Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 42 (2016) 2933–2940
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Properties of regenerated MgO–CaO refractory bricks: Impurity of iron oxide

Gui-bo Qiu[a,b], Ben Peng[a,b], Chang-sheng Yue[b], Min Guo[a], Mei Zhang[a,*]

[a]State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing, China
[b]Central Research Institute of Building and Construction Co., Ltd, MCC Group, Beijing, China

Received 18 September 2015; received in revised form 9 October 2015; accepted 14 October 2015
Available online 20 October 2015

Abstract

Regenerated MgO–CaO refractory brick samples with 0, 1.5, 3.0 wt% iron oxide (Fe_2O_3) addition were prepared by using spent MgO–CaO bricks and fused magnesia as raw materials. The microstructure, flexural strength and corrosion resistance to cement clinker were investigated respectively. It is shown that additions of Fe_2O_3 mainly contributed to forming dicalcium ferrite (C_2F) in the final products. Bulk density, flexural strength at room temperature, and corrosion were enhanced, while the flexural strength at 1573 K decreased along with the increasing of Fe_2O_3 addition, which was beneficial for the improvement in sintering due to the formed C_2F and increased amount of liquid phase. The maximum amount of impurity Fe_2O_3 in regenerated MgO–CaO brick was found to be below 1.57 wt%, considering its flexural strength at high temperature and corrosion resistance property.

Keywords: A. Sintering; B. Electron microscopy; C. Corrosion resistance; D. MgO–CaO

1. Introduction

The long-term extensive use of $MgO–Cr_2O_3$ bricks in cement rotary kiln has resulted in serious environmental problem, especially in China [1]. The Cr(III) in $MgO–Cr_2O_3$ bricks is prone to being oxidized into hypertoxic Cr(VI) when it is exposed to the nature [2,3]. For environmental considera-tion, it is urgent to explore new kinds of free chrome refractory bricks for the application on cement rotary kiln [4].

MgO–CaO bricks belong to a class of refractories that are widely used as a lining in metallurgical refining furnaces such as the argon oxygen decarburization (AOD) furnace [5]. They are also considered as the substitutes of $MgO–Cr_2O_3$ bricks for steel refining process and cement rotary kiln [6–8], because their properties such as high temperature resistance, adherent coating property and resistance to steel slag, etc. [9,10] are similar to that of $MgO–Cr_2O_3$ bricks. However, the hydration of MgO–CaO bricks has restricted their application in cement rotary kiln [11]. Several researches proved that metal oxide such as iron oxide (Fe_2O_3) could improve the hydration resistance of MgO–CaO bricks [12–14].

At present, the accumulation of spent MgO–CaO bricks is becoming a challenge issue due to the presence of impurities such as Fe_2O_3 which makes them unrecyclable in the refining furnace [15]. Till now, very few literatures focused on the reutilization of spent MgO–CaO bricks [15,16]. Regenerated MgO–CaO bricks with an excellent hydration resistance were reported by using spent MgO–CaO bricks that contained impurities such as Fe_2O_3 from AOD furnace in the pilot test [11]. This work provided a new way for utilization of the regenerated MgO–CaO bricks in cement rotary kiln to replace the $MgO–Cr_2O_3$ bricks for their superior hydration resistance.

However, the high temperature properties such as refractori-ness and hot strength could be seriously damaged by too many impurities, especially a large amount of Fe_2O_3 [17]. It is still

*Corresponding author. Tel./fax: +86 1062334926.
E-mail address: zhangmei@ustb.edu.cn (M. Zhang).

http://dx.doi.org/10.1016/j.ceramint.2015.10.076

Table 1
Composition of raw materials (wt%).

Constituents	MgO	CaO	SiO_2	Fe_2O_3	Al_2O_3
Spent bricks	58.24	34.68	3.11	2.09	1.32
Fused magnesia	93.85	2.73	2.39	0.51	0.23
Fe_2O_3 powder	–	–	0.18	98.84	0.07

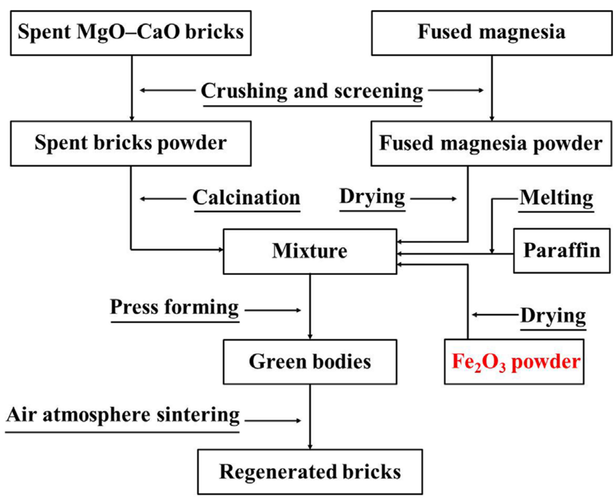

Fig. 1. Preparation process flow diagram of regenerated MgO–CaO bricks.

unknown if the spent MgO–CaO bricks could be reused in the cement kiln substituting the hazardous $MgO–Cr_2O_3$ bricks because of the complex effect of impurity Fe_2O_3.

