Effect Of Sintering Process On Micro-structure And Properties Of Mullite Porous Ceramics Containing magnesium oxide

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Abstract: Mullite porous ceramics with high porosity and good mechanical properties were prepared by foaming method combined with gel casting process using kaolin and alumina as main raw materials and sodium polyoxyethylene ether sulfate as foaming agent. The effects of sintering process and magnesium oxide content on the microstructure and properties of mullite porous ceramics were investigated. The studies show that: With the addition of magnesium oxide, the amount of mullite produced and the compactness of the sample will increase. At this time, the microscopic morphology of mullite is needle-like and prismatic, and the mechanical properties are better. and the pore size distribution gradually tends to be between 0.1-0.2mm and 0.2-0.3mm. The addition of magnesium oxide, The amount of mullite phase increased, the densification degree of the sample increased, and the acicular and prismatic mullite phases with good mechanical properties were mainly formed, and the porosity of mullite porous ceramics decreased and the compressive strength increased. The pore size distribution gradually tends to be between 0.1-0.2mm and 0.2-0.3mm. As the sintering temperature increases, the porosity of mullite porous ceramics decreases and the compressive strength increases. With the extension of the holding time, the amount of mullite phase generated increases, the porosity remains basically unchanged, and the compressive strength increases.

1. Introduction
In recent years, mullite porous ceramics have received great attention [1]. Because of their excellent properties, such as low density, low thermal conductivity, high strength, high thermal shock resistance and high fire resistance. And because of that, mullite porous ceramics have been widely used in engineering[2-4]. Porous mullite ceramics can be used as refractories, catalyst carriers and gas / liquid filters, it has a good application prospect in the field of high temperature applications. The properties and applications of mullite porous ceramics first depend on the properties of the material itself, and the second is the influence of micro-morphology, pore size distribution and porosity of mullite porous ceramics [9-11]. The micro-morphology, pore size distribution and porosity of porous ceramics are usually determined by the preparation process of porous ceramics.

The preparation process of mullite porous ceramics can be divided into three categories [12]: sacrificial template method, particle accumulation method and foaming method. Sacrificial template method can achieve precise design of porous ceramic hole structure, and can prepare ceramic devices.
with complex shape, but the experimental operation is complex, difficult to control, and the experiment cycle is long. The mullite porous ceramics prepared by particle accumulation method have relatively simple process and good mechanical properties, and have a good application foundation. But comparing with other preparation processes, the porosity is relatively low, which can not meet the needs of some applications with high porosity. The foaming method\cite{13} has a simple process, can produce large-size products with complex shape and high porosity, and can be produced on a large scale. However, the bubbles in the ceramic slurry are in an unstable state, and too long time will lead to floatation, delamination, merger and other phenomena, so the foaming slurry needs to be solidified quickly. In this paper, foaming method combined with gel casting process was used to prepare mullite porous ceramics.

As we all know, kaolin can be calcined at high temperature to form mullite. The amount of mullite formation is not only related to the component content of kaolin and the ratio of raw materials, but also to the reaction temperature. Too high temperature will make the experiment more difficult and difficult to control. Some studies have shown that the addition of sintering aids\cite{14} can reduce the sintering temperature, such as magnesium oxide, Calcium oxide, boron trioxide, titanium dioxide, manganese oxide and yttrium oxide. Among them, the addition of magnesium oxide is beneficial to the formation of mullite with equiaxed structure and reduce the experimental temperature.

The purpose of this experiment is to prepare mullite porous ceramics by sintering kaolin and alumina, and to study the effects of magnesium oxide content and sintering parameters on the formation, structure and properties of mullite.

2. Experimental procedure

2.1 Raw materials
In this experiment, Kaolin (analytical purity) and alumina (analytical purity) were used as the main raw materials. The fatty alcohol polyoxyethylene ether sodium sulfate (25%) was used as foaming agent. The sodium fluoride (analytically pure) was used as mineralizer. The sintering additive magnesium oxide (analytical purity).

2.2 Sample preparation
In this experiment, the ceramic preform was prepared by gel casting process, and the molding mold was prepared by special gypsum powder for ceramic mold. The inner dimension of gypsum mold is $\Phi$ 20mm × 40mm.

Metakaolin was obtained by calcining kaolin in a high temperature box furnace (KSL-1100X) at 900 °C for 2 hours.

