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Effects of SiC on the Properties and Microstructures of Closed-Pore Al_2O_3–$MgAl_2O_4$ Refractory Aggregates

ABSTRACT

Closed-pore Al_2O_3–$MgAl_2O_4$ refractory aggregates have been prepared successfully based on the superplasticity of Al_2O_3 ceramic by using a mixed ball-milling method and the gelcasting method. The effects of SiC content on phase composition, porosity and microstructures of the refractory aggregates have been investigated. The properties of Al_2O_3–$MgAl_2O_4$ refractory aggregates fabricated by different methods have been compared to our results. We discuss the influence mechanism of SiC on the refractory aggregate. The results showed that the main phase compositions were corundum and $MgAl_2O_4$ spinel with accompanying small amounts of mullite phase. The closed porosity increased with increased addition of SiC. SiC facilitated the sinterability of materials resulting in a low level of apparent porosity. When compared to the mixed ball-milling method, the closed pore size distribution in the refractory aggregates fabricated by the gelcasting method was more uniform.

1. Introduction

There has been a growing interest in the porous refractory aggregate as a substitute for the dense one in recent years due to its good heat-insulating property, high thermal shock resistance, and the light weight of the metallurgical container [1–3]. Several methods have been used for the fabrication of porous refractory aggregates, such as the pore-forming agent method [4, 5], in-situ synthesis [6, 7], direct-decomposition of inorganic compounds [8, 9] and the reaction-bonding technique [10, 11]. However, the pores of porous refractory aggregates prepared by the aforementioned methods are open. The molten slag may pass through the open pores to erode the refractory should these porous refractory aggregates be used for the working linings of the metallurgical container.

Recently, we fabricated novel closed-pore Al_2O_3–$MgAl_2O_4$ refractory aggregates utilizing the superplasticity of an Al_2O_3-based ceramic. As the Al_2O_3-based ceramic with its fine crystal grains has a superplastic deformation ability at high temperature [12], when SiC is added as a high temperature pore-forming agent, the gases generated by the reaction of SiC are able to provide the pressure to drive grain boundary sliding. Then, the released gases will be enclosed by grain boundaries which results in the formation of closed pores. However, as the closed porosity and the pore size distribution are determined by the SiC, the content and dispersion of SiC in the green body of Al_2O_3-based materials are the main factors that influence the properties and microstructures of the fabricated Al_2O_3–$MgAl_2O_4$ refractory aggregates.

In this study, in order to investigate the effect of SiC dispersion on the properties of a refractory aggregate, a mixed ball-milling method and a gelcasting method are employed to fabricate the refractory aggregate. The gelcasting method is a novel near-net shaping process by which polymerization of organic monomers solidifies the ceramic powder suspensions [13]. In this case, as the SiC powder is dispersed in the suspensions of raw materials, it may be expected to present good dispersion in the green body of the Al_2O_3-based material after drying. Subsequently, a uniform pore size distribution of the closed pores in the refractory aggregate may be obtained. As SiC is the source of the released gases to form the closed pores, the effects of SiC content on the properties of closed-pore Al_2O_3–$MgAl_2O_4$ refractory aggregates are also investigated.

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2. Experimental

Submicron-sized alumina and magnesia powders ($D_{50} \leq 0.5$ µm, Shanghai Chaowei Nano Technology Co., Ltd., China) are used as raw materials because the superplasticity is related to the grain size. Magnesia powders were selected to improve its superplasticity. Submicron-sized SiC ($D_{50} = 0.5$ µm, Shanghai Chaowei Nano Technology Co., Ltd., China) was used as high-temperature pore-forming agent.

The compositions of the samples are listed in Table 1. The preparation procedure for the mixed ball-milling method was that various amounts of Al_2O_3, MgO, and SiC were initially mixed, then ball-milled in ethanol for 24 h using alumina balls as media. After fully mixing and drying, the powders were pressed at 100 MPa using a steel die to obtain cylindrical specimens; then the specimens were sintered at 1600 °C for 6 h with a heating rate of 4 K/min in an electric furnace.

