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Procedia Materials Science 8 (2015) 172 – 179

**Procedia**  
Materials Science[www.elsevier.com/locate/procedia](http://www.elsevier.com/locate/procedia)International Congress of Science and Technology of Metallurgy and Materials, SAM -  
CONAMET 2013

## Effect of Impurities and Sintering Temperature on Properties of MgO-CaZrO<sub>3</sub> Ceramics

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### Abstract

CaZrO<sub>3</sub>-MgO ceramics are useful as refractories in kilns for the cement production. The widely used method of manufacture of such ceramics is by sintering from m-ZrO<sub>2</sub> and dolomite MgCa(CO<sub>3</sub>)<sub>2</sub> mixtures. In this work, electrofused m-ZrO<sub>2</sub> grains (fraction <M 325) and two Argentinean dolomites with different mineralogical compositions were used as raw materials. Ceramics were obtained by the conventional powder method of uniaxial pressing of such mixtures followed by sintering at 1400 to 1680 °C. The influence of the different mineralogy of the dolomites and sintering temperatures on the properties of the composites was investigated. Ceramics had porosity of 20-30 %, the representative microstructure as determined using SEM-EDX was constituted by CaZrO<sub>3</sub> agglomerates of variable size (~100 μm), MgO grains (size < 50 μm) containing some unreacted m-ZrO<sub>2</sub> grains. The elastic modulus and flexural strength of the ceramics were correlated with the presence of impurities of the dolomite, porosity and microstructure.

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Selection and peer-review under responsibility of the scientific committee of SAM - CONAMET 2013

*Keywords:* Dolomite; Zirconia; impurities.

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## 1. Introduction

The effect of addition of m-ZrO<sub>2</sub> to improve the thermal shock resistance of dolomite refractories have been studied previously (Serena et al. 2004). The incorporation of m-ZrO<sub>2</sub> grains improves the thermo-mechanical behavior of these refractory materials (i.e. thermal shock resistance TSR, hot mechanical strength, etc.). The enhancement of these properties is mainly due to the formation of CaZrO<sub>3</sub> in MgO based ceramic. Microcracks can be developed around the CaZrO<sub>3</sub> grains as the reaction resulting from the diffusion of Ca ion in ZrO<sub>2</sub> is expansive. Also, microcracks can occur due to the important difference between the thermal expansion coefficients of the constituent phases (i.e. MgO with  $13.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  and CaZrO<sub>3</sub> with  $5-6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  from 25 to 1000 °C) upon cooling from the sintering temperature. Moreover, the CaZrO<sub>3</sub> is also resistant to corrosion by clinker. Other alternatives to improve the performance of refractories containing dolomite are the addition of sintering aids like fluxes (LiF) or oxides (SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) to the starting composition.

In practice, the application of magnesite/ dolomite refractory products is required to give an adequate combination of high corrosion resistance by clinker /slag with good TSR and mechanical properties at the use temperature. The presence of impurities in natural dolomite controls the formation of compounds with low melting point and decreases the temperature of use.

In this work, two natural dolomites from Argentinean deposits (called DB and DN) are used as raw materials for the preparation of CaZrO<sub>3</sub>-MgO composites. DB dolomite is chemically purer than the DN (1.56 and 5 wt% of impurities content, respectively), in the latter the percentage of SiO<sub>2</sub> is the double and that of R<sub>2</sub>O<sub>3</sub> oxides (Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>) exceeds the ten-fold increase. Therefore, the effect of the impurities of natural dolomites on sintering of the equimolar mixture with m-ZrO<sub>2</sub> and on the characteristics of resultant composites after sintering at temperatures ranging from 1400 to 1680°C was examined.

## 2. Experimental procedure

The CaZrO<sub>3</sub>/MgO composites were prepared from an equimolar (50:50 mol %) mixture of electrofused ZrO<sub>2</sub> and two natural samples of dolomite MgCa(CO<sub>3</sub>)<sub>2</sub>.

