INVESTIGATION OF MECHANICAL PROPERTIES OF AL_2O_3-20 WT % ZRO_2 COMPOSITES AS A FUNCTION OF SINTERING TEMPERATURE

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Abstract

High purity nanocrystalline α-alumina powder was mixed with 20 wt% ZrO_2 by slurry method sintered at temperature (T_s) 1450°C, 1500°C, 1550°C and 1600°C for 2 hour. The density, porosity, structural properties and mechanical properties of Al_2O_3-ZrO_2 composites with respect to sintering temperature have been explored in the present work. The XRD spectra indicate that α-Al_2O_3, t and m-ZrO_2 are the crystalline phases present in 20 wt% ZTA composites for all sintering temperature. It is observed that with higher sintering temperature the intensity of m-ZrO_2 phases increases and the t-ZrO_2 phases decreases. However, t-ZrO_2 retention becomes much easier to trigger the transformation to monoclinic. Higher density of 20 wt% ZTA has been achieved at 1600ºC, whereas the highest porosity was obtained for sintering temperature 1450°C.The microstructures of the samples was studied by using SEM which represents highly homogeneous and finer structure at 1600ºC. The effect of sintering temperature on hardness, elastic modulus and flexural strength were investigated and has been found to increase with the increase of sintering temperature. Maximum hardness, elastic modulus and flexural strength were achieved for the Al_2O_3–20 wt% ZrO_2 composites sintered at 1600°C.

Keywords: XRD; SEM; Vickers microhardness; Flexural strength.

Introduction

A great progress in dental restorations technique has been established by the use of composite materials since the 70's. In some field application, the tendency is the elimination of the metallic substructure, including implant restorations. These composites show relative advantages, like esthetic, biocompatibility and chemical resistance. One problematic aspect of composite materials in particular is their low mechanical resistance and fracture toughness [Munro, 1997]. The metallic abutments used in prosthetic restorations with implants materials compromise the esthetic in some cases [Sadoun et. al., 1997]. To minimize this problem, some implant systems developed composite abutments. The use of alumina and zirconia with high density like biomaterial has been proposed. Alumina has shown excellent biocompatibility and wear resistance however exhibits low flexural strength and toughness [De Aza et. al., 2002]. The pure zirconia cannot be used in the manufacture of parts without the addition of stabilizers [Hannink, 2000]. The yttria-stabilized zirconia polycrystal has become a popular alternative to alumina as biomaterial and is used in dental applications such as endodontic posts [Fischer et. al., 2002], orthodontic brackets [Keith et. al., 1994], crowns and bridges [Cando, 2001 and Ardlin, 2002] and in composite abutments [Prestipino et. al., 1996], beside the extensive experience of using the composite in orthopedic implants [Christel et. al., 1989 and Serra et. al., 2002]. Zirconia presents good esthetic aspects after polishing, is inert in physiological environment, presents greater flexural resistance and toughness and lower Young's modulus when compared with pure alumina [Piconi et. al., 1999]. The ability of Zirconia Toughened Alumina (ZTA) to transform from tetragonal crystalline structure to a more voluminous monoclinic structure and thus obstruct crack propagation, gives the material its strength and toughness [Ardlin, 2002]. The addition of zirconia in the alumina have being used for long time with the objective of alumina based composites densification. It is well known that the mechanical properties of alumina composites can be considerably increased by the incorporation of fine zirconia particles [Claussen, 1976, Shin et. al., 1990, Mullot et. al., 1993, Kishino et. al., 1994]. The toughening mechanisms associated with zirconia toughened alumina are mainly based on the stress-induced tetragonal→monoclinic martensitic transformation toughening.

The main objective of the present work is to incorporate 20 wt% ZrO_2 particles synthesized by the slurry method into high purity alumina matrix and to investigate the effect of ZrO_2 addition on the microstructures and mechanical properties of the Al_2O_3 composites at different sintering temperature.

