Preparation of thermal insulation materials based on granite waste using a high-temperature micro-foaming method

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ABSTRACT
In this study, lightweight thermal insulation materials were successfully prepared in this study using a high-temperature micro-foaming method at 1200°C, where granite waste was the main raw material and SiC was the foaming agent. Further, the thermal insulation material’s macrostructure, microstructure, room temperature, and high-temperature performance have been investigated. This material has a small closed-cell porosity of up to 73.8%, high compressive strength of 18.2 MPa, low thermal conductivity of 0.22 W/(m•K) at room temperature and 0.17 W/(m•K) at 350°C, positive reheating linear change, and the refractoriness under load of 812°C, confirming that these materials can be used as good thermal insulation materials up to ~800°C.

1. Introduction
Thermal insulation materials are widely used in aerospace [1], energy [2], chemical industry [3], metallurgy [4], and many other fields owing to their excellent thermal barrier properties. Thermal insulation materials are generally classified into organic and inorganic thermal insulation materials based on their components [5]. Although organic thermal insulation materials have excellent thermal insulation properties, their poor fire resistance and high-temperature resistance limit their applicability. Inorganic lightweight thermal insulation materials with high porosity, high strength, low thermal conductivity, and excellent high-temperature performance have received extensive attention in recent years [6].

In general, inorganic lightweight thermal insulation materials are made from raw materials such as silica, alumina, fire clay [7], calcium silicate, kaolin, perlite, diatomaceous earth, expanded vermiculite, and aggregates [8]; moreover, they are prepared using the pore former method [9], organic foam dipping method [10], sol–gel method [11], freeze-drying method [12], and in situ decomposition methods [13,14]. Recently, the foaming method [15] has been extensively used for preparing porous materials and thermal insulation materials; a foaming agent is used to produce gas under high-temperature conditions, and these gases cannot be volatilized and wrapped in the material. Note that these pores are formed as the temperature drops [16]. Compared to the other methods, the sample prepared via the foaming method has smaller pores, and the ideal pore size can be obtained by changing the additional amount of foaming agent. The commonly used foaming agents include carbon-containing substances [17], aluminum nitride [18], silicon carbide [19], carbonate [20,21], and sulfate [22]. Yio et al. [23] used coal-fired power station furnace bottom ash and soda–lime–silica glass as raw materials and calcium carbonate as a foaming agent to prepare foam ceramics that can be used for thermal insulation and biological filters for water and wastewater treatment. Fuji et al. [24] thoroughly mixed cordierite ceramic powder and organic foaming agent and then used mechanical stirring in a nitrogen-protected atmosphere to fully foam the ceramic slurry. After drying and firing, the cordierite porous ceramics can be used for treating automobile exhaust gas. Li et al. [25] used calcium carbonate as the foaming agent to prepare closed-cell foam ceramics at 700–800°C, and the ceramic exhibited a high total porosity of 82%, high closed porosity of 78%, low density of 0.48 g/cm³, and compressive strength of 2 MPa. A lightweight ceramic tile with a porosity of 35% and an apparent density reduction of 26% was prepared by Garcia-Ten et al. [26]; they used kaolin, quartz, and albite as raw materials with SiC as the foaming agent. Jiang et al. [27] prepared porous ceramics using granite as a raw material and SiC as a foaming agent; the porosity of the ceramic material was as high as 83.31%; however, the compressive strength of the material is relatively small (~0.85 MPa). Although the abovementioned research yielded good results, the prepared ceramic materials cannot be used as closed-cell refractory aggregates because of their high open porosity, low sintering temperature, or low strength, thus resulting in low refractoriness and poor high-temperature performance.
The high-temperature micro-foaming method was used in our study to prepare lightweight thermal insulation materials, with granite waste as the main raw material and SiC as the foaming agent for generating CO₂. The melting temperature of raw materials matched the oxidation temperature of SiC by adding clay and feldspar, resulting in high porosity as well as uniform and small pores. The prepared thermal insulation materials not only have good room-temperature and high-temperature performances but also allow waste reuse.

