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ScienceDirect

Ceramics International 41 (2015) 14674–14683

CERAMICS INTERNATIONAL

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Correlation of pore structure and alkali vapor attack resistance of bauxite–SiC composite refractories

Ren Bo[a], Sang Shaobai[a,*], Li Yawei[a], Jin Shengli[b]

[a]The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China
[b]Chair of Ceramics, University of Leoben, Peter-Tunner-Straße 5, 8700 Leoben, Austria

Received 13 May 2015; received in revised form 14 July 2015; accepted 30 July 2015
Available online 7 August 2015

Abstract

Alkali attack resistance of cement kiln refractories has become one of the key factors affecting their performance life. In this paper, the correlation between mean pore size, pore size distribution of bauxite–SiC composite refractories and their alkali attack resistance was investigated by means of mercury intrusion porosimetry, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Also, the percolation theory, as well as modeling prediction, was applied associated with thermodynamic calculations. The results showed that quartz phase was generated from the oxidation process of silicon filling in part of pores, which resulted in a significant decrease in both the mean pore size and permeability of the samples. The proposed alkali attack mechanism indicated that K_2CO_3 was firstly reduced to K vapor and then infiltrated into the sample through the open pores. Consequently, the $KAlSiO_4$ phase was formed in the edge part of the samples. When the K vapor permeated into the center of the sample, the $KAlSi_2O_6$ phase was first generated. Afterwards, the decomposition of $KAlSi_2O_6$ in the K-rich atmosphere gave rise to the formation of quartz and $KAlSiO_4$. The decrease of mean pore size and apparent porosity, especially the reduction of the proportion of large pores, helped to prevent the alkali vapor from infiltrating into the samples, bringing about a superior vapor attack resistance at high temperature.

Keywords: Bauxite–SiC composite refractories; Pore size; Silicon powder; Percolation theory; Alkali attack resistance

1. Introduction

In recent years, the substitution of fossil fuels by industrial waste and household garbage as secondary fuels is widely applied in the dry cement production in China. Such fuels comprise a high content of alkali, sulfur and chlorine, which can strongly accelerate the degradation of refractory bricks. This leads to a drastic decrease of performance life, which has become one limitation to high quality cement production [1–6]. Bauxite–SiC composite refractories, which are widely used in the transition zone without the protective coating layer formed on their surface, are more vulnerable to the volatile alkali atmosphere [7–11]. It is well-known that the alkali vapor substance enters the refractories through open pores and ultimately results in the destruction of the materials. Infact, the corrosion by gaseous phases has been found in gasification furnaces [12–15], blast furnaces [16,17], and glass furnaces [18]. The changes mentioned above have driven the refractory industry to create and develop improved refractory lining products against the alkali vapor attack.

In order to minimize these drawbacks, the improvements are related to the optimization of the matrix by careful design of phase combinations and the microstructure characteristics. Baspinar [18,19] reported that the introduction of $ZrSiO_4$ markedly improves the densification and alkali resistance of mullite refractories. Prigent [20] found that incorporation of additives such as andalusite into mullite–SiC composite refractories significantly retards the penetration of alkali vapor into mullite–SiC composite refractory materials. Additionally, the decrease of apparent porosity can also help to reduce the propagation passageway of alkali vapor, and therefore promote the corrosion resistance, according to the research of Yun and Shi [2,3]. Based on the former research of our group [21], the

*Corresponding author. Tel./fax: +86 2768862188.
E-mail address: sangshaobai@126.com (S. Shaobai).

http://dx.doi.org/10.1016/j.ceramint.2015.07.190
0272-8842/

alkali attack resistance of Al_2O_3-C refractories is markedly improved by the decrease of apparent porosity, the mean pore size diameter and the increase of <1 μm pore volume. Therefore, it can be deduced that the pore structure of refractories plays a major role in the alkali attack resistance. Nevertheless, less research has been reported about the relationship between pore structure and alkali attack resistance of refractory.

Taking the above into account, the aim of the present work is to figure out the correlation between the pore structure and alkali attack resistance of bauxite–SiC composite refractories. As reported in our previous work [22], the pore size of bauxite–SiC composite refractories decreased effectively with the addition of silicon. Consequently, in the present work, silicon powder is introduced to adjust the pore size. The alkali attack resistance test was carried out in the graphite crucible together with the powder mixture of carbon black and potassium carbonate (1:1 in mass ratio) at 1000 °C. The relationship between the pore structure and the alkali attack resistance of bauxite–SiC composite refractories is investigated in detail, aiming to make this work a useful step for industrial applications.