Experimental

Sample Preparation

The commercially available powders used in this work were the nanocrystalline, α- Al_2O_3 powder and yttria-stabilized ZrO_2 (3 mol%) powder from the manufacturing company Inframat® Advanced Materials™, USA. Alumina presented crystal size ~40 nm and particle size ~150 nm and zirconia presented average particle size 30-60 nm. To prepare composition, related powders were weighed by following unitary method, keeping the total weight constant.

The nanocrystalline, α- Al_2O_3 powder and 20 wt % yttria-stabilized ZrO_2 (3 mol %) powder have been taken for the preparation of required composite. To attain the composition, mechanical milling was performed in distilled water with 65 wt% of solid content for 24 hours in ball milling, with zirconia ball as a grinding media. Ammonium polyacrylate was used as dispersant. The slurry of the power mixtures was dried in an oven for 24 hours at 100°C and the dried lumps were crushed and passed through a plastic sieve. Hand milling was done for several hours to obtain a homogeneous distribution. Powder compacts with dimension of 5×6×50 mm were confirmed by uniaxiallly pressing at 60 MPa. Before compaction, polyvinyl alcohol (PVA) was mixed as a binder with the powder to provide some green strength for subsequent handling. The withdrawal of the binder was carried through in a muffle furnace with heating rate 6 ºC/min at 600 ºC per 180 min. The sintering was carried out in a box furnace at 1450ºC, 1500ºC, 1550ºC and 1600ºC for two hours with a heating rate of 20ºC/min. The bulk density of the sintered sample was measured from the ratio weight/volume. The sintered specimen was machined longitudinally with a 325 grit-resin bonded diamond wheel at a depth of 5 µm/pass. The final dimension of the specimens was 3×4×35 mm.

Measurements

Phase identification was confirmed by powder X-ray diffractometry (XRD) technique using BRUKER X-Ray Diffractometer of Model D8 Advance with Cu-K_α radiation (λ= 1.54 Å). For each sample a scan has been performed from 20º to 75º with a step size of 0.02º.The volume fraction of monoclinic zirconia (V_m) was calculated according to the following equation:

$$V_m = \frac{I_{(\bar{1}11)_m} + I_{(111)_m}}{I_{(\bar{1}11)_m} + I_{(111)_m} + I_{(111)_t}}$$

Theoretical density ρ_o of the sample was calculated from the actual density of the starting powders and their weight percentages using the rule of mixtures [Bansal et. al., 2003]:

$$\rho_o = \rho_A V_A + \rho_Z V_Z$$

where ρ_A, ρ_Z are the density and V_A, V_Z are the volume fraction of Al_2O_3 and ZrO_2 respectively. Values of ρ_A= 3.97 gm/cm^3 and ρ_Z =6.10 gm/cm^3 have been used here to calculate ρ_o. The measured bulk density ρ_b was determined using the formula:

$$\rho_b = \frac{m}{\pi r^2 h}$$

Where m is the mass, r the radius and h the height of the sample.

The porosity P of the sample was determined using the relation.

$$P = (1 - \frac{\rho_b}{\rho_0}) \times 100\%$$

Microstructures for the samples of different compositions were examined by using Philips XL-30 scanning electron microscopy (SEM). Mean linear intercept length $\bar{l}$ is used to determine the ASTM grain size number, G, by using the linear intercept method:

$$G = -3.2877 + 6.6439 \log_{10} \bar{l}$$

where $\bar{l}$ is in millimeters at 1× Magnification.

The methodology used for the determination of hardness, was in accordance with ASTM C1327-99 [Cecilia et. al., 2004]. Five Vickers impressions had been carried through in the surfaces of each one of the samples, which already were polishing, using an applied load of 2 kgf (19.6141 N) during six seconds. After the diagonal length measurement, the values of the Vickers hardness (GPa) were calculated, by the following equation [Cecilia et. al., 2004, Santos et. al., 2007]:

$$H_v = 0.018544 \times \frac{F}{d^2}$$

Where F is the load in N and d is the average length of the two diagonals of the indentations in mm.