Electrofused ZrO<sub>2</sub> mainly consists of m-ZrO<sub>2</sub> (monoclinic phase) with a low proportion of t-ZrO<sub>2</sub>. The particle size distribution (Malvern, Mastersized 2000, UK) indicated a mean diameter  $d_{50}$  of 98.5 μm. The fraction of particles finer than 32.2 μm was 10 vol% of the sample, the same amount corresponded to sizes larger than 218 μm.

CaMg(CO<sub>3</sub>)<sub>2</sub> is the major constituent of dolomite DB with calcite as impurities, minor amount of plagioclase, and trace amounts of quartz.

Dolomite DN is composed predominantly by CaMg(CO<sub>3</sub>)<sub>2</sub> with quartz and plagioclase as secondary phases. The dolomite component of both samples showed almost stoichiometric proportions of CaCO<sub>3</sub> (50.5 and 49.0 % for DN and DB, respectively). Moreover, the dolomite DB shows a slight enrichment in Mg (i.e. relative Ca deficit) that can be explained by the presence of calcite in the native sample.

Equimolar mixture of the starting powders was homogenized in ethanol suspension. After evaporation of ethanol, the material was dried at 100 °C. Prismatic bars of 10 x 5 x 50 mm dimensions were produced by uniaxial pressing.

Sintering was performed in an electric furnace (Thermolyne model 46200) in a temperature range between 1400 and 1680°C for 2h at heating and cooling rates of 5°C/min.

The identification of the crystalline phases present in the sintered ceramic was made by X-ray Diffraction (XRD) on powdered samples using a diffractometer (Philips model PW3020) with Cu-Kα radiation and Ni filter in the region of  $2\theta = 10-80^\circ$ .

The apparent density of the ceramic was calculated from the weight and volume which was obtained geometrically. Relative density RD was calculated as the ratio between the apparent and theoretical density of the composite. The theoretical density was estimated from the density and the expected volume fraction of each phase present in the composite according to the reaction stoichiometry. Total porosity P was calculated as:  $P = 1 - RD$

The dynamic modulus of elasticity (E) of each composite was measured by the impulse excitation technique using a Grindo Sonic instrument (MK5 model, Lemmens, Belgium). The theoretical elastic modulus of the

composite was calculated using the rule of phases knowing the volume fraction and the elastic modulus at zero porosity  $E_0$  of each phase.

The flexural strength (3-point bending) of prismatic bars was measured with a span length of 35 mm and a speed of 1 mm/min (INSTRON universal testing machine). The microstructure was examined by SEM -EDS (FEI Quanta 200 MK2 Series) on polished surfaces.

### 3. Results and discussion

#### 3.1 Crystalline phases

Figs. 1 and 2 show the XRD patterns of the different m-ZrO<sub>2</sub> and dolomites mixtures after sintering at 1400-1680°C. Composites sintered at 1400 and 1500 °C were mainly composed of CaZrO<sub>3</sub> and MgO accompanied by a low amount of c-ZrO<sub>2</sub> (Ca<sub>0.15</sub>Zr<sub>0.85</sub>O<sub>1.85</sub>). The transformation to c-ZrO<sub>2</sub> of the composite produced from DN was comparatively higher than that of the DB. In the latter, scarce Ca<sub>3</sub>Mg(SiO<sub>4</sub>) and β-Ca<sub>2</sub>(SiO<sub>4</sub>) were identified. Contrarily, a high presence of these phases was found for DN and may be explained by its higher content of impurities. For the composition containing DB, a low content of residual CaO was detected.

Further increase in the sintering temperature to 1600°C and 1680 favored the development of c-ZrO<sub>2</sub> and silicates as the reduction of the proportions of CaZrO<sub>3</sub> and MgO occurred. The increase in the relative content at c-ZrO<sub>2</sub> at 1600 °C and higher temperatures was more pronounced for the composition with DN. In this case, spinel was clearly identified in the XRD diagram.

