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Preparation of Mullite Porous Ceramics by the Composite Method of Foaming and Pore-Forming Agent Method

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Abstract

To prepare mullite porous ceramics with low thermal conductivity and high strength, taking kyanite tailings and α-Al_2O_3 as the main raw materials, the mixture after adding sawdust and foaming agents was cast into shape and heated at different temperatures. The bulk density, porosity and mechanical properties of the sample were tested at room temperature. The phase composition and microstructure were analyzed using X-ray diffraction and scanning electron microscopy. The results show that as the sawdust addition increased, the apparent porosity of the sample increased; the compressive strength and the thermal conductivity decreased. Increasing the firing temperature can promote the densification, improve the compressive strength and increase the thermal conductivity of the sample. When the firing temperature was increased to 1500°C, the ceramic reaction was basically completed. When the sawdust content was low, the sawdust was almost surrounded by the material, and the pore distribution was relatively dispersed. As the sawdust content increased, the pore distribution became more concentrated, and there were more connected pores. When the sawdust addition was 10% (w) and the heat treatment temperature was 1500°C, the mullite porous ceramics would have high compressive strength and low thermal conductivity.

Keywords: Foaming method; Pore-forming agent method; Mullite porous ceramics

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1. Introduction

Porous ceramic materials have these properties such as low bulk density and low thermal conductivity. Related research on porous ceramic materials has attracted more and more attention [1–3]. Porous ceramic materials are widely applied in catalyst carriers [4–5], filtration and separation [6,7], heat insulation [8,9], sound absorption [10], and electronic components [11,12]. Especially in the current situation of extremely severe environmental pollution and energy shortage, the demand for materials with better performance is constantly increasing [13,14]. Due to its porous nature, porous ceramics can reduce thermal radiation and heat convection, thereby lowering the thermal conductivity. It is an excellent thermal insulation material that is of great significance for environmental protection and carbon emission reduction [15].

Widespread technical applications of mullite ceramics stem from their optimal properties such as high thermal stability, excellent thermal shock resistance, low density, low thermal expansion and electrical conductivity, as well as appropriate strength and fracture toughness [16–18]. In addition, mullite ceramics have low gas permeability, optimal creep resistance, high compressive strength, and good corrosion resistance at high temperatures [19]. Due to its optimal thermal and mechanical

Nomenclature

w – share of raw materials, %

Abbreviations and Acronyms

SEM – scanning electron microscopy
XRD – X-ray diffraction

properties, mullite has become an important material for traditional and advanced ceramics [20].

In this work, the foaming method and the pore-forming agent method are combined to form multi-level pores inside the material, aiming to improve the strength and reduce the thermal conductivity of the material. The effects of adding sawdust and heat treatment temperature on the densification, microstructure and physical properties of the samples are studied, aiming to improve the strength of mullite porous ceramic materials and reduce their thermal conductivity.

2. Experiment

2.1. Raw materials

The main raw materials used in this experiment were α-Al_2O_3 micropowder produced by Kaifeng Special Refractories Co., Ltd., China, and kyanite produced in Hainan province, China. The specific chemical compositions of the raw materials are shown in Table 1.

Table 1. Chemical composition of raw materials.

Raw material	*w*, %										Particle size
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	ZrO_2	I.L	µm
Kyanite	35.24	56.73	0.88	0.02	0.81	0.01	0.02	0.02	3.25	3.02	25.72
α-Al_2O_3	0.13	98.88	0.07	0.02	0.02	0.008	0.008	0.005		0.859	2.27

The additives include sawdust (from Hebei province, China, passing through a 0.5 mm sieve, used as a pore-forming agent), polyvinyl alcohol (PVA, analytical grade, used as a binder), aluminium sol (from Shandong province, China, with a solid content of 20%), carboxymethyl cellulose (CMC, analytical grade, used as a thickener), and NG10 (produced by Wuhan Shanda Chemical Co., Ltd., China, used as a foaming agent).

