INTRODUCTION

Refractory ceramic materials are designed to withstand different severe service conditions including high temperatures, corrosive liquids, and gases, abrasion, mechanical and thermal stresses. These are used in a wide range of industries, the most important being metallurgical, glass, and cement [1]. Particularly, cement is strategic and highly demanded by construction and public works. Currently, cement clinker production furnaces are used to incinerate polluting residues (rubber, organics of varied composition). Therefore, their resistance to the attack of corrosive agents from the waste products incinerated in these types of furnaces is an essential requirement for refractories [2]. In the synthesis of the cement clinker, limestone, clays, and other components that provide alumina and silica are used as raw materials. The reactions that take place among the raw materials in the clinkerization furnace are complex (mainly at 1450 °C) and actively involve the refractory lining that covers the interior of the kiln [3].

The development of refractory linings for cement kilns is closely linked to the processing of cement clinker in rotary kilns. In fact, in the 1920s, cement kilns were small and had an insignificant specific thermal load allowing silico-aluminous or high alumina bricks to be used even in hot areas. The development of more advanced technologies for cement production was accompanied by larger furnaces designed to withstand higher thermal loads, which required the development of new refractories capable of withstanding the increase of thermal loads. This requirement was partially addressed by introducing specific basic refractories based on magnesia [4, 5]. When magnesia (the main phase of these refractories) was added with different percentages of SiO$_2$ as a sintering additive, the phases obtained had a high coefficient of thermal expansion, and the resistance to spalling was low. The behavior of these materials at high temperatures depended on the content of the liquid phase and its distribution among solid phases. Therefore, the liquid phases tend to wet the periclase (MgO) grains creating a lubricating film between them that facilitates intergranular sliding resulting in deformation of the material at high temperatures. Adding chromium oxide to the periclase (greater than 15%) came as a partial solution for this problem. Thus, the first generation of spinel of chrome-magnesia refractories was developed. This modification in the composition of refractories significantly improved their characteristics, mainly the thermomechanical and physical abrasion, important properties required in service [6]. Although these materials exhibit acceptable behavior regarding thermomechanical requirements and...
physical abrasion, they were strongly attacked by the cement clinker due to the incompatibility between the chrome spinel with the tricalcium silicate and lime that are part of the cement. The incompatibility of the clinker phases with the chrome spinel of the refractory allows these phases to react forming calcium chromite which, together with other phases present in the refractory that contain silica, form low melting compounds which facilitate the additional attack by chlorides, sulfates, and alkalies present in molten clinker [7].

The reaction of the chrome spinel present in the refractory with the silicates of the clinker under operating conditions produces a change in the chromium oxidation state from Cr$^{3+}$ (non-toxic, non-carcinogenic, and insoluble) to Cr$^{6+}$ (soluble and carcinogenic) [6, 8]. Currently, close attention is focused on the development of new chrome-free refractory materials that can resist not only the complex reactions triggered in the clinkerization process but also the chemical attacks generated by the components of the different alternative fuels used. Furthermore, the composition of the refractory and its microstructure are to be selected to allow raw material on the surface of the refractory to form a layer that covers and protects the material.

Coarse magnesia (MgO) ceramics are of technological interest. It is well known that the high covalence nature of this material is responsible for its difficulty in sintering at relatively low temperatures, ~1300 and 1400 °C, especially when the grain size is over 0.5 mm and lacks a lower content phase acting as a sintering agent that bonds large grains. Magnesia refractory materials, such as spinel, hercynite, and magnesioferrite, show good hot properties and have relatively high melting points to be used in the so-called hot zone of clinkerization furnaces at 1450 °C. These attractive properties were a key factor to their development together with a second-phase with a spinel structure throughout the zone of clinkerization furnaces at 1450 °C. These attractive properties were a key factor to their development together with a second-phase with a spinel structure throughout the zone of clinkerization furnaces at 1450 °C. These attractive properties were a key factor to their development together with a second-phase with a spinel structure throughout the zone of clinkerization furnaces at 1450 °C. These attractive properties were a key factor to their development together with a second-phase with a spinel structure throughout the zone of clinkerization furnaces at 1450 °C.

