

MgAl₂O₄ spinel as an effective ceramic bonding in a MgO–CaZrO₃ refractory

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Abstract

The influence of MgAl₂O₄ spinel addition as a ceramic bonding in the MgO–CaZrO₃ refractory was established by the evaluation of physical and microstructural characteristics in terms of density, porosity, crystalline phases, phase distribution and morphology. X-ray diffraction analyses and scanning electron microscopy with microanalysis have been used. The mechanical behavior has been evaluated in terms of cold crushing strength at room temperature and modulus of rupture at 25 and 1260 °C. Static and dynamic resistances tested by chemical attack of clinker raw constituents have been carried out at 1450 °C. Results showed that thermo-mechanical properties significantly improved with increasing the content of spinel. Microstructural analysis revealed that spinel phase aided to develop a strong bond between MgO and CaZrO₃ refractory aggregates. Finally, the refractory bodies exhibited a good thermal stability and an excellent chemical resistance against the clinker raw material.

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1. Introduction

Magnesia based refractories have been widely used in cement rotary kilns and steel ladles due to their high melting point, no toxicity and good resistance to basic slags and clinker phases. However, they have some disadvantages, such as high thermal conductivity, poor thermal shock resistance and infiltration resistance against chemical attack.^{1–3} In order to improve these properties, some metal oxides and compounds such as SiO₂, CaO, Al₂O₃, MgAl₂O₄, Cr₂O₃, ZrO₂, CaZrO₃ and FeAl₂O₄ have been used as doping agent. These oxides may react with MgO to form a second phase which improves the process of sintering.

In recent years, the burning zone of rotary cement kilns has been exposed to alkali salts and waste by-products such as rubber or other organic products from animal sources; these materials

enhance the corrosion process of refractory bricks. Thus, under the severe service operating conditions present in the rotary cement kilns, industry has demanded the development of new refractory products for increasing the lining life.^{3–12} Many studies conducted by the refractory industry responds to the need for the development and implementation of new chrome-free basic bricks that meet the requirements presented in the kilns.

In other hand, calcium zirconate is one of the most promising high refractory compounds used in the steel and cement industry.¹³ Particularly in the sintering zone, calcium zirconate (CaZrO₃), as a second phase of magnesia refractories works effectively improving the resistance against both clinker phase melting and alkali attack.¹³ Specially, CaZrO₃ presents a high melting point (~2340 °C) and it is compatible with the MgO since does not react at any temperature and does not form a liquid phase up to temperatures higher than 2060 °C.^{14–16} Besides, it is compatible (does not react) with the main phases of Portland cement clinker in the solid state (C₂S, C₄AF and C₃S).¹⁷ Moreover, the solid–solid bonding between the compatible MgO and CaZrO₃ phases is highly resistant to the infiltration of fluxes from the clinker. Previously, Obregón

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et al. demonstrated through corrosion studies, the use of cement clinker with MgO–CaZrO₃ based fine grained materials for these purposes.¹⁷ CaZrO₃ can dissolve in the liquid clinker phase and increases its viscosity. This process restricts infiltration of the cement clinker phase into the refractory.^{18,19}

MgO and CaZrO₃ have been suggested as chrome-free refractories for cement kilns^{20–24} to replace not only magnesia–chromite, but also magnesia-oversaturated spinel refractories currently in use. MgO spinel bricks are highly resistant to thermal shock, non-sensitive against reducing/oxidizing conditions, but vulnerable to thermal overload. Spinel also forms low-melting phases with the result of premature wear.^{25–27} The analysis of MgO–CaZrO₃ composite as refractory materials in rotary cement kilns carried out by Kozuka et al.^{11,12} points out a good behavior on service of this material but peeled off easily in high stressed areas. Recently, the behavior against corrosion by clinker of MgO–CaZrO₃ matrices at high temperatures was established by Serena et al.^{28,29} Their results underline the good corrosion behavior of the MgO–CaZrO₃ materials, and support their use as a matrix in magnesia chrome-free bricks for the burning zone of rotary cement kilns.

Magnesium aluminate spinel is a technologically important material with very attractive properties such as high melting point (2135 °C), high mechanical strength at elevated temperature, high thermal shock resistance and low thermal expansion coefficient.