According to the molar ratio of mullite (3Al$_2$O$_3$ ·2SiO$_2$), weighing the mixtures containing alumina, metakaolin, water, foaming agent, magnesium oxide and sodium fluoride. Then, the mixtures were milled in a ball mill for two hours. After that the prepared ceramic slurry was injected into the prepared gypsum mold. After natural drying for 24 hours, the ceramic embryo was obtained, and then the ceramic embryo was dried in the oven (120 °C for 12 h). The dried ceramic embryos were calcined in a high temperature box furnace (KSL-1700X). The firing system is as follows: the heating rate of 10 °C / min is raised directly to the predetermined temperature, holding for 2 hours, and then cooled with the furnace.

2.3 Experimental analysis

2.3.1 Microstructure analysis
The small particle samples were taken from the broken samples, and the micro-morphology of the samples was observed by SU8020 scanning electron microscope produced by Hitachi Company of Japan.
2.3.2 Phase composition analysis
A small sample is cut from the sample and the powder sample is obtained after grinding. The analysis phase was composed of Bruker D8 advance X-ray diffractometer (XRD, test parameters: Cu target, Ka ray, scanning speed 2 °/ min, tube voltage 40kV, tube current 30mA).

2.3.3 Analysis of mechanical properties
The sample is cut and polished into a cylinder with parallel upper and lower bottom surface, the diameter of the sample is measured by Vernier caliper (measuring accuracy: 0.1mm), the cross-sectional area is calculated, and the tensile and compressive strength of the sample is tested by JBC- LY building thermal insulation material tension and compression performance testing device.

2.3.4 Analysis of pore size distribution
After polishing the section of the sample, the photos were observed and photographed by optical microscope, and the surface morphology of the sample was analyzed by image-pro plus software.

3. Results and discussion

3.1 Organizational structure

3.1.1 Effect of magnesium oxide content on organizational structure of mullite porous ceramics
X-ray diffraction analysis shows that the phase content of the sintered sample is shown in figure 1. When magnesium oxide is not added, mullite phase and corundum phase are the main phases in the sample. The relative content of each phase in the sample is calculated by K value method[15-16] as shown in figure 2. After adding magnesium oxide, the content of mullite phase increases gradually, while the content of corundum phase decreases gradually until it disappears completely. This is due to that after the addition of magnesium oxide, magnesium oxide forms liquid phase during high temperature sintering, which is beneficial to the material transfer during solid phase sintering and positively promotes the rate of sintering reaction, thus increasing the formation of mullite phase. At the same time, the addition of magnesium oxide increases the oxygen vacancy in alumina, which can promote diffusion, facilitate the sintering reaction and increase the formation of mullite phase. A little magnesia-alumina spinel phase appeared in the ceramic sample when the magnesium oxide content reached 4%, and the spinel phase increased slowly with the increase of magnesium oxide content.

The sample was observed by scanning electron microscope as shown in figure 3. From the scanning electron microscope picture, it was observed that the mullite phase without magnesium oxide was mainly flaky (figure 3a). With the gradual addition of magnesium oxide, the resulting mullite gradually changes to acicular and prismatic (Fig. 3b). The addition of magnesium oxide accelerates the
positive progress of the sintering reaction, which promotes the transformation of acicular and prismatic mullite. A little massive spinel was observed after the magnesium oxide content was 4%.

Fig. 3 SEM diagram of sintered sample containing magnesium oxide (a:0% magnesium oxide 1450 °C 2h b:10% magnesium oxide 1450 °C 2h)

### 3.1.2 Effect of sintering temperature on microstructure of mullite porous ceramics

Fig. 4 is the X-ray diffraction pattern of the sample sintered at different temperatures. It can be seen that a small amount of mullite phase was formed in the sample at 1200 °C. With the increase of sintering temperature, the content of mullite phase increased gradually. With the increase of temperature, the surface energy of the system decreases, the bond rearrangement occurs between particles, and the contact state between particles gradually expands from point contact to surface contact, which is beneficial to the positive process of mass transfer and promotes the continuous sintering reaction. As a result, the transformation and formation of mullite phase is improved. Therefore, with the increase of sintering temperature, the content of mullite phase increases while the content of polycorundum phase decreases.

Figure 6 shows the scanning electron microscopic images of the samples sintered at 1200 °C and 1600 °C. It can be seen that the mullite phase formed at 1200 °C is mainly flaky, and there is no obvious acicular and prismatic mullite formation (Fig. 6a). It is observed that most of the mullite formed at 1600 °C are acicular and prismatic (Fig. 6b). When mullite is formed by high temperature sintering, primary mullite and secondary mullite will be formed. The first mullite is formed at about 1200 °C, and the mullite phase is mainly flaky. When the temperature is raised to 1600 °C, a large amount of secondary mullite will be formed, which is mainly prismatic. Therefore, with the increase of sintering temperature, the formation of mullite phase increases and the mullite phase is mainly prismatic.
3.1.3 Effect of holding time on microstructure of mullite porous ceramics

Figure 7 is the X-ray diffraction pattern of the sample after sintering with different holding time. It can be seen that the content of corundum phase is mainly corundum phase after holding for 1h, and the content of corundum phase decreases gradually with the increase of holding time. The content of mullite phase gradually increases as shown in figure 8. With the increase of holding time, it is beneficial to the continuous material transfer, and the sintering reaction also continues to occur. Therefore, the content of mullite phase increases with the increase of holding time.

