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Properties of CaO-ZrO₂ Based Composites

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Abstract

Composites of ZrO₂-CA₂ were sintered by the conventional technique at 1400° C from mixtures of m-ZrO₂ with different amounts of high alumina cement containing CaO. The effect of the change in the composition on some properties such as: density, porosity, size and volume of pores, hardness and elasticity modulus of the composites was analyzed. Young's modulus was determined experimentally by the technique of excitation by impulse and hardness was evaluated by the Vickers method. The main phases identified by XRD were m-ZrO₂, c-ZrO₂ (CaO_{0.15}Zr_{0.85}O_{1.85}) and CA₂ (CaAl₄O₇). An increase in the content of phase c-ZrO₂ (CaO stabilized zirconia) was observed with increasing aluminous cement content. The apparent density decreased whereas porosity and pore volume increased by increasing the content of CaO. Hardness and elasticity modulus showed a clear dependence on composition and porosity of the composites.

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1. Introduction

In the field of refractory composites based on ternary oxide systems, the compositions determined by the ZrO_2 - CaO - Al_2O_3 system were initially studied due to the optimal properties of its components against corrosive environments related to processes of the metallurgical industry (especially the process of casting of steel) (Murakami et al., 2000). However, the available information in the literature about this particular system at present is still limited.

Composites based on the mentioned system starting from a high alumina cement containing CaO and high purity zirconia (m - ZrO_2) as raw materials were developed in this work. The phase composition determined by the mixture of these components results from the reaction of stabilization of zirconia with CaO that leads to the formation of cubic zirconia (c - ZrO_2). The Ca stabilized ZrO_2 presents a substantial improvement of the mechanical properties and conductivity at high temperatures. Depending on the content of cement in the initial mixture, other phase presented was calcium dialuminate (CA_2). This compound, characterized by very low thermal expansion coefficient, was recently used to improve thermal shock resistance in certain refractory formulations (Jonas et al. 1996, 2006).

In this work, different mixtures were prepared from the above mentioned raw materials by varying the content of cement and then sintering at 1400 °C. The m - ZrO_2 has a finer particle size distribution than that used in a previous study (Bruni et al. 2012a) which may be advantageous to improve the sintering, i.e. to increase the degree of densification of the composites.

The dependence of the modulus of elasticity (E) and hardness (D) on the porosity (P) was examined by comparing the experimental data with the properties calculated using a general theoretical model cited in the literature (Baudín, 1987; Lee and Rainforth, 1994) that predicts an exponential decay of these properties with the pore volume fraction (Eqs. 1 and 2)

$$(1) \quad E = E_0 e^{-5P}$$

$$(2) \quad D = D_0 e^{-5P}$$

where E_0 and D_0 are the elasticity modulus and hardness at zero porosity, respectively.

2. Experimental

2.1. Materials and preparation of composites

The composites were prepared from several mixtures of commercial m - ZrO_2 (Saint Gobain, France) and high alumina cement (Secar 71, Kerneos, France) which was composed by 68 wt% of Al_2O_3 and 30 wt% of CaO , the proportion of cement was varied to get composites containing 5, 15, 30 and 50 mol% of CaO in ZrO_2 . The particle size distribution of zirconia used as starting material presented an average particle size of 0.44 μm . In contrast, the high alumina cement (coarser powder) shows a wider particle size distribution containing particles of variable sizes between 1 and 63 μm with an average particle size of 13 μm (Braulio et al., 2011). The mineralogical composition of the Secar 71, which was verified by XRD, consists mainly of calcium monoaluminate $CaAl_2O_4$ (CA , containing 35.4 wt% CaO and 64.6 wt% Al_2O_3) which is also the active phase in the majority of refractory cements. The secondary phase present is the calcium dialuminate $CaAl_4O_7$ (CA_2 , containing 21.7 wt% CaO and 78.3 wt% Al_2O_3) with scarce amounts of Al_2O_3 .

