

## 3YTZP-Al<sub>2</sub>O<sub>3</sub> Powders Synthetized by the Coprecipitation Route

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**Abstract:** The addition of alumina in a zirconia stabilized in a tetragonal phase matrix enhances ceramic hardness and inhibits the tetragonal → monoclinic phase transformation of zirconia when exposed to an aqueous environment. These characteristics are important for applications such as bioceramics and structural materials. For these purposes, the strict control of powder synthesis and the processing conditions are vital to tailor the ceramic characteristics. This work evaluates the influence of 20 wt% alumina in a Y-TZP matrix on powder characteristics, obtained by coprecipitation route, and calcined from 600 to 1200°C for 1 and 3 hours. The powders obtained were characterized by X-ray diffraction, scanning electronic microscopy, laser diffraction and gaseous adsorption (BET). The results reveal that presence of Al<sup>3+</sup> inhibits the crystallization of composite at lower temperatures.

### Introduction

The addition of 3 mol% of yttria in a zirconia matrix produces a solid solution, which keeps the tetragonal form of zirconia at room temperature. At this condition, the TZP (tetragonal zirconia polycrystals) exhibits a very important feature, related to the polymorphic transformation to monoclinic phase when a mechanical stress is applied; this phenomenon, known as transformation toughening, can prevent a crack growth, for instance. It results in a material with high toughness and mechanical strength, however, poor hardness [1]. On the other hand, ceramic bodies made of pure alumina present high hardness but poor toughness [2]. Since zirconia and alumina are insoluble to each other, even at high temperatures [1], it is possible to tailor a ceramic composite, compromising these mechanical properties [2]. The mechanisms involved include inhibition of grain growth during sintering [3, 4] and formation of microcracks [1]. Besides that, in this case, the tetragonal → monoclinic phase transformation is increased when a stress is applied [5].

In addition, the excellent biocompatibility of alumina and TZP ceramics make these materials suitable to biomedical purposes [6, 7], besides its use as structural materials.

To maximize the beneficial effects of the second-phase, the grains must be small-sized and homogeneously dispersed on a well densified matrix. However, this composite is technically difficult to densify as the presence of a second-phase inhibits the crystallization [4, 8]. Hence, it is usually necessary to go through expensive sintering techniques such as hot-pressing [9] and hot-isostatic pressing [10]. As an alternative, chemical methods can be used to obtain powders with higher reactivity than commercial ones, what means better sintering without need of pressure. Some examples of these nonconventional powder preparation techniques are: solvent vaporization, electrochemical reduction [11], solvent combustion [12], coprecipitation [4, 8, 13] and sol-gel [14]. The coprecipitation route consists in preparing an aqueous solution with the metal ions (ex: Al(NO<sub>3</sub>)<sub>3</sub>, ZrOCl<sub>2</sub>) with the desirable composition, and slowly mixing (causing precipitation) with an aqueous base (ex: NH<sub>4</sub>OH). The resulting

gel is filtered and washed with organic solvents then distilled in order to avoid the formation of agglomerates [15].

Due to the possibilities and low cost of this method, the main motivation of the present work was to optimize the synthesis conditions to produce pure, homogeneous and highly reactive powders containing 20 wt% alumina in a 3Y-TZP matrix, via coprecipitation route.

### Experimental Procedure

The powders containing 20 wt% alumina in a 3 mol% yttria-stabilized zirconia matrix were prepared from the following solutions: (a) zirconium oxychloride, obtained by the dissolution of zirconium hydroxide (99.5 wt% purity), from IPEN- Brazil; (b) yttrium chloride, prepared from the dissolution of the oxide (99.9 wt% purity), from Aldrich, EUA; (c) aluminum chloride hexahydrate, (99.9 wt% purity) from Synth, Brazil. Ammonium hydroxide, ethanol and n-butanol were analytical grade.

In order to determine the volume of ammonium hydroxide necessary for maximum efficiency, a titration test was performed, for the three chloride solutions, with  $\text{NH}_4\text{OH}$  3M. For this purpose a digital pH-meter (Micronal, B-474) was employed. From these results, the coprecipitation experiments were set up for production of 35g of mixed oxides.

The coprecipitation of hydroxides was performed with slow addition of mixed chlorides to the base, under vigorous stirring, in order to promote a fast precipitation. The pH of mother liquor was maintained higher than 10. Subsequently, the suspension was maintained under stirring for 15 minutes, to ensure a good homogeneity.