The process for the gelcasting method was similar to that reported previously [14]. A water-soluble epoxy resin and hardener system was chosen for gelcasting. Firstly, various amounts of Al_2O_3, MgO, and SiC were mixed and ball-milled. Ethylene glycol diglycidyl ether (Meryer Chemical Technology Co. Ltd., China), polyethyleneimine (Aladdin Industrial Corporation, China) and distilled water at a mass ratio of 1 : 1.5 : 2 were mixed as the premix solution. Then, the Al_2O_3, MgO, and SiC mixed powders were added to the above premix solution to prepare an aqueous slurry. For dispersion, 0.8 mass-% of ammonium citrate (Shanghai Aibi Chemistry Preparation Co. Ltd., China) was added. Vigorous stirring and ultrasonic shaking was applied to guarantee uniform dispersion. Before casting to the molds, the slurries were degassed in a vacuum chamber to reduce trapped bubbles. Finally, the wet green bodies were dried at room temperature for 24 h, and subsequently the binder was burnt out at 600 °C for 2 h. The sintering process was carried out at 1600 °C for 6 h with a heating rate of 4 K/min.

Table 1 · Chemical composition of the samples (in mass-%)

Samples	Al_2O_3	MgO	SiC
S0	90	10	0
S1	89.5	10	0.5
S2	89	10	1
S3	88.5	10	1.5
S4	88	10	2

The apparent porosity of all samples was determined by the Archimedes method with water as the medium. The closed porosity P_c of the samples was calculated as follows.

(1)

$$P_c = (1- \frac{\rho_o}{\rho}) \times 100\% - P_a$$

Where P_a is apparent porosity ρ_0 is bulk density and ρ is theoretical density.

Phase compositions were identified by X-ray diffraction (XRD, Model D500, Siemens) using CuK_α radiation. The microstructure and morphology of samples were observed by scanning electron microscopy (SEM, Model JSM-6400, JEOL, Japan) with an integrated X-ray energy-dispersive spectroscopy (EDS, Oxford, UK) unit.

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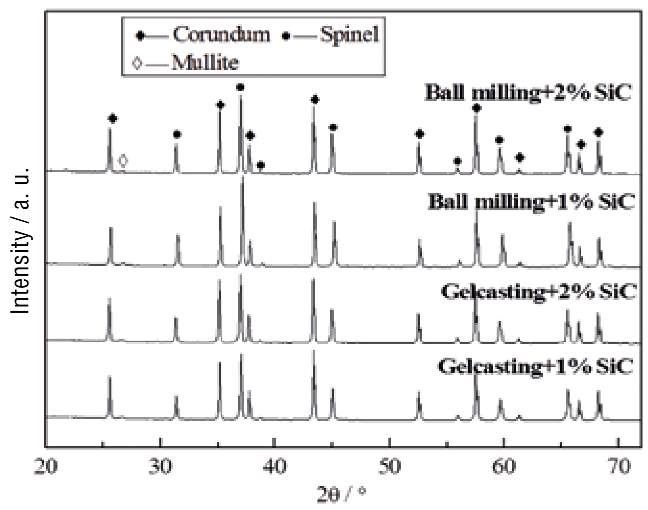

Fig. 1 • The XRD patterns of samples fabricated by two methods with various amounts of SiC

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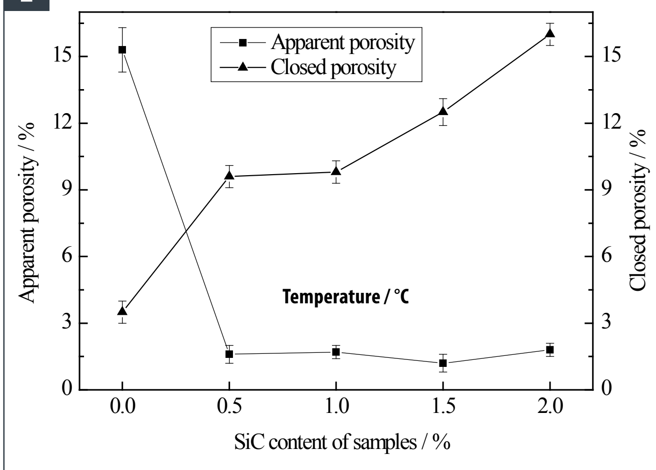