No crystalline compounds with Fe were detected by XRD.

The reaction between pure dolomite and m-ZrO<sub>2</sub> was studied previously (Serena et al. 2004) by Neutron diffractometry up to 1250 °C indicating that the reaction is sequential. Dolomite decomposition occurs in two stages: the formation of MgO and CaCO<sub>3</sub>, and then the decomposition of CaCO<sub>3</sub> corresponding to Eqs. 1 and 2. It was established that the MgO is formed directly without intermediate steps .

- (1)  $\text{MgCa}(\text{CO}_3)_2\text{s} \rightarrow \text{MgOs} + \text{CaCO}_3\text{s} + \text{CO}_2\text{g}$
- (2)  $\text{CaCO}_3 \rightarrow \text{CaOs} + \text{CO}_2\text{g}$
- (3)  $\text{CaOs} + \text{m-ZrO}_2\text{s} \rightarrow \text{CaZrO}_3\text{s} + \text{CO}_2\text{g}$

Therefore, the final composition of the ceramic results from the following reaction:

- (4)  $\text{MgCa}(\text{CO}_3)_2 + \text{m-ZrO}_2 \rightarrow \text{MgO} + \text{CaZrO}_3$

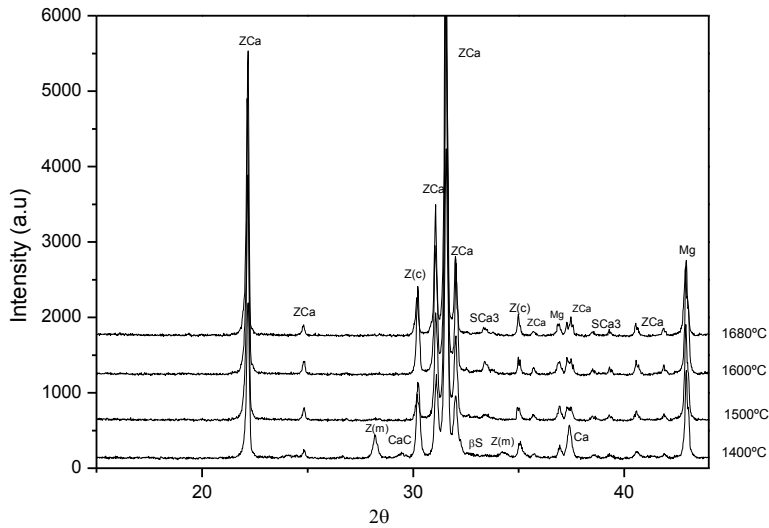


Fig. 1. XRD patterns of ZrO<sub>2</sub>-DB mixture sintered at 1400, 1500, 1600 and 1680 °C; where ZCa: CaZrO<sub>3</sub>, Mg: MgO, Zc: c-ZrO<sub>2</sub>, Ca: CaO, SCA3: Ca<sub>3</sub>Mg(SiO<sub>4</sub>)<sub>2</sub>, βS:β-Ca<sub>2</sub>(SiO<sub>4</sub>)<sub>4</sub>, CaC:CaCO<sub>3</sub>, Z(m): m-ZrO<sub>2</sub>

