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Fabrication of self-reinforcement of porous mullite ceramic using NH_4F as additive from kaolinite

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Self-reinforcement of porous mullite ceramics containing needle-liked whiskers were fabricated from a powder mixture of kaolinite, $Al(OH)_3$ and starch with NH_4F as additive. The effects of the sintering temperature and the content of NH_4F on porosity, phase composition, strength and microstructure of ceramics were investigated. The formation mechanism of needle-liked mullite whiskers by in situ synthesis in ceramic body was discussed. The results indicated that lots of large aspect ratio needle-liked mullite whiskers, especially in the 15% NH_4F additive sample, were observed. An interlocking structure was formed by needle-liked mullite whiskers to enhance the mechanical strength of porous mullite ceramic. And as the content of NH_4F increasing, the bending strength increased. Comparing to the samples without NH_4F additive, porous ceramic fabricated by adding NH_4F showed a higher degree of mullitization. The formation mechanism of the needle-liked mullite in the ceramic was attributed to the reaction among NH_4F and raw materials.

Key words: Mullite, Porous ceramic, Ammonium fluoride, Needle-liked, Kaolinite.

Introduction

Porous ceramics have been widely used as gas filters, insulators, molten steel filters, catalyst supports and separation membranes [1-3]. There has been a growing interest in porous mullite ceramics for such applications due to its low thermal expansion coefficient, low conductivity, good thermal stability, high creep resistance [4, 5]. Various methods have been proposed to fabricate porous mullite ceramics, such as adding pore forming agent, in situ synthesis, gelcasting, combustion synthesis. Different pore size, pore structure and grain morphology have been tailored to meet the requirement of its specific application [6-9]. However, the low mechanical properties limits its application and enhancing the strength of porous mullite ceramic is still the main challenge for the researchers.

In recent years, mullite whiskers have been developed which possess high strength as a candidate for the reinforcement in matrix [10-12]. However, there have been a few reports on the in situ synthesis of needle-liked porous mullite ceramics, which was expected to possess high strength and filtration efficiency. A. J. Pyzik [13, 14] used calcined mullite precursor as raw materials and subjected the green honeycomb body into SiF_4 gas atmosphere, which successfully fabricated acicular porous mullite ceramic and applied in diesel emission applications. However, the raw materials they used were expensive, and the synthesis method was complex. Efforts have been made to reduce its cost using cheap natural mineral materials and adding mineralizer [15]. G. Chen [16] investigated the effect of $Al(OH)_3$ and AlF_3 on the synthesis of mullite ceramic using clay as raw material. Needle-liked porous mullite ceramics were prepared for the membrane support application. S. Li [17] utilized the flyash as raw material, and AlF_3 as additives to prepare porous mullite ceramics through in situ synthesis, the needle-liked mullite whiskers have been also observed in ceramic body and high mechanical strength has been obtained. In all the above works, needle-liked porous mullite ceramic was prepared by using AlF_3 or SiF_4 as additives.

In this research, a novel additive (NH_4F) was selected to add into ceramic body to form needle-liked mullite whiskers, which was expected to self-reinforce the mechanical properties of porous mullite ceramics. In order to reduce the cost and obtain single mullite phase, kaolinite and aluminum hydroxide were used as raw materials. Self-reinforcement of porous mullite ceramic was prepared though in situ synthesis by adding starch as pore-forming agent in this work.

Experimental

Kaolinite (China Kaolinite Company) and $Al(OH)_3$ (Sinopharm, China) were used as raw materials, NH_4F (Sinopharm, China) as additive, and starch as pore-forming agent. The chemical composition of kaolinite is shown in

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Table 1. Chemical composition of kaolinite.

Component (wt%)								
SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	I.L.
46.75	35.51	1.22	0.96	0.15	0.10	0.09	0.07	15.15

Table 1. Kaolinite and $Al(OH)_3$ were weighed with stoichiometric composition of mullite. 0%, 5 wt%, 10 wt% and 15 wt% of NH_4F were separately added to the mixtures. In addition, 10 wt% of starch was also added into the each mixed powder, then ball-milled in ethanol for 24 hrs. After fully mixing and drying, the powders were pressed to obtain cylinder specimens under a 40 MPa pressure using a steel die. And then the specimens were sintered at 1300 ~ 1600 °C for 3hrs with a heating rate of 4 °C/min in electric furnace. After cooling, porous mullite ceramics were obtained.

