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Preparation of self-reinforcement of porous mullite ceramics through in situ synthesis of mullite whisker in flyash body

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Abstract

Self-reinforced porous mullite ceramics were fabricated by a starch consolidation method with flyash, different aluminium sources ($Al(OH)_3$ and Al_2O_3) and the additive AlF_3 as raw materials. The reinforcement mechanism of needle-like mullite whiskers through in situ synthesis in ceramic body was investigated. The bulk density, apparent porosity and bending strength of the samples were tested. Phase compositions and microstructures of the sintered samples were measured by XRD and SEM, respectively. It showed that AlF_3 as additive was helpful to the formation of mullite whiskers at a low temperature. As the aluminium sources, $Al(OH)_3$ was more suitable for the preparation of mullite whiskers than Al_2O_3. The in situ synthesized mullite whiskers formed an interlocking structure, which enhanced the mechanical strength of the porous mullite ceramics. Porous mullite ceramics with bending strength of about 100 MPa and apparent porosity of about 55% were made at 1550 °C.

Keywords: B. Porosity; B. Whiskers; C. Strength; D. Mullite

1. Introduction

Porous mullite ceramics have been extensively studied because of their excellent properties, such as high melting point, low thermal conductivity, moderate thermal expansion coefficient, good resistance to thermal shock and good chemical durability [1,2]. These properties make porous mullite to be widely used in the fields of catalyst carriers, lightweight structural materials and filters for molten metals [3–6]. However, the low mechanical property limited its application. Many efforts have accordingly been made to toughen the mullite ceramics with different methods, such as particle dispersion reinforcing [7,8] and whisker or fiber toughening [9,10]. Among these methods, whisker toughening is an effective approach to reinforce the material. Usually, whiskers are added by mechanical mixing; however, the whiskers are very difficult to be evenly dispersed which strongly affected its reinforcement performance. Therefore, the in situ synthesis method has been adopted to fabricate the whiskers during the sintering process. Chen et al. produced SiC based ceramic foams, which were reinforced by in situ synthesized mullite whiskers [11]. Naga fabricated porous fibrous mullite bodies and the bending strength of the bodies increased from 3.82 MPa to 7.08 MPa (porosity about 90%) [12]. Okada [13] made mullite ceramics by in situ synthesized whiskers in AlF_3 and mullite composition xerogels.

Flyash is a by-product of the coal-fired power plants, which is a serious threat to health by air pollution [5]. Therefore, more and more attentions have been paid to investigate the utilization of flyash. The main compositions of the flyash (Al_2O_3 and SiO_2) are especially suitable for the fabrication of mullite-basic ceramics, which has been proved by many articles [14–18]. Recently, Dong et al. [17,18] fabricated porous mullite ceramics from flyash and natural bauxite, and investigated the low temperature sintering behavior with sintering additives [19]. However, there are few reports on mechanical properties of porous mullite ceramics fabricated from flyash.

In this research, we fabricated porous mullite ceramics by flyash, AlF_3 and aluminium sources through the starch consolidation method. $Al(OH)_3$ added AlF_3 as aluminium source produced preferable needle-like mullite whiskers. These in situ synthesized whiskers formed an interlocking structure

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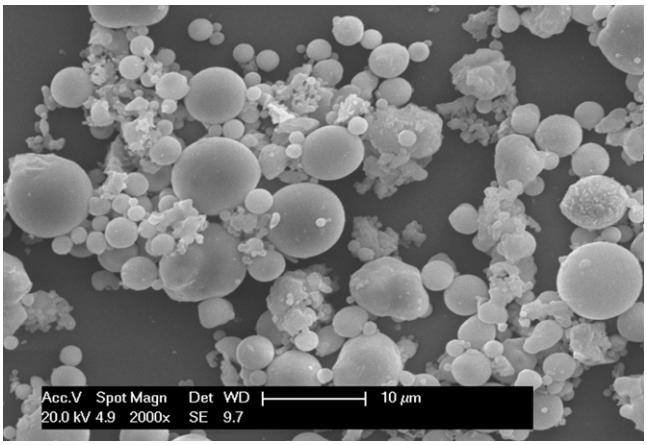

Fig. 1. SEM microphotograph of flyash particles.

and strengthened the porous mullite ceramics. The high strength will promote the industrial application of the porous mullite ceramics fabricated by flyash.