Fig. 2 • The apparent and closed porosity of samples with different amounts of SiC fabricated by the mixed ball-milling method

3. Results and discussion

3.1 Phase composition

Figure 1 shows the XRD patterns of the samples with various amounts of SiC fabricated by the mixed ball-milling and gelcasting methods. The main crystalline phases are corundum and $MgAl_2O_4$ spinel in all samples. This indicates that the added MgO has reacted completely with Al_2O_3 to form $MgAl_2O_4$ spinel. In addition, it can also be seen that small amounts of mullite phase are detected in all samples. This indicates that the added SiC may be firstly partially oxidized and then subsequently reacts with Al_2O_3 to finally form the mullite phase.

3.2 Porosity

The apparent and closed porosity of refractory aggregates fabricated by the mixed ball-milling method as a function of SiC addition from 0 to 2 % are shown in Fig. 2. In the sample without added SiC, the apparent porosity is 15.3 % and the closed porosity is only 3.5 %. This is attributed to the reaction between Al_2O_3 and MgO which generates $MgAl_2O_4$ spinel accompanied by a large volume expansion during the sintering process. This volume expansion suppresses densification which leads to a high apparent porosity. However, after adding SiC, a high closed porosity and low apparent porosity is seen. This indicates that the addition of SiC influences the properties of refractory aggregates in two ways. On one hand, the high closed porosity is formed by the reaction of SiC. On the other hand, the added SiC improves the sinterability of refractory aggregates leading to a relatively lower apparent porosity. With increasing addition of SiC, the closed porosity increases markedly; the sample with 2 % SiC has a closed and apparent porosity of 16.0 and 1.8 %, respectively. Unfortunately, some bumps were found on the surface of the sample with 2 % SiC, that is to say that there are big closed pores in the sample. This is also the reason that the closed porosity increases markedly when the addition of SiC exceeds 1 %. This is related to aggregation of SiC particles, which means more gases are generated by the reaction of SiC at high temperature. This results in formation of a higher pressure which drives grain boundary sliding faster, resulting in the formation of big closed pores.

Figure 3 compares the apparent and closed porosity of refractory aggregates fabricated by the gelcasting method with different amounts of SiC. With the addition of SiC from 0 to 2 %, the tendency of both the apparent and closed porosity of the samples is similar to that of those fabricated by the mixed ball-milling method. The main difference is that the closed porosity increases slowly when the addition of SiC exceeds 1 %; also bumps were not found on the surface of the samples. This indicates that the distribution of SiC powders in the green body is uniform after

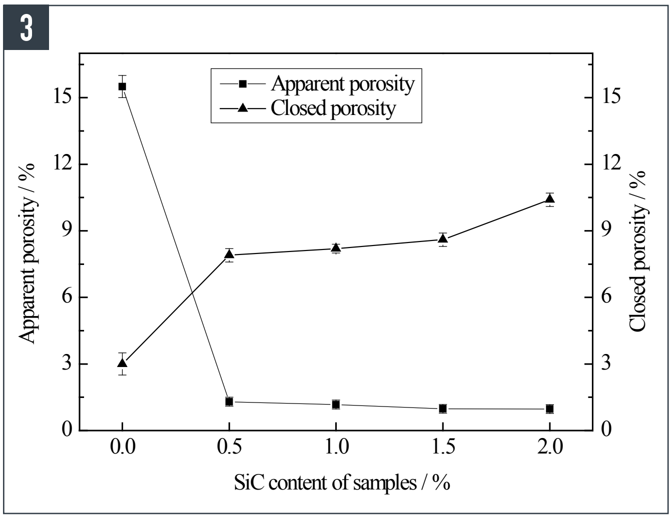

***Fig. 3** • The apparent and closed porosity of samples with different amounts of SiC fabricated by the gelcasting method*

