

Effects of sintering temperature on pore characterization and strength of porous corundum-mullite ceramics

Wen Yan*, Nan Li and Bingqiang Han

The Hubei Province Key Laboratory of Refractories and Ceramics, Wuhan University of Science and Technology, Wuhan, P.R. of China

The effects of sintering temperature on the pore characteristics and strength of porous corundum-mullite ceramics made from $\text{Al}(\text{OH})_3$, kaolinite gangue and MgCO_3 were investigated through an X-ray diffractometer (XRD), scanning electron microscopy (SEM), mercury porosimetry measurement, etc. It was found that the sintering temperature strongly affects the formation of secondary mullite, and then changes the pore characteristics and strength. The formation of secondary mullite takes place extremely quickly at 1500 °C. The pore size distributions are bimodal in samples sintered at 1300 °C and 1400 °C, and mono-modal in samples sintered at 1500 °C and 1600 °C. The strength are the same and low when the sintering temperatures are 1300 °C and 1400 °C, and increase sharply when the sintering temperature is increased to 1500 °C. The most apposite mode is a sample sintered at 1500 °C which has a high mullite content (86.6 wt%), high apparent porosity (42%), high crushing strength (52 MPa) and a homogeneous pore size distribution.

Key words: porous ceramic, corundum-mullite, pore characterization, strength, sintering temperature.

Introduction

Porous mullite ceramics have attracted extensive attention due to mullite's unique properties, such as low thermal expansion, high thermal shock resistance, and remarkable creep resistance as well as excellent mechanical and chemical stability [1-8]. Usually, a porous structure can be achieved by a conventional powder-processing route with the incorporation of some pore-forming agents such as starch, graphite or organic particulates [1], or by gelcasting [2], or by injection molding [9]. Many researchers have prepared porous ceramics by decomposition of starting materials to form pores in situ [6-8, 10-12]. This pore-forming in situ technique is a good way to prepare porous ceramics with well-distributed pores and environment friendly because not producing more carbon oxides [10].

Kaolinite ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) is one of the most used starting materials for aluminosilicate-based ceramics, due to its common occurrence and good availability [6-8, 13, 14]. Kaolinite gangue is a large coal mine waste in China. Utilization of this gangue to decrease pollution of the environment is interesting [6]. Porous corundum-mullite ceramics were prepared using $\text{Al}(\text{OH})_3$ and kaolinite gangue as starting materials by in situ decomposition pore-forming technique [6, 7], and the strength of these porous ceramics were enhanced by introducing MgCO_3 additive [8].

The reaction between kaolinite and alumina is limited

and the primary mullite crystals are formed by the decomposition of meta-kaolinite at temperatures below 1300 °C [14-17]. Usually, the rate of secondary mullite formation is very slow until the formation of eutectic liquid at 1587 °C and extremely rapid at 1600 °C [17]. However, when MgCO_3 is introduced into the mixtures of $\text{Al}(\text{OH})_3$ and kaolinite gangue to prepare porous ceramics, the sintering temperature at which the formation of secondary mullite takes place extremely rapidly must be changed, and the pore characteristics and strength will be affected. This will be addressed in the present paper.

Experimental

The starting materials were $\text{Al}(\text{OH})_3$, kaolinite gangue and MgCO_3 . The chemical compositions of starting materials are listed in Table 1. The average particle size of $\text{Al}(\text{OH})_3$, kaolinite gangue and MgCO_3 measured by a laser particle size analyzer (Mattersizer 2000) were 54.3 μm , 42.3 μm and 16.2 μm , respectively.

A powder mixture was prepared consisting of 54.3 wt% $\text{Al}(\text{OH})_3$ and 45.7 wt% kaolinite gangue which is consistent with a stoichiometric mullite proportion of Al_2O_3 to SiO_2 . The amount of MgCO_3 added to the powder mixture

Table 1. Chemical compositions of $\text{Al}(\text{OH})_3$, kaolinite gangue and MgCO_3 (wt%)

	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	I.L.
$\text{Al}(\text{OH})_3$	64.86	0.08	0.06	0.04	0.02	0.04	0.01	34.44
Kaolinite gangue	36.48	44.52	0.21	0.15	0.15	0.084	0.028	17.89
MgCO_3	0.19	0.05	0.02	0.04	42.69	-	-	57.06

*Corresponding author:
Tel : +86-027-68862511
Fax: +86-027-68862121
E-mail: yanwenref@yahoo.com.cn

was 2.93 wt%. The above starting powders were mixed for 4 h in polyurethane pots using alumina balls. The milled powder was pressed in cylinders with a height of 36 mm and diameter of 36 mm at a pressure of about 100 Mpa and the green compacts after drying to 110 °C were heated to 1300 °C, 1400 °C, 1500 °C, 1600 °C for 180 minutes in an electric furnace.

