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Ceramics International 33 (2007) 1585–1589

CERAMICS INTERNATIONAL

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Oxidation protection of CaO–ZrO_2–C refractories by addition of SiC

Min Chen [a,*], Nan Wang [a], Jingkun Yu [a], Akira Yamaguchi [b]

[a] *School of Materials and Metallurgy, 312#, Northeastern University, 3-11 Wen-Hua Road, Shenyang 110004, China*
[b] *Okayama Ceramics Research Foundation, 1406-18 Nishi Katakami, Bizen, Okayama 705-0021, Japan*

Received 10 October 2005; received in revised form 24 April 2006; accepted 3 July 2006
Available online 18 September 2006

Abstract

The effect of SiC used as antioxidant in carbon-containing CaO–ZrO_2 refractories and the behaviour of SiC in CO gas were studied. SiC was found to react initially with CO to form SiO_2(s) and C(s) at ~1200 °C, and then the formed SiO_2 reacted with CaO in the refractories to form belite ($2CaO{\cdot}SiO_2$). The refractory microstructure was modified by addition of SiC. Due to the deposition of SiO_2 in the large (2–10 μm) pores of the refractory through the reaction of SiO(g) with CO, the percentage of large pores decreased and a dense layer, mainly consisting of belite, was formed near the surface of the refractory after it was heated at high temperature (1500 °C). The oxidation resistance of CaO–ZrO_2–C refractories was improved by reaction of SiC with CO to deposit C(s) and decrease the size of the large pores. The oxidation resistance of such refractories can be improved significantly when such a dense layer is formed near their surfaces.

Keywords: CaO–ZrO_2–C refractories; Oxidation resistance; Oxidation; Antioxidant

1. Introduction

Carbon possesses excellent thermal shock and slag resistance properties, and it has become an important component of commercial refractories, however, carbon suffers the drawback of poor oxidation resistance [1]. To improve the oxidation resistance of carbon-containing refractories, antioxidants, such as metals (Mg, Al, Si), alloys (Mg–Al) and carbides (B_4C, SiC) are often added to them. The antioxidant selected varies according to the matrix type of the carbon-containing refractories. For example, Mg and Al are often added to MgO–C refractories, whereas SiC is often added to Al_2O_3–C refractories [2,3].

Lime has the advantages of being abundant, having a high melting temperature, a low vapour pressure and thermodynamic stability in the presence of carbon. Accordingly, CaO–C refractories have long been regarded as potentially attractive for applications in the metallurgical industries [4,5]. In recent years, lime-containing refractories have shown great advantages in dephosphorization and desulphurization of molten steel [6]. Nevertheless, the application of CaO refractories has been inhibited owing to its poor hydration resistance, and the main attention of lime refractories research has been in this area [7,8]. The present authors have also studied this topic and prepared hydration resistant CaO–ZrO_2 composites through the formation of a protective $CaZrO_3$ layer around CaO grains [9]. Little attention has been paid to improve the oxidation resistance of CaO–C refractories [10,11].

In the present work, the behaviour of SiC antioxidant in CO gas and the mechanism of improved oxidation resistance of CaO–ZrO_2–C refractories were studied.

2. Experimental procedures

2.1. Starting materials

The starting materials in the present work were CaO–ZrO_2 grain prepared by grinding CaO–ZrO_2 clinker (sintered from a mixture of reagent grade $CaCO_3$ and ZrO_2 in the molar proportion CaO:ZrO_2 = 80:20, with relative density of over 99%) [9] to pass 90 μm, carbon (graphite flake, with purity of over 99.7% and average size of less than 0.5 μm) and SiC (with purity of over 99% and average grain diameter of 2–3 μm).

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* Corresponding author. Tel.: +86 24 6368 2241; fax: +86 24 8368 1576.
E-mail address: slakejp@163.com (M. Chen).

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doi:10.1016/j.ceramint.2006.07.004

Table 1
Composition of the CaO–ZrO_2–C refractories, mass%

Batch	CaO–ZrO_2 grain	Graphite	SiC
1	80	20	0
2	75	20	5

2.2. Sample preparation

Two batches of powder were prepared by wet-mixing (in acetone) CaO–ZrO_2 grain, carbon and SiC in the proportions shown in Table 1. Then the mixed powders were shaped to cylindrical compacts of $D15\ \text{mm} \times \sim 15\ \text{mm}$ and plate compacts of $20\ \text{mm} \times 20\ \text{mm} \times \sim 12\ \text{mm}$ by using CIP (cold isostatic pressing) under 100 MPa with 4 mass% phenolic resin as a binder. Cylindrical compacts were pretreated at 800 °C for 5 h in a carbon powder bed for the carbonization of resin before the oxidation test.