The porosity dependence Elastic Modulus can also be measured using the Dewey-Mackenzie relation [Pabst et. al., 2004]:

$$E = E_o(1 - 2P)$$

where E is the effective elastic modulus of the porous composites, E_o is the elastic modulus of the dense composites and P is the porosity of the sample.

The flexural strength of the specimens was determined according with ASTM D790–10 by three-point bending method (Hounsfield Model H10KS-universal test machine), with a span of 30 mm and crosshead speed of 0.5 mm/min at ambient room temperature conditions. The flexural strength was calculated from the following equation.

$$\sigma_{flexural} = \frac{3WL}{2BD^2}$$

where W is the load (N), B is the width (mm) and D is the thickness (mm) of the sample.

Result and Discussion

XRD analysis

The XRD patterns of a ZTA sample containing 20 wt% ZrO_2 sintered at 1450°C, 1500°C, 1550°C and 1600°C are shown in Figure 1, which confirms the formation of different phase in ZTA.

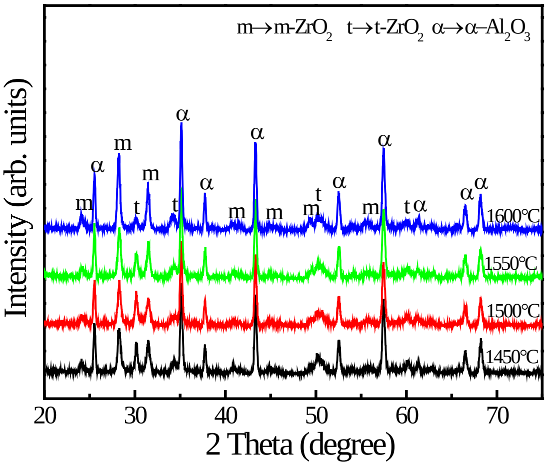


Figure 1. XRD pattern of Al_2O_3-20 wt% ZrO_2 composite sintered at different temperature

XRD analysis of the samples indicates that α-Al_2O_3, t and m-ZrO_2 are the phases present in the composite.From the figure it is observed that with the increase of sintering temperature the intensity of the peaks for Al_2O_3 and ZrO_2 have been changed. It also reveals that with the increase of sintering temperature, the intensity of m-ZrO_2 phases increases, whereas the intensity of t-ZrO_2 decreases. However, t-ZrO_2 retention becomes much easier to trigger the transformation to monoclinic. As a result, its contribution to transformation toughening predominates. The extent of toughening achieved in the composites depend on the grain size of Al_2O_3 and ZrO_2, volume fraction of ZrO_2 retained in the metastable tetragonal phase as well as on the relative distribution of Al_2O_3 and ZrO_2 in the matrix [Bleier et. al., 1992].

Finer particle size of both Al_2O_3 and ZrO_2 will not only enhance the chances of a uniform Al_2O_3 and ZrO_2 distribution, it also increases the possibility of ZrO_2 being retained as metastable tetragonal phase [Garvie, 1965]. So it can be inferred that monoclinic phase is indeed retained at the room temperature due to the presence of the hard alumina matrix around and this phase is responsible for flexural strength improvement by transformation toughening mechanism.

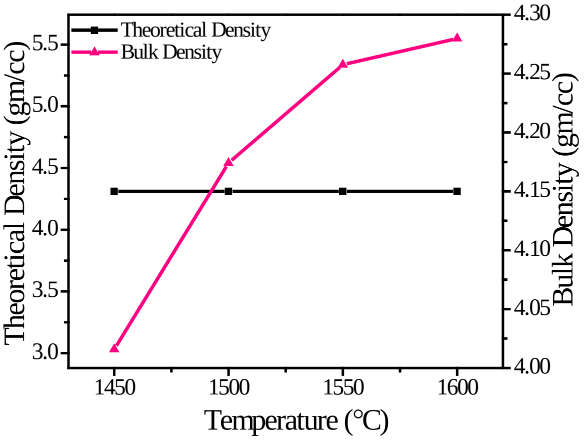


Figure 2. Effects of the sintering temperature on the theoretical and bulk density of Al_2O_3-20 wt% ZrO_2 composite

