Fabrication of porous filter material for the integrated gasification combined cycle

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Abstract. The porous ceramic filter material is the most effective filter materials in the integrated gasification combined cycle. The porous silicon nitride due to its higher mechanical strength, as well as good corrosion resistance, is considered as a promising material in the integrated gasification combined cycle. In this paper, porous silicon nitride ceramics with high porosity and uniform pore structure was prepared by carbothermal reduction reaction between low-cost diatomite and carbon black. The influence of the type of sintering additives and the size of diatomite particles was investigated. Microstructures and mechanical properties of porous silicon nitride ceramics were studied by XRD, SEM and three-point bending measurement. XRD analysis showed that $\beta$-Si$_3$N$_4$ phase, $\alpha$-Si$_3$N$_4$ phase, Sialon phase Si$_5$AlON$_7$ and glass phase Y$_2$Si$_3$O$_3$N$_4$ were detected. SEM analysis showed that porous silicon nitride ceramics was composed of rod-like $\beta$-Si$_3$N$_4$ grains and uniform pores.

1. Introduction

The integrated gasification combined cycle device not only has much higher thermal efficiency than the conventional coal-fired cycle device, but also meets the requirements of environmental protection to the greatest extent. The technology of coal dust filtration at high temperature is one of the key technologies in advanced coal-fired combined cycle gas purification technology. The porous ceramic filtration material is considered to be one of the most promising method in high temperature dust-removing field, and is widely used in advanced coal-fired combined cycle. The porous ceramic filtration material can remove more than 99% of the solid particles in the high-temperature gas to obtain a purified gas with the dust concentration for less than 5mg / Nm$^3$ [1]. This purified gas can meet the safety operation requirements of the gas turbine, and it is fully compliant with the environmental protection standards after working in the gas turbine and discharging to the atmosphere. Therefore, the study on the process of coal-fired combined cycle gas purification with porous ceramic filtration material has attracted extensive attention. Compared with traditional alumina, cordierite, quartz glass and other inorganic materials, porous silicon nitride have absolute advantages in high temperature dust-removing applications [2].

Diatomite is light fine-porous rocks consisting mainly of extremely small opaline skeletons (or their fragments) of diatomic algae diatoms. Their characteristic features are the presence of amorphous active SiO$_2$ on the one hand and a fine-porous structure, lightness and low thermal conductivity on the other hand. The appearance of diatomite particles is shown in figure. 1. There were very large reserves of diatomite in the worldwide, so the production cost of diatomite was very low. This paper report on the fabrication of porous silicon nitride used as the porous ceramic filter material by the carbothermal reduction of diatomite under a nitrogen atmosphere: (3SiO$_2$+6C+2N$_2$$\rightarrow$Si$_3$N$_4$+6CO) [3]. Instead of
SiO₂, diatomite was used as silicon source, which reduced the production cost of porous silicon nitride greatly. The diatomite was very cheaper and easily attainable than SiO₂. The effects of the type of sintering additives and the size of diatomite particles on the microstructure and mechanical properties of porous silicon nitride were investigated.

![Figure 1. Microstructures of diatomite particle](image)

### 2. Experimental Procedure

Diatomite (36µm, 10µm, 1.2 µm) and the rare earth oxide (Re₂O₃ (Re=La, Y, Lu)) were used as the silicon source and sintering additives. Carbon black powder (80nm) and α-Si₃N₄ powder (0.5µm) were used as the carbon source and seeds respectively. The compositions of the starting powder mixture contain a stoichiometric ratio of C and diatomite (2:1 molar ratio), corresponding to different content of Y₂O₃, Lu₂O₃, Y₂O₃ (1wt%) and α-Si₃N₄ seeds (5wt%). The mixed powders were uniaxially pressed to form rectangular bars measuring 46mm×5mm×5mm. The green bodies were sintered at 1750°C for 2 h. The sample compositions are shown in table 1.

**Table 1. The composition of the samples powder**

| Sample | Composition |
|--------|-------------|
| Y-1%-36 | 67.2 wt% diatomite (36 µm) + 26.8 wt% C+1wt% Y₂O₃+5wt% α-Si₃N₄ seeds |
| Lu-1%-36 | 67.2 wt% diatomite (36 µm) + 26.8 wt% C+1wt% Lu₂O₃+5wt% α-Si₃N₄ seeds |
| La-1%-36 | 67.2 wt% diatomite (36 µm) + 26.8 wt% C+1wt% La₂O₃+5wt% α-Si₃N₄ seeds |
| Y-1%-10 | 67.2 wt% diatomite (10 µm) + 26.8 wt% C+1wt% Y₂O₃+5wt% α-Si₃N₄ seeds |
| Y-1%-1.2 | 67.2 wt% diatomite (1.2 µm) + 26.8 wt% + 1wt% Y₂O₃+5wt% α-Si₃N₄ seeds |

The bulk density of the sintered products was measured by the Archimedes displacement method. Crystalline phases were identified by X-ray Diffraction (XRD) analysis. The microstructure was characterized by Scanning Electron Microscope (SEM). The three-point bending strength was measured by an instrument.