2. Experiment

2.1. Materials and chemical reagents

The flyash (FA) was obtained from Shengtou thermal power plant, Shanxi Province, China. The morphology of the flyash is shown in Fig. 1. The XRD patterns are shown in Fig. 2 and it reveals that the major crystalline phases of flyash are mullite and quartz. Table 1 shows the chemical composition of the flyash, which was analyzed by XRF. In addition, Al_2O_3 and $Al(OH)_3$ (purity of 99.9%, Reagent Company, Tianjin, China) were used to adjust the mole ratio of Al to Si in the samples, respectively. AlF_3 (purity of 99.9%, Reagent Company, Tianjin, China) was used as the additive to promote the formation of mullite whiskers. Polyacrylic acid (15 mg/L, Kewei Company, Tianjin, China) was used to make the slurry even and stable.

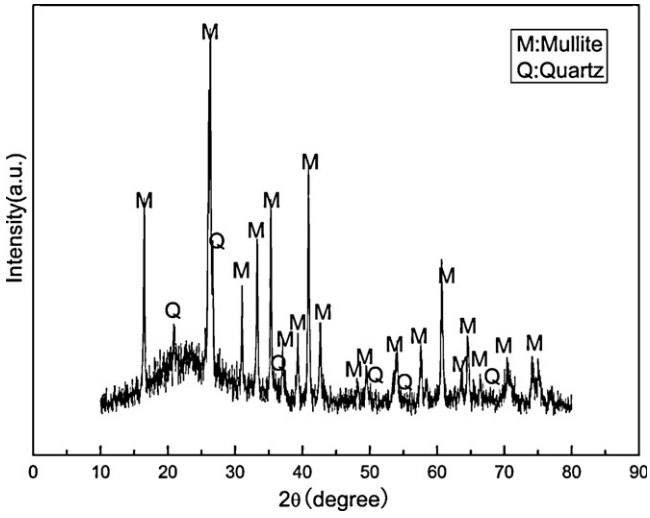

Fig. 2. XRD patterns of flyash.

Table 1
The composition of flyash.

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	P_2O_5
Content (wt%)	50.81	39.85	2.87	2.85	0.32	1.97	0.69	0.64

Table 2
Chemical composition of the green bodies.

Samples	Flyash	Al_2O_3	$Al(OH)_3$ (wt%)	AlF_3	Starch	Al:Si
I-a	36.79	33.21	–	–	30	3
I-b	35.40	27.62	–	6.98	30	3
II-a	29.40	–	40.60	–	30	3
II-b	29.20	–	33.82	6.98	30	3

Potato starch from the supermarket of Tianjin was used as the pore-forming agent and curing agent in this research.

2.2. Experiment process

Firstly, the raw materials were mixed and ball milled for 8 h with certain ratios (Table 2). Then the slurry was injected into the plastic model and covered with a preservative film. After being heated at 85 °C for 2 h, the green bodies were taken out of the mold. The dried green bodies were sintered in high temperature furnace through the following procedure: 5 °C/min from room temperature to the sintering temperature (between 1400 °C and 1600 °C), assisted by holding at 500 °C for 1 h to make the potato starch burning thoroughly and holding at sintering temperature for 4 h to promote mullitization.

2.3. Test and characterization

The X-ray patterns of the samples were tested by X-ray diffractometer (D/Max-2500 Rigaku, Japan) using CuKα radiation (1.5406 Å). The thermal behavior of the green bodies was tested by differential thermal (DTA) and thermogravimetry (TG) analyses on thermal analyzer (STA 449C, Netzsch, Germany). All the thermal analyses were carried out in air at a heating rate of 10 °C/min. Chemical composition of the flyash was analyzed by X-ray fluorescence (XRF-1800, Shimadzu, Japan). Microstructure of the samples was observed by scanning electron microscopy (S-4800, Hitachi, Japan) working at 20 kV. The bulk densities and porosities of the products were determined by Archimedean immersion method. The bending strength of the products was tested through the three-point bending method by a universal materials testing machine (NYL-500A, Jianyi Instrument Company, Wuxi, China) with a loading speed of 1 mm/min, and all the results were given as the mean values of five measurements.