Open porosity and bulk density of all samples were determined by the Archimedes method. Phase compositions were identified by X-ray diffraction (XRD, Model D500, Siemens) using Cu K_α radiation. The microstructure and morphology of porous ceramics were observed by scanning electron microscopy (SEM, Model JSM-6400, JEOL, Japan). Samples were machined to the dimension of 4 × 5 × 25 mm to test the bending strength via the three point bending test (Hounsfield, UK) with a support distance of 20 mm and a cross-head speed of 1 mm/min.

Results and Discussion

X-ray diffraction analysis

Fig. 1 shows the XRD patterns of the samples with 10% NH_4F additive, which were sintered at 1300 °C, 1400 °C, 1500 °C, 1600 °C, respectively. Mullite is the main crystalline phase in all the samples. And the intensity of the mullite phase increases with the sintering temperature increasing. At 1300 °C, the newly-formed mullite with the cristobalite and the quartz phase are detected, and the corundum has not been found. As the sintering temperature increasing, the corundum was formed, and the quartz disappeared. However, the cristobalite phase is undetectable, and the corundum peaks almost disappears at the temperature above 1500 °C. The corundum could be dissolved into the glassy phase contributing to the formation of the secondary mullite [16]. It could be generalized as following reactions.

$$3(Al_2O_3 \cdot 2SiO_2)\ (\text{metakaolin}) \rightarrow (3Al_2O_3 \cdot 2SiO_2)(\text{mullite}) + 4SiO_2(> 1050\ ^\circ C) \quad (1)$$

$$3Al_2O_3 + 2SiO_2 \rightarrow (3Al_2O_3 \cdot 2SiO_2)\ (\text{mullite})\ (> 1300\ ^\circ C) \quad (2)$$

In order to investigate the effect of NH_4F on the phase composition of the porous mullite ceramic, the

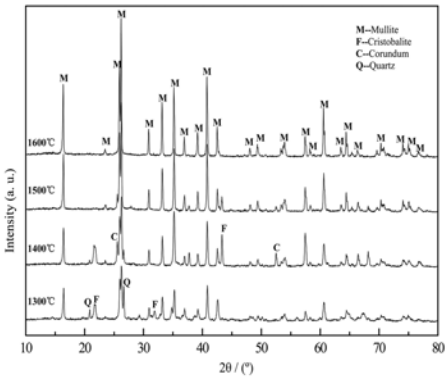

Fig. 1. XRD patterns of the samples with 10% NH_4F additive sintered at different temperatures.

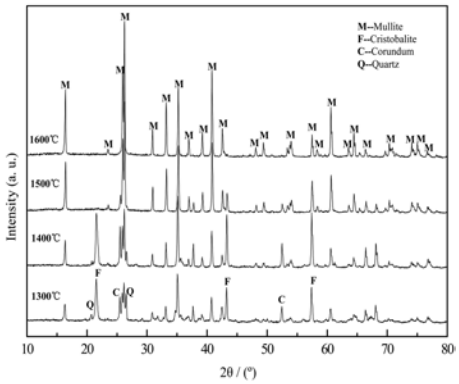

Fig. 2. XRD patterns of the samples without NH_4F additives sintered at different temperatures.

phase compositions of the samples without any NH_4F additives at different temperatures were identified by XRD, as shown in Fig. 2. The ratios of the peak areas of mullite (210) ($2\theta = 26.268^\circ$) to peak areas of corundum (024) ($2\theta = 52.525^\circ$) for each pattern were measured to determine the degree of the mullitization using X' Pert HighScore Plus. At 1300 °C, They are 11.11 (with NH_4F) and 2.25 (without NH_4F). And at 1400 °C, they are 4.41 (with NH_4F) and 2.26 (without NH_4F), respectively. The degree of mullitization of samples with NH_4F is higher than that of the samples without NH_4F. This indicates that the additive of NH_4F in ceramic body can promote the mullitization process of porous ceramic.

