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Effects of composition and temperature on porosity and pore size distribution of porous ceramics prepared from $Al(OH)_3$ and kaolinite gangue

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Abstract

Porous corundum-mullite ceramics were made from $Al(OH)_3$ and kaolinite gangue by the in situ decomposition pore-forming technique. The porosity of the sample increases with increasing $Al(OH)_3$ content in the raw mixture of $Al(OH)_3$ powder and kaolinite gangue. With increasing temperature from 1300 to 1500 °C the porosity of the sample changes a little because of mullite formation. However, when the sintering temperature increases from 1500 to 1600 °C the porosity decreases rapidly. The pores in the samples consist of two groups. One is composed of micropores with maximum diameter of 100 nm. This kind of pores are located in the pseudomorphs of $Al(OH)_3$ and kaolinite gangue. They are derived from the decomposition of $Al(OH)_3$ and kaolinite, and from burning of carbon and organic substance in the gangue. The other is composed of pores with maximum diameter of 1000 nm. They are located among the pseudomorphs of $Al(OH)_3$ and kaolinite gangue. With increase of the $Al(OH)_3$ content in the starting powder mixture the % volume of micropores (pore diameter 250 nm) increases, while it decreases with the increase of the sintering temperature.

Keywords: In situ decomposition; Pore-forming; Porous; Corundum-mullite; $Al(OH)_3$; Kaolinite gangue

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1. Introduction

Recently, there has been an increasing interest in the applications of porous ceramics as filters, desiccants, insulators, catalyst supports, bone replacement, acoustic absorbers, sensors and membrane reactors [1–6].

Porous ceramics can be made by adding pore-forming agents such as sawdust, starch, carbon or organic particulates [7] into the starting powders, or by injection molding [8], or by gelcasting [1]. Deng et al. [9,10] made porous alumina ceramics by decomposition of $Al(OH)_3$. This pore-forming in situ technique exploiting the decomposition of starting powders is a good way to prepare porous ceramics containing well-distributed pores. Mullite has a lower thermal-expansion coefficient [11,12] than alumina. Introducing mullite into corundum ceramics can increase their thermal-shock resistance as well as their mechanical and chemical stability [13,14]. We have used the in situ decomposition pore-forming technique to prepare porous corundum-mullite ceramics, using $Al(OH)_3$ and microsilica as raw materials [15]. On the other hand kaolinite gangue is a large coal mine waste in China. Utilization of this gangue to decrease pollution of the environment is interesting. Compared to microsilica, kaolinite gangue has a pore-forming ability because kaolinite will lose water and the carbon in the gangue will burn out during sintering. It means that the gangue has two pore-forming abilities. Using kaolinite gangue instead of microsilica may increase the porosity of porous ceramics. This article describes the preparation of porous corundum-mullite ceramics, using $Al(OH)_3$ powder and kaolinite gangue. Open porosity and pore size distribution of porous corundum-mullite ceramics were investigated as a function of the composition of the starting powders and the sintering temperature. Comparison of porosity and pore size distribution of samples made from microsilica and gangue will be presented as well.

2. Experimental procedure

The compositions of the starting powders with different kaolinite gangue and $Al(OH)_3$ content are given in Table 1. The starting powders were wet milled for 3 h in a planetary mill using

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Table 1
Main composition of different starting powders (wt%)

	1#	2#	3#
$Al(OH)_3$	54	68	84
Kaolinite gangue	46	32	16
Mullite[a]	100	71	35

[a] Mullite: the content of mullite in sintered specimens was calculated from the composition of starting powders.

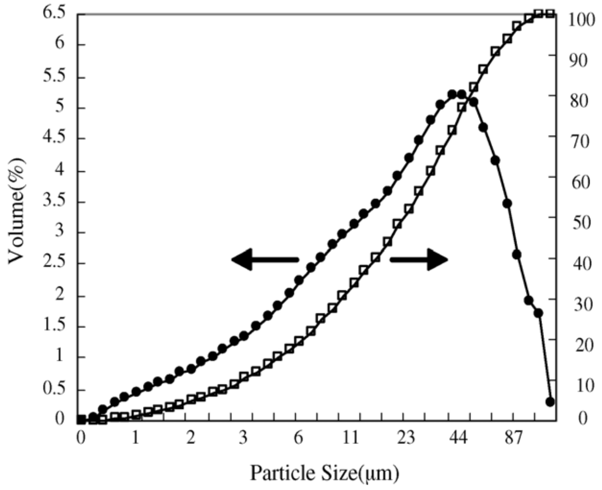


Fig. 1. The particle size distribution of milled starting powder.

alumina balls and pressed to billets with diameter of 36 mm under 50 MPa. The green billets were dried at 110 °C for 24 h, and then heated at 1300, 1400, 1500 or 1600 °C for 3 h, respectively. Particle size distribution of milled powders is given in Fig. 1.