The apparent porosity was detected by Archimedes' Principle with water as the medium. The crushing strength of sintered samples at room temperature was measured. Phase analysis was carried out by an X-ray diffractometer (Philips Xpert TMP) with a scanning speed of 2° per minute. In addition, the relative total content of mullite in the sintered samples was evaluated using the standard-free quantitative method which has been used by Li [18]. This is not an accurate method to evaluate phase content in samples, but it can be used to compare the phase content in samples processed under the same conditions. The pore size distribution and average pore size were measured by mercury porosimetry measurements (AutoPore IV 9500, Micromeritics Instrument Corporation). Microstructures were observed by a scanning electron microscope (Philips XL30). Energy dispersive X-ray spectroscopy (EDS) analysis was processed by EDAX ZAF quantification (standardless).

Results and Discussion

Phase identification

Fig.1 shows the XRD patterns of samples sintered at different temperatures for 3 h to identify the phases formed. In the sample sintered at 1300 °C, the phases are mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), corundum ($3\text{Al}_2\text{O}_3$), cristobalite (SiO_2). By increasing the sintering temperature to 1400 °C, the peaks of cristobalite decrease sharply. However, for samples sintered at 1500 °C and 1600 °C, the cristobalite phase disappears, the peaks of corundum phase decrease, and the peaks of mullite phase increase.

The calculated theoretical primary mullite content from the amount of kaolinite in the starting composition is 31.20 wt%. The secondary mullite content can be obtained

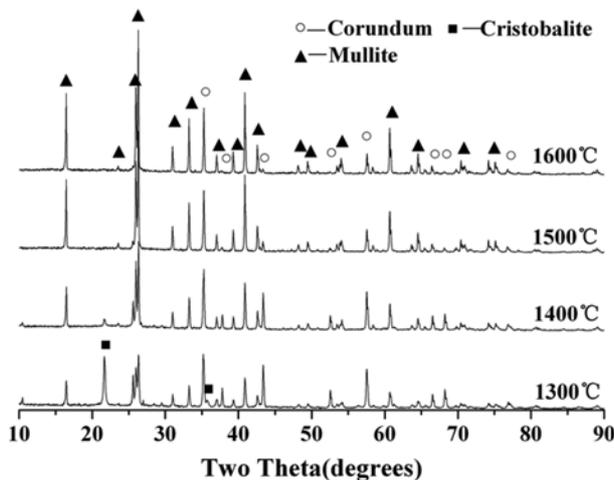


Fig. 1. XRD patterns of the sintered samples.

by subtracting the primary mullite content from the total content. The change of the total and secondary mullite contents as a function of sintering temperature is shown in Fig. 2. As can be seen, the formation of secondary mullite starts at 1300 °C, and the secondary mullite content increases greatly with an increase in the sintering temperature from 1300 °C to 1500 °C, but increases slightly with a further increase in the sintering temperature to 1600 °C. This means, that at 1500 °C the formation of secondary mullite takes place extremely rapidly, and a high mullite content (86.6 wt%) is obtained.

Pore characteristics and crushing strength

Fig. 3 gives the relationship of apparent porosity and average pore size with sintering temperature. The apparent porosity changes little with an increase in the sintering temperature from 1300 to 1400 °C, and is about 45%. When the sintering temperature is increased to 1500 °C, the apparent porosity decreases to 42%. But with a further increase in the sintering temperature to 1600 °C, the apparent porosity decreases sharply. This means that sintering temperatures higher than 1500 °C are not appropriate to prepare porous ceramics with a high porosity from $\text{Al}(\text{OH})_3$, kaolinite gangue and MgCO_3 . The average pore diameter

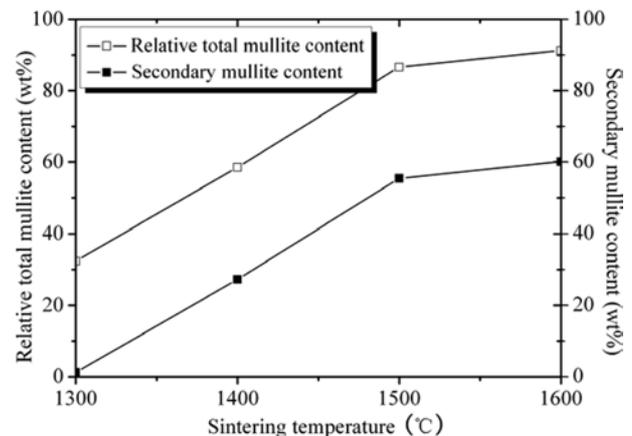


Fig. 2. Relative total and secondary mullite contents in the sintered samples.