3. Results and discussion

3.1. XRD and thermal analyses

Fig. 3 is the XRD patterns of the samples sintered at 1200 °C. The ratios of the peak areas of mullite (2 1 0) ($2\theta = 26.394°$) to

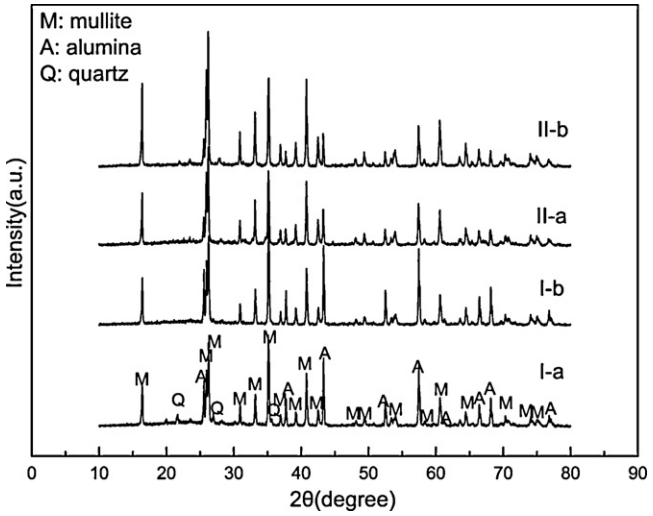

Fig. 3. X-ray diffraction patterns of the ceramics (I-a, I-b, II-a and II-b) sintered at 1200 °C.

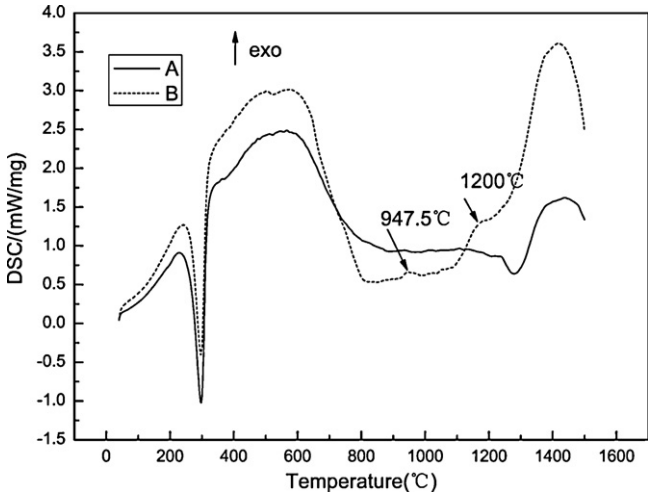

Fig. 4. DSC curves of mixture A (47.5 wt% $Al(OH)_3$ and 52.5 wt% FA) and mixture B (50.5 wt% $Al(OH)_3$, 39.5 wt% FA and 10 wt% AlF_3).

peak areas of corundum (2 2 0) ($2\theta = 53.297°$) for each pattern were measured to determine the degree of the mullitization. They are 3.49 (I-a), 5.27 (I-b), 16.27 (II-a) and 31.09 (II-b), respectively. The degree of the mullitization of samples with AlF_3 (II-b and I-b) was higher than that of the samples without AlF_3. The samples with $Al(OH)_3$ had a higher mullitization degree than that of samples with Al_2O_3. These phenomena indicated that the mullitization degree in FA–$Al(OH)_3$–AlF_3 mixtures was higher than that of the FA–Al_2O_3–AlF_3 mixtures.

According to the results of Okada's investigation, mullitization was largely accelerated by AlF_3 in mullite precursor xerogel. The reactions occurred in mixture of AlF_3 and mullite precursors were shown as follows [13]:

$$6AlF_3 + 3O_2 \rightarrow 6AlOF + 12F \quad (1)$$

$$Al_2O_3 + 2F \rightarrow 2AlOF + 0.5O_2 \quad (2)$$

$$2SiO_2 + 8F \rightarrow 2SiF_4 + 2O_2 \quad (3)$$

$$6AlOF + 2SiF_4 + 3.5O_2 \rightarrow 3Al_2O_3{\cdot}2SiO_2 + 14F \quad (4)$$

This mechanism confirms that the mullitization process was affected by the chemical activity of Al_2O_3 and SiO_2. In the FA–$Al(OH)_3$–AlF_3 mixtures, $Al(OH)_3$ would decompose into Al_2O_3 and H_2O when sintered. This Al_2O_3 had a higher activity than that of the exotic Al_2O_3. Therefore, samples of II-b had a higher mullitization degree than others.