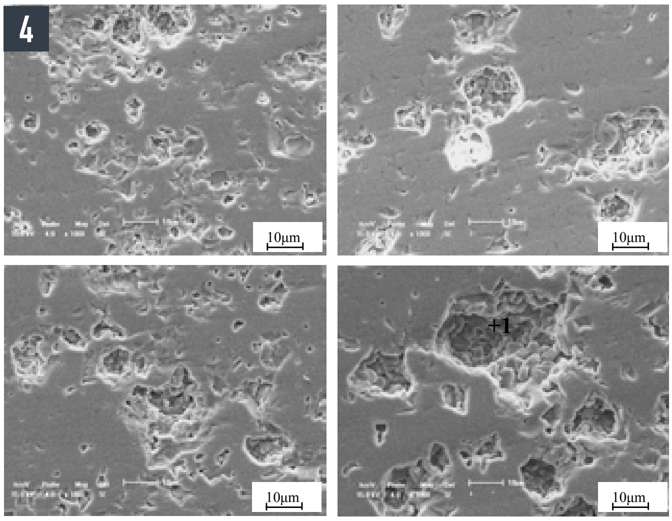

***Fig. 4** • SEM images of fracture surface of samples fabricated by the mixed ball-milling method*

the gelcasting process. Accordingly, the gases generated by the reaction of SiC at high temperature are separated by crystalline grains resulting in closed pores without the big ones. Subsequently, the closed porosity is only about 10.4 % in the sample with addition of 2 % SiC.

3.3 Microstructure

The SEM images of the fracture surface of the Al_2O_3–$MgAl_2O_4$ refractory aggregates fabricated by the mixed ball-milling method are shown in Fig. 4. Lots of pores can be observed on the fracture surface of the samples and the pores are nearly circular and exist relatively independently; also, the crystalline grains on the internal wall of the pores can be observed. These characteristics indicate that there are closed pores. With the increasing addition of SiC, the amounts of pores in refractory aggregates increase and the pore size is obviously larger. This indicates that aggregation between SiC particles has been caused resulting in the formation of big closed pores. The results are consistent with the aforementioned closed porosity of the refractory aggregates fabricated by the mixed ball-milling method.

Figure 5 shows the SEM images of the fracture surface of the samples fabricated by the gelcasting method for comparison with the mixed ball-milling method. Here also a large number of closed pores can be observed in the fracture surface of the samples. However, with increasing addition of SiC, the pore size of the samples has not improved accordingly. Also, the pore size distribution is relatively uniform. The latter indicates that the gelcasting process can obviously improve the dispersion of SiC powders in the green body.

Table 2 shows the EDS spot analysis on the internal wall of closed pores in the samples fabricated by the mixed ball-milling and gelcasting method, respectively. A silicon element has been found on the internal wall of the closed pores. It can thus be proved that the closed pores are formed by the reaction of SiC. In addition, the content of the silicon element of the sample fabricated by the mixed ball-milling method is larger than that of the sample fabricated by the gelcasting method. This also indicates that aggregation between SiC particles has been caused in the green body, finally resulting in more silicon-containing compounds on the internal wall of the closed pores.

Concerning the effects of SiC on the properties and microstructures of Al_2O_3–$MgAl_2O_4$ refractory aggregates, we found that the addition of SiC does not only form closed pores, but also improves the sinterability of the materials. In the initial stage of the sintering process, as the green body had a loose structure, the SiC was partial oxidized in the oxygen-rich atmosphere according to reaction (2).