Figure 2 shows the result of density as a function of sintering temperature. With the continual supply of thermal energy, more and more contact points are created between the particles and the intervening porosity diffuses out of the contact area. Hence a substantial increase in density is resulted. At 1600°C, higher density is achieved than that of other temperature. Densification of powdered particle is a thermally assisted phenomenon due to sintering at various temperatures. We know that matter transport during the sintering of polycrystalline composites occurs by diffusion, a thermally activated process, which can occur along different paths in the solid, giving rise to the different mechanisms of diffusion: lattice, grain boundary and surface diffusion. The density is also influenced by phase transformation of monoclinic to tetragonal zirconia above 1170°C during heating. The density result reveals that the elimination of pore, simultaneous grain growth with grain boundary diffusion and lattice diffusion are the predominant mechanism to compact the material at high temperature. In this work, the relative density have been calculated about 93.15% for 1450°C and about 99.28% for 1600°C. The relative density for other temperatures are in between this values.

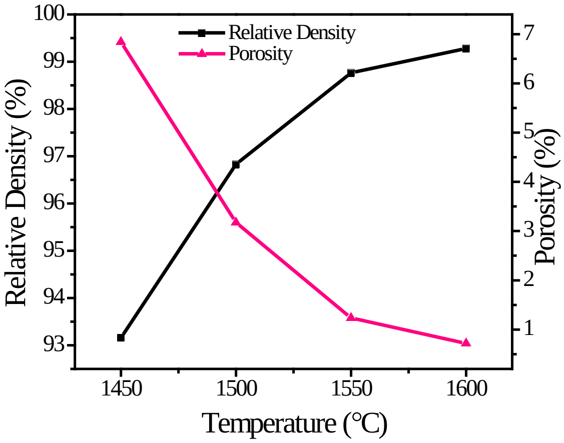
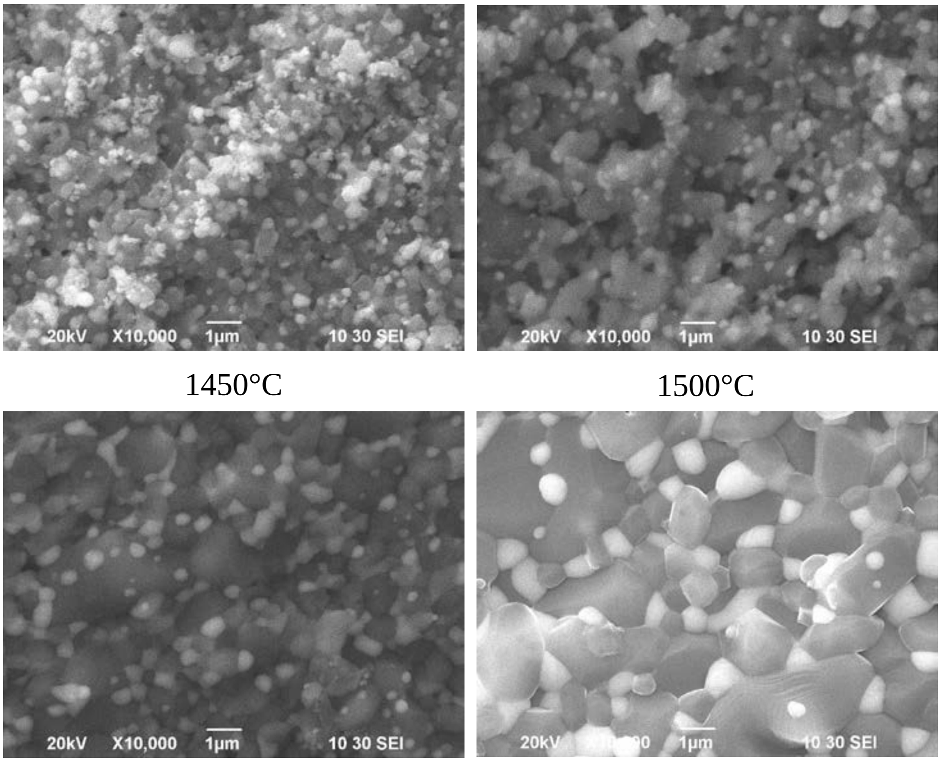