The chemical compositions of the raw materials are listed in Table 2.

The particle size distribution was measured by laser particle size analyzer (Matersizer 2000). X-ray diffractometry (Philips X'pert TMP) was used to analyze the phase composition in the sintered specimens heated at different temperatures. Apparent porosity was detected by Archimedes' Principle with water as medium. The pore size distribution was measured by mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics Instrument Corporation) and the microstructure was analyzed by SEM (Philips XL 30 TMP scanning electron microscopy).

3. Results and discussion

3.1. Effect of the composition of the starting powders on the pore structures of the sintered specimens

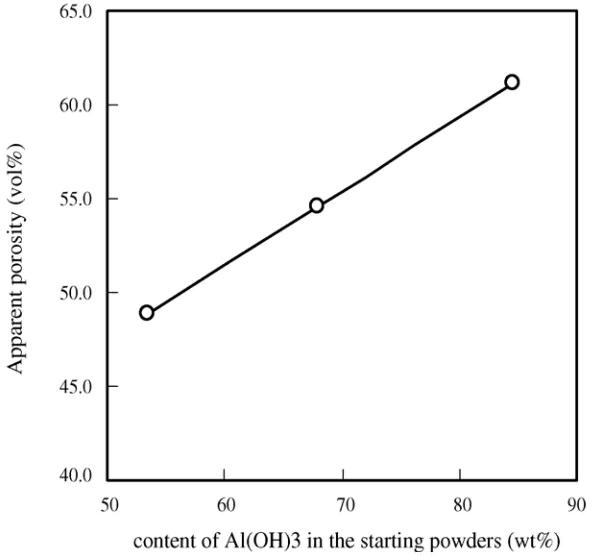


Fig. 2. Variation of the apparent porosities of the specimens sintered at 1500 °C for 3 h with the $Al(OH)_3$ content in starting powders.

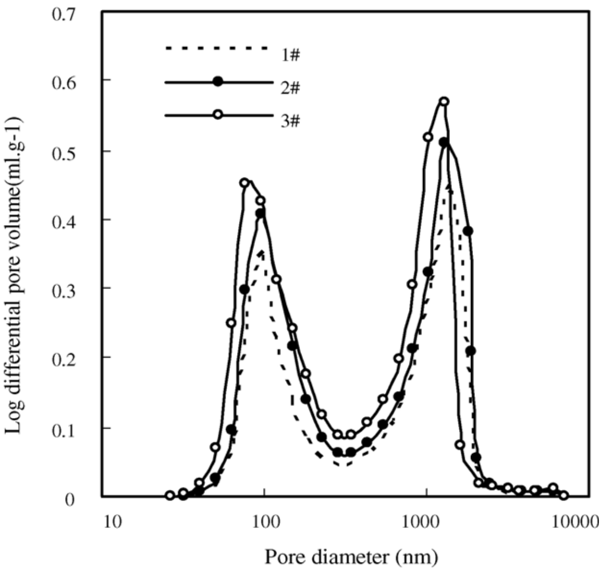


Fig. 3. Variation of the pore size distribution of the porous specimens with different starting powders sintered at 1500 °C for 3 h.

The relationship between the $Al(OH)_3$ content in the starting powders and apparent porosity is shown in Fig. 2. As shown in Fig. 2, with increasing the $Al(OH)_3$ content in the starting powders the apparent porosity of sintered specimens increases.

The pore size distributions of the specimens prepared from different starting powders sintered at 1500 °C are shown in Fig. 3. They are bimodal. One pore group is representative of micropore the diameter of which is mostly about 100 nm and the other is formed by bigger pores the size of which is mostly about 1 μm.