Open porosity and bulk density

The effect of NH_4F on the open porosity and the bulk density of samples sintered at various temperatures are shown in Fig. 3 and Fig. 4, respectively. It can be found that the open porosity increases slightly, but the bulk density increases from 1300 °C to 1400 °C. It could be explained that the secondary mullitization process was proceeding along with 10% volume expansion in the temperature range. Simultaneously, the liquid-phase sintering process was also proceeding, which formed by impurities in raw materials, such as

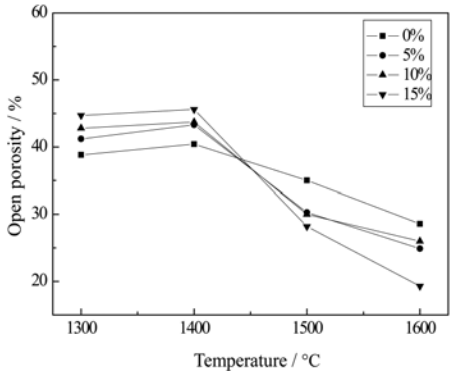

Fig. 3. Open porosity of samples fabricated with different amounts of NH_4F additive.

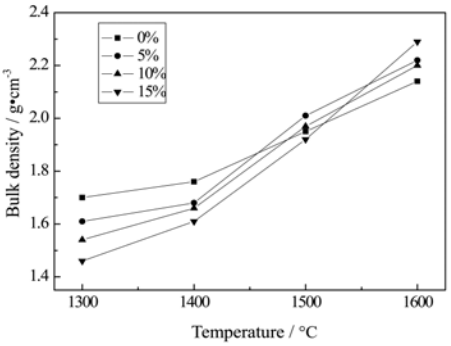

Fig. 4. Bulk density of samples fabricated with different amounts of NH_4F additive.

Fe_2O_3, CaO and TiO_2, etc. When the sintering temperature exceeded 1400 °C, the open porosity decreased, and the bulk density increased with the sintering temperature increasing. This can be attributed to the grain growth and the liquid-phase sintering during the secondary mullitization process.

When NH_4F was added, the open porosity is higher, and the bulk density is lower than those of samples without NH_4F before 1400 °C. As the sintering temperature increasing, the contrary results are obtained. Moreover, with the amount of NH_4F increasing, the open porosity decreased, and bulk density increased at 1600 °C. This indicates that NH_4F could promote the sintering and secondary mullitization process of samples.

Microstructure and mechanical properties

Fig. 5 shows the microstructures of samples sintered at 1500 °C, which prepared with 0%, 5%, 10% and 15% NH_4F additives, respectively. Lots of needle-liked mullite whiskers could be observed in the samples with NH_4F additive. As the amount of NH_4F increasing, the quantity of needle-liked mullite whiskers increased. Especially in the sample with 15% NH_4F, the needle-liked mullite with a high aspect ratio could be found, in which an interlocking structure was formed to provide a good porosity. However, the particles in the sample without NH_4F additive are granular. It has been reported that the mullite have a special crystal

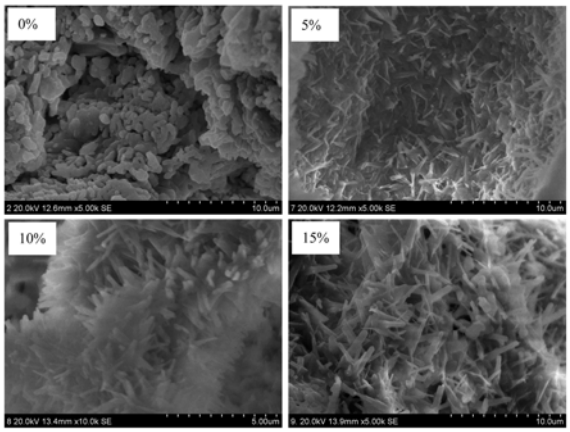

Fig. 5. SEM images of the fracture surface of samples with different amounts of NH_4F.

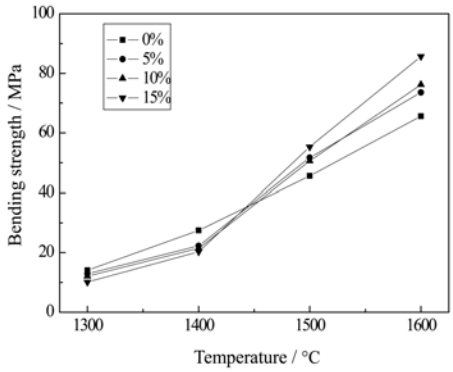

Fig. 6. Bending strength of samples fabricated with different amounts of NH_4F.

structure, where the strong-bounded chains lie along the crystallographic *c*-axis [18]. This allows its grains grow anisotropically in an unconstraint environment. This means that the addition of NH_4F is benefit to the growth of the needle-liked mullite, effectively improving the bending strength (Fig. 6).