Taking into account the previously mentioned, the aim of the present study is to investigate at laboratory and industrial scale the physical, mechanical and chemical properties as well as microstructural characteristics of new free-chrome brick composites of a MgO–CaZrO₃ matrix doped with low contents of MgAl₂O₄ spinel (2.5–6 wt.%) in order to meet the lining requirements present in the rotary cement kiln.^{30–34}

2. Experimental procedure

2.1. Raw materials and refractory formulation

Different raw materials were used for the preparation of the refractory mixtures at laboratory scale. Commercial high

purity magnesia (MgO at industrial grade purity), laboratory synthesized calcium zirconate (CaZrO₃), zirconia (ZrO₂) and MgAl₂O₄ spinel with 98 wt% purity. The chemical analysis of the raw materials obtained by X-ray fluorescence technique is given in Table 1. It is important to mention that all the starting raw materials used in this stage of the investigation have particle size smaller than 45 µm. The addition of a small quantity of fine zirconia particles in all formulations is mainly for avoiding the free lime in the refractory matrix and promoting the formation of an “*in situ*” calcium zirconate phase.

The phase analysis of raw materials at laboratory scale was determined using a Siemens model D5000 diffractometer equipment using, Cu Kα radiation source ($\lambda = 1.54056 \text{ \AA}$) and a setting of 40 kV and 30 mA. All XRD data were collected under the same experimental conditions; in the angular range $5^\circ \leq 2\theta \leq 90^\circ$ using $\theta/2\theta$ configuration with a step scan of 0.05° and 1 s per step exposure time.

At the laboratory scale, the crystalline phases from the raw materials were identified by the X-ray diffraction as: MgO (periclase), CaZrO₃ [calcium zirconate (CaZrO₃) and a zirconium dioxide stabilized by Ca²⁺ ions (Ca_{0.15}Zr_{0.85}O_{1.85})], MgAl₂O₄ [periclase (MgO) and magnesium aluminate spinel (MgAl₂O₄)] and ZrO₂ (baddeleyite).

In the first stage of the present work, the influence of MgAl₂O₄ spinel on MgO–CaZrO₃ properties in a laboratory scale was evaluated through the development of four refractory formulations. Variations carried out in the formulations are reported in Table 2.

The second stage was conducted at an industrial scale. The use of large amounts of high purity raw material was necessary in order to obtain suitable final refractory properties. The chemical composition of the raw material used for the development of new refractory bricks is shown in Table 1. For the sintered commercial magnesia a wide particle size distribution composed by coarse, intermediate and fine grains was used. The particle size distribution of sintered commercial magnesia in mm was: $-4.76 + 2.83 \text{ mm}$ (7%), $-2.83 + 1.19 \text{ mm}$ (29%), $-1.19 + 0.595 \text{ mm}$ (22%), $-0.595 + 0.250 \text{ mm}$ (12%), -0.250 mm (6%) and -0.044 mm (24%). Particularly, in the case of electrofused magnesia–calcium zirconate mixture, which

Table 1
Chemical composition of raw materials.

Raw materials	Oxide compounds (% by weight)							
	MgO	ZrO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O
<i>Laboratory scale</i>								
Sintered MgO	97.90	–	1.64	–	–	0.30	–	–
Sintered CaZrO ₃	–	72.80	26.57	–	–	–	–	–
MgAl ₂ O ₄	28.61	–	0.32	70.36	–	0.51	–	–
ZrO ₂	98.0	–	–	–	–	1.50	–	–
Clinker raw material	0.88	–	44.79	3.03	1.60	11.86	0.47	0.24
<i>Industrial scale</i>								
Sintered MgO	98.91	–	0.85	0.08	0.05	0.11	–	–
Electrofused MgO–CaZrO ₃	50.00	36.43	13.57	–	–	–	–	–
MgAl ₂ O ₄	34.00	–	0.20	64.0	1.0	0.40	–	–
ZrO ₂	–	97.72	–	–	–	2.10	–	–
Clinker raw material	0.88	–	44.79	3.03	1.60	11.86	0.47	0.24

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