Table 2
The chemical composition of raw materials (wt%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	IL
$Al(OH)_3$	0.002	66.85	0.041	0.15	0.04	0.013	0.039	–	32.60
Kaolinite gangue	44.52	36.48	0.21	0.15	0.15	0.084	0.028	0.43	17.89

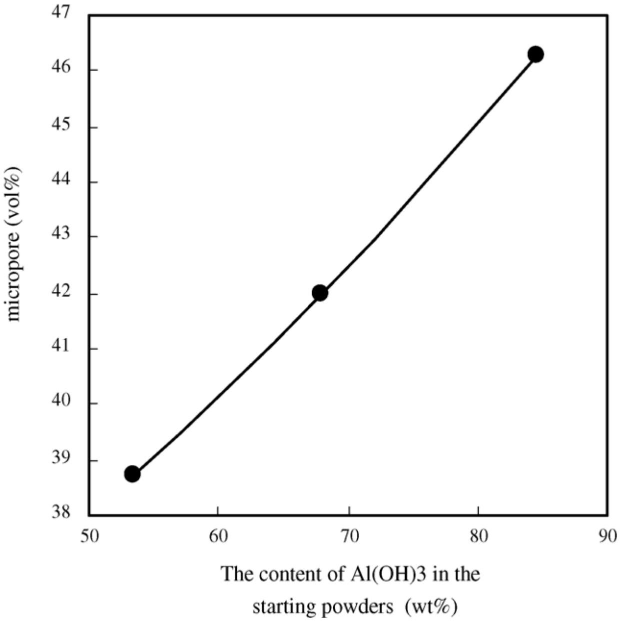


Fig. 4. Variation in the volume percentage of micropores in total pore volume with different starting powders sintered at 1500 °C for 3 h.

Fig. 4 shows the % volume of micropores (pore diameter ≤250 nm). It is found that with the $Al(OH)_3$ content increasing the ratio of micropore volume to total pore volume in sintered specimens increase.

Based on the results we may consider that sample No. 2 is the best in our study because it has higher porosity and more micropores. On the other hand, sample No. 2 has mullite content of 71% which is very close to the apposite content of mullite in mullite-corundum ceramics [14,16,17], so that the composition of sample No. 2 is well-suited to prepare porous corundum-mullite ceramics.

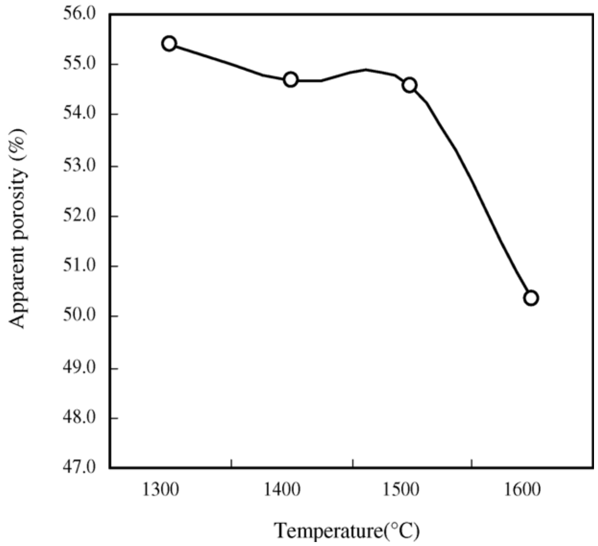


Fig. 5. Variation in the apparent porosity of the specimen No. 2 with the sintering temperature.

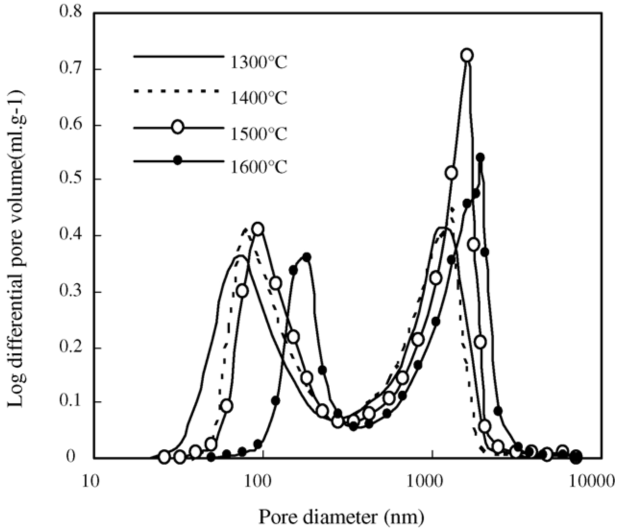


Fig. 6. Variation in the pore size distribution of the specimen No. 2 with the sintering temperature.