The precipitate was washed with water several times until the filtrate indicated the absence of  $\text{Cl}^-$ , and treated with ethanol (to remove the bulk of water) and n-butanol, followed by azeotropic distillation, ensuring a dehydrated precipitate. As a final point, the precipitate was dried at  $80^\circ\text{C}$  for 24h, disaggregated in agate mortar, calcined and milled with zirconia balls for 16h in ethanol.

The nomenclature adopted for calcined samples are shown in Table 1:

Table 1: Nomenclature of 20 wt% alumina/Y-TZP samples.

Sample Code	Calcination conditions	
	Temperature ( $^\circ\text{C}$ )	Holding Time (h)
6/1	600	1
6/3	600	3
8/1	800	1
8/3	800	3
10/1	1000	1
10/3	1000	3
12/1	1200	1
12/3	1200	3

The powders were characterized by X-ray diffraction (Rigaku Multiflex), using 40kV and 20mA of  $\text{Cu-K}\alpha$  radiation, varying  $2\theta$  between  $15^\circ$  and  $110^\circ$  degrees. The determination of specific surface area was carried out using the BET technique (Micromeritics ASAP 2000). The granulometric distribution curves of the powders were measured by laser diffraction

(Beckman-Coulter LS 13320 with tornado DPS module). Particle and agglomerate morphology were observed by scanning electronic microscopy (Phillips XL30).

## Results and discussion

Fig. 1 shows the morphological aspect of the agglomerates of the 20 wt % alumina/Y-TZP powders. It is possible to observe that the powders have sub-micron size. No significant differences from the samples calcined below 1200°C could be noticed. At this temperature, the powder starts to coalesce, evidenced by smoother surfaces of the agglomerates.

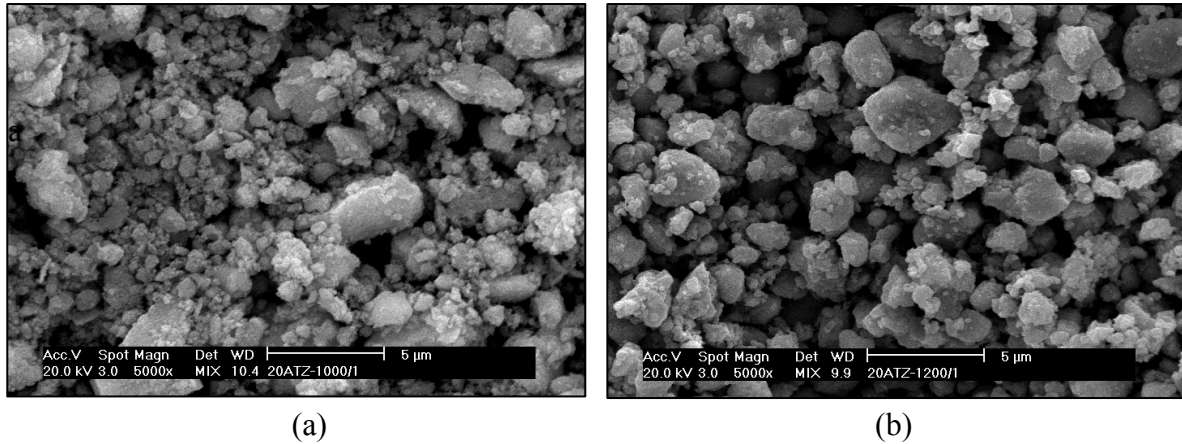


Fig.1: SEM micrographs of powders of 20 wt %  $\text{Al}_2\text{O}_3/\text{Y-TZP}$  calcinated at 1000°C (a) and 1200°C (b), for 1 hour.

The granulometric distributions (Fig. 2) were determined to measure the size of agglomerates. Increasing the calcination temperature, those have a slightly size reduction till 1000°C, probably due to the lowering of electrostatic attractive forces between particles. After this point, the particles start to coalesce, and form bigger agglomerates. The calcination time had a negligible effect on the size of agglomerates.