Figure 3. Effects of the sintering temperature on the relative density and porosity of Al_2O_3-20 wt% ZrO_2 composite

About 1-4% density has been changed due to increase of 50°C temperature. This resembles that after increasing sintering temperature particles become more compact and dense, therefore for the same reason porosity decreases with the same change of temperature. Moreover, increasing temperature, density increases and porosity decreases regularly than that of lower temperature that has been shown in Figure 3. It is observed that the porosity is decreased with sintering temperature. It resembles that the composite are in more compact form at the higher temperatures. During the diffusion process of sintering, the intervening porosity diffuses out, resulting in reduction of porosity. It is observed that the porosity is decreased with sintering temperature. This porosity usually originates from entrapped pore during green slurry. With the increase of temperature, sample becomes more homogeneous. During 50°C interval, porosity decreases sharply from low temperature to high temperature. It is also seen that the percentage of porosity is minimum at the sintering temperature 1600°C for the composites than that of at 1450°C, i.e., it reveals that the sample is more compact at this temperature. The calculated density values are in good agreement with some previous results obtained using pressureless sintering technique [Maca et. al., 2008, Bodisova et. al., 2007, Oungkulsolmongkol et. al., 20010]. The optimum density was also achieved for ZTA sintered at 1600°C for the composition.



1450°C

1500°C

1550°C

1600°C

Figure 5. Microstructure of Al_2O_3-20 wt% ZrO_2 composite sintered at different temperature

Scanning electron microscopy

Figure 5 show the SEM micrographs of the ZTA composites containing 20 wt% ZrO_2 at different temperatures. Micrographs reveals highly homogeneous microstructures with some agglomerates, pores or abnormally grown alumina grains. The micrograph exhibits the Al_2O_3 and ZrO_2 grains as dark and whitish color respectively, where zirconia grains are embedded around the alumina grain uniformly and within the grain. However, small fractions of intragranular zirconia grain are also being noticed.

From the figure, it can also be observed that ZrO_2 particles are uniformly dispersed throughout the alumina matrix. As the temperature increases, the Al_2O_3 and ZrO_2 grain size increases significantly. The ZrO_2 phase creates a pinning effect around Al_2O_3 grain and obstructs its growth. It can also be observed that the grain sizes of ZrO_2 increase and hinders the grain growth of Al_2O_3 at different temperatures, which contributes to the lowering of porosity. A fine grain size and refined microstructure are necessary for improved mechanical properties especially for wear resistance of dental implant. It is observed from Figure 6 that, grain size of Al_2O_3 and ZrO_2 vary with the sintering temperature. In the present work, it is seen that as the sintering temperature was increasing, then the grain size increases regurly.

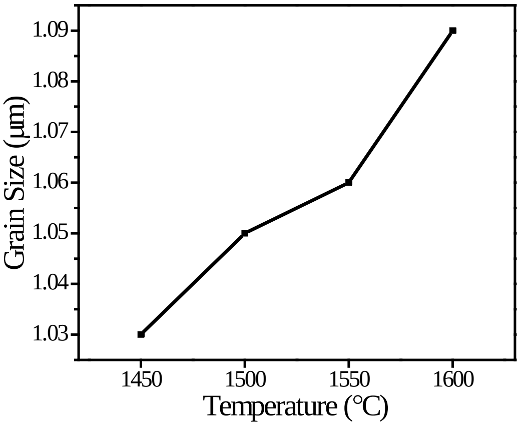


Figure 6. Effects of the sintering temperature on the grain of Al_2O_3-20 wt% ZrO_2 composite