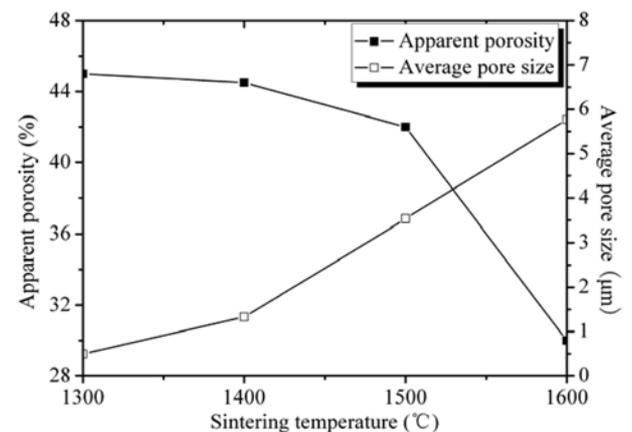


Fig. 3. Variation of apparent porosity and average pore size with sintering temperature.

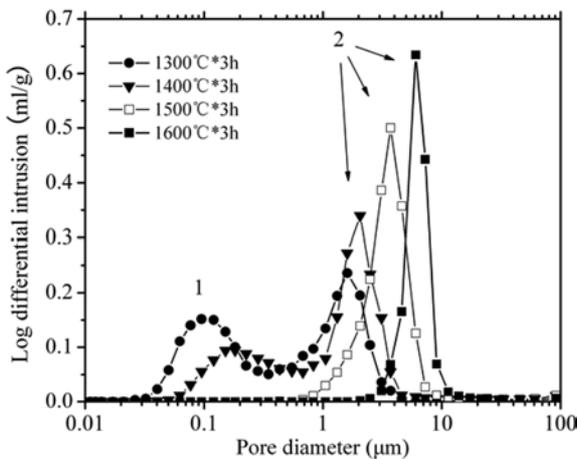


Fig. 4. Pore size distributions of samples as a function of the sintering temperature.

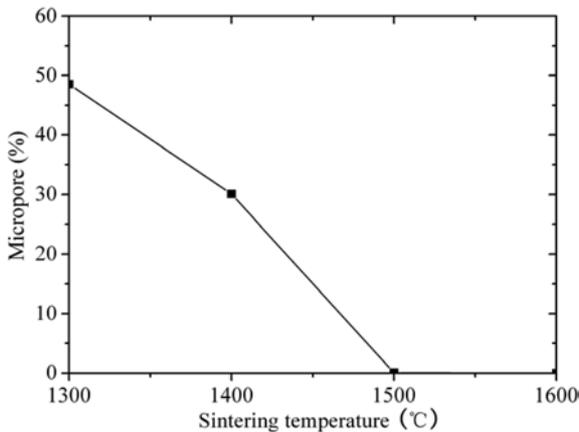


Fig. 5. Variation in the volume percentage of micropores in the total pore volume as a function of the sintering temperature.

of the sample sintered at 1300 °C is about 0.49 μm. With an increase in the sintering temperature from 1400 to 1600 °C, the average pore diameters increase gradually, and are 1.33 μm, 3.54 μm and 5.77 μm respectively.

The pore size distributions of the samples sintered at different temperatures are shown in Fig. 4. Bimodal pore size distributions are observed in samples sintered at 1300 °C and 1400 °C. With an increase in the sintering temperature to 1500 °C and 1600 °C, the pore size distributions become mono-modal and have a homogeneous pore size distribution. The proportion of micropores (pore diameter ≤ 0.45 μm) in the samples was determined (Fig. 5). The ratio of micropore volume to total pore volume in the sintered samples decreases sharply from 30% to zero with an increase in the sintering temperature from 1400 °C to 1500 °C.

The relationship between the sintering temperature and crushing strength of porous mullite ceramics is shown in Fig. 6. The strength changes little with an increase in the sintering temperature from 1300 °C to 1400 °C, but increases sharply with a further increase in the sintering temperature to 1500 °C and 1600 °C.