Ceramic discs of 3 cm in diameter and 0.5 cm thick were conformed from several mixtures of different composition by applying dry uniaxial pressing (20 MPa) and subsequent sintering in an electric furnace (Thermolyne) at 1400 °C for 2 h with a heating/cooling rate of 5 °C/min.

2.2. Characterization methods

The crystalline phases presented in the different ceramics were determined by X-ray diffraction (XRD) using a diffractometer Philips model PW3020 with Cu-K α radiation and Ni filter in the region of 2θ : 5-80 °. Based on the XRD patterns, the relative proportion of the m-ZrO₂ was semi-quantitatively evaluated using the method reported by Garvie and Nicholsson (1972) for mixtures of stabilized and m-ZrO₂. The estimation is based on the relation between the integrated areas of characteristic reflections of the ZrO₂ polymorphs in the range of 2θ from 27 to 33 °.

Apparent density and porosity were determined by immersion in mercury. Relative density (*RD*) was calculated as the ratio between the apparent and the theoretical density of each composite (Bruni et al. 2012 b). Total porosity (*P*) was calculated on the basis of the relative density (*RD*) according to the expression:

$$(3) \quad P=1-RD$$

Volume and average pore size were determined by mercury intrusion porosimetry using the Hg porosimeter (Carlo Erba 2000 , Italy). The dynamic elasticity modulus *E* of each composite was determined at room temperature by the technique of excitation by impulse using the Grindo Sonics MK5 (Lemmens, Belgium). The hardness was evaluated using the Vickers method according to ASTM C-1327 standard with a durometer Buehler. The indentation measurement was performed by applying a load of 0.5 Kgf and 1Kgf for 15 sec. and then, the hardness was estimated as an average of the measurements done.

3. Results and discussion

3.1. Effect of the content of cement on the phases formed and on stabilization of ZrO₂

Fig. 1 shows the XRD patterns for composites with 5 to 50 mol% of CaO in ZrO₂ sintered at 1400 ° C.

The composites of low cement (5 and 15 mol% CaO in ZrO₂) mainly contained m-ZrO₂ with small amount of c-ZrO₂ accompanied by calcium dialuminate (CA₂) a constituent phase of the cement used. The CaAl₂O₄ (CA) (initially presented in the cement) or free alumina were not detected, indicating that both have reacted. Thus, the scarce amounts of CA₂ and low formation of c-ZrO₂ may be explained by the low proportion of cement in these composites.

Stabilization of c-ZrO₂ was based on the reaction in solid state between CaO (resulting from the thermal decomposition of the calcium aluminates of cement) and the m-ZrO₂. The effect of the change in composition determined a higher content of c-ZrO₂ in the samples with 15 mol% of CaO in ZrO₂ in comparison with the composite with 5 mol% CaO.

For composites with 30 and 50 mol% CaO in ZrO₂ , the high cement addition caused a consistent increase in the amount of CA₂ and a marked decrease in the residual m-ZrO₂ due to the significant formation of c-ZrO₂. For the composite with 50 mol% , the CA₂ constituted the major phase followed by c-ZrO₂ and scarce amounts of m-ZrO₂. Moreover, in this case, an additional formation of small content of CaZrO₃ was detected. This compound also developed as a product of the reaction between CaO and the m-ZrO₂ and therefore, the presence of high content of cement as a source of CaO favored its formation.

