Fabrication and microstructures improvement of porous mullite ceramics based on sol-treated sawdust

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Calcined flint clay has a large reserve in China. In this paper, porous mullite ceramics are prepared by calcined flint clay, while the sawdust is pretreated with different concentrations of silica sol. Effects of sintering temperature and silica sol concentrations on physical properties and microstructures of the porous mullite ceramics are studied. Residual skeleton structure cross pores are clearly observed in the scanning electron microscope images, which is established as a key factor in improving the properties of specimens. With the pretreatment of silica sol on sawdust, mechanical properties are enhanced and thermal conductivities could be optimized. Under the firing temperature of 1350 °C, the compressive strength of specimens with sawdust pretreated in 5 wt % concentration of silica sol is 2.4 MPa.

Key-words: Calcined flint clay, Sol-treated, Microstructures design, Thermal insulation, Mechanical improvement

1. Introduction

There is a large reservation of calcined flint clay in Shandong province of China.¹ According to the policy of the energy saving and environment protection from national construction projects, the China clay industry has been one of the most dynamically developing direction in China over the last decade.²,³ Most calcined flint clay in China is deposited from the single mineral type of kaolinite, occupying various phase compositions and stable chemical content of Al₂O₃ and SiO₂.⁴ Because of this special geological formation process, calcined flint clay has several characteristics such as lower water absorption and plasticity, poor dispersion in water.⁵ Several researches have been carried out to study the application of calcined flint clay in the function of expansive agent and hard clay.⁶,⁷ Few studies have been carried out on calcined flint clay of raw materials used for porous ceramic in China.

Porous ceramic is a kind of thermal insulation material with high porosity, low thermal conductivity, low density, combustibility and so forth.⁸,⁹ Concerning the mechanism of pore formation with different porous ceramic materials, the main routes to fabricate porous ceramics can be divided into five categories including: (i) partial sintering,¹⁰ (ii) sacrificial agents,¹¹,¹² (iii) replica templates,¹³ (iv) direct foaming¹⁴ and (v) in situ pore formation.¹⁵,¹⁶ Plant matter is one of the most common options in sacrificial agents, because the burnout of natural plant matter produces CO₂ and H₂O which would not do harm to the environment.¹⁷,¹⁸ However, plant matter usually can not be used for the formation of micropores, due to the high toughness of plant cellulose which is the main reason for the difficulties to be highly processed.¹⁹ On the other hand, the exist of excessive macropores would limit the promotion of mechanical properties.²⁰,²¹

In this paper, calcined flint clay is used as raw materials for the fabrication of porous mullite ceramics, while sawdust is chosen as a kind of cheap plant matter. Further, the sawdust is treated with vacuum impregnated silica sol, aiming to retain skeleton structures after the process of sintering. These skeleton structures would divide the original large pores into several small pores, which might affect the microstructures and properties of porous ceramics. Hence, the effects of silica sol concentrations and sintering temperatures on the physical, mechanical and thermal properties of the products. The porous ceramics prepared at relatively lower temperatures exhibited high porosity, enough strength and low thermal conductivity, which can be recognized as potential candidates for engineering ceramic applications such as thermal insulation and ceramic filter.

2. Material and methods

Firstly, sawdust is soaked in silica sol with different concentrations by vacuum impregnation, while the concentrations of silica sol is 0, 3, 5 and 7 wt %, respectively. The mixtures are curing in room temperature for 24 h, then dried at 80 °C for 48 h to obtain the pretreated sawdust. Secondly, calcined flint clay (Shandong, China), Suzhou

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kaolin, reactive alumina power (Al$_2$O$_3$ $>$ 99.9 wt %), and different sawdust are mixed with the binder to prepare the green bodies for porous mullite ceramics with a model of diameter 36 mm under pressure of 2.5 MPa. The green bodies are dried at 80 °C for 12 h and sintered at 1250, 1300, 1350, 1400 and 1450 °C for 3 h, respectively. The chemical compositions of starting materials and formulations are respectively shown in Tables 1 and 2.

