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DEVELOPMENT OF ZrO_2-Al_2O_3 BIOCERAMIC COMPOSITES

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ABSTRACT

Metallic abutments, used in dental implant prostheses, have shown good mechanical properties, but the metal core affects the aesthetics. To minimize this problem, ceramic abutments can be used. Dental ceramics prosthesis has been introduced with the objective of improving aesthetic restorations, biocompatibility and chemical resistance. In this work, the effects of alumina additions on the properties and citotoxicity of the ZrO_2-Al_2O_3 composites were investigated. Samples of ZrO_2 with varied Al_2O_3 additions were prepared. Powder mixtures were sintered at 1500 and 1600^{0}C in air, for 120 min. Sintered samples were characterized by XRD and SEM. Hardness and K_{IC} were obtained by Vickers indentation method, and in vitro cytotoxicity test was performed as preliminary biological evaluation. In all sintering conditions, samples presented densification higher that 99%TD. Al_2O_3 addition produces an increase of the hardness, reaching values between 1350 and 1600 HV for the addition of 0 and 30% of alumina, respectively. Fracture toughness was near to 8 MPam$^{1/2}$ in all conditions. Since a nontoxic behavior was observed in the cytotoxicity test, this finding suggests that ZrO_2-Al_2O_3 ceramics have potential to be used as a biomaterial for clinical applications.

Keywords: bioceramic, ZrO_2-Al_2O_3 composite, sintering mechanical properties

INTRODUCTION

The most widely used ceramic materials for bioapplications are alumina, Al_2O_3, and zirconia, ZrO_2, because of their excellent biocompatibility. The main advantages of Al_2O_3 is its high hardness and wear resistance, while ZrO_2 exhibits higher strength and fracture toughness, besides its lower Young's Modulus[(1-7)]. Besides mechanical

properties, it become really aesthetically interesting when polished for dental applications.

It is common knowledge that ZrO_2 additions may increase the fracture toughness of ceramic materials. This effect is based on the tetragonal to monoclinic phase transformation of ZrO_2, accompanied with an increase of the specific volume in the order of 3-6%[3]. This volume increase generates stresses in the ceramic matrix, which difficult crack propagation.

Two composite materials are prepared based on the ZrO_2-Al_2O_3 system: ZrO_2 reinforced with alumina particles, ATZ, or alumina reinforced with zirconia particles, ZTA. In both cases, the fracture toughness of the ceramic matrix material as increased[8,9].

This work investigates the influence of sintering temperature and Al_2O_3 content on the physical, mechanical and biological properties of ZrO_2-Al_2O_3 composites, with the aim to develop ceramic components for dental implants.

EXPERIMENTAL PROCEDURE

Tetragonal ZrO_2 powder stabilized with 3% mol of Y_2O_3 (TZ-3YSB, Tosoh Inc. Japan) and Al_2O_3 (SG-1000-Almatis, Alcoa group) were used as starting powders. Different compositions had been prepared with oxide mixture varying the Al_2O_3 addition in ZrO_2 matrix of 0, 10, 20 and 30 wt% in the mixtures. The powder mixtures were prepared by attrition milling for 4 hours using isopropilic alcohol as media and sintered ZrO_2 balls with diameter of 2mm. After milling, the powder mixtures were dried in a heater at 90°C for 24 hours and then, deagglomerated and cold uniaxial pressed under 80 MPa pressure.

Samples of 15mm of diameter were compacted and sintered at 1500°C, and 1600°C. Heating rates varied according to the temperature which were 10°C/min up to 1100°C; 5°C/min up to 1400°C; and 3°C/min until the final temperature. Cooling rate was 5°C/min down to 1400°C; and 3°C/min down to 1100°C, automatically done by the oven. Sintering time kept constant at 120 minutes for all temperatures. The density calculation of sintered samples was made by immersion method, using Archimede's principle.

The sintered samples phases were identified by X-ray diffraction using Cu-Kα radiation in the 2θ ranging on 20° and 80°, with a step width of 0.05° and 2 s of exposure time per position.