3.2. Effect of the sintering temperature on the pore structures of the sintered specimens

Fig. 5 shows the apparent porosities of the specimen No. 2 sintered at different temperatures. As shown, the apparent porosity decreased slightly from 55.4 to 54.7% with the sintering temperature from 1300 to 1400 °C, and maintained stably with the sintering temperature from 1400 to 1500 °C, but decreased to 50.4% with further increase in the sintering temperature to 1600 °C. The pore size distribution of sample No. 2 sintered at different temperature is shown in Fig. 6. The change of the % volume of micropores as a function of the sintering temperature is shown in Fig. 7. When the sintering temperature rose from 1300 to 1600 °C, the curve of the pore

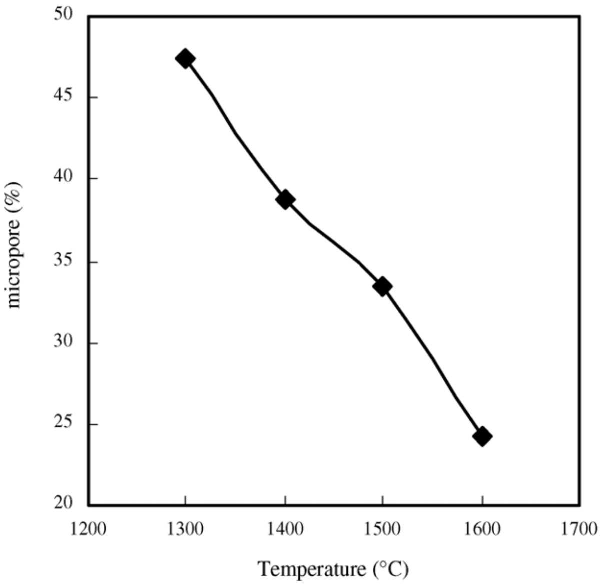


Fig. 7. Variation in the volume percentage of micropores in total pore volume with sintering temperature in the specimen No. 2.

Table 3
Main composition of different starting powders (wt%)

	a	*b*
$Al(OH)_3$	84	86
Kaolinite gangue	16	–
Microsilica	–	14
Mullite[a]	35	70

[a] Mullite: the content of mullite which was calculated from the composition of the starting powders.

size distribution moved towards larger pore size, and the % volume of the micropores decreased.

3.3. Comparison of the effects of kaolinite gangue and microsilica on the pore structures

We have used this pore-forming technique to prepare porous corundum-mullite, using $Al(OH)_3$ and microsilica as raw materials [15].

The comparison of the effects of these two kinds of starting powders on porosity and pore size distribution is shown below. The compositions of the starting powders with kaolinite gangue or microsilica (Elkem Microsilica, Grade 983) and $Al(OH)_3$ are given in Table 3, and the porosity and the pore size distribution are given in Figs. 8 and 9, respectively.

It was found that the porosity of samples with gangue was higher than that with microsilica and the former had more micropores than the latter.

3.4. Discussion

Micrographs of the samples sintered at 1400 and 1500 °C are shown in Fig. 10. The grains in SEM remain the contour of kaolinite gangue and $Al(OH)_3$, they are called ‘‘pseudomorph’’ (A and B in Fig. 10). This phenomenon was found in sintering of MgO made from magnesite [18,19]. Actually pseudomorphs are the aggregates consisting of Al_2O_3 and mullite. These aggregates are called ‘‘secondary grains’’. The pores in the aggregates are micropores and microcracks which formed by decomposition of $Al(OH)_3$ and kaolinite gangue, as well the burning of carbon and organic substance. This type of pores (pore diameter ≤250 nm, with maximum diameter of 100 nm in pore size distribution) we call ‘‘primary pores’’ and the

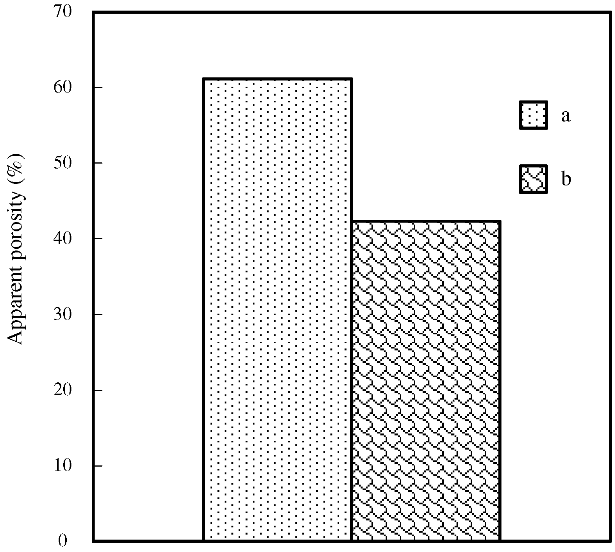


Fig. 8. Variation of the apparent porosities of the specimens with different starting powders sintered at 1500 °C for 3 h.

