EFFECT OF DIFFERENT CERIA CONTENT ON PHASE FORMATION AND PROPERTIES OF MULLITE ZIRCONIA CERAMICS

J. Bruni; M.S. Conconi; L.B. Garrido; E.F. Aglietti

CETMIC (Centro de Tecnología de Recursos Minerales y Cerámica; CONICET- CIC-UNLP). Cno. Centenario y 506, C.C.49, M.B. Gonnet. (B 1897 ZCA) Buenos Aires. Argentina. E-mail: lgarrido@cetmic.unlp.edu.ar

ABSTRACT

Main problems in the reaction-sintering process to produce zirconia toughened mullite ceramics are related with composite microstructure including the grain size control of zirconia inclusions, relative proportion of t-ZrO_2 *and the presence of secondary phases. These factors determine the final properties of the mullite based composite and its possible industrial application.*

In this work, Mullite-ZrO_2 *composites were produced from stoichiometric mixtures of alumina and zircon (molar ratio 3:2) by slip casting and reaction sintering employing cerium oxide as additive (5 to 15 % mol in* ZrO_2*).*

The effect of different ceria content in the starting powder composition and sintering temperature (1400 and 1600ºC-2h) on the densification and conversion as well as the resultant microstructure of composites was examined using the XRD and SEM-EDAX techniques. Crystalline phase development on sintering was quantitatively determined by XRD using the Rietveld method. These measurements allowed the calculation of the conversion of the corresponding reaction products (zirconia and mullite) for different sintering temperatures. Formation of mullite, which occurred at a relatively low temperature, took place in a presence of a liquid phase instead of the usual solid state process.

Keywords: mullite-ZrO_2 ceramics, ceria, Rietveld method, slip casting

INTRODUCTION

According to a chemical reaction in a solid state between zircon and alumina, mixing the stoichiometric amounts of reactives (molar ratio 3:2, respectively) will produce a zirconia with mullite matrix ceramic. The phase distribution expected in resultant composite after complete conversion of stoichiometric mixture of alumina and zircon is 63.4 wt% of mullite (33.4 mol %) and 36.6 wt% of zirconia (66.6 mol %) .

The mechanism of mullite-zirconia formation was earlier described in detail by several authors (1,2,3). These previous studies clearly indicate that the reaction is diffusion controlled and the sequence of reactions consists in several stages. The reaction starts in the grain boundaries of $ZrSiO_4$ which decomposes in the surrounding of Al_2O_3 with a formation of ZrO_2 and amorphous silica. The amorphous siliceous phase dissolves Al_2O_3 and then reacts with it giving mullite in its most stable form (3:2). Nevertheless, several studies reported that initially a transitory amorphous phase of non-crystalline mullite (3,4) is formed and diffusion of Al^{3+} ions within the amorphous silica is a very slow stage. Data reported recently using coarse-grained zircon is consistent with these previous results (5).

For one-step heating cycle, the reaction rate of a submicron powder mixture is rather low at a temperature of 1500 ºC and compacts were incompletely reacted at 1575 ºC whereas by submitting it to a two–step heating cycle with an intermediate step resulted high densificated and full reacted compacts (4-6). Mullite zirconia composites derived by a gel-process from tetraethyl orthosilicate (TEOS), pseudo-boehmite and ZrO_2 sols exhibit higher densification rate at lower sintering temperature and smaller grain size but more shrinkage in a quite expensive process than reaction sintering. Also, zircon, as a reaction product of zirconia and silica, forms as a transition phase in the gel- derived material in the range between 1200 and 1500°C (6).

In this work, the possibility of using ceria as dopant oxide to increase yield of reaction products of the stoichiometric alumina and zircon mixtures and to reduce the sintering temperature was examined. Crystalline phase content of sintered compacts produced from different compositions was quantitatively evaluated by XRD using the Rietveld method. From these measurements, the conversion to zirconia Xz and mullite Xm for different sintering temperatures were evaluated .