2. Experimental

2.1. Raw materials and specimen preparation

The following were used as raw materials, with commercially-available $Al(H_2PO_4)_3$ solution (liquid, the specific gravity is 1.35) as a binder: homogenized bauxite aggregates (5–3 mm, 3–1 mm, 1–0 mm and <0.088 mm, 55 wt% Al_2O_3, 16 wt% SiO_2, 1 wt% Fe_2O_3, 3 wt% TiO_2, Yangquan Jinyutongda Refractory Co., Ltd., China); high grade bauxite (<0.088 mm, 86 wt% Al_2O_3, 8 wt% SiO_2, 2 wt% Fe_2O_3, 3 wt% TiO_2, Xiaoyi Hezhongxing Refractory Co., Ltd., China); SiC(1–0 mm and <0.088 mm, 97 wt% SiC, Shandong Linyi Jinmeng Silicon Carbide Co., Ltd., China); Guangxi clay (<0.075 mm, 30 wt% Al_2O_3, 46 wt% SiO_2, 2 wt% TiO_2, Nanning Guini Mineral Co., Ltd., China); micron-sized α-alumina (2 μm, 99 wt% Al_2O_3, Kaifeng Special Refractory Co., Ltd., China); silicon powder (<0.045 mm, 98 wt% Si, Anyang Yuhong Metallurgy & Refractory Co., Ltd., China). The batch compositions of raw materials are shown in Table 1. Cylindrical specimens (50 mm in height, 50 mm in diameter) were prepared under a pressure of 150 MPa. The specimens were then cured at 110 °C for 24 h in a muffle furnace. Finally, the specimens were fired at 1500 °C for a soaking time of 3 h in ambient atmosphere.

2.2. Testing and characterization

The mass change was calculated according to the formulation: $(m_2-m_1)/m_1\times 100\%$, where specimen mass of m_1 and m_2 before and after firing was measured. The apparent porosity and bulk density of the fired specimens were measured according to the Archimedes method. The cold crushing strength was measured in terms of GB/T 5072.2-2004. The cylindrical specimens with the height of 30 mm were drilled with a 12 mm through-hole along with the axial direction. Subsequently, the top and bottom surfaces were sealed with the special alumina materials after polishing. The tested samples were fixed under 0.2 MPa in case of leakage from top and bottom surfaces and connected with a gas pressure regulator. Therefore, only the permeability of the edge of the specimen during the experiment can be measured. The preparation of samples and permeability test apparatus are shown in Fig. 1. The core of the specimen with a diameter of 30 mm was identified as the center zone and the rest was identified as the edge zone. Each zone of the specimens was cut approximately $6\times 6\times 6$ mm^3 and then examined by Mercury Porosimetry (Autopore IV9500, Micromeritics Instrument Corp., USA). The alkali attack resistance of the specimens was carried out as embedded in pre-mixed carbon black and potassium carbonate (1:1 in mass ratio) powders in graphite crucibles. The graphite crucibles were put in an alumina crucible embedded by carbon powder and fired at 1000 °C for a soaking time of 3, 5 and 10 h respectively. The mass ratio of the specimens to the powder mixtures was 1:1. The phase compositions of the edge and center zones were detected by X-ray diffraction (XRD, X'pert Pro, Philips), using Ni-filtered, Cu Kα radiation at scanning speed of 2°/min at the temperature of 20 °C, using the powders from the milled specimens under a 325 mesh sieve. The phase analysis was conducted with the software of Philips X'pert Pro High Score. All the specimens were cut after firing, and then polishing and coating with gold. The microstructure was observed by using a scanning electron microscope (SEM, Quanta 400, FEI Company, USA) linked with an energy dispersive spectroscopy (EDS, EDAX, Phoenix) system.

Table 1
The batch composition of the samples.

Index	Sample no.				
	S0	S1	S3	S5	S7
Homogenized bauxite aggregates (5-3, 3-1, 1-0 mm)	58	58	58	58	58
SiC (1-0 mm)	10	10	10	10	10
High grade bauxite (≤ 0.088 μm)	20	19	17	15	13
Silicon powder(≤ 0.045 μm)	0	1	3	5	7
Guangxi clay	8	8	8	8	8
Micron-sized α-alumina	4	4	4	4	4
$Al(H_2PO_4)_3$	+3	+3	+3	+3	+3

3. Results and discussion

3.1. Phase composition and microstructure

The physical properties (mass change, bulk density, apparent porosity and cold crushing strength) of the fired specimens are shown in Table 2. It is apparent that the weight gain and bulk density increased simultaneously with the increment of silicon content, and accordingly, the apparent porosity tended to diminish. Meanwhile, a marked enhancement was also observed in cold crushing strength with the increase of bulk density. Since the oxidation of silicon caused the volumetric expansion of fired