Sintered samples were analyzed by the microstructure, through scanning electronic microscopy (SEM), aiming to determine grain size average of ZrO_2 and Al_2O_3 according to sample's composition and sintering temperature. The samples were polished and thermal etched at 1300°C for 15 minutes, in order to reveal the grain boundaries and then, were analyzed with an image analyzer.

The mechanical properties, hardness and fracture toughness, were determinated by Vickers's indentation. For statistical reasons 21 identations per sample were used, under a load of 20 N for 30s. The fracture toughness had been calculated by the equation proposed by Evans[10] for Palmqvist's cracks type.

The biocompatibility of the composites was evaluated by in vitro tests of the cytotoxicity CPCp, according to ISO 10993- part 5, by the neutral red uptake methodology [11]. More details about these cytotoxic tests are obtained in previous works[12].

RESULTS AND DISCUSSION

Fig. 1 presents the results of relative density as function of the sintering temperature and Al_2O_3 contents.

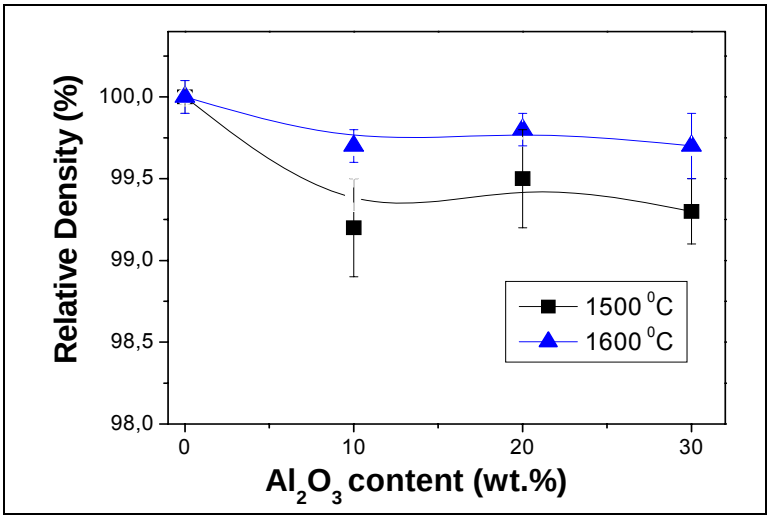

Figure 1. Influence of the Al_2O_3 content and temperature on the relative density of the samples.

A little densification increasing had been observed, according to the increase of sintering temperature, all over the situations. Temperatures higher than 1500°C had shown relative density higher than 99%, which favor the mechanical properties raise the reliability and result in products with increased properties in structural applications.

It had been noticed that the composites presented reduced and close porosity levels, independently the Al_2O_3 contents. In this way, the contents of Al_2O_3 had not influenced the densification levels. This is justifiable because the closed powder mixtures had shown close particle sizes. Besides it, the results of green relative density had not varied by the Al_2O_3 addition, with an average green density around of 50%.

Fig. 2 presents X-ray diffractogram patterns of different samples sintered at 1600°C. Similar diffractogram patterns were obtained for composites sintered at 1500^0C.