When the sintering temperature is 1500 °C, a compromise is reached between apparent porosity (42%) and crushing

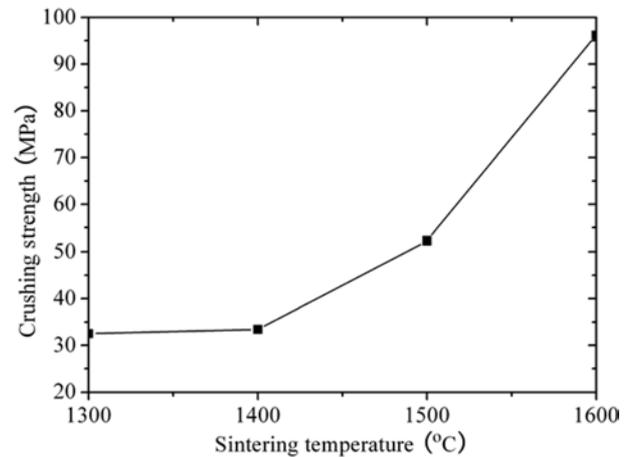


Fig. 6. Variation of crushing strength with sintering temperature.

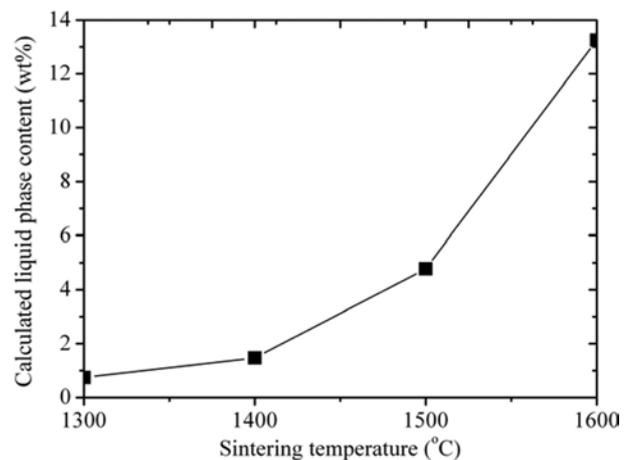


Fig. 7. Calculated liquid phase content in samples at different temperatures.

strength (52 MPa).

Discussion

The sintering temperature affects mullite formation and sintering. The expansion resulting from the formation of primary and secondary mullite and the shrinkage resulting from the sintering, affect the pore characteristics and the strength.

The formation of secondary mullite takes place only by interdiffusion of Al^{3+} and SiO_4^{4-} between the two pseudomorphs. The liquid is a shortcut to diffusion. The liquid phase content in samples at different temperatures is given in Fig. 7, which are calculated by FactSage 5.5 thermochemical software. The liquid phase content is little at 1300 °C, the interdiffusion through the solid is very slow and the formation of secondary mullite is small, and thus the pseudomorphs of $\text{Al}(\text{OH})_3$ and kaolinite gangue are clear and interposed (Fig. 8). With an increase in the sintering temperature to 1500 °C, more liquid is formed and the reaction of formation of secondary mullite is promoted. At the same time, the liquid improves the sintering and rearrangement of particles, resulting in destruction of the pseudomorphs (Fig. 9). This is in accordance with the

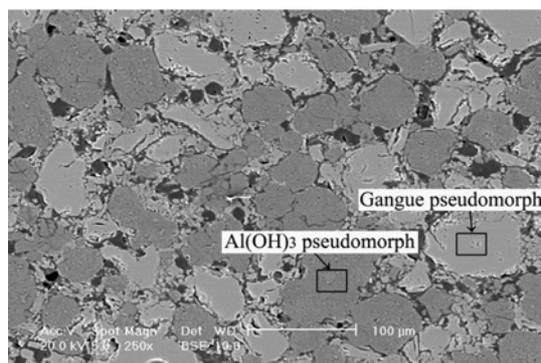


Fig. 8. Microstructure of a sample sintered at 1300 °C.

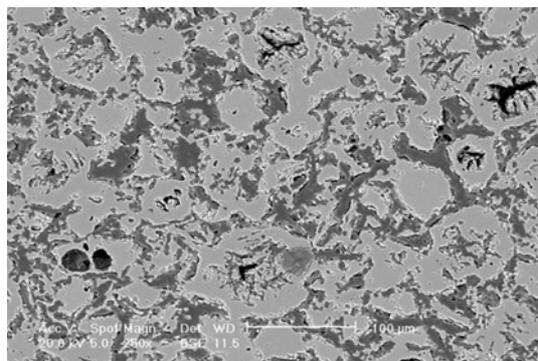


Fig. 9. Microstructure of a sample sintered at 1500 °C.

results shown in Fig. 1 and Fig. 2.