MATERIALS AND METHODS

Starting powders and processing route: three types of ceramics were manufactured using commercial magnesite (MgO) grains (99 wt%, RHI, Brazil) bonded with equimolar mixtures of zirconia (ZirPro, Saint Gobain, China) and dolomite (DBZ); the employed natural dolomite and the other starting powders were fully described elsewhere [3]. The studied materials were called MDBZ1, MDBZ2, and MDBZ3. The processing route was equivalent and the granulometric distribution effect was studied. Mainly, the only difference was in the quantities of the medium and fine fractions (Table I). These compositions were selected for evaluating the influence of different sintering additive quantities (fine fraction) on the processing and properties of the final refractory material. This
study could help to determine the optimal quantity of sintering additives to take into account in the development of commercial refractory material. Coarse and medium fractions were constituted by magnesia grains and the fine fraction (matrix) was formed by the reactive DBZ mixture. Both employed magnesite fractions were characterized by X-ray diffraction (XRD), Rietveld quantitative phase analysis, and scanning electron microscopy (SEM); the fine fraction (DBZ) was characterized in previous works [17, 18]. Initially, grain sizes of coarse and medium fractions (MgO) were adjusted using a ball mill, and then they were screened using ASTM standard sieves in different fractions (Table I). Fig. 1 shows the particle size distribution curves of the individual fractions (coarse, medium, and fine) used in the manufacture of three types of ceramics. (coarse, medium, and fine) used in the manufacture of three types of ceramics.

Characterization methods: identification of crystalline phases in the sintered ceramics was performed by X-ray diffraction (XRD) using a diffractometer (PW 3020/10, Philips) with CuKα radiation and Ni filter from 5° to 80° (20), a step of 0.04° and 2 s/step. The XRD patterns of raw materials were analyzed using the following ICCD PDF files: 36-0426 for dolomite [CaMg(CO₃)₂]; and 37-1484 for m-zirconia. For the sintered samples, the used files were: 35-0790 for calcium zirconate (CaZrO₂); 071-1176 for magnesia (MgO); 026-0341 for calcia-fully stabilized cubic zirconia (c-Cu₃Zr₂O₇); and 35-0591 for merwinite [Me: Ca₄Mg₂(SiO₄)₃]. The crystalline phase contents (wt%) of the materials were determined using the Rietveld method of refinement using the program FullProf v.2019 [19, 20]. The apparent density was measured by the Archimedes method using distilled water [3]. The relative density (D) of the sintered composite was calculated as the ratio between the apparent and theoretical density. Theoretical density was obtained using the rule of mixtures with values of density and volume fraction corresponding to each phase (determined based on Rietveld results). The total porosity was calculated as P=1-D. Microstructural characterization was performed on polished and C-coated specimens using a field emission scanning electron microscope, FE-SEM, with analysis by energy dispersive X-ray spectroscopy, EDX (Jeol, S-4700 I, Japan). The flexural strength or modulus of rupture (MOR) was measured on 10 samples by a 3-point bending test with a 40 mm span and a crosshead speed of 0.1 mm/min using a universal testing machine (5985, Instron, USA) [21]. The dynamic Young’s modulus (E) for each composite was determined at room temperature by the impulse excitation technique (Grindosonic MK5 Industrial, Lemmens, Belgium) following the ASTM C1198 standard [22, 23]. The dynamic Young’s modulus of the composite reported corresponded to the average of 5 measurements according to [24, 25]:

\[ E = 0.94642 \frac{\rho f^2}{t^2} T \]  

(A)

where \( \rho \) is the material’s density, \( l \) is the length of the bar, \( f \) is the fundamental resonant frequency, \( t \) is the thickness of the beam, and \( T \) a correction factor given by Spinner and Telft [24, 26]. The measured E values of the samples were low compared to the moduli at zero porosity (\( E_z \)), which were estimated taking into account the volumetric fraction (\( V \)) and the \( E_z \) modulus of each phase present from the phase rule. The equation that relates to these parameters is as follows:

\[ E = E_z(1-v) + E_{Me}V \]

where \( V \) is the theoretical deformation.

RESULTS AND DISCUSSION

Crystalline phase composition determined by XRD using the Rietveld method: for all compositions (MDBZ1, MDBZ2, and MDBZ3), results of XRD, and the quantitative Rietveld phase analysis are summarized in Fig. 2 and Table II, respectively. \( R_w \) values (Table II) indicated excellent fits.
for refining. In all samples, the major phases were MgO and CaZrO$_3$, and c-ZrO$_2$ (Ca$_{0.15}$Zr$_{0.85}$O$_{1.85}$) and merwinite [Ca$_4$Mg$_8$(SiO$_4$)$_6$] were present in low amounts (<4 wt%), as minority phases; this was expected because the reaction between m-ZrO$_2$ and compound containing calcium and magnesium (dolomite) had been previously reported by a neutron diffraction study [27]. The reaction was shown to be sequential and the decomposition of dolomite occurred in two stages: the formation of MgO and CaCO$_3$, and subsequent decomposition of CaCO$_3$. Also, it was determined that MgO is formed directly without intermediate phases:

$$\text{MgCa(CO}_3\text{)}_{2(s)} \rightarrow \text{MgO}_{(s)} + \text{CaCO}_3\text{)+(CO}_2\text{)(g)} \quad \text{(C)}$$

$$\text{CaCO}_3\text{)(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_2\text{(g)} \quad \text{(D)}$$

$$\text{CaO}_{(s)} + \text{m-ZrO}_2\text{(s)} \rightarrow \text{CaZrO}_3\text{(s)} \quad \text{(E)}$$

The composition of the ceramic results from the global reaction:

$$\text{MgCa(CO}_3\text{)}_{2(s)} + \text{m-ZrO}_2\text{(s)} \rightarrow \text{MgO}_{(s)} + \text{CaZrO}_3\text{(s)} + 2\text{CO}_2\text{(g)} \quad \text{(F)}$$

In the case of CaZrO$_3$ formation using pure dolomite, the kinetics follows a solid-state reaction model controlled by diffusion [27, 28]. In this way, the evolution of the phases formed in all ceramics (MDBZ1, MDBZ2, and MDBZ3) is associated with this mechanism. The contents of MgO and CaZrO$_3$ were different for each ceramic. This can be explained by the different compositions of the starting powders. However, in the minority phases, large variations were not determined for the different compositions studied. This could be due to the error in the quantification method.

Effect of processing variables on textural characteristics of MDBZ1, MDBZ2, and MDBZ3 composites: for all the composites, the achieved density was between 2.5 and 2.6 g/cm$^3$, and the linear shrinkage was low (around 5%), due to low densification (between 65% and 70% of the theoretical density). Thus, these materials exhibited relatively high porosity (between 30% and 35%). This could be improved by modulating more precisely the grain size distribution of the starting powders, for example introducing packing distributions proposed in [29], so as to achieve lower porosities, like commercial refractories, which are lower than 20%. However, the experimental design of this particular study was chosen in order to compare the effect of the change in the proportion of finer fraction (bonding additive) on the sintering properties of these materials of technological interest. Table III shows the results of total porosity, apparent, relative, and theoretical density for the composites studied.

### Table III - Results of total porosity (P), apparent (D$_a$), relative (D$_r$), and theoretical (D$_t$) densities of sintered materials.

| Sample | D$_a$ (g/cm$^3$) | D$_r$ (g/cm$^3$) | D$_t$ (g/cm$^3$) | P (%) |
|--------|----------------|----------------|----------------|------|
| MDBZ1  | 2.52           | 0.65           | 3.82           | 32   |
| MDBZ2  | 2.56           | 0.65           | 3.89           | 35   |
| MDBZ3  | 2.60           | 0.67           | 3.83           | 33   |

#### Mechanical properties of MDBZ1, MDBZ2, and MDBZ3 composites: the values of the elastic modulus corresponding to each phase in the different types of ceramic developed are shown in Table IV [3, 30]. The effect of porosity on modulus E can be estimated by an empirical model that predicts an exponential reduction of E with porosity [31-33]:

$$E = E_o e^{(b\cdot P)}$$  \[G\]

For the typical configuration of a porous structure corresponding to the pore volume between sintered ceramic particles, the constant b is assumed to be 2.73 [31]. Table V shows the results of the modulus of elasticity at zero porosity ($E_o$) and those obtained from the employed model (Eq. G). As shown, the values of the experimental E are far from those predicted by the model ($E_o$). In fact, it was determined that the experimentally measured elastic moduli did not follow the rule of mixture. Therefore, the porosity effect cannot be satisfactorily represented by the Spriggs model. This could be attributed to the large number of pores that lack a defined shape [34], due to the fact that the models were build considering spherical pores. It is well known that finer powders have a higher sintering contraction than coarser powders [35]. The great contraction difference during sintering between the finer fraction and
the bigger magnesia grains could be the cause of the high porosity generated in all the materials. To overcome this, a continuous size distribution should be used, like those studied by Andreassen [29], so as to reach a better packing. Regarding the modulus of rupture (MOR), it was observed that an increase in the finer fraction content produced a higher MOR value. This behavior could be attributed to a higher intergranular bonding (coarse grains) as the sintering additive was increased, although the porosity remained on relatively high values. The sintered MDBZ3 composition reached a MOR value comparable to a typical commercial refractory [36-41].

