Effect of particle size on microstructure and strength of porous spinel ceramics prepared by pore-forming *in situ* technique

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Abstract. The porous spinel ceramics were prepared from magnesite and bauxite by the pore-forming *in situ* technique. The characterization of porous spinel ceramics was determined by X-ray diffractometer (XRD), scanning electron microscopy (SEM), mercury porosimetry measurement etc and the effects of particle size on microstructure and strength were investigated. It was found that particle size affects strongly on the microstructure and strength. With decreasing particle size, the pore size distribution occurs from multi-peak mode to bi-peak mode, and lastly to mono-peak mode; the porosity decreases but strength increases. The most apposite mode is the specimens from the grinded powder with a particle size of $6.53\ \mu\text{m}$, which has a high apparent porosity (40%), a high compressive strength (75.6 MPa), a small average pore size ($2.53\ \mu\text{m}$) and a homogeneous pore size distribution.

Keywords. Porous spinel ceramics; particle size; magnesite; bauxite; microstructure; strength.

1. Introduction

There is a large energy consumption in the metallurgical industry. The high thermal conductivities of traditionally dense refractories as metallurgical furnace lining result in a large energy waste (Wen *et al* 2005). Recently, with increased demand for saving energy, more attention has been paid to lightweight refractories (Wen *et al* 2005; Yan and Li 2006, 2008, 2009, 2010). Traditionally lightweight refractories mainly consisted of $\text{Al}_2\text{O}_3\text{--SiO}_2$ materials, which are acidic and have low strength, and cannot be used as working line in many furnaces (Dunaeva 2006). Basic lightweight refractories with high strength are required.

Usually, increasing strength of lightweight aggregates is beneficial to increasing strength of lightweight refractories (Wen *et al* 2005). The porosity and the pore size distribution affect the strength of porous aggregates. Smaller pore size and homogenous pore distribution are thought to be helpful to improve the strength of aggregates (Wen *et al* 2005). The lightweight $\text{Al}_2\text{O}_3\text{--MgO}$ refractories with high strength and high slag resistance were prepared, using the porous spinel ceramics with small pore size and homogenous pore distribution as aggregates (Yan *et al* 2008, 2009).

Generally, the spinel can be synthesized by an electrofusion method, a sintering method and a mechano-chemical method (Kashcheev and Semyannikov 2000; Dasgupta *et al* 2006; Lodha *et al* 2008), and the porous structure can be achieved by a conventional powder-processing route with the incorporation of some pore-forming agents, or

by injection molding or gel casting (Xie 1998; Liu *et al* 2001; She and Ohji 2003). Porous alumina ceramics were prepared by decomposition of $\text{Al}(\text{OH})_3$ to form pores *in situ* (Deng *et al* 2001). This pore-forming *in situ* technique is a good way to prepare porous ceramics with well-distributed pores, and is environment friendly (Deng *et al* 2001; Li and Li 2005, 2007; Wen *et al* 2005; Yan and Li 2006; Yan *et al* 2010). Porous spinel ceramics have been prepared using magnesite and bauxite powders as raw materials, by the pore-forming *in situ* technique, and the effects of composition and sintering temperature on the microstructure and strength have been investigated (Wen *et al* 2005). Besides composition and temperature, particle size is an important factor in ceramic processing, can affect the particle packing of green compact and mass transport in reaction sintering, and further affect the microstructure and strength. In this paper, the porous spinel ceramics were prepared from the magnesite and bauxite mixtures with different average particle sizes, and some results were obtained.

2. Experimental

The grinded materials were magnesite and bauxite and their chemical compositions are listed in table 1. Five powder mixtures consisted of 39 wt% magnesite and 61 wt% bauxite which is consistent with a stoichiometric spinel proportion of MgO to Al_2O_3 . The above grinded powders were ground using alumina balls for 3h, 6h, 9h, 12h, 15h, respectively. The average particle sizes of grinded powders were

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8.74 μm , 6.53 μm , 4.61 μm , 3.58 μm and 2.56 μm , respectively and the grinded powders were named as A, B, C, D and E corresponding to their average particle sizes. The grinded powders were pressed in cylinders with a height of 36 mm and a diameter of 36 mm at a pressure of about 100 MPa and the green compacts after drying at 110°C were heated at 1340°C for 180 min in an electric furnace, and then furnace-cooled.