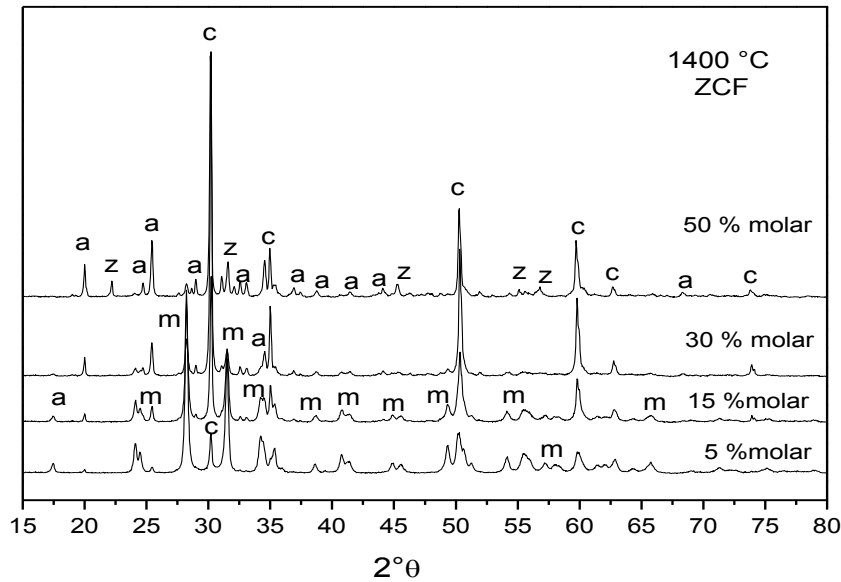


Fig. 1. XRD of the different composites sintered at 1400 °C where a: CA_2 , c: c-ZrO_2 , m: m-ZrO_2 , and z: CaZrO_3

On the other hand, the formation of c-ZrO_2 resulting from a diffusion process depended strongly on the concentration of CaO and sintering temperature. At 1400 °C the diffusion processes involved in this reaction were sufficiently activated at this temperature (Michel et al. 1993), and therefore, its formation was mainly controlled by the availability of the reactant (i.e. the concentration of CaO).

The relative proportion of c-ZrO_2 was determined using the method of Garvie and Nicholson, 1972. In the composites with 5 to 15 mol% of CaO in ZrO_2 the relative proportion to c-ZrO_2 with respect to total ZrO_2 was 9.6 and 39.5%, respectively. In the case of the composites with 30 and 50 mol% of CaO in ZrO_2 , the stabilization of c-ZrO_2 attained approximately 80% and this increase clearly resulted from the combined effect of the high addition of CaO and the effectiveness of the thermal treatment at 1400 °C to enhance the diffusion processes involved in the reaction of stabilization.

Moreover, the final phase compositions of the different ceramics, as determined by XRD, corresponded well to those obtained from the equilibrium phase diagram of the ZrO_2 -CaO- Al_2O_3 system at 1380 °C reported by Muromura and Hinatsu (1986).

3.2. Microstructure

Fig. 2 shows SEM micrographs of the composites with 5 and 30 mol % of CaO sintered at 1400 °C.

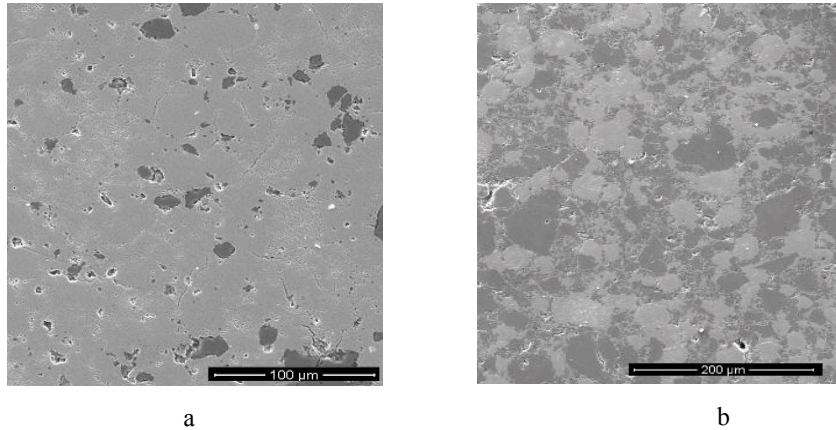


Fig. 2. SEM micrographs showing the microstructure of the composites (a) 5 mol% and (b) 30 mol%CaO.

For the composite with 5 mol% CaO, the predominance of m-ZrO₂ was reflected in the microstructure configuration which was characterized by a dense matrix of fine grained ZrO₂ (light areas) containing a small amount of dispersed CA₂ grains (dark gray areas) .

