CA STABILIZED ZIRCONIA BASED COMPOSITES BY WET CONSOLIDATION OF ZIRCONIA AND HIGH ALUMINA CEMENT MIXTURES.

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ABSTRACT

Composites of the CaO–Al₂O₃–ZrO₂ system are widely used in many industrial applications. In this study, porous Ca stabilized ZrO_2 composites were developed from a starting mixture of m-ZrO₂ and calcium aluminate cement. Ceramics were produced by wet consolidation of aqueous suspensions with and without corn starch as pore former agent and sintering at 1000-1500 °C. The influence of processing parameters on crystalline phases, sintering behavior and textural characteristics was examined. Stabilized c-ZrO₂ formed with the composition of Ca_{0.15}Zr_{0.85}O_{1.85}. The sintering of the mixtures lead to porous composites materials. Textural properties were analyzed considering the initial composition and the present crystalline phases.

Key-words: processing, porous composites, ZrO₂, calcium aluminate cement.

INTRODUCTION

The use of Ca ion to stabilize ZrO_2 is well known. Generally, ZrO_2 and calcia powders by solid state reaction at high temperature are widely used. Milling and solid state process, co precipitation, hydrothermal treatment ,sol gel are very effective methods to produce Ca-ZrO₂ based composites ^(1,2).

Recently, various porous ZrO_2 ceramics were fabricated using a starting mixture of m-ZrO₂ containing different mole proportions of calcium aluminate cement HAC through a conventionally powder processing that consists in uniaxial pressing and reaction sintering at elevated temperature ⁽³⁾. The Ca stabilized ZrO_2 ceramics fabricated by this process have 40 vol% open porosity and pore sizes close to 1 µm. However, dry processing have limited possibilities on geometry of shaped

composites. Also, pore size of these ceramics nearly corresponds to the mean size of particles that were used. Thus, it depends on particle size distribution of the starting powders and therefore, to increase porous structure parameters a relatively coarse powder should be used.

The colloidal processing (i.e. dispersing the ceramic powder in a liquid) overcomes many of these disadvantages allowing the manufacture of components with complex shapes and fine microstructure. Moreover, strength and reliability of the final components are improved.

To ensure suitable porous materials for many industrial applications, several methods exist for increasing the porosity of the bodies. One method commonly employed to fabricate porous ceramics is to add fugitive particles to an initial ceramic mixture ⁽⁴⁾. In this case, the pore size and porosity can be easily controlled by varying the particle size and the volume ratio of fugitive agent /ceramic particles. Starch as pore former is effective to increase the pore volume, mean pore size and interconnectivity of porous structure of ceramics as was previously determined by mercury porosimetry. In this study, the effect of aqueous processing and incorporation of corn starch as fugitive additive on crystalline phases and sintering behavior as well as porous structure of HAC-ZrO₂ mixtures were examined.

EXPERIMENTAL

Materials and methods

Undoped commercial zirconia powder in monoclinic phase (m-ZrO₂, CZE, Saint-Gobain Zir Pro, Taiwan) was used in this study. The mean particle diameter and the specific surface area were 0.44 μ m and 5.6 m².g⁻¹, respectively.

The calcium aluminate cement HAC used is commercially known as SECAR71, the main constituents are AI_2O_3 and CaO, its approximate chemical composition (product data sheet) indicates CaO 26.6–29.2 wt% and AI_2O_3 69.8–72.2 wt%.

From these raw materials, two series of mixtures were prepared by addition of 15 and 30 mole % of CaO in ZrO_2 which are referred as ZrC15 and ZrC30, respectively.

Corn starch, commercially available in Argentina, was used as pore forming agent. The corn granule has a mean diameter of approximately 14 μ m. SEM examination indicated that corn granules were nearly spherical or pentagonal.

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Suspension preparation and consolidation

The powders were dispersed in water to produce 46-71 wt% suspensions with solid volume fractions varying between 0.17 to 0.32 and 0.2 to 0.32 for 15 and 30 mol% CaO respectively. An anionic polyelectrolyte (Dolapix, Zschimmers and Schwartz) was used to regulate the flow behavior. Then, an ultrasonic treatment to suspensions was applied by few minutes.