EXPERIMENTAL

Materials

The stoichiometric powder mixture (molar ratio of $Al_2O_3/ZrSiO_4$ = 3:2) was prepared using alumina (α-Al_2O_3, A-16SG, Alcoa Inc., USA) and zircon ($ZrSiO_4$, Mahlwerke Kreutz, Mikron, Germany)

Ceria (CeO_2, B.D.H Laboratory Chemicals Division, England) was used as dopant oxide. Particle size distribution of ceria particles (d_{50}:2 μm) was similar to that of zircon powder which have average particle size: 1.8 μm; alumina powder was finer (d_{50}:0.5 μm).

Three starting powder compositions with different ceria content were prepared by adding to stoichiometric mixtures of alumina and zircon an equivalent amount of the dopant oxide to obtain 5, 9 and 15 mol% in ZrO_2 which in terms of a weight content corresponds to 2.5, 4.4 y 7.1 wt% of the total solid weight , respectively.

Processing of green compacts by slip casting and sintering

Mullite zirconia composites with a low amount of ceria was prepared by slip casting. Briefly, the procedure starts with the preparation of concentrated aqueous 57 vol% suspensions of alumina and zircon by adding the powders to distilled water containing 0.22-0.26 wt% of anionic polyelectrolyte dispersant (Dolapix, Zschimmers and Schwartz, Germany). The suspension pH was about 9. Suspensions were homogenized and deaglomerated by an ultrasonic process. Then, the ceria in the adequate proportions was mixed. The resulting suspensions were cast in a plaster mold and then the compact was dried at 100 °C.

Green compacts were sintered at temperatures between 1400 and 1600 °C with a heating rate of 5 ºC/min and holding time of 2 h. Cooling rate was 5 Cº /min.

Characterization of sintered composites

Density of sintered compacts was determined using the water absorption method.

Crystalline phase composition of ground sintered samples were examined by XRD (Philips 3020 equipment with Cu-Kα radiation and Ni filter at 40 kV-20 mA). Quantitative crystalline phase content of sintered compacts produced from different compositions was evaluated by XRD using the Rietveld method. These measurements allowed the calculation of the corresponding conversion to zirconia Xz and mullite Xm for different sintering temperatures. The fraction of conversion of reaction products was calculated as the ratio between formed moles of each compound by sintering at a given temperature for 2h , and stoichiometric moles expected when all the alumina and zircon is assumed to have reacted.

Microstructures of polished sintered compacts were examined using SEM-EDAX techniques. (Philips 505-Scanning electron microscope with EDAX accessory).

RESULTS AND DISCUSSION

Reaction

DRX patterns of Figure 1 showed that the compositions containing 5% mol ceria heated at 1400ºC mainly consisted in alumina and zircon; peaks of ZrO_2 appeared while no mullite peaks was observed. For compositions sintered at 1450ºC the intensity of ZrO_2 and mullite increased while that of zircon reduced and disappeared for 15 % mol ceria addition indicating the near completion of the thermal dissociation process. Moreover, Figure 1 shows that some minor amount of cerium pyrosilicate ($Ce_2Si_2O_7$) is formed. Many authors have reported that stabilizing-sintering additives like MgO, TiO_2, dysprosia (7, 8, 9) promote reaction sintering in the presence of transient liquid phase, which is formed in a temperature range. The existence of cerium pyrosilicate may be explained from the $Ce_2Si_7O_5$-Al_2O_3 equilibrium phase diagram (10). An eutectic temperature exists at 1375 ºC, therefore cerium compounds and alumina crystals may be formed as a result of crystallization from the liquid phase during cooling.

For composites sintered at temperatures of 1500-1600ºC, mullite and m-ZrO_2 converted to the major crystalline phases present. Small content of alumina and zircon remained unreacted even for the highest temperature. The absence of $Ce_2Si_7O_5$ at high sintering temperatures was probably due to the effects of high amounts of ZrO_2 which may act as inhibitor of liquid formation due to Ce^{4+} dissolution in the structure (11) and to the high silica consumption to forming mullite.

The behavior of phase development in the other compositions with increasing the ceria content was similar to that showed in Figure 1 for the 5 mol% ceria addition.