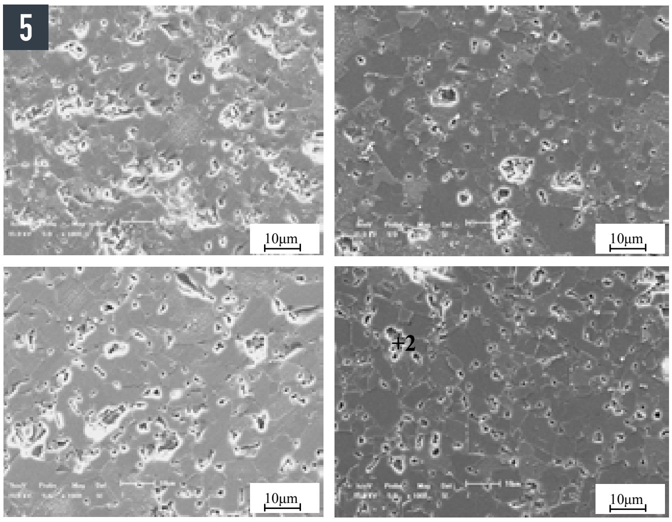

***Fig. 5** • SEM images of fracture surface of samples fabricated by the gelcasting method*

Table 2 · EDS spot analysis results on the internal wall of closed pores in Figs. 4 and 5 (in mass-%)

Position	Mg	Al	O	Si
Point 1	6.38	46.85	42.15	4.62
Point 2	16.39	48.95	33.69	0.97

(2)

$$2SiC(s) + 3O_2(g) = 2SiO_2(s) + 2CO(g)$$

As SiC possesses excellent antioxidant ability, a protective layer of SiO_2 is formed to prevent deep oxidization. With the sintering temperature gradually increasing to 1600 °C, the newly formed SiO_2 diffuses slowly to the grain boundary to facilitate the densification of the sintering and reacts with Al_2O_3 to form mullite. And then, the SiC residue is in an oxygen-poor atmosphere, and would be actively oxidized according to reaction (3).

(3)

$$SiC(s) + O_2(g) = SiO(g) + CO(g)$$

Meanwhile, SiC may also react with the material matrix according to reaction (4), which is feasible in thermodynamics [15].

(4)

$$aSiC + b[n(Al_2O_3)MgO] = (b\text{-}2a)[n'(Al_2O_3)MgO] + 2aMg(g) + aCO(g) + aSiO(g)$$

Hence, because the Al_2O_3-based matrix possesses a superplastic deformation ability, the new formed gases, such as SiO, CO or Mg, lead to pressure which drives grain boundary sliding. Lastly, the closed pores are formed in the Al_2O_3–$MgAl_2O_4$ refractory aggregates.

When the mixed ball-milling method was used, aggregation between SiC particles occurs and accordingly more gases are generated in the high temperature. The pressure was higher as the released gases were greater. Subsequently, the superplastic deformation generated by grain boundary sliding was greater resulting in the formation of bigger closed pores.

When the gelcasting method was used, the SiC particles were dispersed uniformly in the green body. The gases generated by the reaction of SiC are able to obtain an appropriate superplastic deformation, leading to formation of a uniform pore size distribution.

4. Conclusions

Closed pore Al_2O_3–$MgAl_2O_4$ refractory aggregates were fabricated using a mixed ball-milling method and a gelcasting method with SiC as the high-temperature pore-forming agent. The closed porosity of refractory aggregates increased with increasing content of SiC. Comparing to the mixed ball-milling method, the refractory aggregates fabricated by the gelcasting method possess a more uniform closed pore size distribution. Because of the superplastic deformation ability of of Al_2O_3-based ceramic, the gases released by the reaction of SiC at high temperature could provide a pressure to drive grain boundary sliding resulting in the formation of closed pores. The main phase compositions are corundum and $MgAl_2O_4$ spinel with accompanying small amounts of mullite. As SiO_2 could be generated in the sintering process, the addition of SiC could also improve the sinterability of Al_2O_3–$MgAl_2O_4$ refractory aggregates resulting in a low level of apparent porosity.

Acknowledgments

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