Fig. 4 is the DSC curves of mixture A ($Al(OH)_3$ of 47.5 wt% and FA of 52.5 wt%) and mixture B ($Al(OH)_3$ of 50.5 wt%, FA of 39.5 wt% and AlF_3 of 10 wt%). It shows that curve B has two obvious exothermic peaks at 947 °C and 1200 °C respectively compared to curve A. These two exothermic peaks on curve B are formed because of the mullite formation caused by the addition of AlF_3. Firstly, AlF_3 reacted with O_2 and became AlOF, and then AlOF reacted with the reaction product SiF_4 and produced mullite at a lower temperature. This also proved that AlF_3 could accelerate the mullite formation by the gas–solid reaction with SiO_2 [13].

3.2. Sintering character

The bulk density and open porosity of different samples (I-a, I-b, II-a and II-b) sintered at different temperatures are shown in Fig. 5. With the increasing of the sintering temperature, the open porosity decreased and the samples became densified. This can be explained by the grain growth and the grain

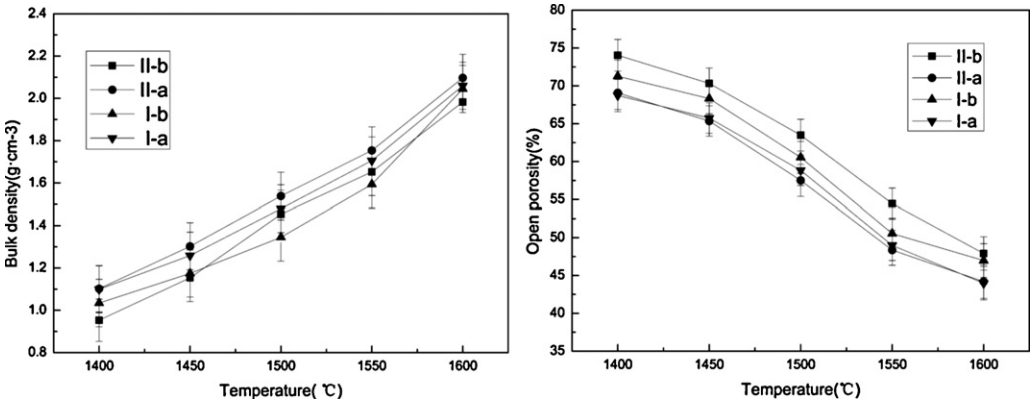

Fig. 5. Density and open porosity of the samples (I-a, I-b, II-a and II-b) sintered at different temperatures.

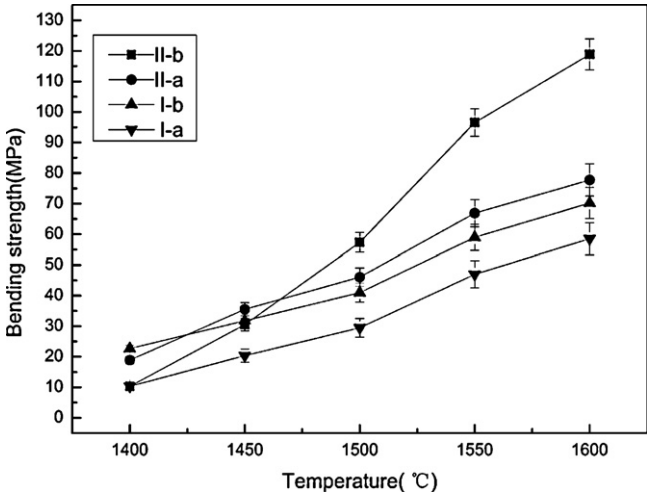

Fig. 6. Bending strength of samples (I-a, I-b, II-a and II-b) sintered at different temperatures.