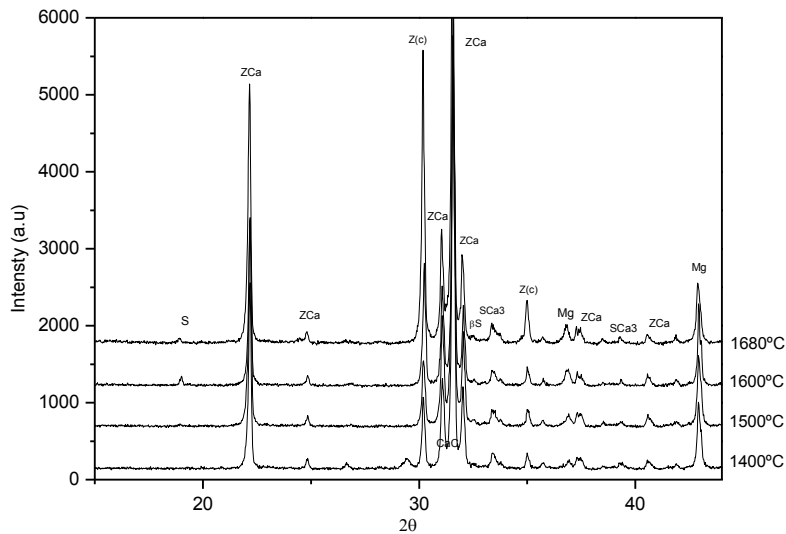


Fig. 2. XRD patterns of ZrO<sub>2</sub>-DN mixture sintered at 1400, 1500, 1600 and 1680 °C; where ZCa: CaZrO<sub>3</sub>, Mg: MgO, Zc: c-ZrO<sub>2</sub>, Ca: CaO, SCA3: Ca<sub>3</sub>Mg(SiO<sub>4</sub>)<sub>2</sub>, βS: β-Ca<sub>2</sub>(SiO<sub>4</sub>)<sub>4</sub>, CaC:CaCO<sub>3</sub>, S: spinel

Thus, the CaZrO<sub>3</sub> formation using pure dolomite (Eq.4) follows to a kinetic model of solid state reaction controlled by diffusion (Serena et al. 2004). The evolution of phases formed with temperature for sample DB (Fig.1) indicated that this mechanism probably occurred. Nevertheless, the presence of compounds with low melting point, detected by XRD, for composites produced from DN suggested that a liquid phase probably originated at elevated temperatures which favored the formation of c-ZrO<sub>2</sub> (Fig.2).

### 3.2 Microstructure

According to the phase identification performed by XRD, the composite sintered at 1400 °C contained CaZrO<sub>3</sub>, MgO and minor amounts of c-ZrO<sub>2</sub>. Following the stoichiometry of reaction (Eq. 4), the expected phase contents in the composite are 76 vol. % of CaZrO<sub>3</sub> and 23 vol % of MgO. Fig. 3 shows the microstructure (SEM- EDX) of the composite sintered at 1400 °C containing the different phases: CaZrO<sub>3</sub> agglomerates (light areas) and MgO (dark gray areas) showing some heterogeneity in the distribution. The particle size distribution of DN ( $d_{50} = 14 \mu\text{m}$ ) was finer than that of the DB ( $d_{50} = 48 \mu\text{m}$ ) but a fraction (10 vol. %) consisting of particles larger than 82 and 265  $\mu\text{m}$ , respectively was found in both samples. In addition, the electrofused m-ZrO<sub>2</sub> (reactant) exhibited a coarser and broader particle size distribution ( $d_{50} = 98 \mu\text{m}$ ). Thus, the CaZrO<sub>3</sub> agglomerates having sizes larger than 100  $\mu\text{m}$  present in the microstructure of composite corresponded well with the large particle size of initial ZrO<sub>2</sub> powder. Moreover, Fig.3 a shows that CaZrO<sub>3</sub> agglomerates were constituted of smaller individual grains (rounded) which appeared surrounded by secondary phases. The low melting silicates often tends to segregate at grain boundaries or triple points (Contreras et al., 2005; Rodriguez et al., 2012) and consequently, they were probably located surrounding the CaZrO<sub>3</sub> grains.