Bulk density and apparent porosity are detected by Archimedes drainage method in distilled water. Cold crushing strength (CCS) is tested on a hydraulic universal testing machine (HT-9051, Hung Ta Instrument, Taichung, Taiwan), and thermal conductivity is performed on the disk-shape specimens (20 mm in thickness, 180 mm in diameter), at 300, 600, 900 °C, respectively, by using water flow plate thermal conductivity apparatus (PBOR-02, Precondar, China). All the testing values are obtained from the average of six specimens. Thermodynamics calculation are based on the software of FACTSAGE 6.2, with setting the concentrations of silica sol as the variable. Phase compositions of sintering specimens are identified by X-ray diffractometry (XRD, X’Pert PRO, Philips, Netherlands). Microstructures of specimens are observed by scanning electron microscope (SEM, JSM-6610, JEOL, Japan).

3. Results and discussion

Physical properties of the varied specimens under different firing temperatures are shown in Fig. 1. With the increasing of silica sol concentrations in sawdust, the volume expansion of specimens could be effectively inhibited [Fig. 1(a)]. At the same time, apparent porosity shows a trend to decrease and the bulk density slight increase in Figs. 1(b) and 1(c). Its worthy to be mentioned that CCS of specimen S7 could be greatly improved from 1.5 to
3.2 MPa by the increasing of silica sol in sawdust. As the sintering temperature rising from 1250 to 1450 °C, all the specimens show better performance in mechanical properties, almost have larger linear shrinkage. When the sintering temperature is 1350 °C, the specimens show lower linear shrinkage than 1300 °C, that might relate with the continuous growth of mullite crystal and the promotion from liquid sintering reaction.\(^{(7)}\),\(^{(20)}\)

XRD patterns of specimens with sawdust unpretreated in silica sol under different firing temperatures are shown in Fig. 2(a), while XRD patterns of specimens with sawdust pretreated in different concentrations of silica sol under firing temperatures of 1350 °C are shown in Fig. 2(b). As the sintering temperatures increasing, the phases evolution of specimens is obvious in Fig. 2(a). Most diffraction peaks of corundum phase initially disappear in 1450 °C, along with the disappearance of cristobalite and tridymite, indicating the formation of mullite. Finally, all the phases can be detected as mullite and corundum. As shown in Fig. 2(b), phase compositions of sintered specimens could be little affected by the change of silica sol concentrations in sawdust. But the intensity of corundum diffraction peaks decreases with the increase of silica sol concentrations. This may result from that the pretreated silica sol in sawdust could combine with clay and kaolin, then transfer to mullite phase.

In order to further detect the promotion of sintering temperature on phase evolution, microstructures of specimens with sawdust pretreated in 5 wt% silica sol under different firing temperatures are shown in Fig. 3. The specimens initially show a needle-like crystalline morphology at 1250 °C. When the firing temperature gets to 1300 and 1350 °C, the microstructures become more compact and dense, indicating the phase transformation from XRD patterns. The SEM images show that the mullite crystals grow larger and more uniform as the temperature increases.

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**Fig. 2.** XRD patterns of specimens vs. firing temperature and concentration of silica sol (a: without silica sol pretreated; b: 1350 °C).

**Fig. 3.** SEM images of specimens S5 under different firing temperatures.
1350 °C, specimens have obvious needle-like mullite crystal combined columnar crystal to form a network structure. As the sintering temperature is 1450 °C, the grains size shows the maximum than other specimens. The increase of temperature promotes the liquid sintering and the growth of mullite grains,22) accelerates the linear shrinkage of specimens, and the densification of solid phase improves the CCS of the specimens (Fig. 1).

Aiming to verify the effects of silica sol concentrations in sawdust and firing temperatures on the properties of specimens, thermodynamic software FactSage 6.2 is used in thermodynamics calculation.10) FACT OXIDE database is chosen for the simulation of thermal chemical reaction, and the results of calculation are shown in Fig. 4. According to the chemical and batch compositions shown in Tables 1 and 2, the chemical compositions of sawdust would change as the setting concentrations of silica sol ((19.59 + A) SiO₂ + 5.14 Al₂O₃ + 48.0 CaO + 4.57 MgO + 3.85 K₂O). As the variable (A) range from 0 to 100 g, standing for the situation of without silica sol and with excessive silica sol. With increasing sintering temperature from 1250, 1350 to 1450 °C, the amount of different phases and compositions in the reaction simulation are quite different, which can be reflected in Fig. 4 as Y-axis. Along with the increase of (A), liquid phase increase sharply and the kinds of solid phases decrease. This indicates that the proper concentration of silica sol is essential to enhance the liquid sintering and promote the densification of residual skeleton from sawdust. However, too higher sintering temperature may cause partial contraction to form cracks and defects while the only exist phase in 1450 °C is liquid. Compare the data of thermal simulation and the experiments, the pretreated concentration of silica sol for sawdust should set in the range of 3–5 wt % and the proper sintering temperature can be set as 1350 °C.