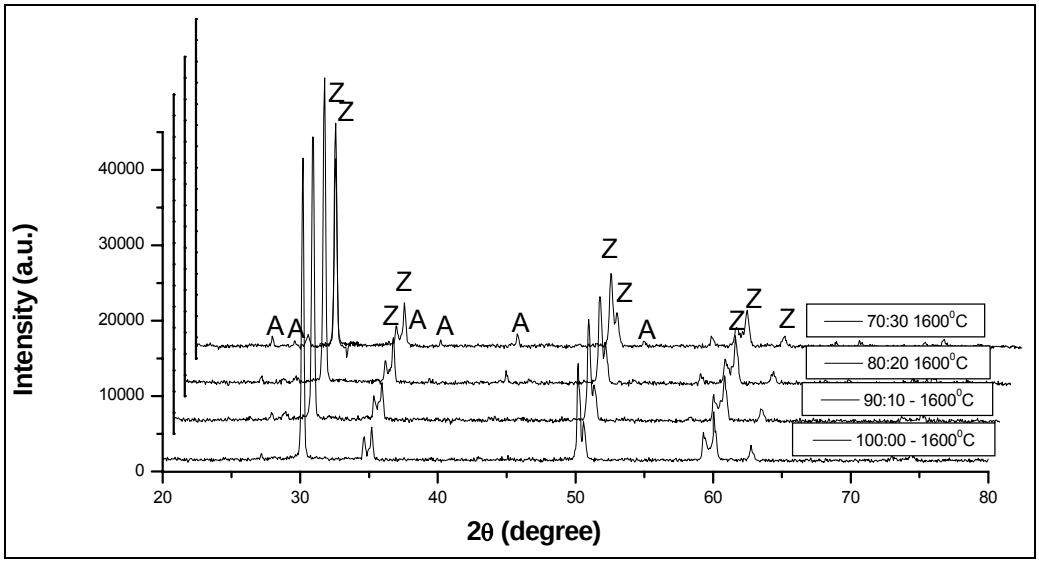

Figure 2. X-Ray diffractogram patterns of the ZrO_2-Al_2O_3 composites, sintered at 1600^0C.

It is observed in different composites, only the tetragonal ZrO_2 phase, showing that the percentage of monoclinic ZrO_2 in the starting powder had been totally transformed. It also can be seen in ZrO_2-Al_2O_3 composites, the absence of monoclinic ZrO_2, which indicate a total stabilizing of tetragonal phase, during cooling. This shows that Al_2O_3 had not influenced phase's transformation rates during the sintering process. There is also an increase of the Al_2O_3 peak intensity as function of Al_2O_3 increasing on the ZrO_2 matrix.

It is known[3] that the application of compressive stresses under a tetragonal ZrO_2 surface during sanding and polishing can be to start the tetragonal-monoclinic, T-M transformation. X-ray difraction of the polished surfaces were performed. In the results, it is not noticed the monoclinic ZrO_2 presence, characterized by diffraction peaks at 2θ =28° and 2θ=31°. In this way, can be deduced that the T-M

transformation's content is nule or lower than 2% vol, limit of deteccion of difrractometer.

Fig. 3 presents micrographs of the ZrO_2-Al_2O_3 composites sintered at 1600°C, for different Al_2O_3 contents. Furthermore, Table I present the summarized microstructural parameters related to the ZrO_2-Al_2O_3 composites. These results are graphically showed in Fig. 4.