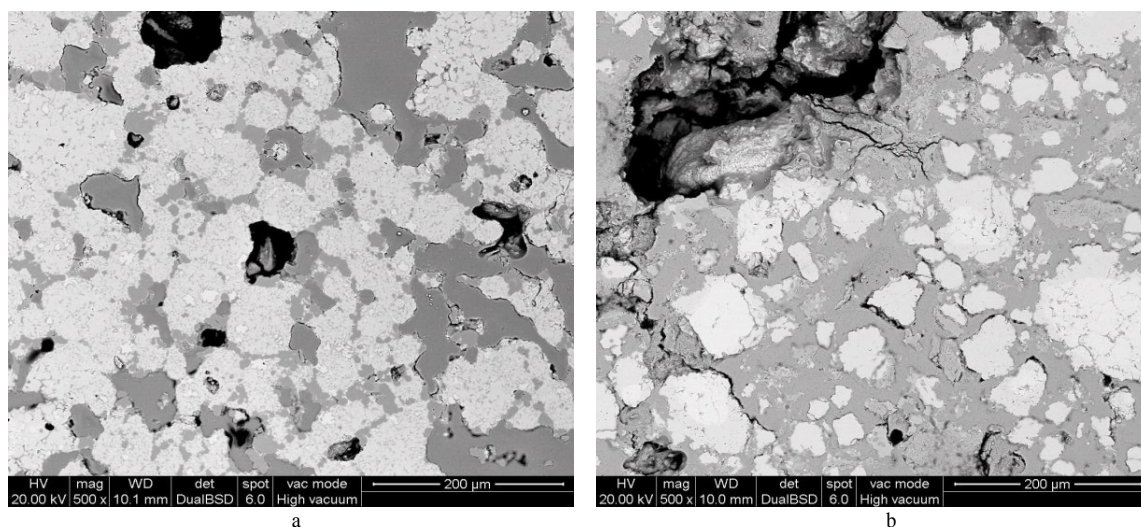


Fig. 3. Microstructure SEM of different composites sintered at 1400 °C. a: DN, b: DB.

There were small white grains inside CaZrO<sub>3</sub> agglomerates attributed to unreacted m-ZrO<sub>2</sub>. There also existed some cracks and pores (black areas).

### 3.3 Effect of sintering temperature on the physical properties

Fig. 4 shows the variation of the porosity with the sintering temperature for the composites prepared with DN and DB dolomites. In both cases, porosity gradually reduced with temperature due to the enhancement of the sintering process and neck growth which in turn increased densification. The porosity of the composite formed with DN was 34% at 1400 °C, reached near to 20% after sintering at 1500 °C and then remained approximately constant up to 1600 °C. In contrast, the porosity of the ceramics produced from DB showed little change with temperature (50 to 45 %) and was significantly higher than the respective values of the series with DN. The porosity of this ceramic probably increased by development of cracks (Fig 3b) due to the greatest tendency for degradation of unreacted CaO (Fig. 1). This effect was significant even in the ceramic sintered at 1680 °C.

Fig. 5 shows that linear shrinkage for DN series markedly increased between 1400 and 1500 °C and approximated to 20% at 1500°C in agreement with the increase in the densification degree as the sintering process developed. However, the relative density achieved near to 80 % even by sintering at 1600 °C whereas the shrinkage

remained nearly constant. Thus, the lower densification attained clearly shows the difficulties in sintering dolomite powders which decomposed and generated large voids that cannot be eliminated during sintering remaining in the microstructure. Nevertheless, composites produced from DB exhibited a significantly lower degree of densification even at 1600 °C. Thus, ceramics showed a different sintering behavior depending on the purity of the dolomites.

The XRD, porosity and shrinkage measurements confirmed that reactive sintering of dolomite and m-ZrO<sub>2</sub> mixtures mainly occurred in sequential steps (although some overlapping probably existed). The reaction occurred prior to any significant sintering: high conversion to CaZrO<sub>3</sub> and MgO as reaction products (with minor amounts of residual m-ZrO<sub>2</sub>), while an initial stage of sintering was found at 1400 °C. With further increase in temperature above 1400 °C, the densification of the reaction products started in agreement with a previous study using dolomite-zircon mixtures (Obregón et al., 2011).

Dolomite DN having the highest content of impurities promoted the sintering process occurring in a presence of a liquid phase. Thus, liquid phase formation in such compositions with DN favored densification.