2.2. Sample preparation

The ingredients were prepared according to the ratio of m(kyanite):m(Al_2O_3 micropowder) = 74.57:25.43. First, the prepared raw materials, PVA (3.5% (*w*)) and CMC (0.1% (*w*)) were placed into a planetary ball mill for grinding. The ratio of grinding ball, material and water was 3.6:3:1. Then, 5% (*w*), 10% (*w*), 15% (*w*) and 20% (*w*) sawdust was added separately to the ball-milled materials, followed by the foaming agent. After rapid stirring, the mixture was poured into moulds. After drying at room temperature for 24 hours, the samples were demoulded and further dried at 110°C for 24 hours. Finally, the samples were heat-treated in a high-temperature furnace at 1450°C and 1500°C, respectively, as shown in Fig. 1.

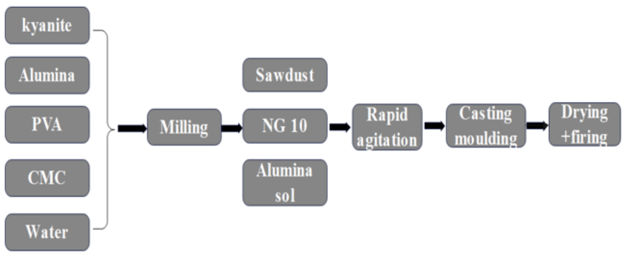

Fig. 1. Preparation process of mullite porous ceramics.

2.3. Analysis and testing

According to GB/T 2997-2000, the apparent porosity and bulk density of the heat-treated samples were measured using an apparent porosity and bulk density tester (Model XQK-04, Luoyang Precondar Instruments for Testing Refractoriness Co., Ltd., China). According to GB/T 5072.2-2004, the compressive strength of the heat-treated specimens at room temperature was tested using a microcomputer-controlled electronic universal testing machine (Shenzhen WANCE Testing Equipment Co., Ltd., China). According to GB/T 5988-2007, the linear change rate of the samples heat-treated at 1450°C and 1500°C was measured. Referring to the international standard ISO 22007-2, the thermal conductivity of the specimens at room temperature was measured using a Hot Disk thermal property analyser (Model TPS2500S, Hot Disk AB, Sweden).

3. Results and discussion

3.1. Effects of heat-treatment temperature and sawdust addition on the phase changes of samples

Figure 2 shows the variation rules of the phases of mullite porous ceramics with different sawdust additions at different heat-treatment temperatures.

It can be observed from the X-ray diffraction (XRD) patterns of the three samples that an increase in the heat-treatment temperature is conducive to the formation of the mullite phase. Specifically, the peak values of the characteristic peaks of the mullite phase in the mullite porous ceramic samples prepared at 1500°C are higher than those prepared at 1450°C. Therefore, from the phase growth trend of the samples, the quantity of the mullite phase is higher when the heat-treatment temperature is 1500°C. This indicates that the combination of various phases is better at this temperature, resulting in the formation of more mullite phases. The internal reaction of the mullite porous ceramic prepared by heat-treatment at 1500°C is basically completed. Specifically, kyanite reacts with α-Al_2O_3 micropowder to form mullite, and zircon decomposes and reacts with α-Al_2O_3 micropowder to form mullite and zirconia. As a phase that can undergo phase transformation at high temperatures to improve and toughen materials, the formation of zirconia in materials is beneficial for improving their thermal shock resistance.

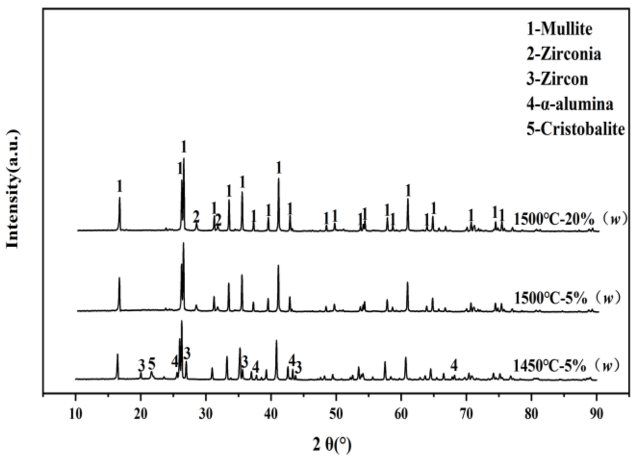

Fig. 2. XRD patterns of mullite porous ceramics prepared with different amounts of sawdust added at different sintering temperatures.