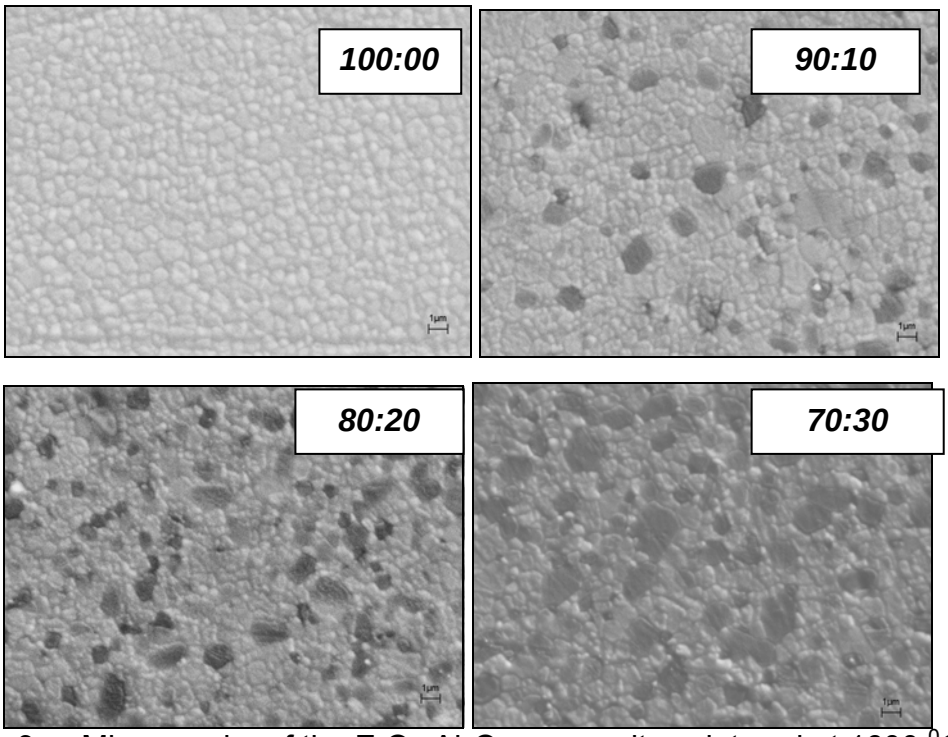

Figure 3 - Micrographs of the ZrO_2-Al_2O_3 composites sintered at 1600 ^{0}C, for different Al_2O_3 contents. (Magnification – 8000x)

Table I: Microstructural parameters of the ZrO_2-Al_2O_3 composites, sintered at 1600^{0}C.

Composition ZrO_2-Al_2O_3	**Grains density (Grains/ μm^2)**		**Grain Size Average (μm)**
70-30	Al_2O_3	0.18	1.67
	ZrO_2	1.07	0.65
80-20	Al_2O_3	0.15	1.29
	ZrO_2	1.51	0.53
90-10	Al_2O_3	0.13	0.77
	ZrO_2	2.02	0.50
100-00	ZrO_2	2.08	0.48

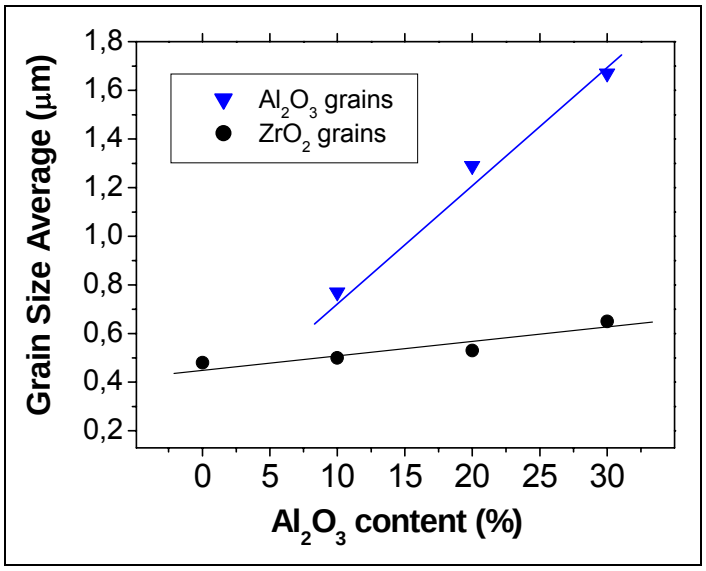

Figure 4. Grain size average as function of Al_2O_3 contents.

It can be seen the presence of the two distinct phases, ZrO_2 and Al_2O_3. It can be observed a coherent increasing of Al_2O_3 grains as a dark phase on the global microstructure, as function of the Al_2O_3 addition. The increasing of Al_2O_3 on the composition of ZrO_2-Al_2O_3 composites leads to the grain size increasing in both phases, ZrO_2 and Al_2O_3. In the Fig. 4, the different inclination of the lines of grain size average of ZrO_2 and Al_2O_3 phases indicates different grain growth rate as function of the Al_2O_3 additions. It can be observed that the grain growth rate of the Al_2O_3 phase is higher than ZrO_2 phase.

Table II presents results of Vickers hardness and fracture toughness, K_{IC}, of samples at different sintering temperatures.

Table II: Hardness and fracture toughness of the sintered sample.

% Al_2O_3	1500 ^{0}C		1600 ^{0}C	
	Hardness (HV)	Fracture Toughness (K_{IC})	Hardness (HV)	Fracture Toughness (K_{IC})
0	1340 ± 16	8.05 ± 0.24	1353 ± 10	8.15 ± 0.26
10	1401 ± 6	7.97 ± 0.37	1408 ± 5	8.21 ± 0.21
20	1509 ± 9	7.82 ± 0.33	1520 ± 7	8.02 ± 0.26
30	1585 ± 12	7.87 ± 0.22	1610 ± 5	7.98 ± 0.14

It can be observed at Fig. 1 that, in all the temperatures had been reached a relative density higher than 99%, so the sintering temperature had not influenced the increasing of hardness of the composite. It also had been noticed through Table 2

that Al_2O_3 addition causes an increasing on the hardness, reaching values between 1350 and 1600 HV for a addition of 0 and 30% of Al_2O_3 respectively, which means 20% of hardness increasing with 30% of Al_2O_3 addition. The results of standard deviation indicate homogeneity of hardness values, inside the sample.

