4.94 ± 0.01	12,87 ± 0,17
ZYT30-10	4.83 ± 0.01	5.61 ± 0.17
ZYT30-20	4.48 ± 0.01	14.42 ± 0.07
ZYT30-30	4.12 ± 0.01	20.67 ± 0.08

From the observation of SEM micrographs of polished and thermally etched samples of series ZYT10 in low (fig. a, b and c) and high (fig. d, e, and f) magnification, shown in figure 03, it can be seen that ceramic keeps the same microstructure even after the addition of pore formers, and is composed of small grains ranging about 01 micron. According to table 03, pore volume is proportional to added rice starch but image show that pores are inhomogeneously distributed. This

can be attributed to an excessive milling, causing collapses and probably, an agglomeration of rice starch particles.

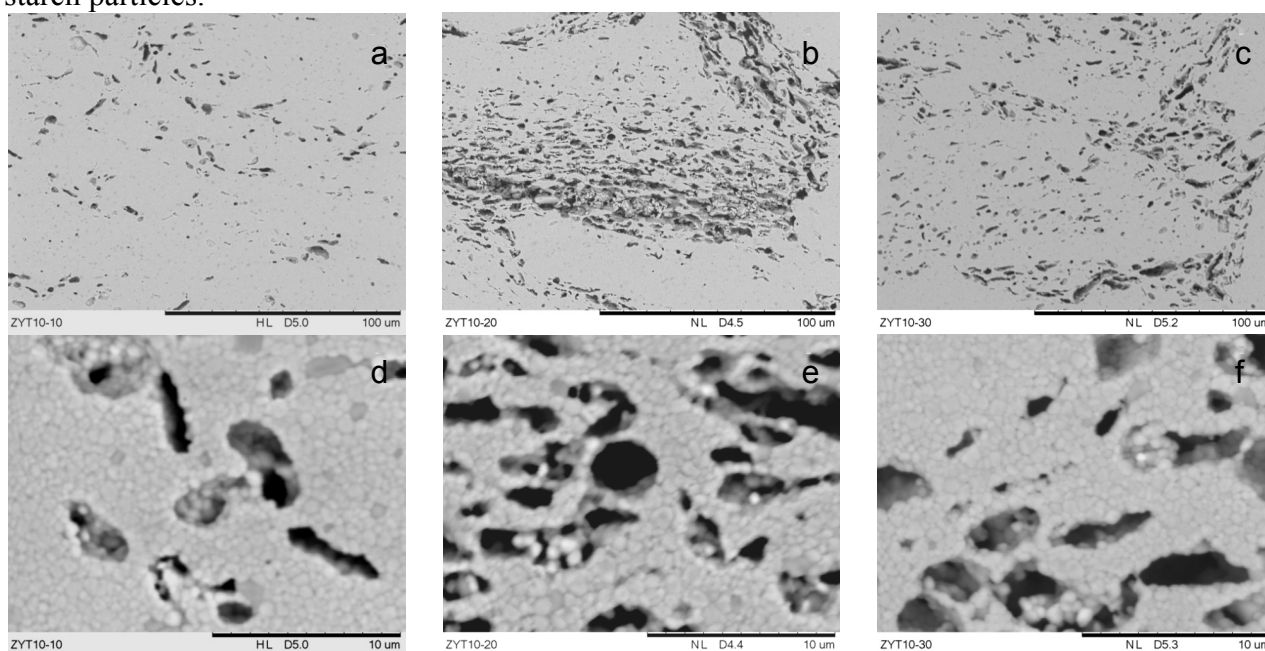


Fig. 03. SEM micrographs of polished and thermally etched surface (a, b and c) and (d, e and f) of samples ZYT10-10, ZYT10-20 and ZYT10-30 with low and high magnification, respectively.

Conclusions

ZYT powders were successfully synthesized by coprecipitation and after forming and sintering, resulted in dense ceramic bodies with fine grains. Influence of titanium content is not much visible in micrograph images and X-ray diffraction patterns, indicating a formation of solid solution. Addition of rice starch kept the ceramic characteristic, i.e, small and homogeneous grains and resulted in formation of porosity proportional to the pore former amount. Pore distribution is, however, inhomogeneous, indicating that milling time was excessive. To overcome these problems, reduction of milling time and use of pore formers with different properties are planned.

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