3.2. Effects of heat-treatment temperature and sawdust additions on the permanent linear change rate of sample heating, apparent porosity and bulk density

Figure 3a shows the permanent linear change rate upon heating of the prepared mullite porous ceramics with different sawdust addition amounts at different heat-treatment temperatures. With the increase of the heat-treatment temperature, the permanent linear change rate shows a downward trend. Taking the sawdust addition amount of 5% (*w*) as an example, the permanent linear change rate upon heating of the specimen prepared by heat-treatment at 1450°C is –0.22%, and that of the specimen prepared by heat-treatment at 1500°C is –0.44%. With the increase of the heat-treatment temperature, the diffusion coefficient increases, and the mutual reaction between the raw materials in the mullite porous ceramics proceeds more completely. The shrinkage of the specimen intensifies, resulting in a decrease in the permanent linear change rate upon heating. When the heat-treatment temperature is the same, as the sawdust addition increases, the permanent linear change rate of the samples after heating increases. As the sawdust addition increases from 5% (*w*) to 20% (*w*), the permanent linear change rate of the specimen after heating prepared by heat-treatment at 1450°C increases from –0.22% to –0.01%, and that prepared by heat-treatment at 1500°C increases from –0.44% to –0.19%. This change is caused by two aspects: First, as the sawdust addition increases, the relative content of the solid matrix in the sample decreases. Since the deformation of the sample is mainly borne by the solid matrix, the reduction in the matrix content implies a decrease in deformation. Therefore, under the same temperature, the permanent linear change rate of the sample will increase (with the absolute value decreasing). Second, the pores in the sample can accommodate the shrinkage of the matrix. When the matrix shrinks, the pores, by virtue of their own cavity structures, provide additional space for the shrinking matrix. To a certain extent, the shrinkage of the matrix is alleviated, and from a macroscopic perspective, the samples have a relatively high permanent linear change rate.

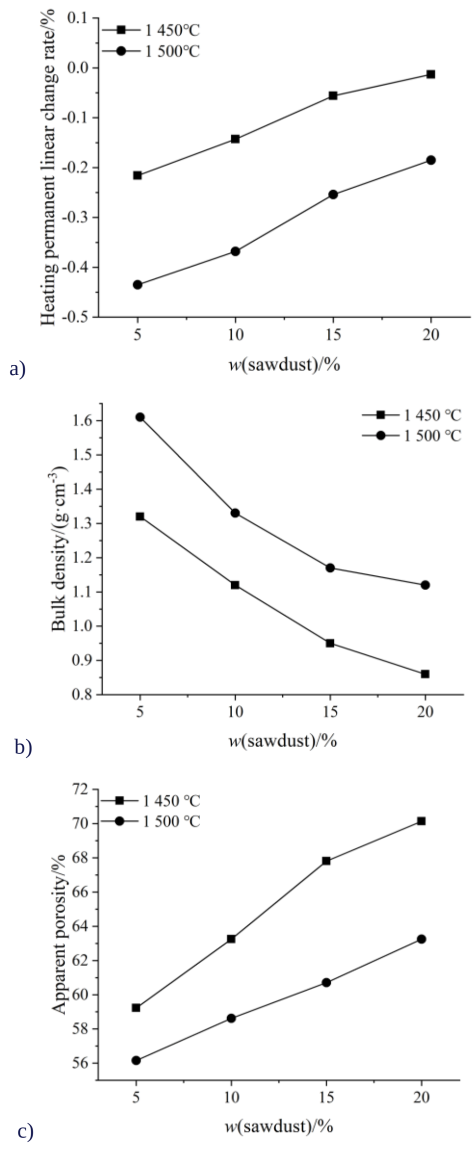

Fig. 3. The physical properties of mullite porous ceramics prepared by sawdust addition at different heat treatment temperatures: a) Heating permanent linear change rate, b) Bulk density change, c) Apparent porosity change.