Hardness and elastic modulus

Figure 7 shows the variation in Vickers hardness of 20 wt% ZTA composite with the change of temperature. Hardness increases with the increase in temperature. As higher sintering temperature offers better densification, hardness value increases as a whole. Similar trend in hardness has been observed by R. P. Rana [Rana, 2009]. Similar trend in hardness has also been observed by Basu et al. [Basu et. al., 2005]. At 1600°C, maximum hardness shows 11.52 GPa. However, at 1450°C, minimum hardness shows 9.61 GPa. The above increase in the hardness value of the Al_2O_3-ZrO_2 composite is related to the density increment. It appears that the phases of the sintered composite have least influence on the hardness.

Elastic modulus of the composite depends on the volume fraction of the phases present and their individual modulus of elasticity. At 1450°C, densification of the composites is improved by reducing pore volume fraction of the matrix and as a result of which the modulus of elasticity improves. Alumina has a higher modulus of elasticity compared to zirconia. So, samples containing 20 wt% zirconia have the highest modulus of elasticity at 1600°C. Simultaneously, the grain size of zirconia increases and hinders the grain growth of alumina at 1600°C, which contributes to the change of elastic modulus. Nicholson [Khaund et. al., 1980] established that both Young's modulus and hardness of ZTA composites containing particles of zirconia stabilized with 0.3 mol% MgO followed a linear rule of mixtures.

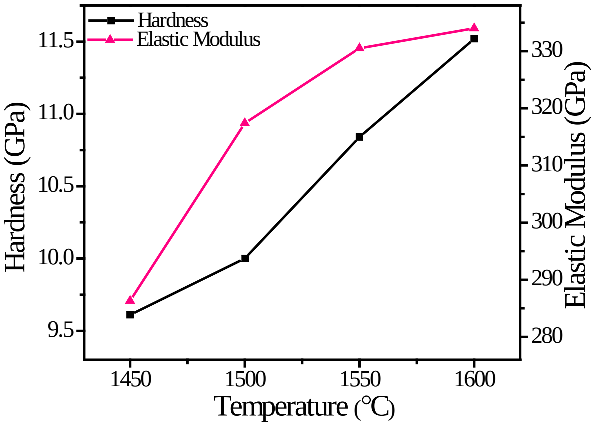


Figure 7. Effects of the sintering temperature on the relative density and porosity of Al_2O_3-20 wt% ZrO_2 composite

Flexural Strength

The Flexural strength increases almost linearly with increasing sintering temperature that has shown in Figure 8. The flexural strength was found around 728 MPa sintered at 1600°C and that of 688 MPa sintered at 1450°C for 2 hours.

The martensitic transformation and frontal process zone are predominant mechanisms to increase the flexural strength of Al_2O_3-ZrO_2 nanocomposite. Since the tetragonal zirconia grains do not undergo the stress-induced transformation to the monoclinic form when grain size is smaller than a critical size. The particle sizes lower than the critical value does not affect the strength. The reduction of size improves the bulk density but not the transformability of the tetragonal zirconia grains. Usually, the effect of grain size on strength in transformation-toughened composites is a complex phenomenon [Orange et. al., 1988]. An increase in grain size improves the transformability, therefore, increasing strength. Microstructure reveals that the zirconia grain size increases with increasing zirconia content. The m-ZrO_2 phase increases with increase in sintering temperature. The retention of t-ZrO_2 varies during fracture and t-ZrO_2 fraction decreases with increasing temperature. However, t-ZrO_2 retention becomes much easier to trigger the transformation to monoclinic. As a result, its contribution to transformation toughening predominates although retention of m-ZrO_2 aids to microcrack toughening.