Subsequently, the adequate amount of starch was added to the suspension of ZrO_2 -HAC and mixed by hand followed by ultrasonication for 1 minute. Suspensions resulted with solid volume fractions ranging from 0.25-0.42 and 0.23 to 0.40.

After ultrasonication, the resultant suspension was poured into a cylindrical plastic container which was in contact with a plaster plate. The resultant compacts were dried at room temperature and then at 100 °C. Sintering was performed at a heating rate of 5°C / min and temperatures of 1000-1500°C for 2h.

Characterization of green and sintered products

The HAC suspension (water to solids weight ratio 0.8 using ultrasonication) and various dried casts containing 15 and 30 mol% CaO dried at room temperature and then at 100 °C were powdered and also analyzed by differential (DTA) and thermal gravimetric (TG) analysis (Model STA 409, Netzsch Inc., Germany) at a heating rate of 10 °C/min .

X-ray diffraction analysis (XRD) was carried out using a Philips diffractometer model PW3020 with radiation Cu-K α and Ni filter in the region °2 θ = 10-80 °. The relative proportion of m-ZrO₂ phase was determined semi quantitatively from the XRD diagrams using the method of Garvie and Nicholson⁽⁵⁾ for mixtures of stabilized zirconia and monoclinic.

The density of dried and sintered compacts was measured by Hg immersion. Density values of 5.95, 5.56, 2.93 and 1.43 $g.cm^{-3}$ for $m-ZrO_2$, c- ZrO_2 , HAC and starch, respectively were used to calculate the theoretical density of composites.

The textural properties of the sintered product was determined by the Hg porosimetry.

RESULTS AND DISCUSSION

Properties of dried casts

Phases and hydrated products of HAC: XRD and DTA-TG

XRD diffraction patterns of the HAC suspensions dried at 100 °C and those of the ZrO₂-HAC mixes are show in Figure 1. The diffractogram of the dried HAC suspension confirmed that the calcium aluminates CA (°2θ=30.14) and CA2 (CaAl₄O₇, ° 2θ = 25.5) were the major constituents. Also, the main reflections in the 17-21 °2θ region distinguished the development of C₃AH₆ and Al Hydroxides (gibbsite). These peaks appeared in the respective diagrams of the two compositions studied but with considerable low intensity.





Figure 1: XRD of dried HAC suspensions of commercial HAC and mixtures with ZrO2 , where X :CA2, , :m-ZrO2, M :CA, \blacktriangle :Hydrates, Λ :Al Hydroxide

Figure: 2. ATD-TG of dried HAC suspension (ultrasonicated by few minutes).

Thermal decomposition of the commercial HAC (Figure 2) and that of various HAC suspension dried at 100 °C were examined. The TG of the dried samples could be mainly divided in four steps ⁽⁶⁾.

The initial weight loss up to 200 °C indicated the low content of adsorbed water, CAH_{10} , C_2AH_8 and AI gel which decompose below 175-200 °C. DTA curve showed the corresponding endothermic peak centered at 130 °C. This agreed well with the presence of C3AH6 and crystalline AI hydroxides as determined by XRD.

Secondly, an important weight loss of 6.9 wt% was observed from 200 to 350 $^{\circ}$ C. This is related with the strong endothermic peak centered at 327 $^{\circ}$ C in the DTA curve due to the elimination of crystallization water of the C3AH6 and the transformation of Al hydroxide to Al₂O₃.

The third step from 350 up to 550 °C corresponded to a gradual weight loss of 0.9 wt% due to the loss of the rest of crystallization water of the C_3AH_6 and the formation of transition alumina from AI hydroxides. This is associated to a weak/ broad endothermic peak at 516 °C as well as with the formation of CaO from CaOH at 440°C.