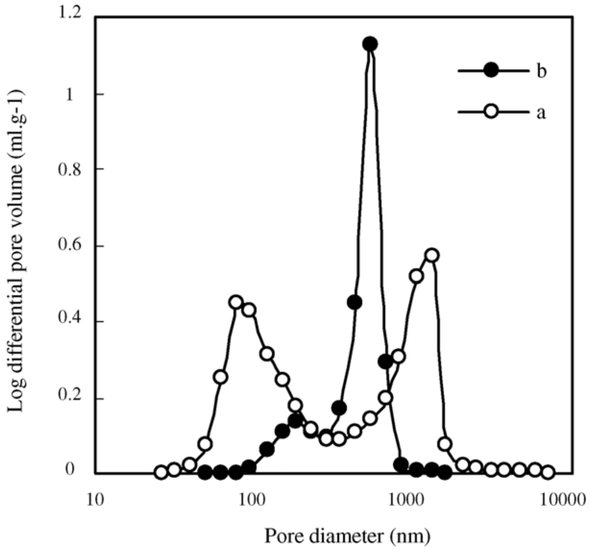
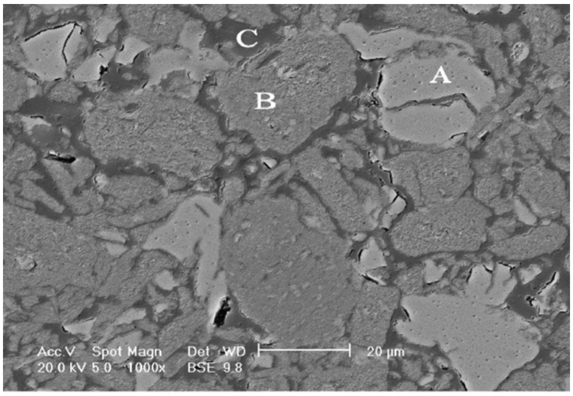
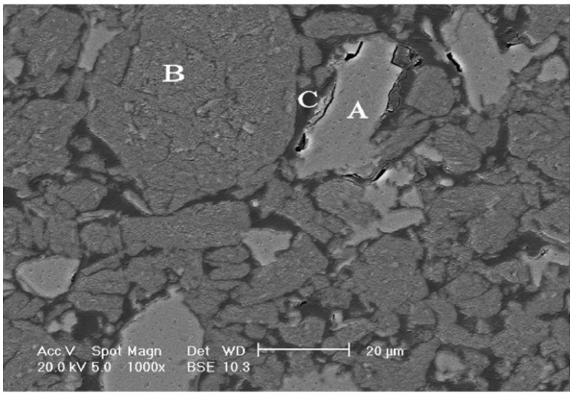


Fig. 9. Variation of the pore size distribution of the porous specimens with different starting powders sintered at 1500 °C for 3 h.



1400°C



1500°C

Fig. 10. SEM images of the specimen No. 2 sintered at 1500 °C for 3 h.

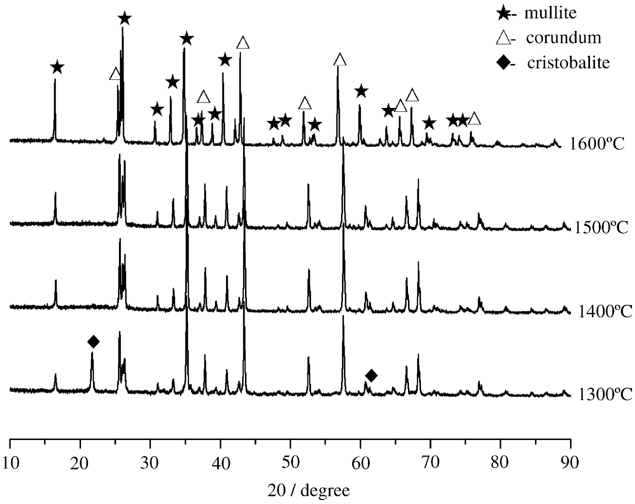


Fig. 11. The XRD analyses of the specimen No. 2 sintered at different sintering temperatures.

