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Phase Stability of 3Y-TSZ Ceramics after Different Surface Treatments

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Abstract. The ability of zirconia ceramics to develop a bioactive surface is of great importance for biomedical applications. For that, it is also required to control phase stability (i.e. to avoid the tetragonal to monoclinic phase transformation) of zirconia surfaces in order to impart a high mechanical resistance. In this work, the phase stability of dense 3 mol% yttria stabilized-zirconia (3Y-TSZ) ceramics after acid and hydrothermal treatments was examined. Ceramic discs were prepared by slip casting from well dispersed 52 vol% suspensions, and subsequently sintered to 1300-1500 °C. The effect of various synthesis parameters and 0.25 wt% alumina doping on the phase transformation after acid and hydrothermal treatments was semi-quantitatively evaluated by XRD. The 3Y-TSZ sintered to 1500°C exhibited higher t→m transformation than samples sintered at lower temperatures. The phase transformation up to10h of hydrothermal treatment occurred by nucleation and growth mechanisms in which the nucleation process predominated. The presence of 0.25 wt% alumina in 3Y-TSZ sintered at 1500°C slightly enhanced the resistance to acid treatment.

Introduction

The Y_2O_3-stabilized tetragonal ZrO_2 (3Y-TSZ) is an important structural and functional ceramics [1,2]. Commonly, these ceramics are produced by the conventional powder processing techniques that involve mixing, pressing and subsequent sintering. Mechanical properties (fracture toughness, strength, and hardness) as well as phase transformation during aging of the final product are strongly dependent on microstructure including the extent of densification, grain size and shape, introduction of an inert material, etc. Through a careful processing a desirable microstructure can be obtained. Colloidal processing is an alternative route to ensure a uniform microstructure with a reduction in porosity and grain size leading to significant improvements in the ceramic. The addition of 0.25 wt% of alumina accelerates densification of 3Y-TSZ. The alumina particles locate at the ZrO_2 grain boundaries and change the diffusion sintering mechanism from grain-boundary to volume diffusion preventing grain coarsening [3]. Additionally, phase stability of such 3Y-TSZ after hydrothermal treatment may be enhanced.

In this study, dense 3Y-TSZ ceramics were developed by slip casting in a plaster mold and subsequently sintered at different temperatures. The effect of hydrothermal and acid treatments on tetragonal to monoclinic (t-m) phase transformation and microstructure were evaluated by XRD and SEM-EDX and compared with that of 0.25 wt% alumina doped ZrO_2.

Experimental

Materials. Two commercially available ZrO_2 doped with 3 mol% Y_2O_3 stabilized in tetragonal phase (Saint Gobain ZirPro, HanDan) were used. One of these 3Y-TSZ powders was doped with 0.25 wt% alumina (3Y-TSZA) and has a finer average particle size of 0.21 μm whereas that of 3Y-TSZ without alumina was 0.6 μm.

Processing of 3Y-TSZ Compacts and Sintering. Green compact in a shape of disc (10-12 mm in diameter, 3-4 mm height) was prepared by slip casting. The processing consisted in the preparation of well dispersed aqueous 52 vol% suspensions of 3Y-TSZ by adding to the powder distilled water containing 0.20 wt% of anionic polyelectrolyte dispersant (Dolapix, Zschimmers and Schwartz, Germany). The suspension pH was about 9. After mixing, deagglomeration of the suspension was performed by ultrasonication.

Concentrated aqueous suspension of 3Y-TSZA was prepared using an ammonium polyacrylate solution as a dispersant. Experiments on the dispersion of this alumina doped 3Y-TSZ particle in aqueous solutions have been discussed in a previous work [4].

The resulting suspensions were cast in a plaster mold and then the compact were dried at 100 °C. Green compacts were sintered at temperatures between 1300 and 1500 °C with a heating rate of 5 ºC/min and holding time of 2 h. Density of green and sintered compacts was determined using Hg immersion and the water absorption method, respectively. The relative density RD was determined from the ratio between the apparent and theoretical density (6.05 g/cm^3).

Characterization Methods. Crystalline phase composition of sintered surfaces were examined by XRD (Philips 3020 equipment) with Cu-Kα radiation in Ni filter at 40 kV–20 mA. The relative proportions of both monoclinic and stabilized phases were semi-quantitatively determined by XRD analysis using the Garvie and Nicholson method [5] and then the relative volume fraction of m-ZrO_2 was calculated [6].

Microstructure of the sintered compacts was observed by a scanning electron microscope SEM (FEI Quanta 200 MK2 Serie) and microanalysis (EDX) using the polished surface of the sintered ceramics (transversal section).

