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Fabrication and characterization of lightweight foam ceramics from rare earth tailings

Zhuohao Xiao[1, 2*], Xiuying Li[1], Xiaofeng Dong[1], Wenyan Luo[1], Ling Bing Kong[1, 2*]

[1] School of Materials Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333001, China

[2] School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue 639798, Singapore

*corresponding author e-mail address: ***xiaozhuohao@126.com, elbkong@ntu.edu.sg***

ABSTRACT

Utilization of waste resources is currently a hot research topic in materials science and engineering. In this work, by using tailings of ion-absorption rare earth as the main raw material, supplemented by potassium feldspar, black soil, lithium porcelain stone and talc, together with silicon carbide abrasive waste as foaming agent, lightweight foam ceramics were prepared through high temperature foaming. The effects of sintering temperature on the structure and properties of the foam ceramics were elaborated. It is found that the maximum amount of the rare earth tailings can reach 60 wt.% and the sintering temperatures can be optimized in the range of 1160 ~ 1180 °C. Both density and thermal conductivity of the foam ceramics are reduced with increasing sintering temperature. The main crystal phase in the foam ceramics is quartz, whose content is decreased rapidly with increasing sintering temperature. Specifically, the sample sintered at 1180 °C for 10 min has a bulk density of 0.37 g/cm^3, thermal conductivity of 0.021 W/m·K and compressive strength of 11.2 MPa.

Keywords: *Foam ceramic; Rare earth tailing; Thermal conductivity; Porous ceramic*.

1. INTRODUCTION

Rare earth resources in China was very abundant, accounting for about 75 % of the world's reserves in 1970 [1]. However, due to the uncontrolled exploitation, the reserve ratio of rare earth in China drops to 23 % of the world's reserves in 2011 [1, 2]. The arbitrary mining of rare earth leads to the formation of immeasurable tailings in mountains and plains, resulting in serious environmental pollution and ecological problems in the mining areas, which has become a critical bottleneck restricting the sustainable development of local economics and society [3]. One of the ideal ways to solve the pollution issue of rare earth tailings is to convert it into useful industrial raw materials [4].

Foam ceramics is generally serviced in thermal insulation fields, especially widely used as an energy-saving building exterior insulation material, duo to their low bulk density, low thermal conductively and incombustibility [5,6]. Clay is traditionally used as the main raw materials to develop foam ceramics, which not only consumed large amount of high-quality resources but also led to high cost products.

In the present work, with rare earth tailings as the main raw material, highly porous foam ceramics were successfully prepared by using the high temperature foaming method. We believe that the conversion of large scale rare earth tailings to foam ceramics will an effective way to significantly mitigate their pollution issue. At the same time, the cost of foam ceramics can be drastically reduced by using rare earth tailings as the raw materials.

2. EXPERIMENTAL

2.1. Raw Materials. Ion-absorption rare earth tailing (120 mesh, Ganzhou, China) was used as the main raw material to develop the foam ceramics. Chemical compositions of the tailings are listed in Table 1. It can be seen that the total content of silica and alumina is more than 85 wt. % in the tailings. In order to prepare foam ceramics, a sufficient high temperature is required to make the raw materials to be fluidic, so that some low temperature fluxes are also required. In this study, potassium feldspar, black soil, lithium porcelain stone and talc were used as the fluxing agent. To further decrease the cost of the raw materials, silicon carbide abrasive waste was employed as the foaming agent. The detail raw materials ratios for the foam ceramics are listed in Table 2.

2.2 Sample Preparation. The raw materials listed in Table 2 were thoroughly mixed with appropriate amount of water and milled for 1 h with a planetary ball mill. The ratio of the raw materials, ball and water is 1:2:1. The obtained slurry was sieved through 200-mesh sieve and dried at 150 °C. An arboxymethyl cellulose (CMC) solution with concentration of 6.0 wt.% was used as binder, whose content was about 0.5 wt.%.