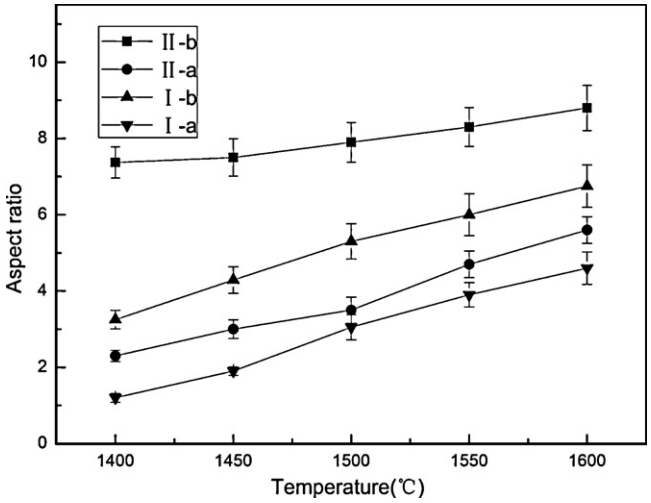

Fig. 7. Aspect ratios of the whiskers in samples (I-a, I-b, II-a and II-b) sintered at different temperatures.

boundary motion during the mullitization process. As shown in Fig. 5, the samples with AlF_3 (I-b and II-b) had lower density and higher porosity than the samples without AlF_3 (I-a and II-a) at the temperature lower than 1500 °C. This can be attributed to the anisotropy growth of mullite, which is obvious in the samples with AlF_3.

3.3. Mechanical properties and the analysis of microstructures

Fig. 6 shows that the bending strength of the porous mullite ceramics increased with the increasing of sintering temperature. The bending strength of the samples without AlF_3 was lower than that of the samples with AlF_3, and the strength of the samples with $Al(OH)_3$ was higher than that of samples with Al_2O_3. This can be ascribed to two factors: (a) $Al(OH)_3$ and AlF_3 could accelerate the mullitization process, which was shown in Section 3.1. (b) The in situ synthesized mullite whiskers constructed an interlocking structure (Fig. 9, II-b), which enhanced the bending strength.

Figs. 8 and 9 show the microstructures of the samples sintered at 1400 °C and 1600 °C respectively. It shows the samples with AlF_3 formed mullite whiskers at 1400 °C (Fig. 9, I-b and II-b), but the particles of the samples without AlF_3 was

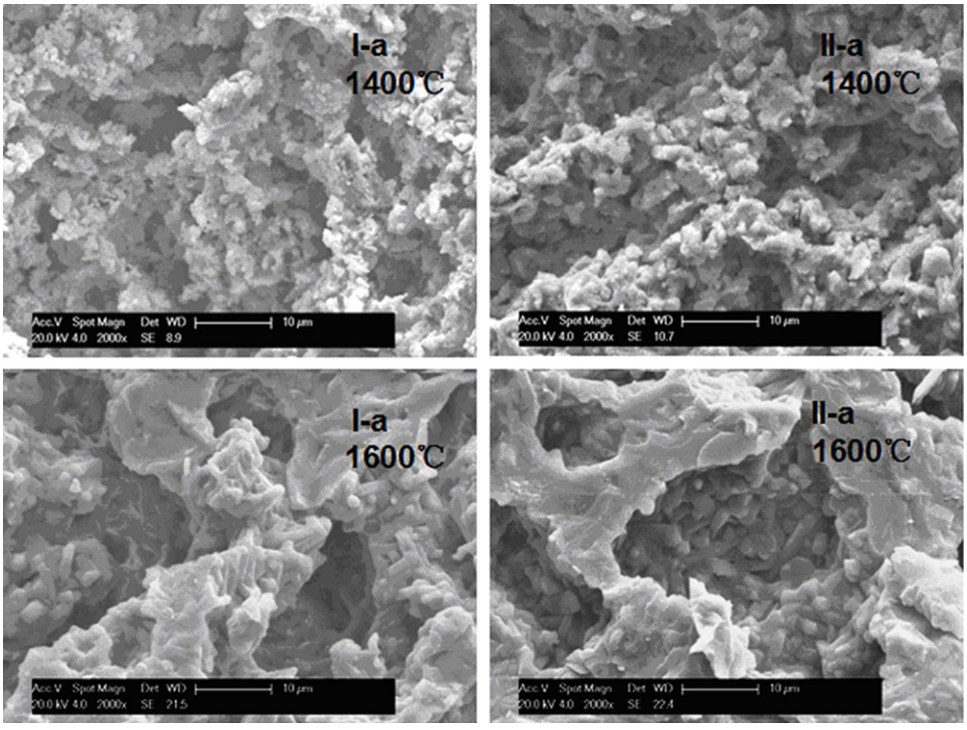

Fig. 8. Microstructures of fracture surface of I-a and II-a (no AlF_3) sintered at 1400 °C and 1600 °C.