Results and Discussion

The relative density of green compacts produced from well dispersed suspension by slip casting was approximately 0.628. The relative density of 3Y-TZP compacts sintered at 1300°C increased to 0.88, and higher densification of 0.98 achieved at 1400°C. Both 3Y-TSZ and 3Y-TSZA compacts exhibited nearly full densification at 1500°C. Thus open porosity reduced at 1400 °C and most pores were closed.

The X-ray diffraction patterns (Fig. 1) of 3Y-TSZ confirmed that it mainly consists in tetragonal phase but in the 2θ range from 27 to 32 º a trace of monoclinic phase was detected for all samples. According to Fig. 2 a minor amount of cubic phase formed after sintering at 1500 ºC.

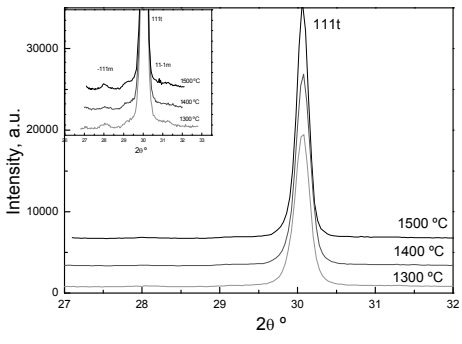

Fig.1: XRD patterns of 3Y-TZP sintered at different temperatures. Detail showing trace of monoclinic phase.

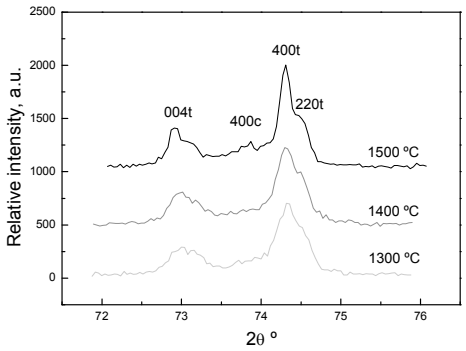

Fig. 2: XRD patterns in the 2θ range 72-74º for 3Y-TZP sintered at different temperatures.

The existence of cubic phase in 3Y-TSZ ceramics stabilized in tetragonal was previously confirmed by XRD [7,8]. Matsui et col. [9] showed that relative content of cubic phase attained up to 12.7 and 18.6 wt% for 1300 and 1500 ºC, respectively and it correlated with the distribution of the Y^{3+} ions inside the zirconia grains, which depends on several processing conditions such as sintering temperature. Particularly, this study shows that Y^{3+} ions resulted homogeneously distributed in most grains of the compact sintered at 1300 ºC , whereas a higher amount Y^{3+} ions appeared to concentrate within large grains after sintering at 1500 ºC. Therefore, the formation of cubic phase started to originate in certain regions at which Y3+ ions had segregated (i.e. grain boundaries and triple junctions).

Effect of Hydrothermal Treatment on Phase Stability. The transformation rate at which the tetragonal phase is transformed to monoclinic phase is an indication of the hydrothermal sensitivity of the ZrO_2 containing ceramics. The effect of hydrothermal treatment on phase stability of dense 3Y-TSZ casts sintered at different temperatures was examined. The evolution of XRD patterns

with time after hydrothermal treatment for all samples showing an increase in monoclinic peak intensity with time. Fig. 3 shows the variation of the volume fraction of monoclinic phase with time for the different 3Y-TSZ samples with and without alumina doping.

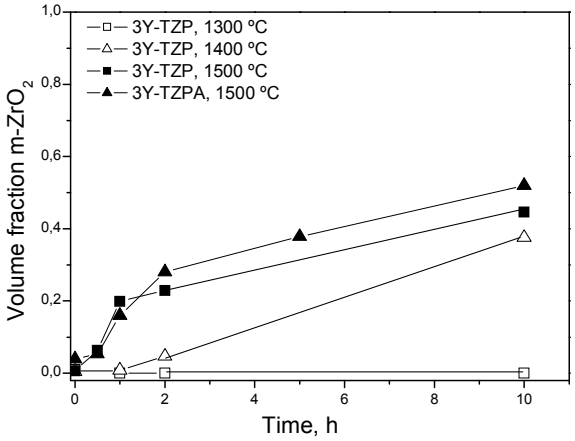

Fig. 3: Volume fraction of monoclinic phase vs. time for 3Y-TZP sintered at different temperatures and 3Y-TZPA doped with 0.25 wt% alumina sintered at 1500 ºC.