The particle size was measured by laser particle size analyser (Mattersizer 2000). Apparent porosity was detected by Archimedes' Principle with water as medium. Compressive strength of sintered specimens at room temperature was measured. Phase analysis was carried out by X-ray diffractometer (Philips Xpert TMP) with a scanning speed of 2° per minute. The content of spinel in specimen A was obtained by the X-ray diffractometer using α -quartz as an internal standard. Pore size distribution and average pore size were measured by a mercury porosimetry measurement (AutoPore IV 9500, Micromeritics Instrument Corporation). Microstructures were observed by a scanning electron microscopy (Philips XL30). The liquid phase content in specimen was calculated from the Equilib Mode of MgO–Al₂O₃–SiO₂–CaO–TiO₂–Fe₂O₃ system by the FactSage 6.1 thermochemical software. In this calculation, ELEM, FACT 53 and FToxid database were used, and the liquid phase came from FToxid-SLAGA.

3. Results and discussion

3.1 Phase identification

Figure 1 shows the XRD pattern of specimens sintered at 1340°C for 3h to identify the formed phases. In specimen A, the phases are: major spinel (MgAl₂O₄, 89 wt%, JCPDS # 75-1797) and minor magnesium aluminum titanium oxide (MgAl₂Ti₃O₁₀, <11 wt%, JCPDS # 05-0450). With a decrease in particle size, the peaks of spinel and magnesium aluminum titanium oxide change a little. It means that the spinel ceramics were synthesized successfully and the effect of particle size on phase composition was not obvious. The liquid phase content of specimens at 1340°C is 7.13 wt% and not too high, calculated by FactSage thermochemical software. It would not give strong effects on the properties of the materials at elevated temperature.

3.2 Pore characterization

Figure 2 gives the relationship of apparent porosity with particle size. With decreasing particle size, the apparent porosity decreases gradually but the apparent porosities are more than 35% when particle size is >4.61 μm , with further decreasing particle size, the apparent porosity is <30%, which is associated with higher extent of sintering.

Table 1. Chemical compositions of magnesite and bauxite (wt%).

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	IL
Magnesite	1.02	2.51	0.22	0.35	46.3	0.14	0.13	0.14	49.33
Bauxite	5.25	74.21	0.92	0.25	0.29	0.076	0.021	4.38	14.46

Figure 1. XRD pattern of specimens sintered at 1340°C for 3h.

Figure 2. Apparent porosity of specimens sintered at 1340°C.

Figure 3. Pore size distribution of specimens sintered at 1340°C.

Figure 4. Microstructure of specimen prepared from grinded powder A sintered at 1340°C.

The pore size distributions of the sintered specimens prepared from grinded powders with different particle sizes are shown in figure 3. The average pore sizes of these specimens from grinded powders A, B and E are $4.38 \mu\text{m}$, $2.53 \mu\text{m}$ and $1.32 \mu\text{m}$, respectively. The multi-peak mode of pore size distribution is observed in specimen from grinded powder A with a particle size of $8.74 \mu\text{m}$, consisting of three peaks. The bi-peak modal of pore size distribution is observed in specimen from grinded powder B with a particle size of $6.53 \mu\text{m}$. When the particle size is $2.56 \mu\text{m}$, the pore distribution becomes mono-peak mode of pore size distribution. It indicates that with a decrease in particle size, the pore size distribution becomes narrower and the pores are homogenous.

In order to investigate the change of the pore distribution, the microstructures of the specimens prepared from grinded powders with different particle sizes are given in figures 4–6. As can be seen in these figures, the microstructures of these specimens are rather different. In specimen from the grinded

Figure 5. Microstructure of specimen prepared from grinded powder B sintered at 1340°C.