It can be noticed that Al_2O_3 content in ZrO_2 matrix had not affected the composite's fracture toughness. In this case, the martensitic transformation of ZrO_2 phase can be contributing for the high fracture toughness. Furthermore, the Al_2O_3 phase, which presents thermal expansion coefficient different from ZrO_2, generates a stress field around the grains during cooling, which blocks the crack propagation in ZrO_2 matrix. The results presented are really promissing with fracture toughness varying between 7.8 and 8.2 $MPam^{1/2}$. Low values of standard deviation gives to material a better reliability.

The evaluation of the biological compatibility of the ZrO_2-Al_2O_3 composite was done by the incorporation of the "Neutral Red", in the citoplasmatic and lisossomatic membranes of the cells, which were contact with the ceramic material.

Plotting the average percentage of survival of the cells in function of the concentration of the extract, a curve is obtained which shows the cytotoxicity index ($CI_{50\%}$). It is know, that the negative control simulates an environment where the cell has total capacity of development and to born colonies, while the positive control simulates an environment totally adverse to its development.

Fig. 5 shows the results obtained for the sintered samples at 1600^0C and the controls used. Similar behavior was observed for samples sintered at 1500°C.

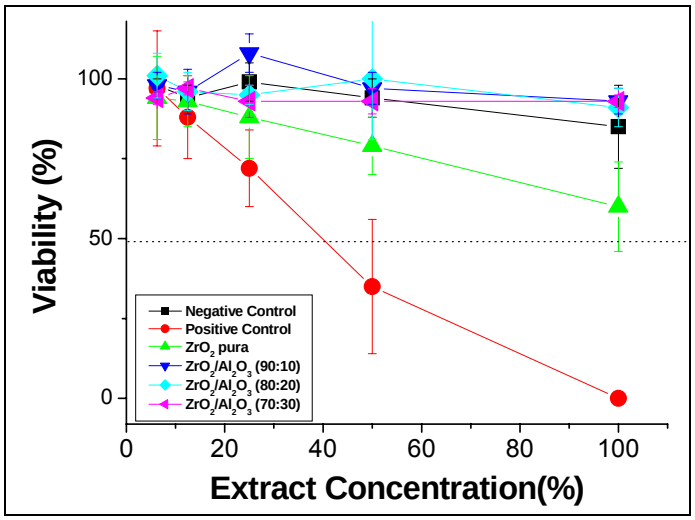

Figure 5. Viability curves of sintered ZrO_2- Al_2O_3 composite ceramics sintered at 1600°C in the cytotoxicity test by neutral red uptake assay.

This analysis showed promising results because the viability over 80% corresponds to an excellent biocompatibility of the material, and the samples presented viability around 80%. In this way, is possible to affirm that ZrO_2-Al_2O_3 ceramic composites developed at this study do not cause death or damage to the cells population, and can be classified as non-cytotoxic, thus having great potential for possible applications in implants. Besides, through this test, is guaranteed that had not contamination at significant quantity during processing, which does not compromisse the experiment.

CONCLUSIONS

Based on the present results, it could be observed that the addition of different Al_2O_3 contents, leads to a considerable hardness increasing of ceramic composites. At the studied temperatures, the addition of Al_2O_3 in ZrO_2 does not influence the densification of ceramic samples. All over the cases, samples with relative density over 99% were obtained. The values of fracture toughness were about 8 $MPam^{1/2}$ at all the conditions. As the cytotoxicity tests indicated that these composites studied are non-cytotoxic, ZrO_2-Al_2O_3 composites presented promising properties for use as components for implant systems.

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