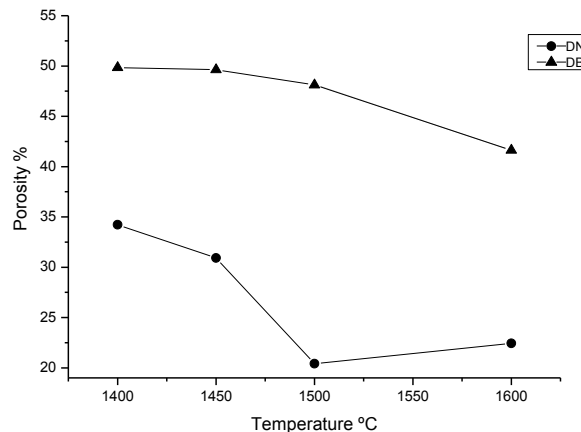


Fig. 4. Porosity vs. sintering temperature for DB and DN compositions

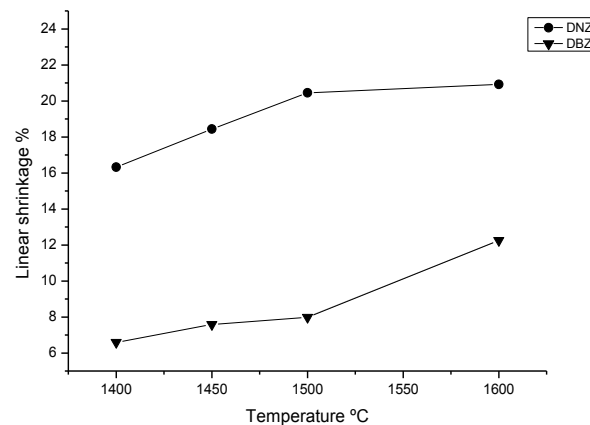


Fig. 5. Linear shrinkage vs. sintering temperature for DB and DN compositions

### 3.4 Mechanical properties: Dynamic elastic modulus and Modulus of Rupture MOR

The evolution of the elastic modulus E and flexural strength (MOR) with the sintering temperature for DB and DN compositions are shown in Figs. 6 and 7, respectively. The elastic modulus increased with increasing sintering temperature from 1400 to 1500 °C. This result may be correlated with porosity and composition because E depends

on the volume fraction and the individual modulus of elasticity at zero porosity  $E_0$  of each phases present. At 1500 °C, the increase in the elastic modulus was caused by the reduction in the pore volume fraction as shown in Fig. 4.

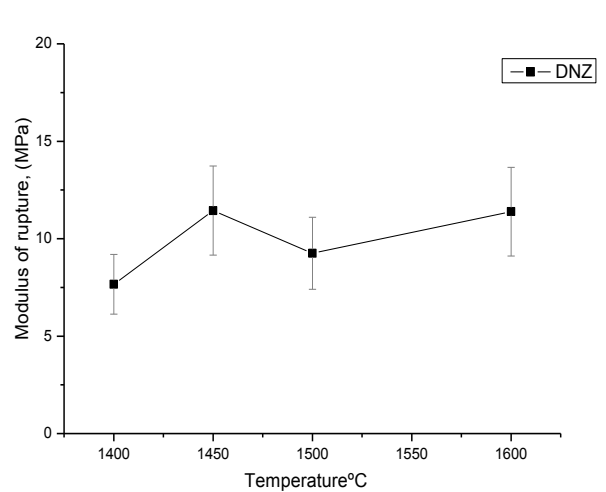
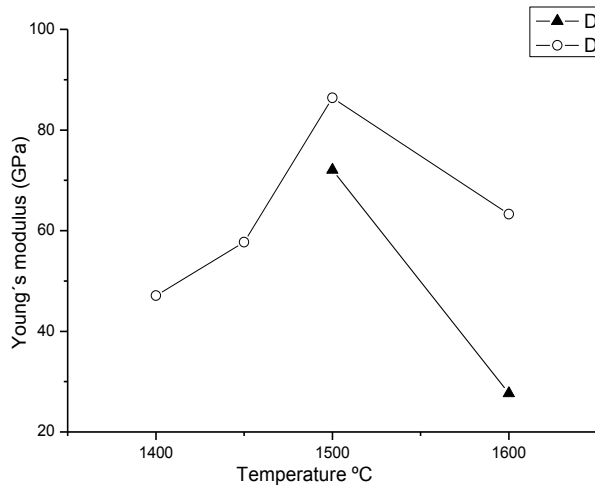