In the present paper, the regenerated MgO–CaO bricks with different Fe_2O_3 addition were prepared. The phases, microstructure, flexural strength at room and high temperature, and corrosion resistance to cement clinker were investigated.

2. Experimental

2.1. Materials

The raw materials of regenerated MgO–CaO bricks and their compositions are shown in Table 1, among which spent bricks were from AOD refining furnace, fused magnesia was from the refractory factory, and the Fe_2O_3 powder (≤ 0.088 mm) was analytically pure Fe_2O_3.

The preparation process of regenerated MgO–CaO bricks is shown in Fig. 1. Three kinds of green bodies of regenerated MgO–CaO bricks were obtained using spent MgO–CaO bricks powder and fused magnesia powder as raw materials, 0, 1.5 and 3.0 wt% analytically pure Fe_2O_3 as an extra additive respectively, 6 wt% paraffin as a binder. The composition of green bodies is shown in Table 2. All green bodies were prepared by press-forming at 100 MPa into size of 60 mm × 8 mm × 8 mm, and then sintered at 1873 K for 2 h under air atmosphere. Finally, three kinds of regenerated MgO–CaO brick samples with 0, 1.5, 3.0 wt% Fe_2O_3 addition were obtained after furnace cooling, and they were named as sample F0, F1.5, F3.0 respectively. Considering the in-situ

Table 2
Composition of green bodies of the regenerated MgO–CaO bricks (wt%).

Samples	MgO	CaO	SiO_2	Fe_2O_3	Al_2O_3	Fe_2O_3 addition	Total Fe_2O_3
F0	70.00	24.13	2.87	1.57	0.96	–	1.57
F1.5	70.00	24.13	2.87	1.57	0.96	1.5	3.02
F3.0	70.00	24.13	2.87	1.57	0.96	3.0	4.44

Fe_2O_3 in the raw materials (spent brick and fused magnesia), the total Fe_2O_3 content of sample F0, F1.5 and F3.0 was 1.57 wt%, 3.02 wt% and 4.44 wt% respectively (Table 2).

2.2. Characterization

The phase identification of regenerated samples was studied by MXP21VAHF X-ray diffraction (XRD) analysis. The microstructure and linear scanning of regenerated samples were observed by MLA 250 mineral liberation analyzer equipped with scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). The flexural strength of regenerated samples at room temperature and 1573 K were carried out by three point bending method using the WDW-10E microcomputer control electronic universal testing machine and mechanical coupling testing machine respectively.

The corrosion resistance of regenerated samples was evaluated at 1823 K for 3 h under normal air atmosphere using 425 ordinary Portland cement clinker as corrosion source. The test method of the corrosion resistance experiment is shown in Fig. 2. The regenerated MgO–CaO brick was cut into two sections and then the fracture surfaces were polished to smoothness. One gram of cement clinker with 5 wt% analytically pure K_2SO_4 was sandwiched between the two sections of the regenerated sample, and they were combined into an experimental sample. The sample was sintered at 1823 K for 3 h under normal air atmosphere subsequently, and the microstructure of the junction between cement clinker and regenerated sample after furnace cooling was used to evaluate its corrosion resistance.

3. Results and discussions

3.1. Phases analysis of regenerated MgO–CaO bricks

Fig. 3(a) shows the XRD patterns of sample F0, F1.5 and F3.0, respectively. It can be seen that the main phases were MgO, free CaO (f-CaO), Ca_3SiO_5 (C_3S) and Ca_2FeAlO_5 (C_4AF). Besides, $Ca_2Fe_2O_5$ (C_2F) was also observed in sample F1.5 and F3.0. It is indicated that different Fe_2O_3 addition did not cause noticeable changes of the main phases of regenerated samples.

Fig. 3(b) shows the XRD patterns of regenerated samples in the range of 28–42°. It can be observed that the intensities of characteristic diffraction peaks (200) of f-CaO ($I_{CaO(200)}$) and (111) of MgO ($I_{MgO(111)}$) gradually changed with increasing addition of Fe_2O_3. The relative intensities $I_{CaO(200)}/I_{MgO(111)}$ were calculated and the comparison result is shown in Fig. 4. It