The composite with 30 mol% of CaO exhibited a change in the microstructure in relation to that corresponding to the low CaO concentration, as the high cement addition provided a high amount of CA₂. In this microstructure, large CA₂ grains appeared interconnected with grains of c-ZrO₂ (along with small amount of grains of m-ZrO₂). It also noted higher porosity in the 30 mol% composite.

3.3. Linear shrinkage and densification

Table 1 shows physical properties of the different composites sintered at 1400 °C .

Table 1. Linear shrinkage and density of different composites sintered at 1400 °C

Properties	Compositions (CaO in ZrO ₂ , Mol%)			
	5	15	30	50
Linear Shrinkage (%)	19	16	12	9
Apparent Density (g/cm ³)	4.9	4.2	3.4	2.8
Density (g/cm ³)	5.58	4.98	4.34	3.72
Relative density	0.89	0.85	0.81	0.76

Linear shrinkage decreased from 19 to 9 with increasing cement content. At high cement contents a reduction in apparent density occurred but this variation resulted more evident with 30 mol% CaO in the composition due to the presence of more CA₂.

The effect of the presence of CA₂ on the reduction in density may be explained by its comparatively low theoretical density (3.1 g/cm³) in relation to that of zirconia (6-5.6 g/cm³) (Bruni et al. 2012b). Moreover, the coarser and wider particle size distribution of cement with the largest grain size determined a lower efficiency of particle packing than that existing when increase the fraction of m-ZrO₂. The fine ZrO₂ filled interstices between particles and also promoted sintering.

Moreover, the variation of the relative density of the composites with increasing cement addition was clearly observed in Table 1. For composite with 5 mol% CaO (with m-ZrO₂ as principal component) the relative density attained 0.89 and then, a further increase in CaO concentration to 50 mol% (with CA₂ as the major phase) produced a significant reduction in density to 0.76, indicating a different degree of sintering. The densification of

finer zirconia particles became more effective in comparison to densification of the coarser CA_2 phase, as the driving force for sintering strongly depends on the reduction of surface area of powders.

Table 2 shows the textural properties of the composites studied.

Table 2. Textural properties of the composites

Properties	Compositions (CaO in ZrO ₂ , Mol %)			
	5	15	30	50
Pore volume (mm ³ /g)	2.82	15.74	38.4	73.72
Mean pore size (µm)	0.015	0.41	0.78	1.75
Open porosity (%)	2.3	6.2	8.3	17.5
Total porosity (%)	11	16.5	21.5	25

The increase in the content of cement from 5 to 50 mol% produced, as expected, a high pore volume ranging between 2.82 and 73.72 mm³/g. Moreover, the mean pore size showed the same tendency increasing significantly from 0.015 to 1.75 µm . Porosity increased from 11 to 25% whereas open porosity varied from 2.3 to 17.5%. Minimum pore volume and average pore size as well as the low open to total porosity ratio corresponded to the composite with 5 molar of CaO consisting mainly of ZrO₂. In this case, the SEM microstructure clearly shows the continuous ZrO₂ phase forming a highly dense matrix. The extended contact between individual particles was caused by sintering at 1400 °C. Contrarily, high increase in volume and average pore size notably developed for composites produced from 50 mol% CaO (containing CA_2 as the main phase), as well as higher open to total porosity ratio, which may be explained by the combined effect of both the composition and the different particle size on the different degree of sintering.

3.4. Elasticity modulus and hardness

The modulus of elasticity at zero porosity (E_0) of the different composites was calculated using the rule of phases knowing the volume fraction of each phase in accordance with the final phase composition determined by XRD and its individual E_0 reported in literature (Bruni et al., 2012a). Then, the theoretical modulus of elasticity for each composite was estimated using eq. (1) from porosity values of Table 1.

The E_0 of different composites decreased from 192 to 153 GPa with increasing the proportion of CaO, as a result of the increase in CA_2 which has the lower E_0 in comparison to the other phases present. The experimental E of the composites measured by the dynamic method reduced from 114 to 40 GPa for 5 to 50 mol% of CaO, respectively and showed a significant dependence on the composition.