Finally, the weight loss of 2.9 wt% in a range of 550 to 800°C occurred with the presence of a broad endothermic peak near to 780°C. The Ca12A7 formation from reactive alumina and CaO takes place around 600°C. The wide exothermic band at 950°C may be assigned to CA formation between $C_{12}A_7$ and alumina. The CA was detected by XRD analysis in our samples sintered at 1000°C as will be mentioned below. The CA is instable and reacts with alumina to form CA₂ above 1080 °C; CA₂ presence was confirmed in samples sintered at 1300 °C and higher temperatures. CA₆ did not appear in our samples.

HAC in dried composites showed a similar decomposition behavior.

Sintering

The crystalline phases present in sintered composites was analyzed by XRD. Reaction did not start at 1000° C, m-ZrO₂ remained accompanied with minor amounts of CA and CA₂; both are the main phase constituents of the high alumina cement and therefore CA2 increased in the composition with 30 mole % CaO.

The relative intensity of c-ZrO₂ peaks increased when sintering temperature was above 1300°C. For ZC30 the relative content of Ca stabilized ZrO₂ appreciably increased as compared with ZC15 due to the higher content of cement and hence of CaO in the starting composition. The diffusion of calcium from CaO phases of high alumina cement promoted the m \rightarrow c-ZrO₂ phase transformation with stabilization of a Ca solid solution (cubic, Ca_{0.15}Zr_{0.85}O_{1.85}). For the two compositions, the stabilization of the cubic phase was partial and the monoclinic phase predominated. The main reflections of CA₂ slightly increased while the absence of CA indicated the formation of CA₂ by reaction of CA with alumina above 1000°C.

For ZC15 composites sintered at 1400 °C, c-ZrO₂ was the predominant phase but a significant m-ZrO₂ remained unreacted. For ZC30 the transformation of m to c-ZrO₂ was nearly completed as scarce m-ZrO₂ was detected. Then, c-ZrO₂ and CA2 were the major constituents of composites with 30 mole % CaO. Since the reaction took place mainly through a solid state mechanism, the increase of HAC content in the powder composition (causing an increase in surface area) favored the reaction between ZrO_2 and Ca ions.

Sintering at 1500 °C, lead to minor compositional changes for both samples. For ZC15 the relative intensity and crystallinity of c-ZrO₂ slightly increased.

Figure 3 shows the evolution of the relative $c-ZrO_2$ content with sintering temperature for ZrC15 and ZrC30 samples. The relative $c-ZrO_2$ content of the ZrC15 composite sintered between 1300 and 1400 °C ranged between 5 and 30%, respectively while that of the ZrC30 increased from 6 to 84%. The maximum $c-ZrO_2$ content at 1500°C attained 56 % for the ZrC15 and total transformation resulted for ZrC30.



Figure 3: The relative c-ZrO₂ content vs. sintering temperature for ceramics containing 15 and 30 mol %CaO in ZrO_2

Figures 4 and 5 show the evolution of porosity with sintering temperature for ZC15 and ZC30 composites produced from mixed suspensions containing different solid contents (46 to 71 wt%). Similar sintering behavior was observed for the two compositions studied; an important reduction in the porosity was found up to 1400 °C followed by a lesser reduction with further increasing of the sintering temperature. Porosity at 1500 °C remained near to 10 and 6 % for ZC15 and ZC30, respectively. Previous study of sintering behavior of YSZ samples indicated that nearly dense compacts (98% TD) could be achieved at 1400 °C.

The low solid volume fraction suspension caused slightly higher porosity in the matrix. Moreover low cement in the composition lead to higher reduction in densification. The high water to cement ratio favored the formation of hydration products of HAC and their thermal decomposition during sintering (water loss) promoted the development of pores causing the small increase in porosity.

The sintering shrinkage of the composites at a given temperature could be directly related to the solid content of suspensions. Suspensions with low solid content gave comparatively high shrinkage attaining near to 50 vol% at 1500 °C for ZC15 and up to 56 vol% for ZC30. The higher water to cement ratio for the composites which increase cement hydration reduced the solid packing density within the matrix, thereby increasing the sintering shrinkage.