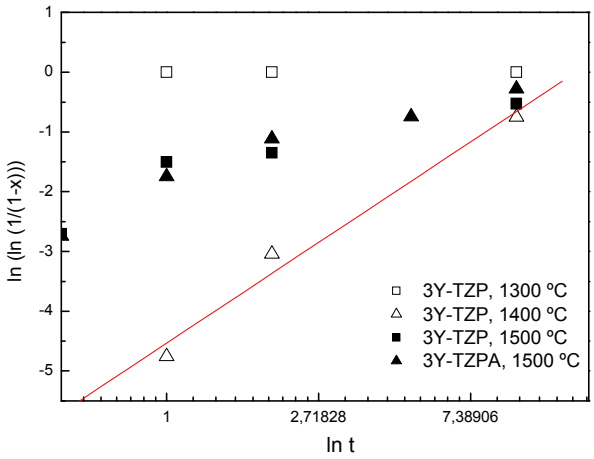

Fig. 4: ln (ln (1/ (1-x))) vs. ln t using experimental data of Fig. 3.

Only scarce content of monoclinic fraction was detected for 3Y-TSZ sintered at 1300 ºC after hydrothermal treatment up to 10 h. For curves of samples sintered at 1400 ºC the volume fraction of monoclinic phase remained very low for times below 2h and then increased up to 0.35 after 10 h. At 1500 ºC, the curves show a nearly sigmoid shape in which the monoclinic content slowly increased at low and high times and it increased rapidly at an intermediate time. In this case, the relative monoclinic fraction reached 0.2 for 1 h resulting in a higher content than those of the other samples. This sample exhibited the lower phase stability as transformation started at times lower than 1h; the curve also presented a much higher slope and thus the intermediate part of the curve appeared for times >1 h , for that the monoclinic volume fraction approximated to 0.45 for 10 h. This rapid degradation behavior was consistent with the presence of cubic phase detected by XRD (Fig. 2).

The relation between cubic phase and accelerated aging in 3 mol% yttria-stabilized zirconia was previously found. Previous works [2, 7-9] indicated that phase stability of sintered 3Y-TSZ to hydrothermal treatment improved with reducing porosity and grain size.

There is a critical grain size of 0.3 μm for 3 mol% yttria content of stabilizing agent below which phase transformation does not occur. Therefore, a good combination between high sintering temperatures to attain high densification and that required to avoid an increase in the grain size as well as heterogeneity in Y distribution may be favorable to retain t-ZrO_2.

Previous studies suggested a nucleation and growth kinetics to describe the variation of monoclinic volume fraction x with time [2, 7, 9-11]. The model equation contain two parameters which can be derived from the linearized ln(ln(1/(1-x))) vs. ln t . The Fig. 4 shows the approximately linear relation, from which the exponent n and a parameters involved in the model equation [2, 7, 9-11] can be obtained. The calculated results using experimental data of sample sintered at 1400 ºC are shown by a line in Fig. 4. The resulting parameter n near to 1.70 was lower than that expected value of ~ 3-4 considering that phase transformation proceeds via homogeneous nucleation and growth mechanism [10]. However, the n value between 1 and 2 corresponded well to a nucleation and one-dimensional growth process [3]. The samples sintered at 1500 ºC exhibited a reduction in the slope (i.e. a low n value). According to [12], the low n value suggested a different mechanism in which nucleation predominated and growth proceeded at slower rates. There was not a clear indication that alumina doping provided high phase stability as was previously reported for

small amount of silica doping on 3Y-TSZ ; this difference can be attributed to a low grain size of 0.55 μm [3].

Effect of Acid Treatment on Phase Stability. Figures 5 and 6 show the effect of the acid treatment on phase stability for 3Y-TSZ sintered at different temperatures and that doped with 0.25 wt% alumina sintered at 1500 ºC. XRD patterns of samples after acid treatment showed the decrease of tetragonal peak intensity and the increase of monoclinic one with sintering temperature indicating the t to m phase transformation. The highest phase transformation after acid treatment was found in the 3Y-TSZ sintered at 1400 and 1500 ºC as monoclinic volume fraction resulted close to 0.83 compared with 0.62 for compacts sintered at 1300 ºC. Although in the latter, more pore surface was exposed to acid, high porosity did not correlate with the results of phase transformation. Monoclinic content of these samples in acid solution was higher than those after hydrothermal treatment (vol. fraction ~0.44).

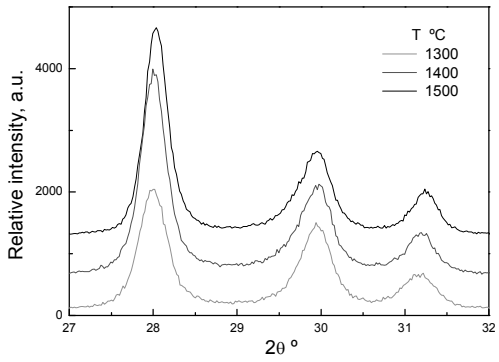

Fig. 5: XRD patterns of 3Y-TSZ sintered at different temperatures after acid treatment.