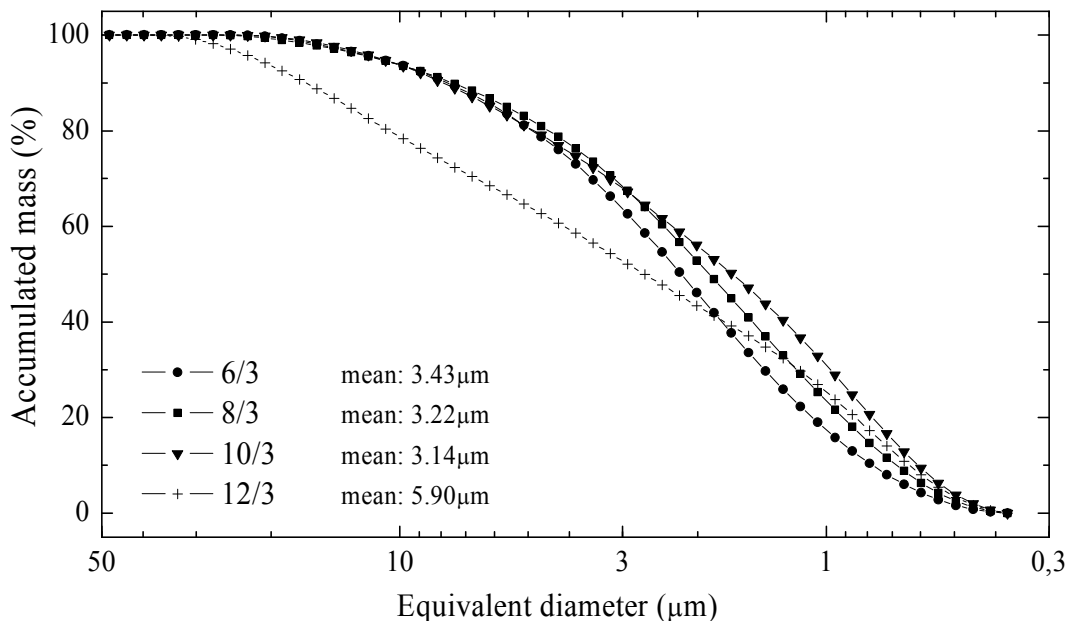


Fig.2: Cumulative size distribution curves of 20 wt %  $\text{Al}_2\text{O}_3/\text{Y-TZP}$  powders calcined from 600°C to 1200°C for 3 hours.

The specific surface area results (Fig. 3) revealed an exponential decrease as the temperature is raised, mainly for the powder calcined at 1200°C. At this temperature, the driving forces of sintering start to take place, accomplished of coarsening and sintering of particles. As it is observed in Fig. 3, the variation from 1 to 3 hours in calcination time does not affect significantly the surface area of the powders.

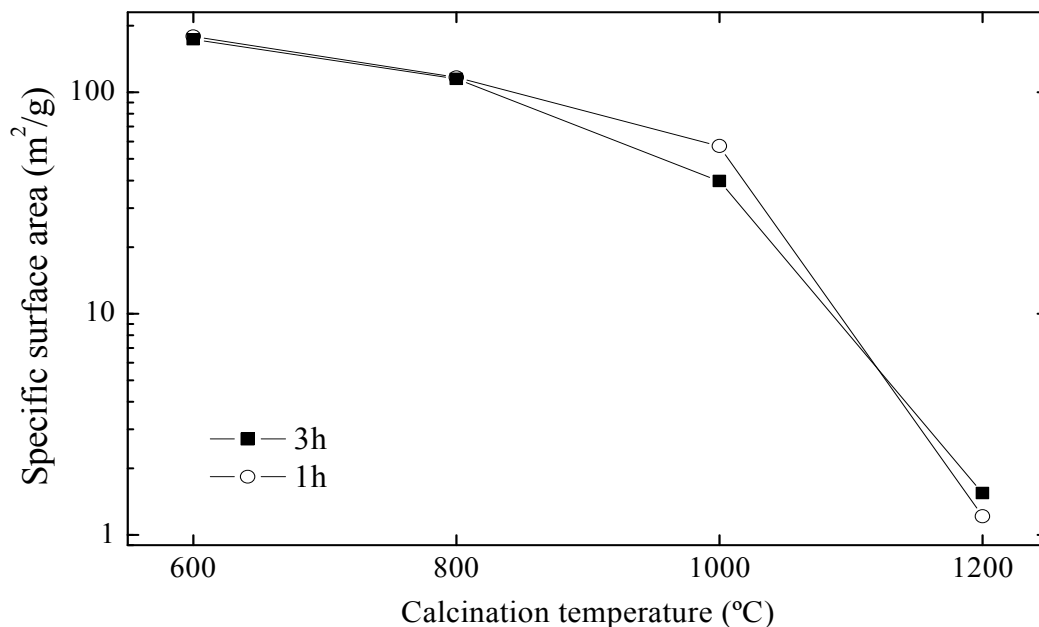


Fig.3: Specific surface area of 20 wt % Al<sub>2</sub>O<sub>3</sub>/Y-TZP powders, calcined in several conditions.