Figure 9 shows the scanning electron microscopic image of the sample after sintering for 1 h and 6 h. It can be seen that the mullite phase formed after holding for 1 h is mainly flaky (figure 9a), and the mullite crystal phase tends to grow and dense when holding for 6 h (figure 9b). According to the principle of solid phase sintering, with the increase of holding time, the grain size of the sintered phase will continue to grow, and the mullite phase tends to grow and dense.

![Figure 7 X-ray diffraction patterns of sintered samples with different holding time](image7)

![Figure 8 Mullite phase content of sintered samples with different holding time](image8)

![Figure 9 SEM diagram of sintered samples with different holding time](image9)
3.2 Porosity and pore size distribution

3.2.1 Effect of magnesium oxide content on porosity and pore size distribution of mullite porous ceramics

The porosity of the calcined samples was measured by Archimedes drainage method. The change trend of porosity is shown in figure 10, and the porosity of mullite porous ceramics decreases gradually with the addition of magnesium oxide. This phenomenon is mainly caused by the addition of magnesium oxide as sintering additive and the increase of liquid phase formed between grains, which promotes the elimination of pores in the sintered body and improves the densification degree of the sample. At the same time, the addition of magnesium oxide can react with alumina to form magnesia-alumina spinel at the grain boundary, reduce the growth of discontinuous grains, restrain the abnormal grain growth, reduce the grain boundary separation of interstitial grains, and promote densification. Therefore, the porosity of mullite porous ceramics decreases gradually with the addition of magnesium oxide.

The surface morphology of the sample was analyzed by image-pro plus software. The pore size distribution of the sample containing 0% magnesium oxide is shown in figure 11. The pore size range of the sample is mainly between 0.1-0.4mm, of which 0.1-0.2mm and 0.2-0.3mm account for the most. With the addition of magnesium oxide, the proportion of pore size between 0.1-0.2mm and 0.2-0.3mm increased at first and then decreased as shown in figure 13. After the addition of magnesium oxide, the shrinkage of the sample becomes larger and the pore size tends to be concentrated, and the larger the

![Fig.10 porosity of sintered sample containing magnesium oxide](image1)

![Fig. 11 pore size distribution of 0% magnesium oxide sintered sample](image2)

![Fig. 12 pore size distribution of 2% magnesium oxide sintered sample](image3)

![Fig.13 0.2-0.4mm pore size distribution](image4)
pore diameter is, the greater the pore shrinkage is. The pores with a large proportion of pores in the range of 0.2-0.3mm and 0.3-0.4mm gradually changed to 0.1-0.2mm and 0.2-0.3mm, and some tiny pores will disappear due to the shrinkage of the sample. Thus, with the increase of magnesium oxide content, the multi-pore size distribution gradually concentrated between 0.1-0.2mm and 0.2-0.3mm, and then gradually changed to a smaller range. Therefore, the proportion of pore size range between 0.1-0.2mm and 0.2-0.3mm increased at first and then decreased.

3.2.2 Effect of sintering temperature on porosity and pore size distribution of mullite porous ceramics

Figure 14 shows the change trend of porosity of samples after sintering at different temperatures. It can be seen that when the sintering temperature of mullite porous ceramics is changed, the porosity decreases gradually with the increase of sintering temperature, and the range of change is small. With the increase of temperature, the amount of mullite phase formation increases, the ceramics are relatively dense, and the porosity decreases relatively. At the same time, with the increase of temperature, the shrinkage of the sample increases, the compactness of the ceramic body increases, and the porosity decreases relatively.

![Fig. 14 porosity of samples sintered at different temperatures](image)

The surface morphology of the sample was analyzed by image-pro plus software, and the pore size of the sample was mainly distributed in the range of 0.1-0.4mm. With the increase of sintering temperature, the proportion of pore size in the range of 0.1-0.2mm and 0.2-0.3mm remains basically unchanged. With the increase of temperature, the decrease of porosity is small, and the shrinkage of the sample increases, so the change of pore size distribution is also small, basically unchanged.