2.3. High temperature behaviour of SiC added to CaO–ZrO_2–C refractories

Approximately 1.5 g of the mixture with SiC addition (with composition of sample 2) was heated in a tube furnace at a heating rate of 10 °C/min. After soaking at different temperatures for 2 h and at 1500 °C for 2–6 h, the heated sample was cooled in the furnace to room temperature at a rate of 10 °C/min. CO gas was bled into the furnace at a flow rate of 0.2 L/min for the duration of the heat treatment. The phase composition of the heat treated mixture was analyzed by using powder XRD (X-ray diffraction, Cu target, 20 kV, 20 mA) and the mass change was measured using an electric balance.

2.4. High temperatures oxidation testing

The oxidation test was carried out by heating the cylindrical bricks in a TG (thermogravimetric) furnace in air (Fig. 1a), with the same heating and cooling rate of 10 °C/min. The pore size distribution of the bricks was examined using mercury porosimetry, and the phase composition of the samples after heating was analyzed using XRD. Cross sections of the heated samples were observed under optical microscopy and SEM (scanning electron microscopy).

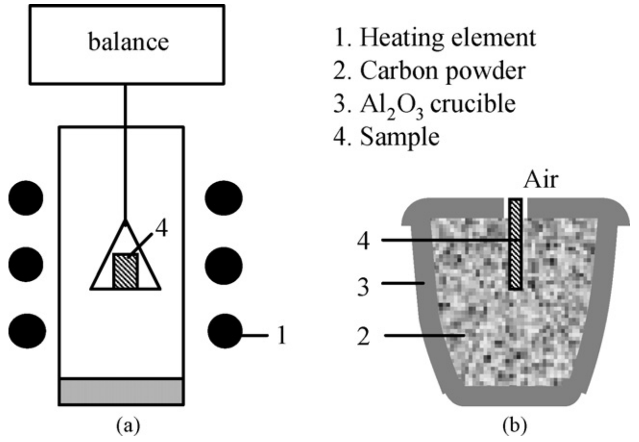

Fig. 1. Schematic diagram of reaction vessel for oxidation test of the CaO–ZrO_2–C refractories.

Because of the low pressure used, the relative density of the brick was so poor that the cylindrical compact was completely oxidized before it reached the higher temperature (1500 °C). To investigate the oxidation behaviour of the refractory with SiC addition at a higher temperature, the oxidation test was also carried out in another electric furnace by embedding most of a plate compact in carbon powder while keeping its top surface exposed to air, as shown in Fig. 1b. The sample was heated to 1500 °C at a rate of 10 °C/min and kept at this temperature for 4 h. After heating, the microstructure was observed under optical microscopy and the composition near the surface was obtained by spot analyses with interval of 200 μm using EPMA (Electron Probe Micro Analysis).

3. Results and discussion

3.1. Behaviour of SiC added to CaO–ZrO_2–C refractories

It is known that the main gaseous species in the refractories is CO when the oxides coexist with condensed carbon. Therefore, the present work investigated the behaviour of SiC added to the refractories in CO gas. Fig. 2 shows the phase change of the CaO–ZrO_2–C refractories with SiC addition after heating at different temperatures for 2 h and at 1500 °C for 2–6 h in CO gas. The intensity of SiC began to decrease significantly above 1200 °C, and, simultaneously, the intensity of CaO decreased and belite (Ca_2SiO_4) began to be detected. This indicates that the SiC reacted with CO to form SiO_2(s) and C(s) according to reaction (1) from ~1200 °C. The identification of belite indicates that the formed SiO_2 reacted further with CaO. For $CaZrO_3$, no change of its intensity after heating at different temperatures confirmed that it was stable in these