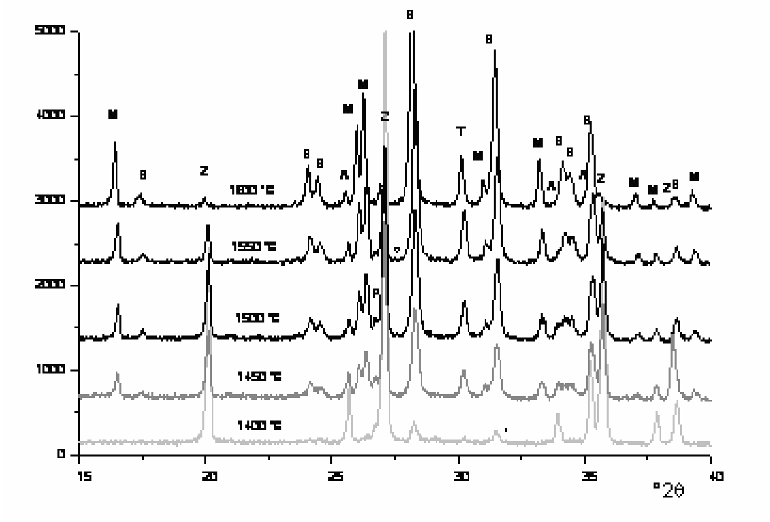

Figure 1: XRD patterns of composition with 5 mol% ceria after sintering at different temperatures. M, mullite; B, m-$Zr0_2$; T, t-$Zr0_2$; Z ,zircon ;A, α-Al_2O_3 , P, cerium pyrosilicate.

The crystalline phase content of sintered compacts prepared from different initial mixtures was quantitatively evaluated by XRD using the Rietveld method for sintering temperatures ranging between 1400 and 1600 ºC. The conversion to mullite and zirconia was estimated from these data and considering the complete reaction of amounts of reactants added. Figures 2 - 4 show the variation of conversion to mullite and zirconia of the composites with sintering temperatures for the different ceria content. Conversion of reaction products increased with temperature: up to 1400 ºC the extent of reaction was very low, a significant progress of the reaction was observed in compacts sintered at 1450-1500 ºC and a slow increase in conversion resulted at 1550-1600 ºC. Mixtures with ceria exhibited a low temperature end of the curve which is associated with the beginning of zircon thermal dissociation. The ceria doping reduced the temperature at which ZrO_2 conversion attained a nearly constant value because zircon decomposition process was nearly complete. Thus, the zirconia conversion was total, particularly for 9-15 mol% ceria at 1450-1500 ºC, before the mullite transformation finished. Sample compositions at the maximum temperature were similar .

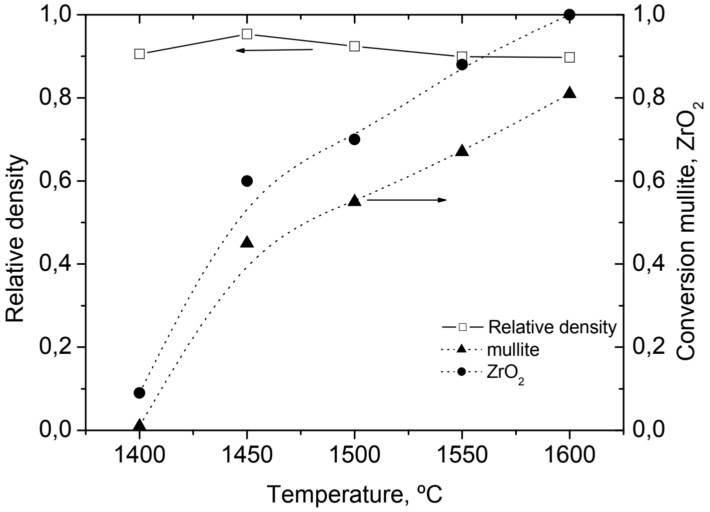

Figure 2: Relative density of slip cast prepared using 5% mol ceria composition – mullite, zirconia conversion versus sintering temperatures. Conversion equal 1 gives the value of complete mullite or zirconia formation.