Fig. 3 shows the variation of the E/E_0 ratio of the composites with porosity for both experimental E and theoretical value estimated by eq. (1).

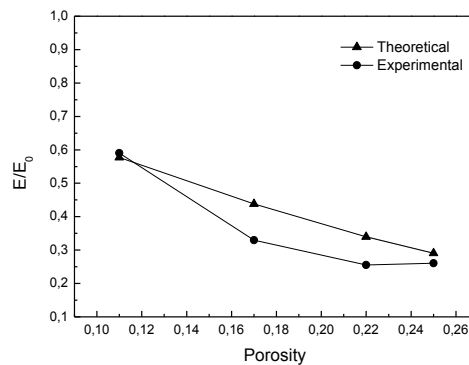


Fig. 3. Modulus of elasticity on experimental and theoretical vs. porosity.

There was a satisfactory agreement between the experimental and theoretical the E/E_0 values, indicating an exponential decay of the elasticity modulus with increasing porosity between 11 and 25 %. The deviation between experimental and theoretical values ranged from 2 to 25 % depending on the composition indicating that the fitting was more adequate for the composites with 5 and 50 mol% of CaO.

On the other hand, the remarkable difference between elastic moduli E of 114 and 40 GPa for samples with 5 and 50 mol% CaO respectively, may be explained by the increase in porosity (10 and 25% ,respectively) and the change in phase composition containing mainly $m\text{-ZrO}_2$ (E_0 : 200 GPa) and CA_2 (E_0 : 124 GPa), respectively. In addition both composites showed marked differences in volume and size of pores and open porosity, as shown in Table 2.

The elasticity modulus of composites developed in the present work were higher than the E values ranging between 6 and 37 GPa for ceramics of identical compositions but prepared from a coarser $m\text{-ZrO}_2$ (d_{50} : 8 μm) previously reported (Bruni et al. 2012a). The use of the $m\text{-ZrO}_2$ with submicrometer particle size (d_{50} : 0.4 μm) improved of the sintering process and enhanced densification at 1400 ° C.

Table 3 shows the Vicker's hardness of the different samples, except for the composite with 50 mol% CaO because of the high pore volume and open porosity prevented the evaluation. According to bibliographic data, the hardness at zero porosity (D_0) of the individual phases are: 10 GPa for $m\text{-ZrO}_2$ (Gritzner and Steger, 1993) , 11 GPa for the CA_2 (Asmi and Low,1998) and 12 GPa for $c\text{-ZrO}_2$ (Nath et col., 2008) .

The relative hardness D/D_0 experimentally determined was similar to the value theoretically calculated using Eq. (2) that predicts an exponential decay of the hardness with increasing pore volume fraction.

The hardness of composites with 5 and 15 mol% CaO approximated to 6 GPa, while hardness of the sintered sample with 30 mol% CaO reduced due to its higher porosity.

Table 3. Hardness of the composites measured by Vickers method and theoretically evaluated.

CaO in ZrO_2 Mol %	D_0 (by rule of phases) GPa	D (Vickers) GPa	Experimental (D/ D_0)	Theoretical (D/ D_0)
5	10.33	$5.9 \pm 0.26^*$	0.57	0.58
15	10.76	$5.7 \pm 0.52^*$	0.53	0.44
30	10.78	$3.8 \pm 0.34^*$	0.35	0.34

* standard deviation

4. Conclusions.

Composites of the ZrO_2 -CaO- Al_2O_3 system were developed from a mixture of $m\text{-ZrO}_2$ and a variable proportion of high alumina cement containing CaO by conventional sintering at 1400 °C. The effect of the change in composition on the microstructure, texture and mechanical properties such as hardness and modulus of elasticity was examined . Total and open porosity and mean pore size increased with increasing cement content due to the coarser particle size and the high presence of CA_2 which has low density in relation to zirconia. The decrease of the elasticity module and hardness may be explained by the same effects. The variation of such mechanical properties with porosity was satisfactorily described with an exponential decay model.

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