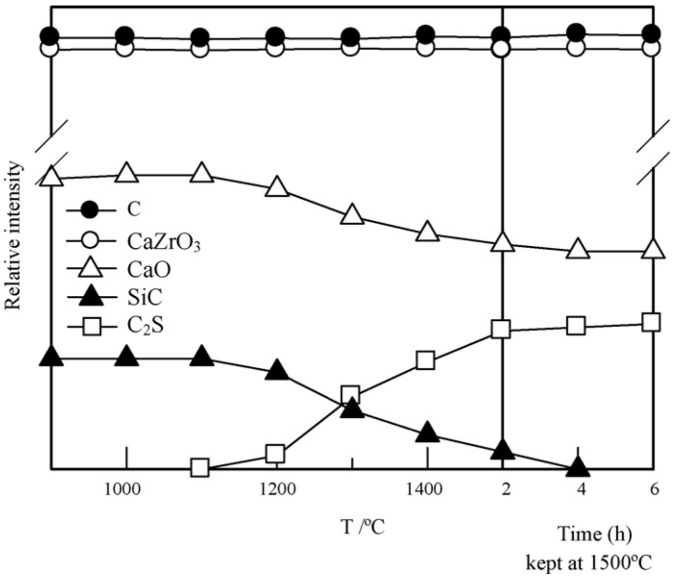

Fig. 2. Phase change of the CaO–ZrO_2–C refractories with SiC addition heated at various temperatures for 2 h and at 1500 °C for different time.

atmospheres and temperature conditions. The intensities of CaO and belite reached a constant value when the sample was heated at 1500 °C for 6 h, indicating the completion of the reaction in the refractories.

$$SiC(s) + 2CO(g) = SiO_2(s) + 3C(s) \quad (1)$$

Fig. 3 shows the mass change of the mixture with SiC addition (with composition of sample 2) after heating at different temperatures for 2 h and at 1500 °C for 2–6 h in CO gas. The abrupt increase of mass gain from 1200 °C also confirmed the occurrence of reaction (1) from this temperature. As previously reported, it is considered that the occurrence of reaction (1) proceeded in the following two steps [2]:

$$SiC(s) + CO(g) = SiO(g) + 2C(s) \quad (2)$$

$$SiO(g) + CO(g) = SiO_2(s) + C(s) \quad (3)$$

Because a part of the SiO(g) volatilized to the atmosphere, it did not completely condense as SiO_2 within the refractories. As a result, after the refractory was heated in CO gas for 6 h, the mass gain of the refractory was only 5.8 mass%, which was less than the theoretical value of 7.0 mass%.

3.2. Improved oxidation resistance of the $CaO–ZrO_2–C$ refractories

Fig. 4 shows the mass changes of the $CaO–ZrO_2–C$ refractories heated to 1300 °C and kept at this temperature for 2 h in air at a heating rate of 10 °C/min. Mass decreased in a similar manner for both samples at lower temperatures, but from 1200 °C, the mass decrease was obviously suppressed and a plateau was found for samples with SiC addition. For samples without SiC, the mass reached a constant value after 11 min at 1300 °C, whereas it was 32 min for samples with SiC. These results indicate that the oxidation of carbon was effectively suppressed by the deposition of C(s) when SiC was added.

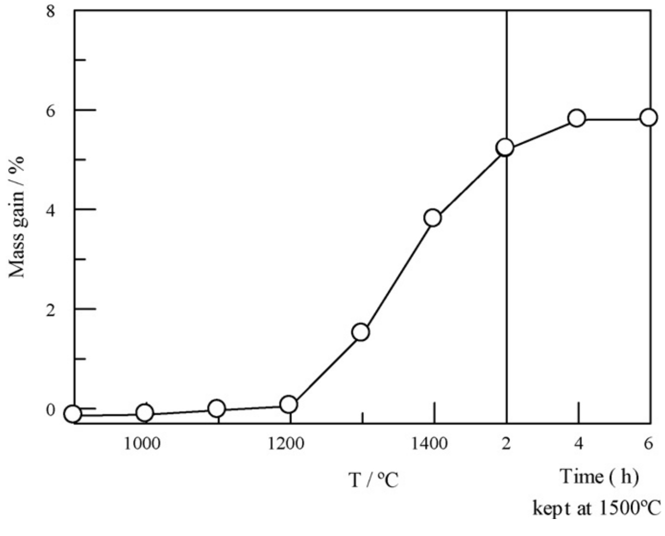

Fig. 3. Mass change of the $CaO–ZrO_2–C$ refractories with SiC addition heated at various temperatures for 2 h and at 1500 °C for different time.