Figures 3b and 3c show the changes in the bulk density and apparent porosity of the prepared mullite porous ceramic specimens with different sawdust additions at different heat-treatment temperatures. As the heat-treatment temperature increases, the apparent porosity of the prepared mullite porous ceramics decreases, while the bulk density increases. Taking the sawdust addition of 10% (*w*) as an example, the bulk density and apparent porosity of the specimen prepared by heat-treatment at 1450°C are 1.12 g·cm⁻³ and 63.25%, respectively, and those at 1500°C are 1.33 g·cm⁻³ and 58.62%, respectively. As the heat-treatment temperature increases, then the intensification of the mutual reaction between raw materials in mullite porous ceramics leads to a decrease in the permanent linear change rate during heating. This is the main reason for the above-mentioned results. When the heat-treatment temperature is the same, as the sawdust addition increases, the bulk density of the prepared mullite porous ceramics decreases, and the apparent porosity increases. As the sawdust addition increases from 5% (*w*) to 20% (*w*), the bulk density of the specimen prepared by heat-treatment at 1450°C decreases from 1.32 g·cm⁻³ to 0.86 g·cm⁻³, and the apparent porosity increases from 59.23% to 70.14%.The bulk density of the specimen prepared by heat-treatment at 1500°C decreases from 1.61 g·cm⁻³ to 1.12 g·cm⁻³, and the apparent porosity increases from 56.16% to 63.25%.

3.3. Effects of heat-treatment temperature and sawdust addition on the compressive strength at room temperature and thermal conductivity of samples

Figure 4a shows the effects of different heat-treatment temperatures and sawdust additions on the compressive strength of the samples at room temperatures. As shown in Fig. 4a, as the heat-treatment temperature increases, the compressive strength increases. Taking the sawdust addition of 15% (*w*) as an example, the compressive strengths of the specimens prepared by heat-treatment at 1450°C and 1500°C are 7.23 MPa and 7.56 MPa, respectively. As the heat-treatment temperature increases, the density of the mullite porous ceramics increases, and the pores decrease. At the same time, the intensification of the reaction between raw materials leads to high bonding strength. This is the main reason for the above-mentioned results. When the heat-treatment temperature is the same, as the sawdust addition increases, the compressive strength decreases. When the sawdust addition increases from 5% (*w*) to 20% (*w*), the compressive strength of the specimen prepared by heat-treatment at 1450°C decreases from 9.85 MPa to 6.39 MPa; that at 1500°C decreases from 10.65 MPa to 6.75 MPa. The increase in sawdust addition leads to a decrease in the density of the mullite porous ceramics and an increase in the pores after heat-treatment, ultimately resulting in a decrease in the compressive strength of the material.

Figure 4b shows the effects of different heat-treatment temperatures and sawdust additions on the thermal conductivity of the specimens at room temperature. As shown in Fig. 4b, as the heat-treatment temperature increases, the thermal conductivity increases. Taking the sawdust addition of 20% (*w*) as an example, the thermal conductivity of the specimens prepared by heat-treatment at 1450°C and 1500°C is 0.210 W·(m·K)⁻¹ and 0.214 W·(m·K)⁻¹ respectively. As the heat-treatment temperature increases, the density of the mullite porous ceramics increases. Since the heat-transfer efficiency of the solid phase is much higher than that of the gas phase, the decrease in the porosity is the main reason for the increase in the thermal conductivity. When the heat-treatment temperature is the same, as the sawdust addition increases, the thermal conductivity of the prepared mullite porous ceramics decreases. As the sawdust addition increases from 5% (*w*) to 20% (*w*), the thermal conductivity of the specimen prepared by heat-treatment at 1450°C decreases from 0.227 W·(m·K)⁻¹ to 0.210 W·(m·K)⁻¹; that at 1500°C decreases from 0.269 W·(m·K)⁻¹ to 0.214 W·(m·K)⁻¹. The increase in sawdust addition leads to a decrease in the density of the mullite porous ceramics and an increase in the porosity, thereby reducing the heat conducted by the solid phase and ultimately resulting in a decrease in the thermal conductivity of the material.