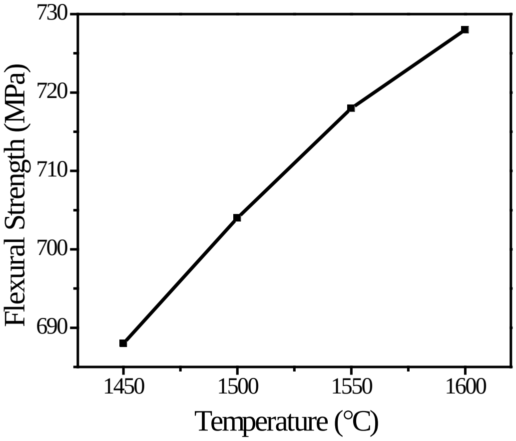


Figure 8. Effects of the sintering temperature on the flexural strength of Al_2O_3-20 wt% ZrO_2 composite

Conclusion

This work presents the variation in structural and mechanical properties of 20 wt% ZTA in the temperature range from 1450°C to 1600°C. All samples in this work have been prepared by slurry method.The X-ray diffraction studies clearly showed the formation of α-Al_2O_3, t and m-ZrO_2 phases in the ZTA composites. The density has been found to increase with increasing sintering temperature, while porosity decreases with the same change of temperature. SEM images show the microstructures of prepared ZTA which reveals that the grains are homogeneous and uniformly distributed. It can also be observed that the grain sizes of ZrO_2 increase and hinders the grain growth of Al_2O_3 at 1600°C compared to that of at 1450°C, which contributes to the lowering of porosity. Hardness and elastic modulus was found to be increased with sintering temperature. The Flexural strength increases with sintering temperature. The predominant mechanisms for the improvement of the mechanical properties of the ZTA materials are the stress-induced transformation toughening and process flaws eliminating. The change of sintering temperature was also found to have a significant effect on structural and mechanical properties of ZTA composite.

References:

Munro R.G., J. Am. Ceram. Soc. , 80, 1919, 1997.

Sadoun M., Perelmuter S., “Alumina-zirconia machinable abutments for implant-supported single-tooth anteriorcrowns”,*Practical Periodontics and aesthetic dentistry*,v. 9, n. 9, 1047-1053, 1997.

De Aza A.H., Chevalier J., Fantozzi G., et al., “Crack grouth resistance of alumina, zirconia and zirconia toughened aluminaceramics for joint prostheses”, *Biomaterials*, v. 23, 937-945, 2002.

Hannink R.H.J., “Transformation toughening in Zirconia-Containing Ceramics”, *J. Am. Ceram. Soc.*, v. 83, n. 3, 461-487, 2000.

Fischer H., Rentzsch W., Marx R., “Elimination of low-quality ceramic posts by proof testing”, Dental *Materials*, v. 18, n. 8, 570 - 575, 2002.

Keith O., Kusy R.P., Whitey J.Q., “Zirconia brackets: an evaluation of morphology and coefficients of friction” *Am. J. Orthod. Dentofacial Orthop*, v. 106, n. 6, 605 - 614, 1994.

Cando D.C., “Zirconia: una alternativa fiable”, *Labour Dental*, v. 4, n. 2, 1-7, 2001.

Ardlin B.I., “Transformation-toughened zirconia for dental inlays, crowns and bridges: chemical stability and effect of low temperature aging on flexural strength and surface structure”, *Dental Materials* v. 18, n. 8, 2002, 590-595.

Prestipino V. and Ingber A., “All-ceramic implant abutments: Esthetic indications”, *Journal of Esthetic Dentistry* v. 8, 255-262, 1996.

Christel P., Meunier A., Heller M., Torre J.P., Peille C.N., “Mechanical properties and short-term in vivo evaluation of yttrium-oxide-partially-stabilized zirconia”, *J. Biomed. Mater. Res*,v. 23, 45-61, 1989.