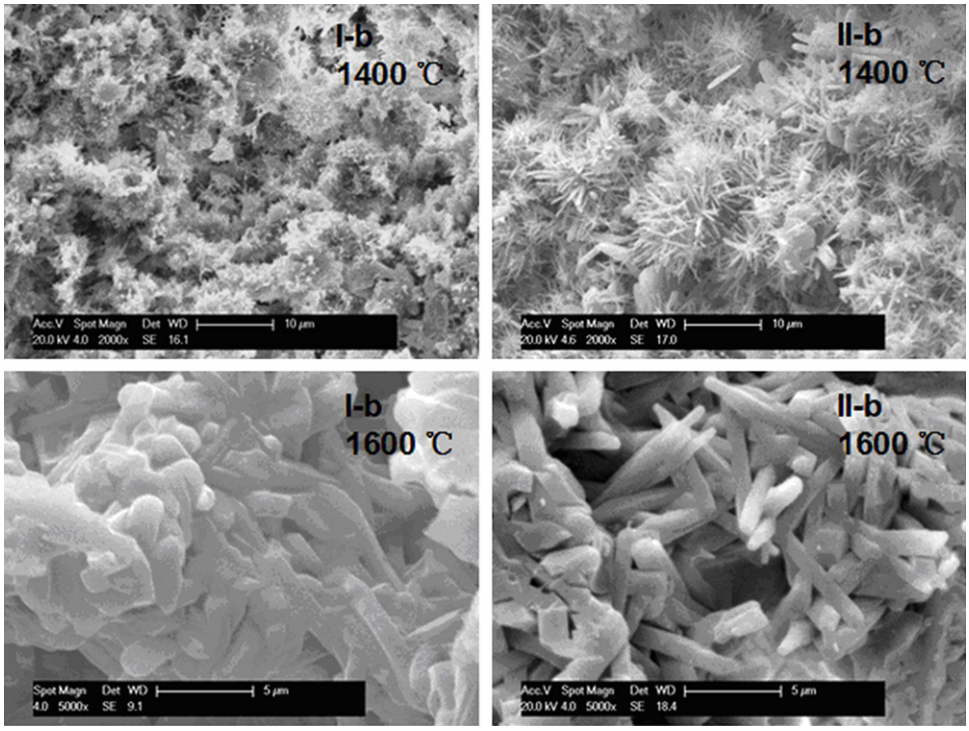

Fig. 9. Microstructures of fracture surface of I-b and II-b (contain AlF_3) sintered at 1400 °C and 1600 °C.

granular (Fig. 8, I-a and II-a). Meanwhile, the whiskers were long in the samples made with $Al(OH)_3$ (Fig. 9, II-b), but the whiskers were short in the samples made with Al_2O_3. These phenomena were consistent with what Fig. 7 shows, which is AlF_3 as the additive could improve the aspect ratios of the whiskers obviously. The whiskers of sample II-b had the highest aspect ratios at different sintering temperature. This is why sample II-b had the best mechanical properties after 1500 °C.

It is reported that mullite has a special crystal structure, where strong-bounded chains lie along the crystallographic *c*-axis, which allows its grains grow anisotropically in an unconstraint environment [20]. Therefore, when the heating temperature increased to 1600 °C, mullite whiskers grew stronger and formed an interlocking structure (Fig. 9, I-b and II-b). This structure enhanced the bending strength effectively (Fig. 6).

4. Conclusion

In this paper, self-reinforced porous mullite ceramics were fabricated by starch consolidation method with flyash, different aluminium sources and the additive AlF_3 as raw materials. Compared with Al_2O_3, $Al(OH)_3$ and flyash could fabricate preferable needle-like mullite. AlF_3 as the additive is helpful to form mullite whiskers at a low temperature. These needle-like mullite whiskers constructed an interlocking structure, which enhanced the bending strength of the porous mullite ceramics effectively. Finally, porous mullite ceramics with bending strength about 100 MPa and apparent porosity about 55% were got at 1550 °C.

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