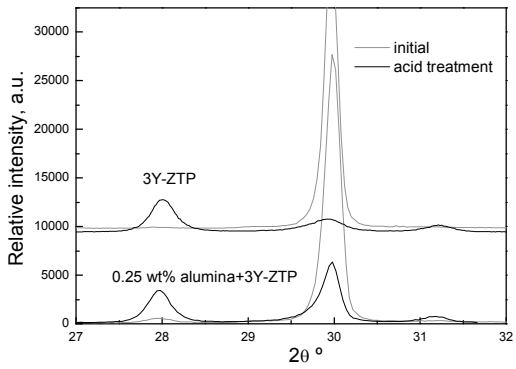

Fig. 6: XRD patterns of 3Y-TSZ and that doped with 0.25 wt% alumina sintered at 1500 ºC and after acid treatment

Negligible amount of m-ZrO_2 phase was initially found in 3Y-TSZA sintered at 1500 ºC but the volume fraction of this sample increased to 0.53 after acid treatment which is a relatively low value as compared with the other samples.

Fig. 7 a and b show the SEM microstructures (transversal section) showing the modification below the 3Y-TSZ surface after acid treatment .

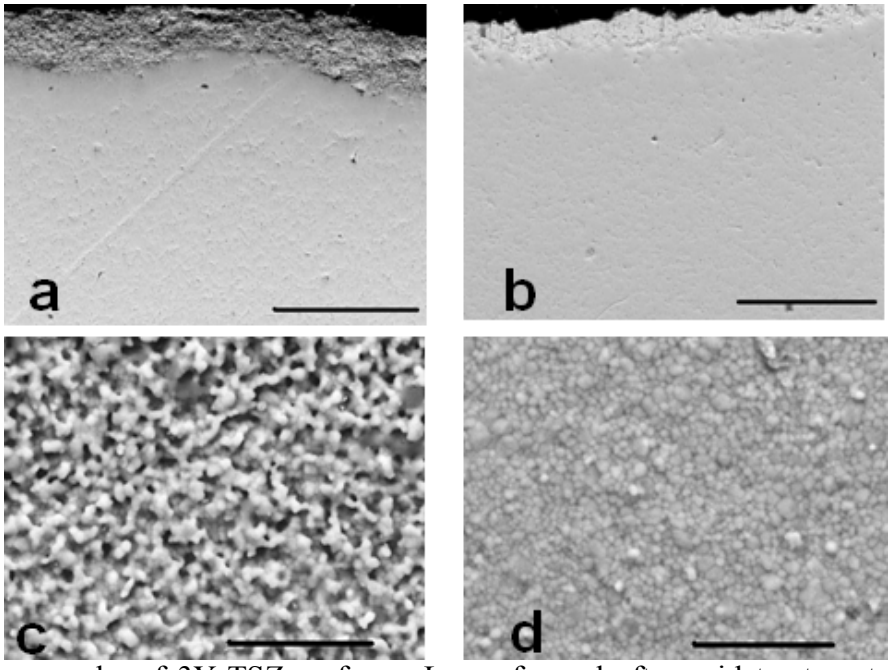

Fig. 7. SEM micrographs of 3Y-TSZ surfaces. Layer formed after acid treatment a: surface in contact with the mold; b: top surface. (Bar: 100 μm); Without treatment c: surface in contact with the mold; d: top surface. (Bar: 10 μm)

For samples sintered at 1500 ºC, however a different behavior was found between the surface which was in contact with the plaster mold and the top surface of the sintered compacts (Figs. 7 a and b, respectively). Below the top surface, a layer with small thickness was observed. The top surface of this ceramic before treatment was smooth and brilliant due to the presence of very fine particles and low porosity (Figs. 7 c and d) causing a positive effect on resistance to acid treatment.

Conclusions

Phase stability of dense 3Y-TSZ with and without 0.25 wt% alumina doping processed by slip casting after hydrothermal treatment and in phosphoric acid was examined. The processing conditions have a critical role on phase stability. Sintering at temperatures below 1400 °C limited the t to m phase transformation of 3Y-TSZ surface after 10 h of hydrothermal treatment. On the contrary, such treatment led to marked increase in the phase transformation of samples sintered at 1500 °C which contained scarce cubic phase. Similar effects caused the acid treatment. For 3Y-TSZ sintered at 1500 ºC , the volume fraction of m-ZrO_2 exceeded the respective value found after treatment in autoclave 10 h. Doping with alumina was more effective to improve resistance to phase transformation by treatment in phosphoric acid**.**

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