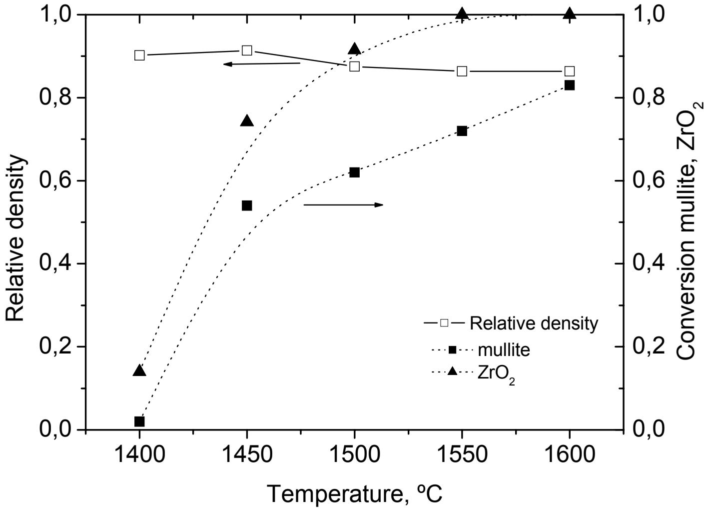

Figure 3: Relative density of slip cast prepared using 9 %mol ceria composition – mullite , zirconia conversion versus sintering temperatures. Conversion equal 1 gives the value of complete mullite or zirconia formation.

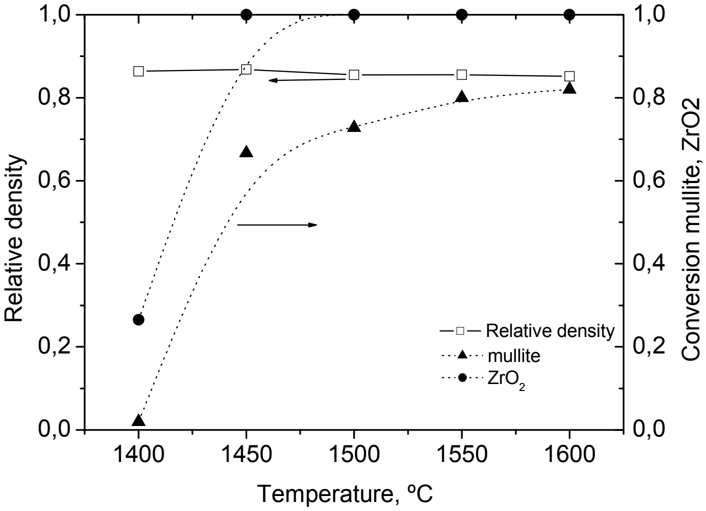

Figure 4: Relative density of slip cast prepared using 15 %mol ceria composition – mullite , zirconia conversion versus sintering temperatures. Conversion equal 1 gives the value of complete mullite or zirconia formation.

Density

Relative density (using the theoretical density calculated according to the Rietveld data) of sintered compacts as a function of sintering temperatures are also shown in Figures 2-4 for different ceria content used. Density–sintering temperature dependence followed a similar behavior for the three starting compositions. Densification of compacts exhibited a maximum which shifted to lower temperature with increasing ceria addition, and then, density slightly reduced with further increase in temperature. Highly densificated compacts resulted by sintering at 1400-1450 ºC as compared with those without additive. Contrarily, compacts with ceria sintered at 1550 and 1600 ºC showed a gradual reduction in density which is the opposite tendency obtained for mixtures without doping from which a nearly dense material resulted at temperatures higher that 1500 ºC.