The formation of crystalline structures was inhibited mutually by the presence of a second phase. The diffraction patterns of the samples show that this composite has low crystallinity when calcined at temperatures below 1200°C (Fig. 4). Otherwise, pure TZP, obtained by the same route, usually reveals good crystallinity when calcined above 600°C [4, 16]. Similarly, pure alumina crystallizes at 400-500°C as  $\gamma$ -alumina, shifting to  $\theta$  polymorph at 900°C. At 1100°C  $\alpha$ -alumina starts to take place. [8]. For the composite studied, alumina seemed amorphous for the samples calcined below 1200°C, and at this temperature was detected the formation of  $\theta$  (theta) and  $\alpha$  (alpha) phases, with raise of concentration of  $\alpha$ -alumina when calcined at 1200°C for 3 hours.

Fig. 5 illustrates the X-ray diffraction pattern of the sample 12/3, and diffraction data from ICDD files from reference materials. It is interesting to observe that, although zirconia does not form a solid solution with alumina [1], it seems that, due to the employed synthesis route, alumina causes a deformation of zirconia lattice leading to the formation of a metastable phase. This behavior is evidenced by the dislocation of diffraction peaks, specially the ones with  $2\theta$  higher than 50°. The occurrence of monoclinic reflections of zirconia can be considered usual for TZP powders. It results from un-stabilized zirconia, and tends to disappear on sintering [16].

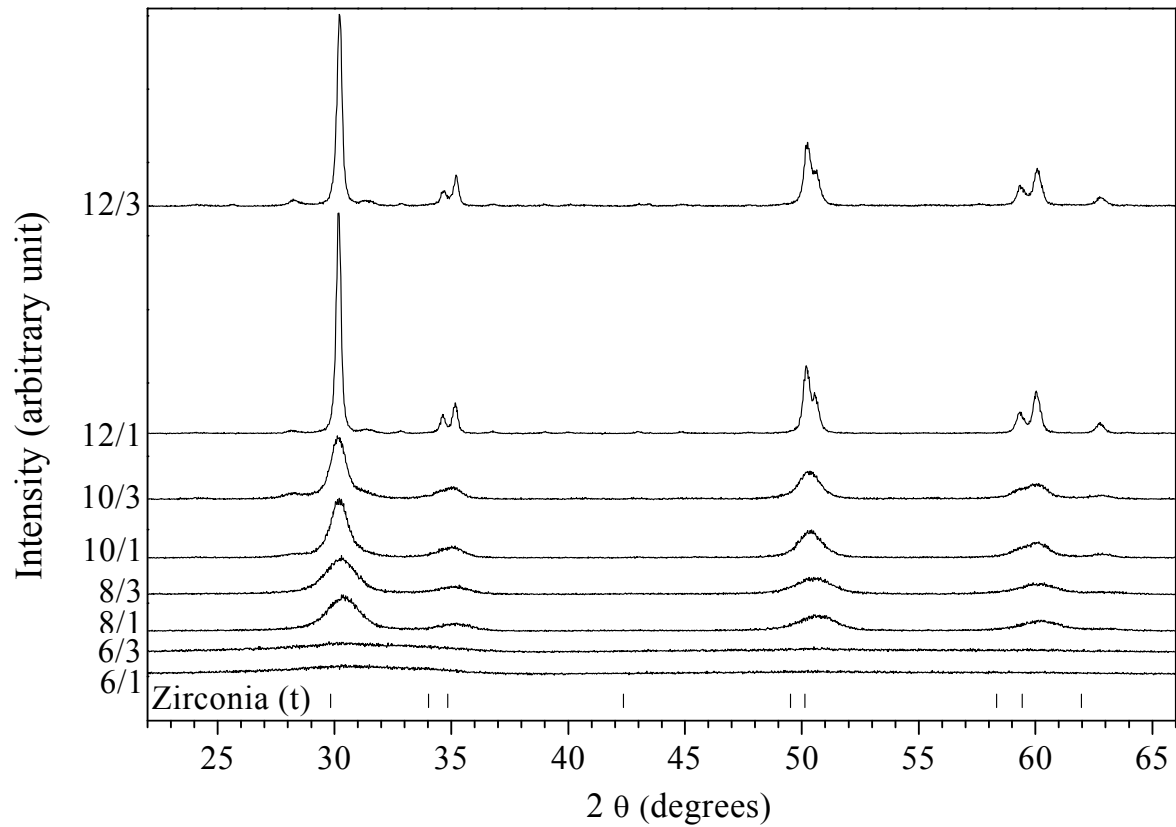


Fig.4: Diffraction patterns revealing the crystalline evolution of 20 wt%  $\text{Al}_2\text{O}_3/\text{Y-TZP}$  powders, calcined under several conditions.