The green bodies were pressed into disks, with a dimension of Φ120 mm × 20 mm, at a pressure of 10 MPa. Then, the green bodies were treated at 300 °C for 1 h to remove the residue water and CMC, so as to prevent the samples from cracking caused by the rapid evaporation of moisture. The samples were further sintered at 1100-1200 °C in air for 10 min.

Table 1. Chemical composition of the Rare earth tailings (wt. %).

Composition	**SiO_2**	**Ai_2O_3**	**K_2O**	**Na_2O**	**MgO**	**SO_3**	**CaO**
Content	65.96	19.99	2.55	0.81	0.21	0.04	0.1
Composition	TiO_2	Cr_2O_3	MnO	Fe_2O_3	NiO	ZrO_2	Loss
Content	0.7	0.05	0.09	0.94	0.05	0.1	8.41

2.3. Characterization. The foam ceramic samples were grinded into powders (200 mesh) for phase composition characterization by using a D/Max-2500 diffractormeter with nickel-filtered Cu/Kα radiation at a tube voltage of 40 kV. The scan range was over 10° - 70° with a step size of 0.02°. To take sectional images, the samples were cut and polished to reveal their inner porous structure. Thermal conductivity of the samples was measured by using the flat heat conduction method, with sample size to be Φ110 × 10 mm. Each sample was tested for three times, while the average value was used. Compression property was tested to examine mechanical strength of the samples, with a dimension of 30×30×10 mm3. In order to apply the load uniformly, rubber pads were attached on the tested surfaces of the foam ceramic samples. Four samples were measured for each group to obtain the average value. The water absorption was calculated by the waterlogged method, in which the samples masses before and after saturation with water were weighed. Bulk density of the sintered foam ceramics was measured by using the Archimedes' method with a DA-600M model density meter.

Table 2. Raw materials ratios of the foam ceramic (wt. %)

Raw materials	Rare earth tailings	Potash feldspar	Talcum powder	Black soil	Lithium porcelain stone	Foaming agent
Content /wt.%	60.00	15.00	12.00	8.00	4.00	1.00

3. RESULTS & DISCUSSION

3.1. Porous Structure Evolution with Sintering Temperature. It is well known that the performance of a material is dependent on its structures. For foam ceramics, the properties are mainly characterized in terms of their porous structures, including pore size, size distribution and connection characteristics. Figure 1 shows photographs of the foam ceramics sintered at different temperatures, illustrating the porous structure evolution as a function of sintering temperature. The pores have an average size of about only 1 mm, with an average distance between every two adjacent pores to be about 2 mm, as the sintering temperature is 1140 °C. This means that the wall thickness of the pores is also about 1 mm. All the pores are independent one another in the matrix and virtually no open or through holes are present (Figure 1 A). When the sintering temperature was increased to 1160 °C, the size of the pores was significantly increased to 1 - 4 mm, while the thickness of the walls was reduced to about 0.2 mm. Meanwhile, some of the pores were merged to form larger ones. Also, the sample had a rather wide pore size distribution. However, most of the pores are still about 1 mm (Figure 1 B). As the sintering temperature was further increased 1180 °C, the pore size distribution of pores was slightly narrowed. Although some large pores were still observed, the number of small pores was significantly reduced (Figure 1 C). After sintering at 1200 °C, an obviously different pore structure can be observed, as shown in Figure 1 D. A large number of pores were fused and merged together. As a result, the size of the pores was increased evidently. Furthermore, the thickness of pore walls was obviously increased.

According to the pore structure evolution of the samples, it can be deduced that sintering temperature is the key factor to affect the size and distribution of the pores in the matrix. In order to promote the generation of pores, two requirements must be satisfied at the same time. Firstly, the sintering temperature should be appropriate to ensure that the matrix is softened but not flowing. In other words, an easily deformable matrix is favorable to form pores.

However, an excessive high sintering temperature would cause the matrix to flow or melt, so that the pore size is not stable. Secondly, an appropriate amount of foaming agent is also important to control the porous structures. The foaming agent produces a large amount of gas at an optimal temperature, which is remained in the matrix so as to form pores. If the sintering temperature is increased in an unreasonable manner, the gas in the pores will expand rapidly and thus the pores will merge together. Therefore, our present results indicate that the optimal sintering temperatures of the foam ceramics should be in the range of 1160-1180 °C.