Microstructure of composites and transformability of m to t-ZrO_2

The effect of sintering temperature on microstructure for the composition containing 5 mol% ceria is showed in Figure 5. The microstructure of composites sintered at 1400 ºC (Figure 5a) consists in a nearly dense material with uniform distribution of zircon and alumina phases (as light and dark grey areas, respectively). Both grains appeared diffuse and interconnected due to the relatively low sintering temperature. Sintering at

1500 ºC produced important changes in the microstructure (Figure 5 b) that agreed well with changes in phase composition determined by XRD . Dense matrix was composed by mullite, as grey grains, in which alumina and large zircon grains (black and dark grey, respectively) remained homogeneously distributed. Zirconia particles (white grains) appeared dispersed as very fine grains with rounded morphology. Most of ZrO_2 (intergranular) was located in the boundary region of zircon grains. Zirconia grains were rounded and isolated and appeared to have a larger average size with increasing temperature to 1600 ºC. A rounded grain morphology for zirconia was attributed to growing in a non crystalline matrix (3,6,8), whereas an elongated mullite crystals predominates in the presence of a liquid phase. Microstructures of samples sintered at 1600 ºC was characterized by rounded ZrO_2 grains (light) uniformly distributed in a dark mullite matrix. S.E.M micrographs revealed that similar microstructural evolution, except for grain size, for the other compositions was caused by increasing temperature. S.E.M. micrographs of 15 mol% CeO_2 composite (Figure 6) show the increase in zirconia grain size occurred at elevated temperatures and the anisotropic growth of mullite crystals.

The average grain sizes were approximately doubled by the addition of 5 to 15 mol% ceria regardless of sintering temperature.

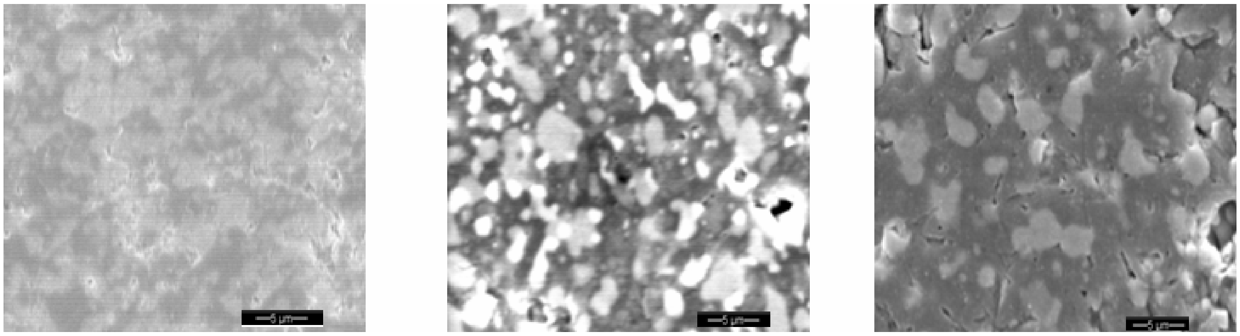

Figure 5: S.E.M. microstructure of slip casts prepared using 5 mol% CeO_2 in starting composition and sintered at different temperatures, 2 h (scale bar = 5 µm), (a) 1400ºC, (b) 1500ºC, (c) 1600ºC

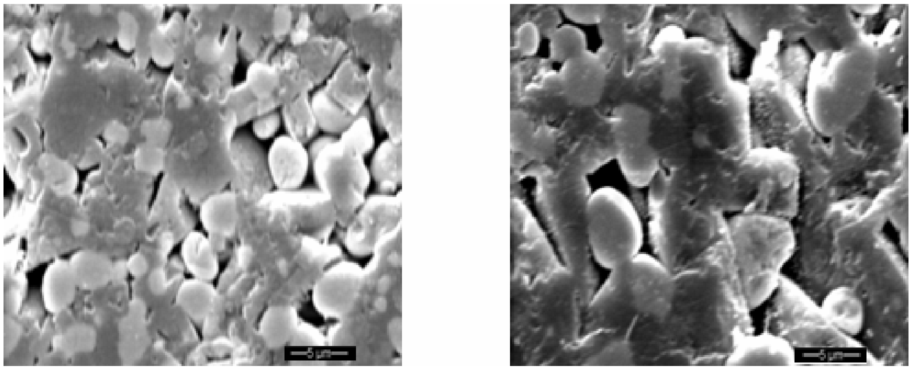

Figure 6: S.E.M. micrographs of 15 mol% CeO_2 composite showing the increase in grain size occurred at elevated temperatures (scale bar = 5 μm), (a) sintered at 1500 ºC ; (b) 1600 ºC, 2h.