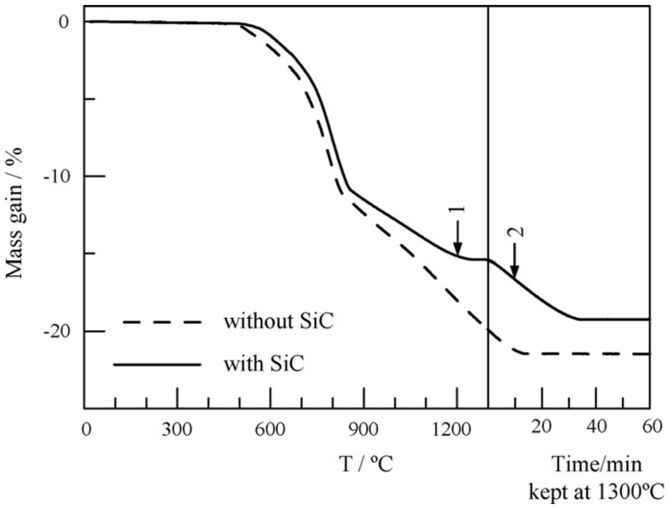

Fig. 4. Mass change of the $CaO–ZrO_2–C$ bricks heated in air at a rate of 10 °C/min.

Fig. 5 shows XRD of the air quenched samples with SiC addition after heating to 1200 °C and holding at 1300 °C for 10 min in air (corresponding to positions 1 and 2 in Fig. 4). It is observed that SiC was still found and no alite or belite [12] formed when samples were heated to 1200 °C, but SiC disappeared and there was an obvious increase in the intensity of alite peaks after the sample was held at 1300 °C for 10 min. Similar to the results shown in Fig. 3, this shows that SiC began to react with CO at ~1200 °C. Because of the occurrence of this reaction, mass loss by carbon oxidation was counterbalanced by deposition of carbon. Thus the oxidation rate was decreased, and a plateau formed (in Fig. 4). Due to the mass increasing while SiC was oxidized to SiO_2, the mass loss of the SiC added refractory was always less than that of the sample without SiC after they were completely oxidized (Fig. 4).

Fig. 6 shows the optical photographs of the $CaO–ZrO_2–C$ refractories after heating at 1300 °C for 10 min. For the sample

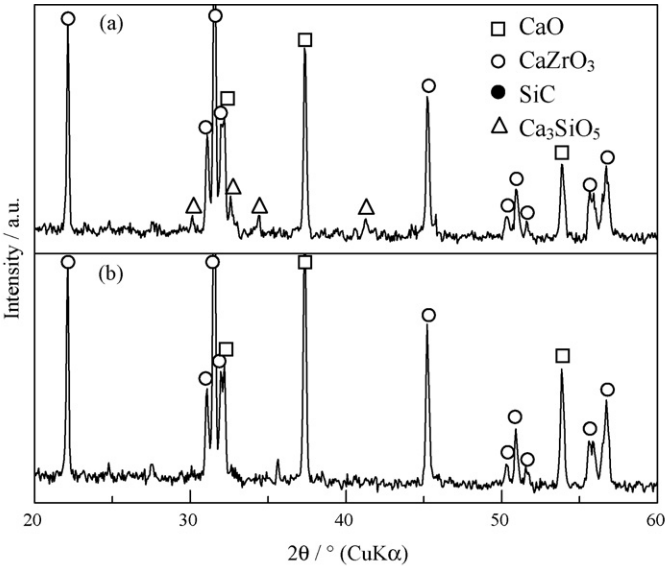

Fig. 5. XRD of the SiC added $CaO–ZrO_2–C$ refractories heated to (a) 1200 °C and (b) kept at 1300 °C for 10 min.

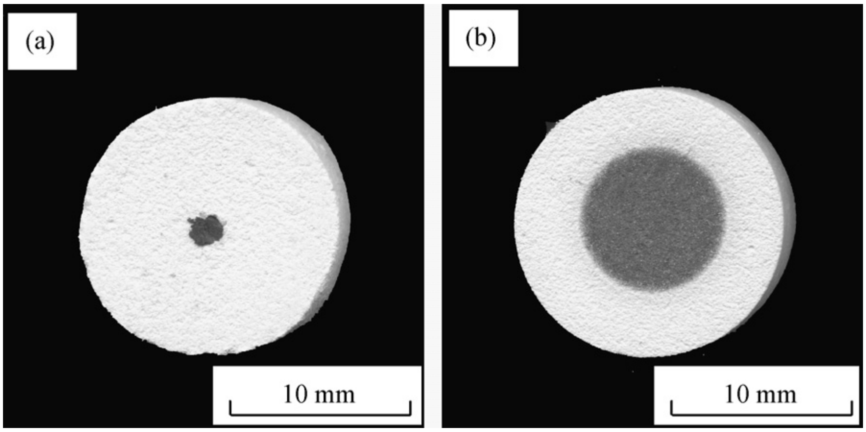

Fig. 6. Section of (a) SiC free and (b) SiC added CaO–ZrO$_2$–C refractories heated at 1300 °C for 10 min in air.

without SiC, the refractories were almost completely oxidized (the central black zone is the unoxidized core). But for the sample with SiC, a large unoxidized zone was still observed. This result also confirmed that the addition of SiC effectively improved the oxidation resistance of the refractories.