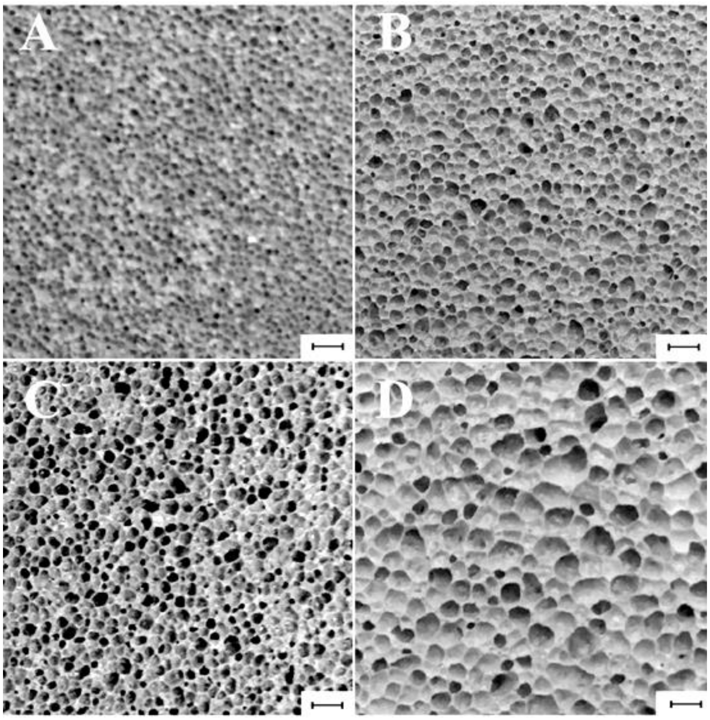

Figure 1. Optical photographs of the foam ceramic samples sintered at different temperatures for 10 min: (A) 1140°C, (B) 1160 °C, (C) 1180°C and (D) 1200°C. The scale bars are all 5 mm.

3.2. Phase Composition. It is generally acknowledged that ceramics mainly consist of crystalline phase, glassy phase and pores. The coexistence of glassy phase and pores is the key to develop the porous structure of foam ceramics. At the same time, the crystalline phase is also an important factor to affect the physical properties and performances of foam ceramics. For a given composition, crystalline phase usually has better physical properties than the glassy phase, duo to the close packing of atoms in crystals [7, 8]. Therefore, an appropriate volumetric content of crystals is necessary to maintain the performances of foam ceramics at a desired level. Figure 2 shows XRD patterns of the samples sintered at different temperatures. The presence of diffraction peaks indicates that there are crystalline phases in the samples.

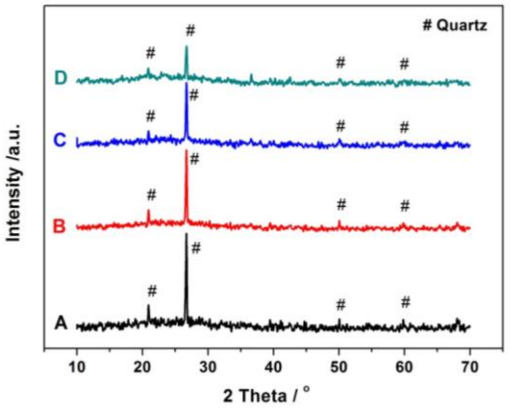

Figure 2. XRD patterns of the foam ceramic samples sintered at different temperature for 10 min: (A) 1140°C, (B) 1160°C, (C) 1180°C and (D) 1200°C.