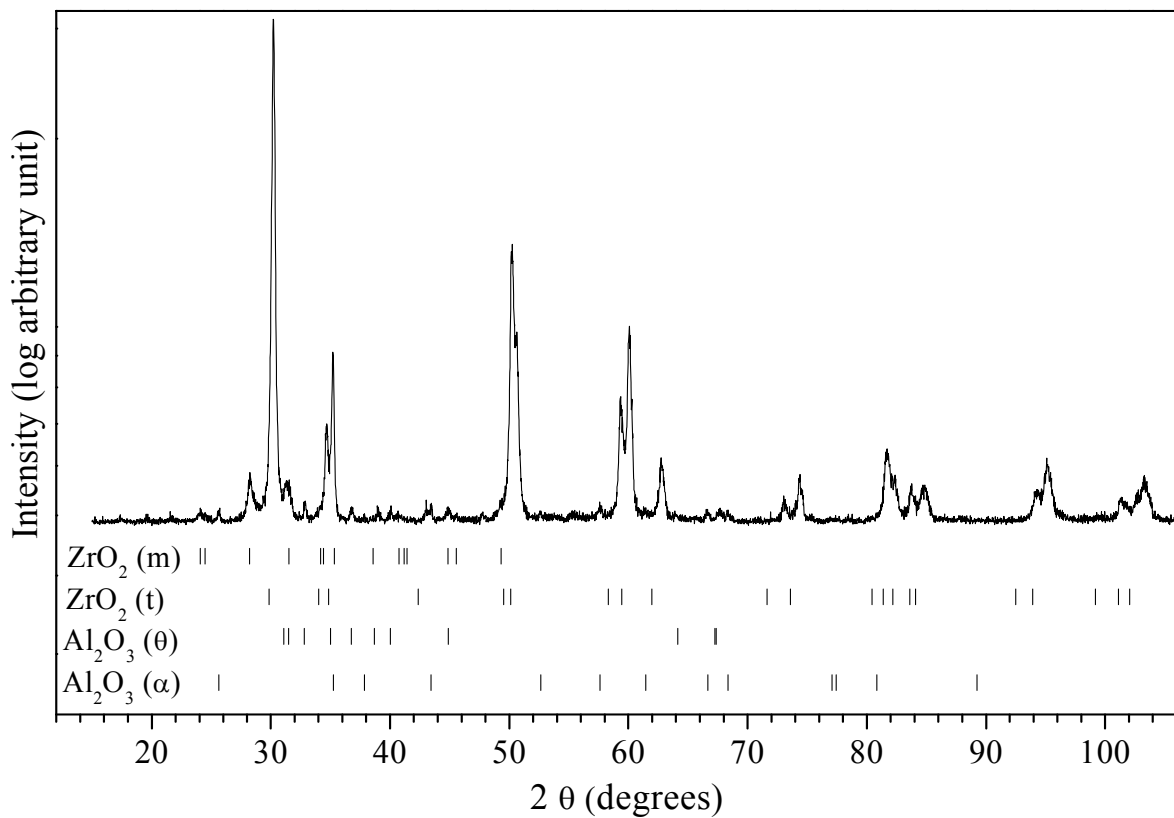


Fig.5: Diffraction pattern of 20 wt %  $\text{Al}_2\text{O}_3/\text{Y-TZP}$  powders, calcined at  $1200^\circ\text{C}$  for 3 hours

## Conclusion

20 wt % alumina/ Y-TZP powders, obtained by coprecipitation route, have high specific surface area and low agglomeration state, consequently good reactivity. The employed calcination time, 1 to 3 hours, did not promote significant changes on powders characteristics, except for the sample calcined at 1200°C. Even with such high calcination temperature, all the powders remained with submicron-sized particles. The TZP matrix exhibited low crystallinity when calcined at temperatures below 1000°C. In samples calcined at 1200°C,  $\theta$ -alumina metastable polymorphic form and  $\alpha$ -alumina were detected. No crystalline phases of alumina were observed in samples calcined below this temperature. Considering that the mechanical properties of sintered ceramics are strongly dependent on physical characteristics of starting powders, these results show a very promising possibility of cost reduction on producing high quality materials.

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