2. Experimental

2.1. Materials

The primary raw materials for the experiment include granite waste, feldspar, and clay as well as silicon carbide powder as a foaming agent. Table 1 shows the chemical compositions of these raw materials as determined via X-ray fluorescence. Figure 1 shows the X-ray diffraction patterns for granite waste, feldspar, and clay. The primary phases of granite waste are clearly quartz, albite, and microcline; the primary phases of feldspar are albite and microcline and the characteristic peaks of kaolin in clay are visible, followed by pyrophyllite.

2.2. Design and preparation

Granite waste, feldspar, and clay were sieved to <75 μm and silicon carbide (foaming agent) was sieved to 13 μm [28]. For mixing, an experimental ratio of 85-wt% granite waste, 10-wt% of feldspar, 5-wt% clay, and 0.8-wt% SiC was used. After drying and sieving, the raw materials are granulated into particles with particle sizes of 0.2–0.8 mm, and 80 g of the mixed powders were placed in a corundum crucible of 7 cm × 7 cm × 4 cm. After flattening the surface, they were placed in a muffle furnace and fired in an air atmosphere. The temperature was increased from room temperature to 1000°C at a rate of 5°C/min, to 1200°C at a rate of 3°C/min for 30 min, and then naturally cooled to room temperature. After the samples drill and sand mill, cylinder samples with a diameter of 50 mm and height of 20 mm were obtained for subsequent performance testing; the process is depicted in Figure 2.

2.3. Testing and characterization

A pressure testing machine was used to determine the compressive strength of the samples at room temperature. The samples were pressurized at a rate of 10 mm/min until they cracked, and the instantaneous maximum load was measured. At room temperature, the compressive strength of the sample can be calculated using Equation (1):

\[ \sigma = \frac{F_{\text{max}}}{S} \]  

(1)

where \( \sigma \) is the compressive strength at room temperature (MPa); \( S \) is the cross-sectional area of the sample (mm²); and \( F_{\text{max}} \) is the instantaneous maximum load (N).

The linear change rate on reheating was measured by heating the samples to 1000°C in a muffle furnace and holding it for 4 h after cooling. The linear change rate on reheating of the samples can be calculated using Equation (2):

\[ Lc = \left( \frac{L_1}{L_0} \right) \]  

(2)

Table 1. Chemical compositions of granite waste, feldspar and clay (wt%).

|                | SiO₂ | Al₂O₃ | Fe₂O₃ | K₂O | CaO | Na₂O | Loss |
|----------------|------|-------|-------|-----|-----|------|------|
| Granite waste  | 67.31| 17.02 | 3.63  | 2.97| --  | 4.85 | 0.28 |
| Feldspar       | 65.04| 18.52 | 0.2   | 12.35| 0.1 | 3.24 | 0.28 |
| Clay           | 45.82| 35.93 | 2.85  | 0.97| 0.68| 0.37 | 9.35 |

![Figure 1](image.png)  

Figure 1. XRD patterns of granite waste, clay, and feldspar.
where $L_c$ is the linear change rate on reheating, $L_1$ is the length (mm) of the samples after heating, and $L_0$ is the length (mm) of the samples before heating, mm.

Thermogravimetry and differential thermal analysis (TG-DTA) of the raw materials used a thermal analyzer (NETZSCH STA 449F3 Jupiter), and the temperature was raised from room temperature to 1200°C at 10°C/min in an air atmosphere. The refractoriness under load (RUL) was investigated on cylindrical samples according to the standard YB/T370-1995. The load was set in order to achieve a compressive stress of 0.05 MPa. The furnace was heated up at a rate of 5 K/min, and the temperature was recorded when the sample was compressed by 0.6% of the original height from the maximum degree of expansion, $T_{0.6}$. Apparent density and water absorption were measured using the Archimedes method. True density and apparent density were used to calculate porosity, and true density was tested and calculated using the pycnometer method. The sample’s thermal conductivity was tested using a thermal conductivity meter (Hot Disk TPS 2500S). The macrostructure was observed using a digital camera and morphology observation of the sample was taken on a scanning electron microscope, SEM (ZEISS EVO HD15). The phase composition was analyzed by X-ray diffractometer system (Philips X’Pert-Pro), the tube voltage was 40 kV, working current was 30 mA, scanning speed was 0.33°·s⁻¹, step length was 0.013°, and scanning range was 10–80°.