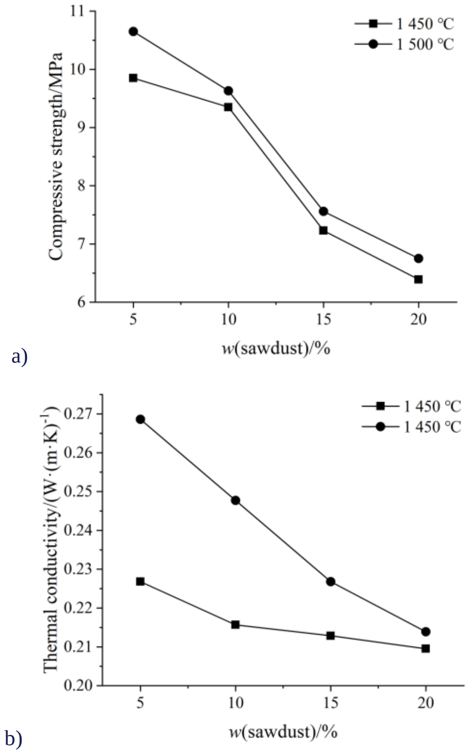

Fig. 4. The influence of sawdust additions on the compressive strength and thermal conductivity of mullite porous ceramics at different sintering temperatures: a) Compressive strength, b) Thermal conductivity.

3.4. Effects of heat treatment temperature and foaming-pore former composite method on the microstructure of samples

Figure 5 shows the scanning electron microscopy (SEM) images of specimens prepared with different sawdust additions after heat treatment at different temperatures. As shown in Figs. 5a–5d, the pores formed by sawdust have irregular shapes, rough contours and certain unevenness on the pore walls. The pores formed by the foaming agent are mostly spherical or approximately spherical. This is because gas tends to form a spherical shape with the minimum surface energy in a homogeneous medium. The pores formed by the combustion of sawdust are relatively large, with pore diameters concentrated around several hundred micrometers. In contrast, the pores generated by the decomposition of the foaming agent are smaller, usually around tens of micrometers. Pore diameters of the samples show a bimodal distribution of large and small pores. Small pores distributed in the gaps of large pores help to increase the number of pores within a limited space, thereby further increasing the porosity and specific surface area of the porous ceramics. As the sawdust addition increases, the average size of pores in the samples increases. This is the main reason for the increase in the porosity and the decrease in the strength of the samples.

Comparing Figs. 5b and 5d, it can be seen that the skeleton of the mullite porous ceramics prepared by heat treatment at 1500°C is denser. At the same time, due to sintering densification, the pores are interconnected. Comparing Figs. 5e and 5f, it can be seen that the skeleton of the mullite porous ceramics prepared by heat treatment at 1500°C is denser, with only a small number of closed pores in the skeleton. The skeleton of the mullite porous ceramics prepared by heat treatment at 1450°C is relatively loose, and most of the pores inside the skeleton are connected pores. This is a factor for the lower strength of the mullite porous ceramics prepared at 1450°C.