Serra E., Tucci A., Esposito L., Piconi C., “Volumetric determination of the wear of ceramics for hip joints”, *Biomaterials*, v. 23, 1131-1137 , 2002.

Piconi C., Maccauro G., “Zirconia as a ceramic bio-material”, *Biomaterials* v. 20, 1-25, 1999.

Claussen N., *J. Am. Ceram. Soc.*, 59, 49 , 1976.

Shin D. W., Orr K. K., Schubert H., *J. Am. Ceram. Soc.*, 73, 1181 , 1990.

Mullot J., Lecompte J.P., Montanaro L., A. Negro, J. Euro. Ceram. Soc. 11, 309, 1993.

Kishino J., Nishiyama A., Sakuma T., J. Mater. Sci., 31, 4991, 1994.

Bansal N.P., Choi S.R. “Processing of Alumina-Toughened ZrO_2 Composite”, *NASA/TM -212451*, 2003.

Maria Cecilia, Carlos Nelson EliasI, Jamil Duailibi FilhoII, Leandra Guimarães de OliveiraII, “Mechanical properties of Al_2O_3-ZrO_2 composites for composite abutments”, *Mat. Res.*, Vol. 7, No. 4, 643-649, 2004.

Santos C., Souza R.C., Daguano J.K.M.F., Elias C.N., Rogero S.O., “ Development of ZrO_2 -Al_2O_3 Composite”, *The 51st Brazilian Congress on Composites*, 2007.

Pabst W., Gregorova E., Ticha G., Tynova E., “Effective Elastic Properties of Al_2O_3 – ZrO_2 Composite Composites Part 4. Tensile Modulus of Porous Al_2O_3 and ZrO_2”, *Composites − Silikáty* Vol. 48, No. 4, 165-174, 2004.

Bleier A., Becher P.F., Westmoreland C.G. and Alexander K.B., “Effect of aqueous processing conditions on the microstructure and transformation behavior in Al_2O_3 – ZrO_2 (CeO_2) composites”, *J. Am. Ceram. Soc.*, Vol. 75, 2649-58, 1992.

Garvie R.C., “Occurrence of metastable tetragonal zirconia as a crystallite size effect”, *J. Phys. Chem.*, Vol. 69, 1238-43,1965.

Maca K., Pouchly V. and Shen Z.J., “Two-step sintering and spark plasma sintering of Al_2O_3, ZrO_2 and $SrTiO_3$ composites”, *Integrated Ferroelectrics*, 99, 114–124, 2008.

Bodisova K. and Sajgalik P., “Two-stage sintering of alumina with submicrometer grain size”, *J. Am. Ceram. Soc.*, 90, 330–332, 2007.

Oungkulsolmongkol T., Salee P. and Buggakupta W., “Hardness and fracture toughness of Al_2O_3-based particulate composites with ZrO_2 and strontia additives”, *J. Met., Mat. Min.*, 20, 71-78, 2010.

Rana R.P., “Powder processing, densification behaviour, microstructure and mechanical properties of Al_2O_3- 50 vol% ZrO_2 composites”, Ph. D. Thesis, National Institute of Technology Rourkela, 2009.

Basu B., Venkateswaran T., Sarkar D., “Pressureless sintering and tribological properties of WC–ZrO_2 composites”, *J. Eur. Ceram. Soc.*, 25 (9), 1603–10, 2005.

Khaund A.K., Nicholson P. S., “Fracture of a brittle composite: Influence of elastic mismatch and interfacial bonding”, *J. Mater. Sci.*, 15, 177, 1980.

Orange G., Fantozzi G., Homerin P., Thevenot F., Leriche A., “Thermomechanical Properties of Zirconia-Toughened Alumina Materials: Effect of Microstructure and Temperature on Toughening Mechanisms”, *Advances in Composites*, Vol24B, Science and Technology of Zirconia III, Edited by A. Somiya, N. Yamamoto, H. Yanagida, *The American Composite Society*, Inc. Westerville O.H., 1075-82,1988.