3. Results and discussion

3.1. Macro- and Micro-Structure of the Thermal Insulation Materials

Figure 3 shows a macroview of the thermal insulation materials. The prepared insulation materials were composed of continuous solid and gas phases, had high porosity, and the pores were small and uniform, as shown in Figure 3. Pore walls existed between the pores, and the entire sample was divided into countless small units, each of which was independent of others while existing as a unified whole. The SEM images of the thermal insulation materials are shown in Figure 4. From the images, the pore walls of the three large pores form regular “Y”s that can be seen clearly (Figure 4b). These “Y”s form the skeleton of the sample, which is of great importance for alleviating the external pressure. However, the pore walls between the holes were scattered with many uneven and isolated small pores (Figure 4c). On the one hand, these small pores can destroy the uniformity of pore walls, making the pore walls thinner and negatively affecting the strength; on the other hand, these holes can have a positive effect and can reduce the thermal conductivity of the material. Moreover, the inner wall of some pores was very smooth; however, some of them had through holes (Figure 4d), which could increase the water absorption rate of thermal insulation materials.

The prepared lightweight thermal insulation materials had a good structure, high porosity, and small pore size because of the high matching between the melting temperature of the raw material and the oxidation reaction temperature of SiC. Figure 5(a) shows the TG-DTA curve of granite waste. This figure indicated that the weight loss rate of granite waste is only 0.78% until heated to 1200°C; the heat release at 595.7°C can be attributed to the phase change of...
plagioclase. The granite waste started to melt at ~1100°C; Figure 5(b) shows the TG-DTA curve of SiC. At ~800°C the quality of SiC started to significantly increase, indicating that it was oxidized. As the temperature increased, the oxidation rate gradually decreased. When the temperature was >1150°C, the oxidation rate increased rapidly, accompanied by an increase in quality. SiC can be effectively oxidized at a temperature of >1150°C. Furthermore, feldspar and clay were present in raw materials and they decreased
3.2. Room-temperature Thermal insulation

The porosity, for that reason, finally, the melting temperature of the mixture. Finally, the melting temperature of the raw materials was closely related to the oxidation temperature of SiC. After the raw material was melted, SiC started to oxidize, producing bubbles and getting wrapped in the melt, and finally, by adjusting the sintering temperature and holding time to prevent further bubble merger and growth. After cooling, uniform and tiny closed pores that are formed in situ.

3.2. Room-temperature Performance of the Thermal Insulation Materials

For a lightweight thermal insulation material, high porosity, high mechanical strength, low apparent density, and low thermal conductivity are important. The room-temperature performance of the thermal insulation materials was tested and has been listed in Table 2. As can be observed in the table, thermal insulation materials with an apparent density of 0.6 g/cm³, compressive strength of 18.11 MPa, closed porosity of 73.8%, water absorption of 0.36%, and the thermal conductivity at room temperature of 0.22 W/(m·K) were obtained. The gas phase is an important component of thermal insulation materials; the number, size, shape, and connectivity of pores have a significant impact on the apparent density, compressive strength, thermal conductivity and other properties [29]. The thermal conductivity of the material decreases almost linearly as the porosity increases; when the porosity reaches a certain value, the rate of decrease slowly and eventually stabilizes. However, with an increase in porosity, the material’s strength decreases [30]. Therefore, while ensuring porosity, the effect on the strength should be considered and the best value of the two should be selected. Ceramic foams used commercially available α-Si₃N₄ as a raw material and short-chain surfactant n-propyl gallate as a foaming agent, which was prepared by Du et al. [31]. The porosity of the sample was as high as 90.8–96.4%; however, the compressive strength was only 0.37–5.53 MPa. Huo et al. [32] used a particle-stabilized direct foaming method to prepare highly porous zirconia ceramics with porosity as high as 98.1% and thermal conductivity as low as 0.027 ± 0.004 W/(m·K); however, the strength of the product was only 0.26 ± 0.05 MPa. Compared to previous studies, high-strength, high-porosity, and low thermal conductivity insulation materials provide the possibility for a wider range of applications.