The relative proportion of t-ZrO_2 with respect to total ZrO_2 content of compacts with the different ceria addition was determined using the Rietveld method for the sintering temperatures studied. Despite of the different the matrix-composition and structure observed for the resultant composites, m-ZrO_2 was the dominant ZrO_2 phase (see Figure 1). Retention of tetragonal zirconia slightly increased from proper sintering temperature. According to microstructure showed in Figure 6, instability of tetragonal grains by sintering at 1600ºC cannot be avoided probably due to the significant ZrO_2 grain coarsening observed.

CONCLUSIONS

The use of ceria as additive caused a strong influence on the high temperature properties of mullite zirconia composites due to the formation of glassy phase.

Slip cast compacts produced from mixtures even with 5 mol% ceria addition and sintered at the relatively low temperatures exhibited high densification (near to 95%TD). The presence of a liquid phase that developed from the mixture containing ceria during the heating process caused the strong reduction in porosity. Consequently, the relative density was higher than those materials produced from the stoichiometric mixture. However, further temperature increase to 1600ºC was detrimental for densification of composites which exhibited similar composition but higher porosity and significant grain coarsening than those conventionally prepared without doping.

The extent of high temperature reactions between alumina and zircon with different ceria content was enhanced particularly over a temperature range of 1450-1500 ºC.

REFERENCES

1. CAMBIER, F.; BAUDIN DE LA LASTRA, C.; PILATE, P.; LERICHE, A. Formation of microstructural defects in mullite-zirconia and mullite-alumina-zirconia composites obtained by reaction-sintering of mixed powders. ***Br. Ceram. Trans. J.*** v. 83, p. 196-200, 1984.
2. DESCAMPS, P.; SAKAGUCHI, S.; POORTEMAN, M.; CAMBIER, F. High-temperature characterization of reaction-sintered mullite–zirconia composites. ***J. Am. Ceram. Soc.,*** v. 74, p. 2476-2481,1991,.
3. WALLACE, J. S.; PETZOW, G.; CLAUSSEN, N. Microstructure and Property Development of In situ-Reacted Mullite-Zirconia Composite. In: Claussen, N.; Ruhle, M.; Heuer, A.H. (Eds.), ***Advances in Ceramics v. 12: science and technology of zirconia II,*** Westerville, OH,The Am. Ceram. Soc.,1984, p. 436-442.
4. ZHAO, S.; HUANG, Y.; WANG, CH.; HUANG, X.; GU, J. Mullite formation from reaction sintering of $ZrSiO_4$/α-Al_2O_3 mixtures. ***Mat. Lett.***, v. 57, p.1716-1722, 2003
5. BRADECKI, A.; JONAS, S. Investigation of high-temperature reactions within the $ZrSiO_4$–Al_2O_3 system. ***Ceram. Inter***. v.36, p. 211–214, 2010.
6. EBADZADEH, T.; GHASEMI, E. Influence of starting materials on the reaction sintering of mullite–ZrO_2 composite. ***Mat. Sci. Eng. A,*** v. 283, p. 289–297, 2000.
7. WEN-CHENG, J.; WEI, H.; KAO, C.; LO, M.H. Phase Transformation and Grain Coarsening of Zirconia/Mullite Composites. ***J. Eur. Ceram. Soc.***, v.16, p. 239-247, 1996.
8. DAS, K. ; DAS, S.K.; MUKHERJEE, B. ; BARNERJEE, G. Microstructural and mechanical properties of...mullite-zirconia composites with magnesia as additive. ***Interceram,*** v.47, p. 304-308, 1998.
9. DAS, K.; BANERJEE, G., Mechanical properties and microstructures of reaction sintered mullite–zirconia composites in the presence of an additive—dysprosia. ***J. Eur. Ceram. Soc.*** v.20, p. 153-159 , 2000.
10. TAS, A.; AKINC, M.; Phase Relations in the System Al_2O_3─$Ce_2Si_2O_7$ in ***J. Am. Ceram. Soc.,*** v. 76, p. 1595-1601, 1993.