Table IV - Young modulus, E (GPa), of the phases present in the sintered materials [3, 30].

| Phases         | E (GPa) |
|----------------|---------|
| CaZrO3         | 231     |
| MgO            | 270     |
| c-ZrO2         | 218     |
| Ca3Mg(SiO4)2   | 116     |

Table V - Results of flexural strength (MOR), Young’s modulus (E), Young’s modulus at zero porosity (E₀), and elastic modulus calculated from the empirical model as a function of porosity (Eₘ) of sintered materials.

| Sample  | MORᵃ (MPa) | Eᵇ (GPa) | E₀ᵇ (GPa) | Eₘᶜ (GPa) |
|---------|------------|----------|-----------|-----------|
| MDBZ1   | 6.2 (±0.2) | 11.3 (±2.0) | 264.4     | 125       |
| MDBZ2   | 9.0 (±1.0) | 16.8 (±3.0) | 260.0     | 113       |
| MDBZ3   | 11.4 (±1.0)| 20.0 (±2.0) | 262.9     | 123       |

ᵃ: experimental;ᵇ: Eq. B;ᶜ: Eq. G.

**Developed microstructure:** The coarse magnesia microstructure was distinguished; Fig. 3 shows the microstructures of the 3 types of ceramic sintered at 1450 °C/2 h at low magnification. The SEM images show that the microstructures were mainly made up of a gray phase (grain of variable size: 20 to 500 μm) attributed to magnesia grains. In a smaller proportion, bordering the gray grains and dispersed throughout the microstructure, the second phase of white color was distinguished; this could correspond to the calcium zirconate. Finally, the third region of darker color was observed, throughout the microstructure of variable size and shape compatible with the continuous porosity of the studied materials. At higher magnification (Fig. 4), the light gray phase showed to contain small dark gray dots. This phase corresponded to the fine fraction of the ceramic named DBZ, whose composition, characteristics, and properties were described in previous work [17]. The SEM images showed that this gray color phase was found in a greater proportion in the MDBZ3 ceramic. The result was expected according to the formulations studied (Table I) indicating that it had the highest amount of DBZ fine fraction (50 wt%) formed by m-ZrO₂ (monoclinic zirconia) and CaMg(CO₃)₂ (dolomite) 1:1 molar ratio. In this case, phenomena of dolomite decarbonation, reaction, and sintering with m-ZrO₂ occurred to form CaZrO₃ and c-ZrO₂ during the heating stage, as previously reported [27].

The EDX analysis confirmed that the gray phase corresponded to MgO grains and the gray and white spots located on the grain border corresponded to the CaZrO₃/c-ZrO₂ phase. The dark color region corresponded to the composition of the resin infiltrated in the samples for the
polishing stage, showing that it filled the open pores in the microstructure. The observed porosity was between 32% and 35% (Table III) and the pore structure was present in the three studied materials, showing the mentioned lack of packing of the coarse magnesia grains. Apparently, the pore channels were interconnected throughout the material. The observed pore diameter was below approximately 50 μm. Finally, some closed pores were observed within the magnesia grains, especially in the bigger coarse grains. From a detailed observation of SEM images, no cracks or loss of the microstructure integrity were observed within the magnesia grains and the calcium zirconate grains, showing a good reaction sintering process that ensured the consolidation of the ceramics.

CONCLUSIONS

Coarse magnesia (MgO) ceramics are of technological interest, especially for the cement industry. This type of material with a high content of MgO exhibits some difficulty to achieve sufficient bonding among grains as their optimum sintering temperature is over 1500 °C, especially if the grain size is relatively large and does not have a second bonding phase. Considering this fact, a new bonding strategy based on a zirconia dolomite reaction sintering was proposed and studied with firing at 1450 °C. No significant shrinkage was observed in the fired samples and the porosity remained relatively high (30%) in the studied composition range. The developed crystalline phases and microstructure features were described and the effect of the proportion of bonding starting powders was observed. The thermochemical processes were established as well. The ceramics showed good mechanical properties. It was concluded that with the increase of fine fraction, the MOR (modulus of rupture) value increased, showing a better bonding effect, yet with higher raw materials cost. The developed ceramics fired at 1450 °C seem suitable for use as refractories in the cement manufacturing industry.

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