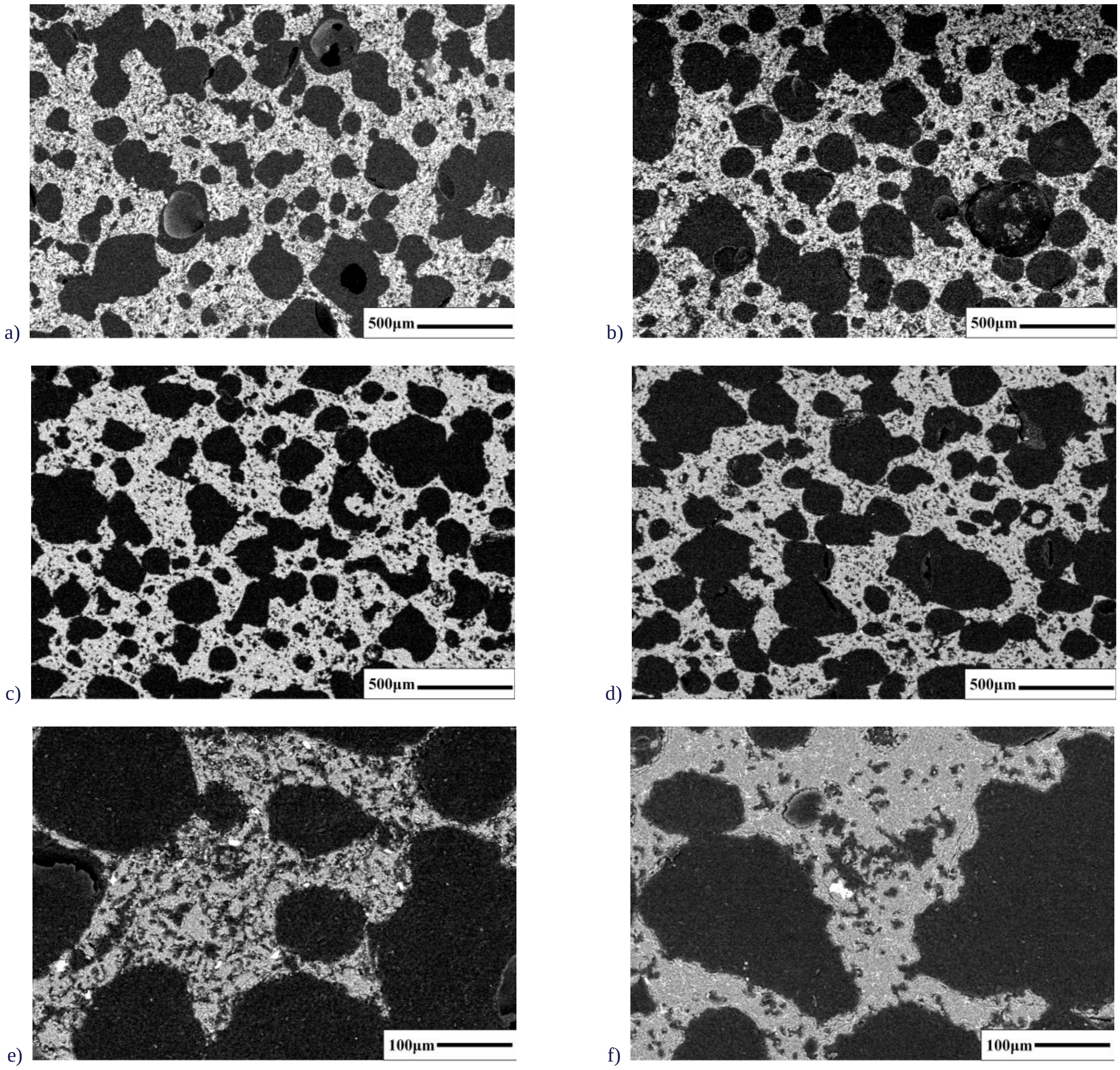

Fig. 5. SEM images of polishing samples prepared by different sawdust additions after heat treatment at different temperatures.
Sawdust: a) 5% (*w*) –1450℃, b) 20% (*w*) – 1450℃, c) 15% (*w*) – 1500℃, d) 20% (*w*) – 1500℃, e) 10% (*w*) – 1450℃, f) 10% (*w*) – 1500℃.

Figure 6 shows the SEM images of the cross-sections of specimens prepared with different sawdust additions after heat treatment at different temperatures. Comparing Figs. 6a and 6c, it can be seen that as the heat-treatment temperature increases, the thickness of pore walls becomes thinner, but more compact. Comparing Figs. 6b and 6d, it can be seen that the microstructure of the mullite porous ceramics prepared by heat treatment at 1450°C is relatively loose. Moreover, the particle morphology is diverse. Combining with the XRD results in Fig. 2, it can be determined that the raw materials have not completely reacted. The microstructure of the mullite porous ceramics prepared by heat treatment at 1500°C is relatively dense, and the difference in particle morphology is low. Combining with the XRD results in Fig. 2, it can be determined that the reaction between raw materials has been completed.