3.2.3 Effect of holding time on porosity and pore size distribution of mullite porous ceramics

When the holding time of mullite porous ceramics is changed, the porosity of the sample is shown in figure 15. With the increase of holding time, the porosity fluctuates relatively smoothly and remains basically unchanged. It shows that the extension of holding time has little or no obvious effect on the porosity of mullite.

![Fig. 15 porosity of sintered samples with different holding time](image)

The surface morphology of the sample was analyzed by image-pro plus software, and the pore size of the sample was mainly distributed in the range of 0.1-0.3mm. With the increase of holding time, the proportion of aperture range between 0 and 0.1mm remains basically unchanged at 1h-4h, it decreased.
after 5 hours. The proportion of 0.1-0.3mm increased at first and then decreased. The proportion of 0.5-1mm decreased gradually. According to the principle of solid phase sintering, with the increase of holding time, it will promote grain growth and improve the compactness of the sample, some very small pores will gradually disappear, and larger pores will gradually shrink. Therefore, the pore size ratio between 0.1-0.3mm increased at first and then decreased, and that between 0.5-1mm decreased gradually. At the same time, the increase of holding time has little effect on porosity, and the corresponding effect of pore size distribution is also small.

3.3 Compressive strength

3.3.1 Effect of magnesium oxide content on compressive strength of mullite porous ceramics

The compressive strength of the calcined samples was tested, and the mechanical properties of mullite porous ceramics were studied. It is concluded that the change trend of compressive strength is shown in figure 16, with the gradual addition of magnesium oxide, the mechanical properties of mullite porous ceramics are improved, and the compressive strength increases. When magnesium oxide was gradually added to the sample, the phase composition of the sample changed, the amount of mullite increased, the porosity decreased, the shrinkage of the sample increased and the structure became denser. Therefore, the compressive strength increases gradually. At the same time, with the gradual addition of magnesium oxide, most of the mullite phases are needle-like and prismatic, with compact structure and good mechanical properties. To sum up, the compressive strength of mullite porous ceramics increased with the addition of magnesium oxide.

![Fig.16 compressive strength of specimens with different magnesium oxide content](image1)

3.3.2 Effect of sintering temperature on compressive strength of mullite porous ceramics

Fig.17 shows the change trend of compressive strength of mullite porous ceramics when the sintering temperature is changed. It can be seen that the compressive strength increases gradually with the increase of sintering temperature. With the increase of sintering temperature, the amount of mullite increases, and the main mullite phases are acicular and prismatic mullite phases, and the mechanical properties are improved. At the same time, with the increase of temperature, the shrinkage of the sample increases, the compactness of the sample increases, and the strength also increases. To sum up, the compressive strength of mullite porous ceramics increases with the increase of sintering temperature.

![Fig.17 compressive strength of specimens with different sintering temperatures](image2)
3.3.3 Effect of holding time on compressive strength of mullite porous ceramics

When the sample is calcined at 1450 °C, change the holding time during sintering. The compressive strength of the sample is shown in figure 18, and the compressive strength of the sample increases gradually with the extension of holding time. According to the principle of solid state sintering, prolonging the holding time is helpful to the formation of main crystal phase and grain growth of the sample. The amount of mullite phase is increased, the compactness and mechanical properties of ceramics are improved. To sum up, with the increase of holding time, the compressive strength of mullite porous ceramics increases gradually.

4. Conclusion

(1) The addition of magnesia promotes the sintering reaction rate, the formation of mullite phase increases, and the flaky mullite phase is transformed into acicular and prismatic mullite phase with good mechanical properties. At the same time, the addition of magnesium oxide accelerates the elimination of pores in the sintered body and improves the densification degree of the sample. Therefore, the porosity of mullite porous ceramics decreases and the compressive strength increases. The pore size distribution gradually tends to be between 0.1-0.2mm and 0.2-0.3mm. A little magnesia-alumina spinel phase appeared in the ceramic sample when the magnesium oxide content reached 4%, and increased with the increase of magnesium oxide content.

(2) The increase of sintering temperature is beneficial to the positive process of mass transfer and promotes the continuous sintering reaction, the amount of mullite phase increases and transforms from flake to prism with good mechanical properties, the compactness of the sample increases, the porosity decreases, and the strength increases. The change of pore size distribution is small and remains basically unchanged. The aperture range is mainly distributed between 0.1-0.2mm and 0.2-0.3mm.

(3) The increase of holding time is conducive to the continuous material transfer, the sintering reaction also continues to occur, the amount of mullite phase increases, the compactness of the sample increases, the change of porosity is small, and the compressive strength increases. The pore size range is mainly distributed between 0.1-0.2mm and 0.2-0.3mm, and the proportion increases at first and then decreases.

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