In our earlier paper [8], we reported that there were two types of pores in the samples made from $\text{Al}(\text{OH})_3$ and kaolinite gangue. One was what we called primary pores. They are in the pseudomorphs of $\text{Al}(\text{OH})_3$ and kaolinite gangue grains. Their size is smaller than $0.45 \mu\text{m}$. The other pores were formed by packing of pseudomorphs of $\text{Al}(\text{OH})_3$ and kaolinite gangue. We called them secondary pores. Their size is bigger than $0.45 \mu\text{m}$. In the sample sintered at 1300 °C, the pseudomorphs are clear and separated, and the kaolinite pseudomorph seems the denser (Fig. 8). This means that the primary pores are mainly in the $\text{Al}(\text{OH})_3$ pseudomorph, corresponding to peak No.1 in Fig. 4. With an increase in the sintering temperature to 1400 °C, secondary mullite formation fills in the primary pores of the $\text{Al}(\text{OH})_3$ pseudomorphs, resulting in decrease of the primary pores (peak No.1 in Fig. 4). With a further increase in the sintering temperature to 1500 °C, the liquid content is high enough to improve mullite formation and sintering, well-developed necks are formed, resulting in the disappearance of primary pores, and then a mono-modal pore size distribution appears. When the temperature is raised from 1500 °C to 1600 °C, the rate of secondary mullite formation becomes slow, but the sintering occurs very rapidly because of the large liquid phase content. Also then the shrinkage resulting from the sintering overrides the expansion resulting from mullite formation, leading to a decrease of the porosity.

The samples sintered at 1500 °C have both high strength and high porosity for three reasons: the first is the formation

of well-developed necks; the second is the good-distribution of pore size; and the third is the strength of the dense mullite grains [8].

Conclusions

The sintering temperature strongly affects the formation of secondary mullite, and then changes the pore characteristics and strength. The formation of secondary mullite takes place extremely rapidly at 1500 °C. The pore size distributions are bimodal in samples sintered at 1300 °C and 1400 °C, and mono-modal in samples sintered at 1500 °C and 1600 °C. The strengths are the same and low when the sintering temperatures are 1300 °C and 1400 °C, and increase sharply when the sintering temperature is increased to 1500 °C.

The most appropriate mode is the sample sintered at 1500 °C which has a high mullite content (86.6 wt%), high apparent porosity (42%), high crushing strength (52 MPa) and a homogeneous pore size distribution.

Acknowledgements

We wish to express our thanks to the Puyang Refractories Co., Ltd for financially supporting this work.

References

1. J.H. She and T. Ohji, *Mater. Chem. Phys.* 80 (2003) 610-614.
2. Y.F. Liu, X.Q. Liu, H. Wei and G. Y. Meng, *Ceram. Int.* 27 (2001) 1-7.
3. R. Barea, M. I. Osendi and P. Miranzo, *J. Am. Ceram. Soc.* 88[3] (2005) 777-779.
4. R. Barea, M.I. Osendi, J.M.F. Ferreira and P. Miranzo, *Acta Mat.* 53 (2005) 3313-3318.
5. H. Abe, H. Seki and A. Fukunaga, *J. Mat. Sci.* 29 (1994) 1222-1226.
6. S. Li and N. Li, *Ceram. Int.* 33 (2007) 551-556.
7. S. Li and N. Li, *Sci. Sinter.* 37 (2005) 173-180.
8. W. Yan and N. Li, *Am. Ceram. Soc. Bull.* 85[12] (2006) 9401-9406.
9. Z.P. Xie, J.L. Yang and Y. Huang, *Bull. Chin. Ceram. Soc.* 2 (1998) 18-21.
10. Y. Wen, L. Nan and B.Q. Han, *Am. Ceram. Soc. Bull.* 84 (2005) 9201-9203.
11. Z.Y. Deng, T. Fukasawa, M. Ando, G. J Zhang and T. Ohji, *J. Am. Ceram. Soc.* 84 (2001) 485-491.
12. Z.Y. Deng, T. Fukasawa, M. Ando, G. J Zhang and T. Ohji, *J. Am. Ceram. Soc.* 84 (2001) 2638-2644.
13. K.C. Liu and G. Thomas, *J. Am. Ceram. Soc.* 77 (1994) 545-552.
14. H.R. Rezaie, W.M. Rainforth and W.E. Lee, *Trans. Br. Ceram. Soc.* 96 (1997) 181-187.
15. L. Montanaro, J.M. Tulliani, C. Perrot and A. Negro, *J. Eur. Ceram. Soc.* 17 (1997) 1715-1723.
16. A.K. Chakraborty and D.K. Ghosh, *J. Am. Ceram. Soc.* 61 (1978) 170-173.
17. K.C. Liu and G. Thomas, *J. Am. Ceram. Soc.* 77 (1994) 545-552.
18. S. Li, N. Li and Y.W. Li, *Ceram. Int.* 34 (2008) 1241-1246.