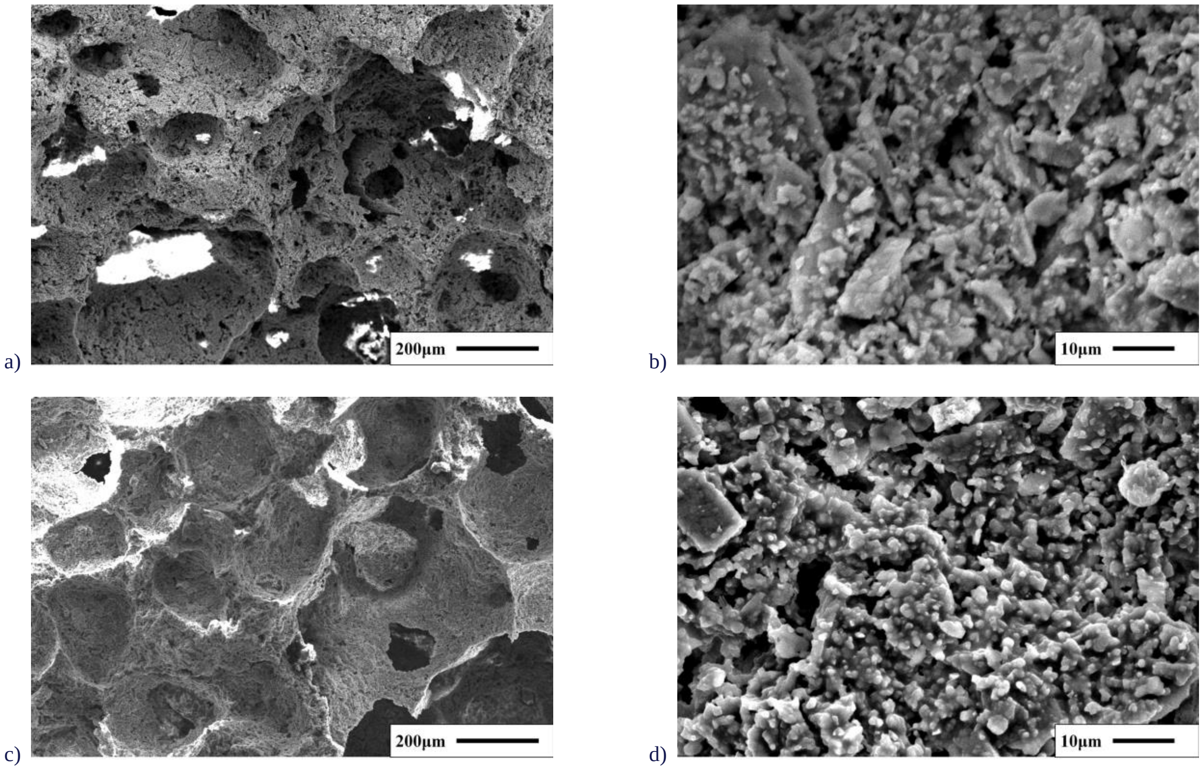

Fig. 6. SEM images of the fracture surface of the samples prepared by different sawdust additions after heat treatment at different temperatures. Sawdust: a) 5% (*w*) – 1450℃, b) 5% (*w*) – 1450℃, c) 5% (*w*) – 1500℃, d) 5% (*w*) – 1500℃.

4. Conclusions

Comprehensively comparing the mullite porous ceramic materials prepared with different sawdust additions and heat-treated at different temperatures, the following conclusions can be drawn:

1) When the sawdust addition was the same, the mullite porous ceramics prepared by heat-treatment at 1500°C have a more compact microstructure. The mutual reaction between the raw materials was more sufficient, with higher bulk density, lower apparent porosity, higher strength and relatively higher thermal conductivity;
2) The compressive strength of the prepared mullite porous ceramic materials was 6.39–10.56 MPa, and the thermal conductivity was 0.210–0.269 $W\cdot(m\cdot K)^{-1}$;
3) When the sawdust addition was 10% (*w*) and the heat-treated temperature was 1500°C, the sample had the best comprehensive performance. At room temperature, its bulk density, apparent porosity, compressive strength and thermal conductivity were 1.33 $g\cdot cm^{-3}$, 58.62%, 9.63 MPa and 0.248 $W\cdot(m\cdot K)^{-1}$, respectively.

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