Figure 4: Porosity of ceramics with 15 mol %CaO in ZrO_2 vs. sintering temperatures for different solid content (closed symbols indicates using corn starch as pore former)

Figure 5: Porosity of ceramics with 30 mol % CaO in ZrO_2 vs. sintering temperatures for different solid content (closed symbols indicates using corn starch as pore former)

Effect of the starch addition on sintering behaviour and texture of composites

Figures 4 and 5 also show that porosity significantly increased when starch as pore former agent was added to the starting composition. In this case, the volume fraction of starch in the dried body Xst ranged between 0.185 to 0.205 for ZC15 and resulted close to 0.17 and 0.19 for ZC30 composites. Lower Xst than that the expected from volume fraction of added starch was obtained due to the increase in

the volume of the dried compact by formation of hydrated products of HAC and porosity.

Figure 6 shows the experimental porosity of composites produced using starch and the value theoretically predicted from the sum of porosity of sintered samples without starch and Xst. In this case, the increase in porosity by starch addition achieved a nearly constant value of 0.18-0.2

Total porosity followed a linear increase with respect to ceramics produced without starch as predicted by the Xst that was in agreement with results previously reported using several organic inclusions as fugitive pore former ^{(7).}





Figure 6: Total porosity vs predicted value for porous samples produced from suspensions with different solid volume content

Figure 7: Cumulative Hg porosimetry curves of ceramics with 15 and 30 mol % CaO in ZrO₂ (closed symbols indicates with corn starch addition)

Starch granules as pore former agent create pore with sizes considerably larger than the interparticle voids between ceramic particles of the matrix. Therefore, porosity originated by such large pores remains constant during sintering. When the ceramic matrix achieved the complete densification (that is, no interstitial pores exist between ceramic particles) pore volume is identical to the volume fraction of starch in the dried product ⁽⁸⁾.

The effect of corn starch addition on textural properties of the composites sintered at 1400°C was examined by Hg intrusion measurements. Fig. 7 shows that maximum pore volume increased with starch addition from 28-40 to 125- 150 mm³ Hg /g for ZC15 and ZC30, respectively. Thus, composites sintered at 1400 °C

exhibited a volume fraction of open porosity of 0.11- 0.13 indicating that most of pores (70 %) remained open.

CaO in ZrO ₂ mol %	Apparent density g.cm- ³	Open Porosity	OP/TP	Dp
15	4.10	0.11	0.73	0.6
15-starch	3.00	0.37	0.99	2.8
30	3.40	0.13	0.68	1
30-starch	2.60	0.39	1	3

Table 1 Textural characteristics of composites sintered at 1400°C. OP/TP: open to total porosity , Dp: mean pore diameter, μm

Composites processed using starch had open porosity of 0.37-0.39 with open to total porosity ratio near to 1 indicating the total interconnection between pores. A similar effect of starch on pore size was observed. The most frequent pore size increased from 0.6 to 2.8 μ m for ZC15 and from 1 to 3 μ m for the ZC30. Pore size distribution became narrower at high CaO content .

CONCLUSIONS

Porous Ca stabilized zirconia composites (68 and 48vol% of total ZrO_2) were developed by wet consolidation of aqueous suspensions of m-ZrO₂ and HAC mixtures. The CaO concentration and sintering temperature controlled the c-ZrO₂ transformation (cubic, Ca_{0.15}Zr_{0.85}O_{1.85}). For the ZrC15, the relative c-ZrO₂ content strongly increased attaining between 25 and 56% with increasing temperature from 1300 to 1500 °C while c-ZrO₂ completely formed for ZrC30. The composites sintered at 1400°C had moderate porosity (20 vol%) with typical pore size of 1µm. Such pore structure parameters were slightly affected by the solid content of suspensions (i.e. water to cement ratio) and the high cement addition.

Corn starch addition enhanced pore volume, mean pore size and interconnection between pores. The increase in porosity was close to that predicted for the starch content of the dried compact.

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