Fig. 6. Young's modulus  $E$  vs. sintering temperature for DB and DN compositions. Fig. 7. MOR vs. sintering temperature for DN composition

The  $E_0$  of MgO is comparatively higher (270 GPa) than that of CaZrO<sub>3</sub> (230 GPa) (Obregón et. al., 2011; Hou et al., 1994). Then, the theoretical module of the composite  $E_0$  calculated using the rule of phases was 240 GPa. The effect of porosity on module  $E$  can be estimated by applying an empirical model that predicts an exponential reduction of  $E$  with porosity (i.e.  $E = E_0 \exp(-bP)$ ). The constant  $b$  depends on the shape of pores. For the typical configuration of a porous structure corresponding to the pore volume between sintered ceramic particles, the constant  $b$  was assumed to be 5. For this case, the effective  $E$  calculated was 44 GPa at 1400 °C. Considering the higher densification achieved at 1500 °C, the predicted modulus  $E$  increased to 88 GPa. Thus, the  $E$  calculated from  $E_0$  of the composite resulted similar to the experimental  $E$  (Fig.6). Therefore, the  $E$  experimentally measured satisfied the rule of phases and the effect of porosity can be estimated satisfactorily by an exponential model.

Nevertheless, the experimental  $E$  decreased at 1600 °C (Fig. 6) probably due to relative increase in the content of silicate phases as porosity remained nearly constant. The lower  $E_0$  of  $\beta$ -Ca<sub>2</sub>(SiO<sub>4</sub>) and Ca<sub>3</sub>Mg (SiO<sub>4</sub>) reported are 130 and 116 GPa, respectively which caused a reduction in the theoretical module  $E_0$  of the composite.

Composites obtained from dolomite DB exhibited significant lower  $E$  than those of the composites produced using DN, this result may be explained by the relatively high porosity and the cracks which originated by the hydration of residual CaO.

Fig. 7 shows that the MOR of composite containing DN sintered at different temperatures remained approximately constant at 8-12 MPa, being similar to that reported for refractory bricks with porosity of 20% which were fabricated from electrofused CaZrO<sub>3</sub>-MgO grains (Rodriguez et al., 2012). On the other hand, the composites produced from mixed ZrO<sub>2</sub>-DB dolomite powder had a tendency to degradation and therefore flexural strength cannot be evaluated.

#### 4. Conclusions

Porous CaZrO<sub>3</sub>-MgO composites were developed by reaction sintering of electrofused m-ZrO<sub>2</sub> grains and two natural dolomites with different mineralogical composition. The highest content of impurities of DN dolomite favored the formation of compounds of low melting points (mainly silicates of Ca, Mg) which in turn promoted high densification of ceramics due to a liquid phase sintering. The lower porosity originated high (dynamic) elastic

modulus of the composites. The E experimentally measured followed the rule of phases and its reduction with porosity can be described by an exponential decay function.

The modulus of rupture of the composites processed from DN remained approximately constant with increasing temperature. The modulus of elasticity and mechanical strength resulted comparable with properties of CaZrO<sub>3</sub>-MgO based refractories with 20% of porosity.

The composite produced from the purer dolomite with scarce calcite as impurity exhibited a high porosity and susceptibility to hydration which limited its application.

### Acknowledgements

The authors thank CONICET for financial support.

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