3.3. Modification of microstructure

Fig. 7 shows the pore size distribution of the refractories with and without SiC heated at 1300 °C for 2 h. It is observed that although there was no obvious change in apparent porosity (it was 50% and 49% for the sample without and with SiC addition, respectively), the percentage of large pores (2–10 μm) was decreased when SiC was added. The microstructure observation also identified that the amount of large pores decreased when SiC was added, as shown in Fig. 8.

The modification of microstructure was considered to occur by the reaction of SiC turning to SiO$_2$. Because of diffusion of SiO(g) at high temperature, SiO(g) was considered likely to condense as SiO$_2$(s) in the pores. As a result, the pores were filled with SiO$_2$ (which further reacted with CaO to form belite) and the pore size decreased.

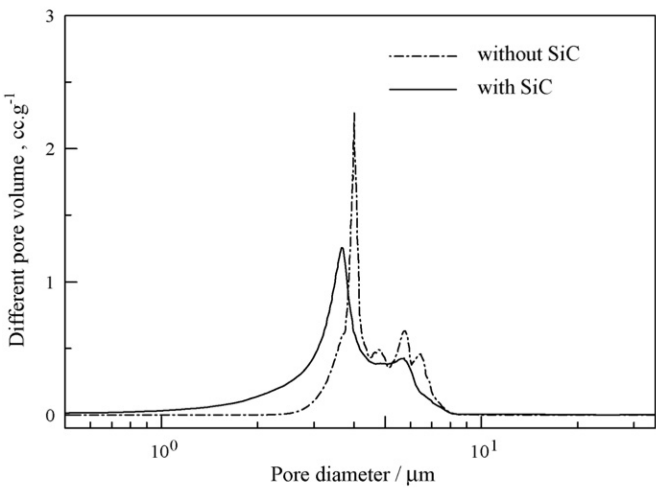

Fig. 7. Pore size distribution of the CaO–ZrO$_2$–C bricks after 2 h at 1300 °C.

It is known that the partial pressure of $P_{\mathrm{SiO(g)}}$ is strongly dependent on temperature. For example, it is calculated that $P_{\mathrm{SiO(g)}}$ is 270 Pa at 1300 °C, increasing to 535 Pa when the temperature is elevated to 1500 °C. Because of the low $P_{\mathrm{SiO(g)}}$ and limited time of SiC coexisting with carbon due to the complete oxidation of carbon at 1300 °C, SiO(g) would be expected to diffuse only a short distance. As a result, SiO(g) reacted with CO gas to condense as SiO$_2$ (reaction (3)) just at the original SiC site or the pores nearby.

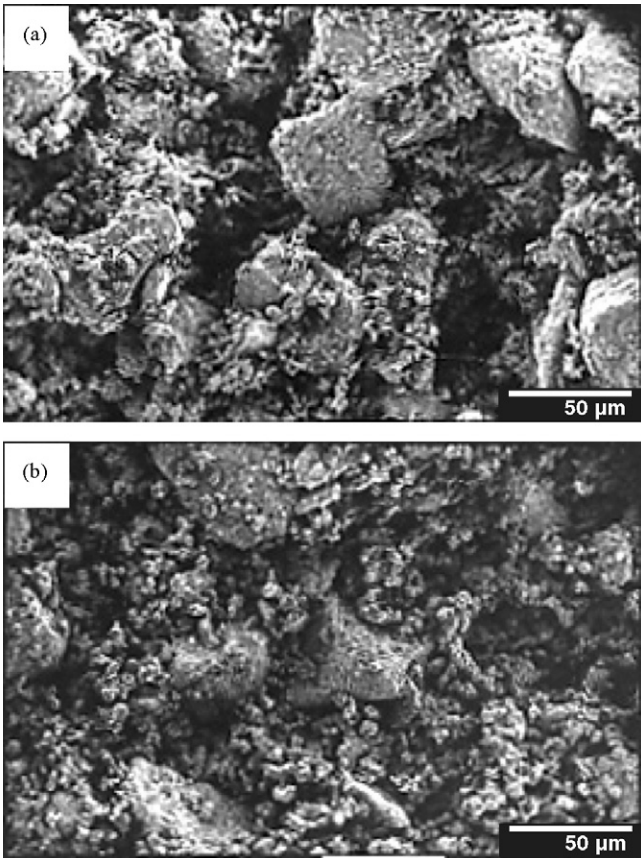

Fig. 8. SEM photographs of the fractured surface of CaO–ZrO$_2$–C bricks (a) without and (b) with SiC addition after heating at 1300 °C for 2 h.