### 3. Results and discussions

Variations in the weight loss, linear shrinkage, porosity, flexural strength with different the type of sintering additives and the size of diatomite particles are shown in table 2. Because the decomposition of organic impurities in diatomite during the sintering process, the actual weight loss were higher than the calculated theoretical weight loss. Because the liquid phase which formed by La₂O₃ has a lower eutectic temperature and viscosity, which facilitated the particle rearrangement and densification, resulting in the higher linear shrinkage and the lower porosity of La-1%-36. So, the linear shrinkage of La-1%-36 is higher than the linear shrinkage of Y-1%-36 and Lu-1%-36. Due to the higher porosity of the samples, the effect of the sintering additives on the linear shrinkage and porosity is very obvious for the carbothermal reduction reaction,
For the samples with different sintering additives, because the amount of sintering additives is relatively small, so it has no effect on the green density of the samples. Under a certain forming pressure, the green density of the samples with different sintering additives was the same basically. For the samples with different the size of diatomite particles, as the size of diatomite particles decreased, the surface energy increased and the green density decreased. The green density of the samples with different diatomite particle size is shown in table 3. As the size of diatomite particles decreased, the surface area and the surface energy increased, resulting in sintering driving force and linear shrinkage increased. There is no significant difference in the weight loss, the porosity of porous silicon nitride is determined by the combined effects of the green density and the linear shrinkage. Although, as the size of diatomite particles decreased, the green density decreased, but the linear shrinkage showed a more significant effect on the porosity, so the porosity of the samples gradually decreased.

| Samples  | Weight loss / % | Linear shrinkage / % | Porosity / % | Flexural strength/MPa |
|----------|-----------------|----------------------|--------------|----------------------|
| Y-1%-36  | 52              | 10.2                 | 75.2         | 11.2                 |
| Lu-1%-36 | 51              | 5.5                  | 78.6         | 10.8                 |
| La-1%-36 | 47              | 14.2                 | 65.7         | 15.5                 |
| Y-1%-10  | 46              | 16.1                 | 68.6         | 15.2                 |
| Y-1%-1.2 | 47              | 19.2                 | 63.1         | 19.7                 |

Table 3. Green density of the samples

| Samples   | Y-1%-36 | Y-1%-10 | Y-1%-1.2 |
|-----------|---------|---------|----------|
| Green density (g/cm³) | 1.23 | 1.15 | 0.89 |

The β-Si₃N₄ phase, minor of α-Si₃N₄ phase and different grain boundary phase were detected by XRD analysis as shown in figure. 2. It showed that the phase compositions were the same for the samples with different the size of diatomite particles. The grain boundary phase was identified as crystalline Y₂Si₃O₄N₄ which was apparently formed by the reaction between Y₂O₃, SiO₂ and α-Si₃N₄. Sialon phase Si₃AlON₇ which was apparently formed by the reaction between Al₂O₃ and α-Si₃N₄. For the sample of La-1%-36 and Lu-1%-36, the explanation is that grain boundary phase was in such small quantities that it could not be detected by XRD analysis.

Figure 3 give SEM images of fracture surfaces of the sintered samples with different sintering additives and the size of diatomite particles. As the size of diatomite particles decreased, the grain size of α-Si₃N₄ decreased. Because the size of diatomite particles decreased, the specific surface areas and activity of the diatomite particles increased, the direct contact areas between the diatomite and carbon black particles increased, which promotes the carbothermal reduction reaction, resulting in a uniform and fine microstructure. The pores between the grains become finer and uniform, and the samples become dense. Compared with Y-1%-36 and Lu-1%-36, the abnormally grown equiaxed α-Si₃N₄ grains of La-1%-36 is serious, and it is unfavorable to the mechanical properties of porous silicon nitride ceramics. It was obvious that Lu-1%-36 showed a typical microstructure composed of fine elongated β-Si₃N₄ grains with a high aspect ratio and a uniform pore structure. The rod-like β-Si₃N₄ grains are overlapped to form a three-dimensional interlocking network structure with a uniform pore structure, so the porous silicon nitride has excellent mechanical properties[4, 5]. As the ionic radius of
the rare earth element Me$^{3+}$ increased, the rod-like morphology changes from a high aspect ratio to a low aspect ratio. So with an increase in the ionic radius of the rare earth element Me$^{3+}$, the densification degree increased, the aspect ratio of rod-like $\beta$-Si$_3$N$_4$ grains became lower, the pores became less. The equiaxed $\alpha$-Si$_3$N$_4$ grains were converted into the rod-like $\beta$-Si$_3$N$_4$ grains with the higher aspect ratio by dissolution-diffusion-precipitation [6]. The growth of rod-like $\beta$-Si$_3$N$_4$ grains was mainly controlled by diffusion and interface reaction. According to the Einstein formula:

$$\eta = \frac{kT}{nD}$$  \hspace{1cm} (1)

where $\eta$ is liquid viscosity, K is proportional constant, D is diffusion constant and $\alpha$ is diffusion activity. It can be seen from equation (1) that the liquid viscosity and the diffusion constant are inversely proportional. If the liquid viscosity is higher, and the diffusion constant is much lower than the interface reaction constant, the growth of rod-like $\beta$-Si$_3$N$_4$ grains is mainly controlled by diffusion. If the liquid viscosity is lower, the diffusion constant is much higher than the interface reaction constant, the growth of rod-shaped crystals is mainly controlled by the interface reaction. The growth of rod-like $\beta$-Si$_3$N$_4$ grains controlled by the interface reaction is conducive to grow along the [210] crystal orientation of the (001) crystal plane, and the growth of rod-like $\beta$-Si$_3$N$_4$ grains controlled by diffusion is conducive to grow along the [001] crystal orientation of the (100) crystal plane. The growth of rod-like $\beta$-Si$_3$N$_4$ grains is considered to be caused by the anisotropic growth of hexagonal silicon nitride grains that maximize the area of the (100) crystal plane. When the liquid viscosity is higher, the diffusion control is beneficial to the growth of rod-like $\beta$-Si$_3$N$_4$ grains. As the ionic radius of the rare earth element decreased (La$^{3+}$ 108.1 Pm, Y$^{3+}$ 88 Pm, Lu$^{3+}$ 84.8 Pm), the melting point of the rare earth oxide increased, the liquid viscosity increased, and the aspect ratio of the rod-like $\beta$-Si$_3$N$_4$ grains gradually increased.

Figure 2. XRD patterns of the samples (1) Y-1%-36 (2) Y-1%-10 (3) Y-1%-1.2

(a) (b)
Because the rare earth oxide $\text{La}_2\text{O}_3$ has the lowest melting point and is the easiest to form a liquid phase with good fluidity and promote densification. So compared with Y-1%-36 and Lu-1%-36, La-1%-36 has the lowest porosity and the highest flexural strength. The sample Lu-1%-36 has higher porosity and is mainly composed of the higher aspect ratio of the rod-like $\beta$-$\text{Si}_3\text{N}_4$ grains, so it has good synergy between mechanical properties and porosity. As the size of diatomite particles decreased, the particle rearrangement and densification of the porous silicon nitride ceramics increased, the porosity decreased and the flexural strength increased accordingly.

4. Summary

Porous silicon nitride ceramics which used as the porous ceramic filter material with higher porosity and excellent mechanical properties were fabricated by the carbothermal reduction reaction between diatomite and carbon, and has a good application prospect in the field of integrated gasification combined cycle. With a decrease in size of diatomite particles, the porosity decreased, and the flexural strength increased accordingly. The sample La-1%-36 has the lowest melting point, forms a low-viscosity liquid at higher temperature, which is beneficial to densification. The sample Lu-1%-36 with higher melting point is beneficial to obtain the higher aspect ratio of the rod-like $\beta$-$\text{Si}_3\text{N}_4$ grains.

5. References

[1] Rahele M, Marti D, Robin A 2019 *Ceram. Int* **45** 986-997.
[2] Nura Y, Osman 2010 *Adv. Powder. Technol* **24** 697-702.
[3] Lu Y, Yang J F, Lu W Z 2010 *Mater. Manuf. Process* **25** 998-1000.
[4] Liu N, Zhang J 2019 *J. Eur. Ceram* **44** 1927-1933.
[5] Matsunaga C, Zhou Y, Kusano D 2020 *J. CERAM. SOC JPN* **128** 75-79.
[6] Anil K, Aditya G, Sudarsan G 2019 *Mat. Sci. Eng* **750** 132-140.