Pore size distributions of specimens with sawdust pretreated in different concentrations of silica sol after fired at 1350 °C are illustrated in Fig. 5. As shown, pore size of the specimens are mainly bimodal distributed in the range of 1–10 and 10–50 µm. In the range of 1–10 µm, pore volume of relative small pores increase rapidly by the rising concentration of silica sol (S5 and S7). Meanwhile, the position and volume of relative larger pores in the range of 10–50 µm show different unregular change than smaller ones, because the amount of relative bigger pores in specimens S5 is less than others. Based on the statistical data of pore size distribution, the beneficial function of silica sol pretreated sawdust can be confirmed that proper concentrations of silica can contribute plant porogen to remain solid skeleton in the pores, forming several smaller pores and supporting structure.

Further, thermal conductivities of specimens with sawdust pretreated in different concentrations of silica sol under firing temperature of 1350 °C are illustrated in
Fig. 6. As the concentrations of silica sol are increasing, the thermal conductivities of specimens S0 and S7 show the maximum and minimum, respectively. It is worthy to be mentioned that specimens S3 show lower thermal conductivities than S5. With the volume increase of relative smaller pore in Fig. 5, the enlarge of heat transfer area could effectively increase the channels to prevent the loss of energy in specimens. Even though the higher concentrations of silica sol pretreated would contribute to the increase of liquid phase and the densification of solid phase, the formed solid skeleton in the pores of specimens with pretreated sawdust could partly enhance the insulation efficiency and prevent the linear shrinkage.

In order to further detect the optimization from silica sol pretreated on microstructures evolution, microstructures of specimens with sawdust pretreated in different concentrations of silica sol under firing temperature of 1350 °C are shown in Fig. 7. It can be observed that the relative larger pores (S0) are gradually divided into several smaller pores (S3, S5 and S7) with the changing of silica sol concentrations. Especially for specimens S5, the optimized microstructures show more uniform distribution than others, remaining proper skeleton to divide the space and support the strength. This beneficial evolution of microstructures can be related to the balance of linear shrinkage in Fig. 1 and the improvement of thermal insulation in Fig. 6. Implementation of these functions, the optimization mechanism of pretreated sawdust with silica sol can be promoted and the schematic diagram are shown in Fig. 8. With the pretreatment of silica sol, sawdust retains its original plant morphology and forms solid skeleton structures to support the pores. The optimized structure can contribute to resist volume shrinkage from liquid sintering.

![Fig. 6. Thermal conductivities of the specimens with sawdust pretreated in different concentrations of silica sol after fired 1350 °C.](image)

![Fig. 7. Microstructures of specimens with sawdust pretreated in different concentrations of silica sol at firing temperatures of 1350 °C.](image)

![Fig. 8. Schematic diagram for microstructures design and properties improvement of unpretreated and sol-treated plant pore formers in porous ceramics.](image)
ing and enhance the mechanical properties of specimens. At the same time, more complex microstructures could increase heat transfer area and heat transfer distance, promoting the thermal insulation of specimens.

4. Conclusions

Porous mullite ceramics with improved mechanical properties, lower thermal conductivity and well-designed microstructure are successfully fabricated by sacrificial agents, with the sawdust pretreated in silica sol used as the pore-forming agent.

Sawdust pretreated by different concentration of silica sol has a great influence on physical properties, thermal properties and microstructures of the porous mullite ceramics. Observed from the SEM images, the pretreated sawdust would form solid skeleton in the pores to divide it into several smaller ones. The formation of residual skeleton contributes to keep the volume stability and enhance the CCS. Meanwhile, larger pores are divided into more smaller pores, it contributes to the decrease of thermal conductivity. When the firing temperature is 1350 °C and the pretreated concentration of silica sol is 5 wt %, the prepared mullite ceramics have CCS of 2.4 MPa and thermal conductivity of 0.23 W/(m·K) at the 900 °C. Therefore, this special pore structure not only reduces heat transfer, but also reduces stress concentrations within the specimens.

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