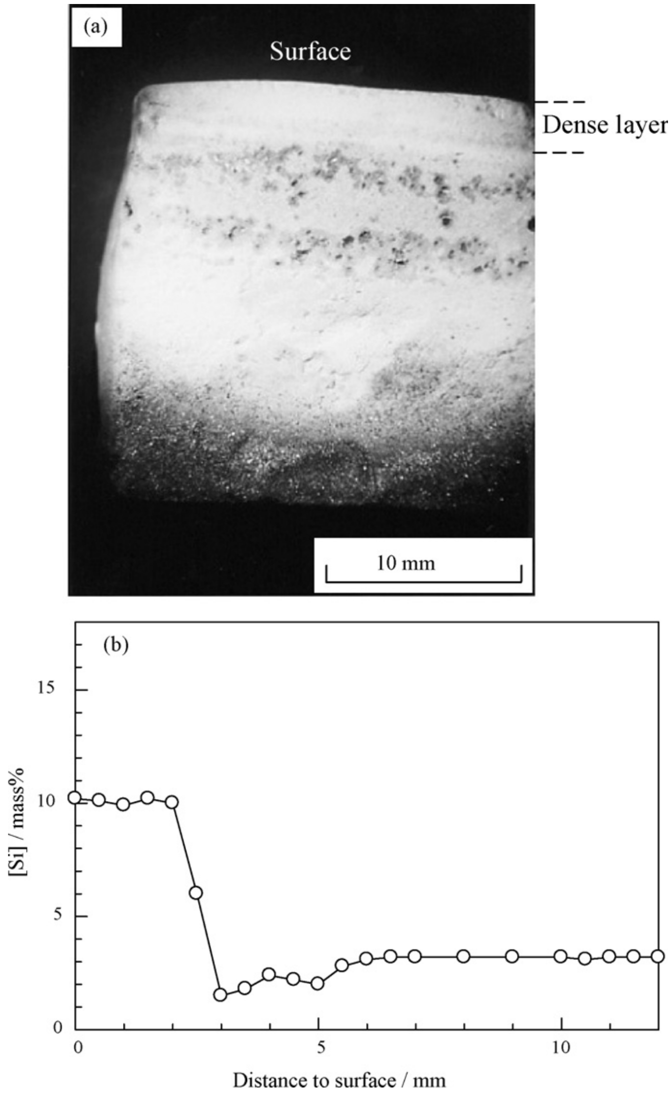

Fig. 9. Reflected light photograph (a) and result of EPMA analysis (b) of the SiC added CaO–ZrO_2–C refractories after heating at 1500 °C for 5 h in carbon bed.

However, when the sample was heated at a higher temperature and SiC coexisted with carbon for a sufficiently long time, the formed SiO(g) diffused continuously to the surface of the refractory and condensed to form SiO_2. Thus, a dense protective layer near the surface of the refractory was formed, as shown in Fig. 9a. EMPA analyses showed that the silicon content in the dense layer was much higher than that in the bulk (Fig. 9b). This confirms that the dense layer formation near the surface arises by the condensation of SiO(g). It is considered that the formation of a dense protective layer can effectively suppress the diffusion of oxygen into the refractories and improve its oxidation resistance.

4. Conclusions

Based on the above results, the following conclusions were drawn when SiC was added as an antioxidant to the CaO–ZrO_2–C refractories:

(1) SiC begins to react with CO gas at ~1200 °C, forming C(s) and SiO_2(s). The latter further reacts with CaO to form belite. Due to the diffusion and condensation of SiO(g), the microstructure was modified. The percentage of large pores (2–10 μm) is decreased and a dense protective layer is formed when SiC coexists with condensed carbon in the refractory at higher temperature (1500 °C) for enough time.

(2) The addition of SiC improves the oxidation resistance of CaO–ZrO_2–C refractories by reaction of SiC with CO gas to deposit carbon and modification of the microstructure. In particular, a dense protective layer formed near the refractories surface is effective in improving the oxidation resistance.

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