Figure 6. Microstructure of specimen prepared from grinded powder E sintered at 1340°C.

powder A with a particle size of $8.74 \mu\text{m}$, there were two types of pores, as shown in figure 4, one located in the particles (1 in figure 4) which mainly comes from the decomposition of magnesite, the other located at particle intersections (2 in figure 4) which resulted from the particle packing. These two types of pores were also observed in the porous mullite ceramics fabricated by the same method, and the evolution of pores was explained (Yan and Li 2006). Obviously, the latter pore size is larger. When the particle size decreased to $6.53 \mu\text{m}$, the difference between the two types of pores is not obvious. With further decrease in particle size to $2.56 \mu\text{m}$, there is no any difference between the two types of pores. It was in accordance with the results of figure 3.

The porosity and pore size distribution of the specimens depend on four factors (Wen *et al* 2005): (i) porosity of green compact which depends on the particle size distribution of raw powder and the pressure of compacting, (ii) decomposition of magnesite which finishes at temperature below

Figure 7. Compressive strength of specimens sintered at 1340°C.

700°C, (iii) expansion caused by formation of spinel and (iv) sintering.

Among four factors mentioned above, factors 2 and 3 can be ignored because the five grinded powders have same compositions. The particle size plays three roles. Firstly, smaller particle can decrease the size of pore resulting from particle packing. Secondly, smaller particle also decreases the porosity of green compact. Lastly, smaller particle can enhance sintering by promoting mass transport. With decreasing particle size, on the one hand, the difference between the two types of pores become smaller, and then the pore size distribution takes place from multi-peak mode to bi-mode, and lastly to mono-peak mode; on the other hand, the porosity decreases and the neck between particles grow (Yan and Li 2006).

3.3 Compressive strength

The relationship between the particle size of the grinded powders and compressive strength of porous spinel ceramics is shown in figure 7. The strength increases with increasing particle size of the grinded powders. The increase of strength may come from three hands. The first is the decreasing porosity (figure 2). The second is the well distribution of pore size

(figure 3). The last and most important is the formation of well-developed neck between the particles (figures 4–6).

4. Conclusions

The porous spinel ceramics were prepared from magnesite and bauxite by the pore-forming *in situ* technique, and the effects of particle size on microstructure and strength were investigated. It is found that particle size affects strongly on the microstructure and strength. With decreasing particle size, the pore size distribution takes place from multi-peak mode to bi-peak mode, and lastly to mono-peak mode; the porosity decreases but strength increases. The most appropriate mode is the specimens from the grinded powder with a particle size of 6.53 μm, which has a high apparent porosity (40%), a high compressive strength (75.6 MPa), a small average pore size (2.53 μm) and a homogeneous pore size distribution.

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References

- Dasgupta S, Kim K B, Ellrich J, Eckert J and Manna I 2006 *J. Alloys Compd* **424** 13
- Deng Z Y, Fukasawa T, Ando M, Zhang G J and Ohji T 2001 *J. Am. Ceram. Soc.* **84** 485
- Dunaeva M N 2006 *Refract. Ind. Ceram.* **47** 199
- Kashcheev I D and Semyannikov V P 2000 *Refract. Ind.* **41** 9
- Li S and Li N 2005 *Sci. Sinter.* **37** 173
- Li S and Li N 2007 *Int. Ceram.* **33** 551
- Liu Y F, Liu X, Wei H and Meng G Y 2001 *Ceram. Int.* **27** 1
- Lodha R, Troczynski T and Oprea G 2008 *Interceram* **57** 324
- She J H and Ohji T 2003 *Mater. Chem. Phys.* **80** 610
- Wen Y, Nan L and Han B Q 2005 *Am. Ceram. Soc. Bull.* **84** 9201
- Xie Z 1998 *Bull. Chin. Ceram. Soc.* **2** 18
- Yan W and Li N 2006 *Am. Ceram. Soc. Bull.* **85** 9401
- Yan W, Li N and Han B 2008 *Int. J. Appl. Ceram. Tech.* **5** 633
- Yan W, Li N and Han B 2009 *Sci. Sinter.* **41** 275
- Yan W, Li N and Han B 2010 *J. Ceram. Process. Res.* **11** 388