Fig. 6 shows the bending strength of porous mullite ceramics prepared with different amounts of NH_4F. Since the crystalline grain grew, and the liquid-phase sintering proceeded, the bending strength increased with the sintering temperature increasing. After 1500 °C, the bending strength of the sample with NH_4F is apparently higher than that of the sample without NH_4F. An interlocking structure constructed in the needle-liked mullite could be explained to enhance its bending strength.

Discussion

Generally, needle-liked mullite ceramics were fabricated mainly using AlF_3 as an additive, or putting the ceramics into SiF_4 atmosphere gas [13-17]. The mechanism could be explained that the needle-liked topaz would be synthesized firstly and then decomposed into the needle-liked mullite at high temperature. However, it has been not reported that the needle-liked

mullite was prepared using NH_4F as an additive, and the reaction process between NH_4F and kaolinite is still unclear in synthesis of mullite. Abdel-Rehim reported that the different products obtained from the reaction of kaolinite and NH_4F, depending upon the sintering temperature and the amount of NH_4F [19]. The mechanism of the reaction might be considered as following.

$$Al_2Si_2O_5(OH)_4 + 24NH_4F = 2(NH_4)_3AlF_6 + 2(NH_4)_2SiF + 14NH_3 + 9H_2O \quad (3)$$

$(NH_4)_3AlF_6$ and $(NH_4)_2SiF_6$ are unstable and would decompose at the high temperature, as shown in the following reactions (4) and (5).

$$(NH_4)_3AlF_6 = AlF_3 + 3NH_3 + 3HF \quad (4)$$
$$(NH_4)_2SiF_6 = SiF_4 + 2NH_3 + 2HF \quad (5)$$

The overall reaction can be written as reaction (6).

$$Al_2Si_2O_5(OH)_4 + 14NH_4F = 2AlF_3 + 2SiF_4 + 14NH_3 + 9H_2O \quad (6)$$

In this work, only single mullite phase could be obtained attributing to the addition of $Al(OH)_3$ into the kaolinite, which was expected to consume the residual silica. $Al(OH)_3$ was firstly decomposed to Al_2O_3, and then tended to react with the reaction products of kaolinite and NH_4F, according to reaction (7).

$$3SiF_4 + 2Al_2O_3 = 4AlF_3 + 3SiO_2 \quad (7)$$

Thus, the AlF_3 gas would react with the residual silica from kaolinite to form the needle-liked topaz. After the dissociation of topaz, the needle-liked mullite could be obtained as shown in reactions (8) and (9).

$$AlF_3 + SiO_2 = Al_2(SiO_4)F_2 + SiF_4 \quad (8)$$
$$6Al_2(SiO_4)F_2 + SiO_2 = 2(3Al_2O_3 \cdot 2SiO_2) + 3SiF_4 \quad (9)$$

The above reactions occurred continuously until the off-gases were consumed completely. When the adding amount of NH_4F increased, the off-gases of AlF_3 and SiF_4 would increase to form much more needle-liked mullite whiskers. This was also proved by the analytical results from SEM images in Fig. 5.

Conclusions

Needle-liked mullite ceramics were directly fabricated through in situ reaction sintering using the kaolinite and $Al(OH)_3$ as raw materials, starch as pore-forming agent and NH_4F as additive. Attribution to NH_4F, the pore structural and stiff skeleton needle-liked mullite was formed to provide the better pore structure and higher bending strength in the porous ceramics than those of the samples without NH_4F. As the amount of NH_4F increasing, the content of the needle-liked mullite whiskers increased. During the sintering process, NH_4F could react with the kaolinite and $Al(OH)_3$ in a series of reactions. Lots of fluoride might exist in the system, and finally the topaz was formed. The forming mechanism of the needle-liked mullite in porous ceramic could be that the needle-liked topaz was firstly formed, and then dissociated to the mullite.

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