grains in the secondary grains are called ‘‘primary grains’’, i.e. one ‘‘pseudomorph’’ contains many ‘‘secondary grains’’, and furthermore, one ‘‘secondary grain’’ contains many ‘‘primary grains’’. The size distribution of ‘‘primary pores’’ depends on crystal sizes of $Al(OH)_3$ and kaolinite in gangue, the volume contraction of $Al(OH)_3$ during decomposition and the size of carbon and organic substance in the kaolinite gangue, as well mullite formation. It is almost no relationship with packing of $Al(OH)_3$ and kaolinite gangue particles and pressure of press. The bigger pores (pore diameter >250 nm, with maximum diameter of 1 μm in pore size distribution) among the aggregated powder are called ‘‘secondary pores’’ (C in Fig. 10). They are formed by pile of particles of $Al(OH)_3$ and kaolinite gangue.

With increase of the $Al(OH)_3$ content in the raw powder the ‘‘primary pore’’ amount increases because the $Al(OH)_3$ can produce more pores than kaolinite gangue and experience a 60% volume contraction during decomposition [9]. It results in the apparent porosity and the % volume of micropores (pore diameter ≤250 nm) increase (Figs. 2–4).

With increasing the sintering temperature from 1300 to 1400 °C, the porosity decreases slightly(Fig. 5) but the % volume of micropores (pore diameter ≤250 nm) decrease (Fig. 7) and the diameters of micropores grow observably (Fig. 6). In this stage the velocity of mullite formation is small because this reaction takes place on the boundary between Al_2O_3 aggregates and aggregates of kaolinite gangue calcined, but the sintering in the Al_2O_3 aggregates and aggregates of kaolinite gangue calcined occurs fast because of high activity. The ‘‘primary pores’’ in the aggregates transfer to ‘‘secondary pores’’ by sintering. With increasing sintering temperatures, the mullite formation takes place fast. The expansion of mullite formation balances the shrinkage resulting from sintering to maintain the size and shape of secondary grains and microstructure of the samples. It makes the porosities of the samples sintered at 1400 and 1500 °C almost similar. From Fig. 11 it can be found that most of the mullite is formed at temperatures between 1400 and 1500 °C. At the same time the ‘‘primary pores’’ grow up to make the % volume of micropores (pore diameter ≤250 nm) decrease. When the sintering temperature increases from 1500 to 1600 °C, the porosity of the sample and the % volume of micropores (pore diameter ≤250 nm) of the sample decrease rapidly. In this case mullite formation is finished at lower temperature, the shrinkage resulted from sintering makes the porosity of the samples and the % volume of micropores (pore diameter ≤250 nm) of the samples decrease.

When the kaolinite gangue is used instead of microsilica, the primary pores increase because of decomposition of kaolinite gangue and burning of carbon and organic substance in the kaolinite gangue. That means that addition of kaolinite gangue is beneficial to make porous corundum-mullite ceramics.

4. Conclusions

The porous corundum-mullite ceramics were made from $Al(OH)_3$ and kaolinite gangue by the in situ decomposition pore-forming technique. The porosity of the sample increases with the increasing $Al(OH)_3$ content in the raw mixture of powder of $Al(OH)_3$ and kaolinite gangue. From 1300 to 1500 °C, the porosities of the sintered samples change a little because of mullite formation. However, when the sintering temperature increases from 1500 to 1600 °C the porosity decreases rapidly.

The pore size distribution is bimodal. The first group consists of micropores with maximum diameter of 100 nm. They located in the pseudomorphs of $Al(OH)_3$ and kaolinite gangue and issued from the decomposition of $Al(OH)_3$ and kaolinite, and from burning of carbon and organic substance in gangue. The other group issued from the pores with maximum diameter of 1000 nm. These pores located among the pseudomorphs of $Al(OH)_3$ and kaolinite gangue. With increasing of the $Al(OH)_3$ content in the starting powder mixture the % volume of micropores (pore diameter ≤250 nm) increases, while with the increase of the sintering temperature it decreases.

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