3.3. High-temperature Performance of the Thermal Insulation Materials

3.3.1. Linear change on reheating

For thermal insulation materials, slight volume expansion can resist thermal stress caused by high temperatures and prolong the service life of the material [33]. By calculation, the linear change rate after reheating was ~0.7%. The operating temperature should be set at ~1000°C to ensure that the thermal insulation materials have little deformation and have a long service life under high temperatures. Figure 6 shows that the phase composition of the sample after 4 h of reheating at 1000°C is basically the same as that of the sample after 0 h of reheating with the primary phases being a-quartz, hematite, Al₉Fe₃Si₉O₂₇, and anorthite sodian.

Table 2. Room-temperature performance of the thermal insulation materials.

| Item          | Closed porosity | Average pore size | Apparent density | Water absorption | Compressive strength | Thermal conductivity at room temperature |
|---------------|------------------|-------------------|------------------|------------------|----------------------|------------------------------------------|
| Value         | 73.8%            | 0.68 mm           | 600 kg/m³        | 0.36%            | 18.11 MPa            | 0.22 W/(m·K)                             |

Figure 6. XRD patterns of the samples reheating for 0 h and reheating for 4 h.
3.3.2. Thermal conductivity of 350°C
The material’s high-temperature thermal conductivity shows its thermal insulation performance at a high temperature. The thermal conductivity of the thermal insulation material tested at 350°C was 0.17 W/(m·K). Moreover, the value was lower than the thermal conductivity at room temperature. This phenomenon of decreased thermal conductivity may be attributed to phonons in the solid phase [34,35], which causes the phonon collisions to generate thermal resistance [36].

3.3.3. Refractoriness under load
The RUL level shows the strength of the material’s ability to withstand high temperatures under load and to identify the maximum working temperature of the material [37]. In addition to the viscosity of liquid phase within the sample, the factors that affect the refractoriness of the sample under load are related to the pores inside the sample [38]. RUL (T₀.₆) of the thermal insulation material was determined by the test to be 812°C. This is attributed to the sample’s high porosity, which reduces the effective force-receiving area when stressed and increases the pressure per unit area of the sample, thus resulting in a lower RUL.

4. Conclusion
In this study, lightweight thermal insulation materials with high closed-cell porosity and excellent performance were prepared using a high-temperature micro-foaming method using granite waste, clay, and feldspar as raw materials and SiC as the foaming agent. The closed porosity of thermal insulation materials was as high as 73.8% and had a high compressive strength of 18.2 MPa as well as low thermal conductivity of 0.22 W/(m·K) at room temperature and 0.17 W/(m·K) at 350°C; the linear rate of change after reheating at 1000°C for 4 h was 0.7% and the RUL was 812°C. Compared with other research on thermal insulation materials under the guarantee of low thermal conductivity, the thermal insulation materials prepared in this study also had higher compressive strength and better high-temperature performance; hence, these materials have a wider range of applications; however, because the firing temperature was 1200°C and the RUL was 812°C, these materials are destined to be used only up to ~800°C. To improve the application of thermal insulation materials at higher temperatures, in-depth research will be conducted by examining the various compositions of raw materials and ratios in future.

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