According to standard XRD data, all the diffraction peaks observed in the patterns are attributed to the characteristic peaks of quartz. Interestingly, the intensity of diffraction peaks was gradually decreased with increasing sintering temperature. This is contradictory to the relationship between crystal content and sintering temperature that is commonly observed in ceramics and glass-ceramics [9, 10]. Based on the compositions of the raw materials, it can be seen that the content of low temperature flux is rather high, which would promote the formation of eutectic mixtures, thus lowering the melting temperature of the ceramics. However, as the main crystalline phase in the rare earth tailings, quartz has a melting point of as high as 1726 °C [11]. The quartz crystals could not be completely engaged to form a eutectic mixture with the fluxes when the sintering temperature is not sufficiently high. As a consequence, quartz crystals are preserved in the foam ceramics. With increasing sintering temperature, the amount of the eutectic mixture was raised, thus resulting in a gradual weakening in the characteristic peaks of quartz in the samples.

3.3. Physical Properties. As an idea candidate material for exterior walls of buildings, the fundamental advantages of foam ceramics are their light weight and incombustibility. Low bulk density is not only conductive to reducing heat conduction, but also helpful to decrease the weight load of buildings. Physical properties of the foam ceramics sintered at different temperatures are listed in Table 3. Figure 3 shows water absorption and bulk density of the foam ceramics as a function of sintering temperature. After sintering at 1120 °C, the foam ceramics has a bulk density of 0.84 g/cm^3. With increasing sintering temperature, the bulk density of the samples was declined significantly. It is only 0.33 g/cm^3 when the sintering temperature is 1200 °C. However, the ratio of water absorption of the samples rises obviously with sintering temperature.

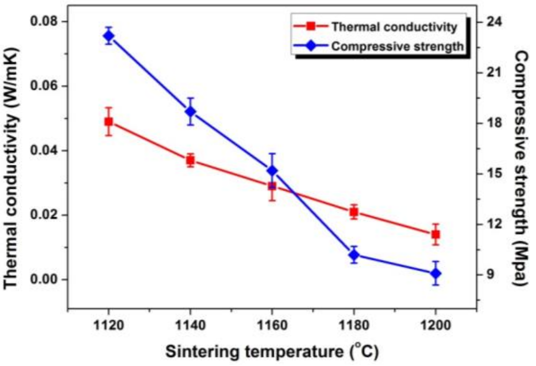

Figure 3. Figure 3 Water absorption and bulk density of the foam ceramics as a function of sintering temperature.

From the optical photographs of the foam ceramics, it can be seen that the pores of the samples are almost all closed (Figure 1), which can hardly absorb water. In fact, there are a large number of pores on the surface of the samples, resulting in the high water absorption of the foam ceramics. A lot of air is enclosed in the pores when the samples are in contact with water, so that the ceramics with smaller size of pores have lower water absorption. However, the interconnected pores can preserve much water, thus leading to the increased water absorption of the foam ceramics.

Thermal conductivity and compressive strength are the most important parameters of foam ceramics for building applications. As a thermal insulation material for the exterior walls of energy-saving buildings, foam ceramics are expected to have a thermal conductivity to be as low as possible. At the same time, in order to prevent the foam ceramics from being damaged and cracked during transportation and construction, they are also expected to have a compressive strength to be as high as possible.

Table 3. Physical performances of the foam ceramics sintered at different temperature.

Sintering temperature	1120	1140	1160	1180	1200
Bulk density (g/cm^3)	0.84	0.65	0.44	0.37	0.33
Water absorption (%)	3.5	6.2	8.4	8.7	9.5
Thermal conductivity (W/m·K)	0.049	0.037	0.029	0.021	0.029
Compressive strength (MPa)	17.5	15.7	12.9	11.2	10.9

Thermal conductivity of the foam ceramics as a function of sintering temperature is shown in Figure 4. It can be seen that the thermal conductivity of the foam ceramics was in the range of only 0.021-0.049 W/m·K, over the sintering temperature range of 1120-1200 °C, which is much lower than those of the similar foam ceramics reported in the open literatures [12, 13]. This is mainly resulted from the uniform distribution of the closed pores in the matrix of our foam ceramics. Obviously, because of the low thermal conductivity, our foam ceramics will the promising candidate for building energy-saving insulation applications. With increasing sintering temperature, the thermal conductivity of the foam ceramics was decreased gradually, which is attributed to the increase in porosity and the decrease in density of the foam ceramics. For example, after sintering at 1200 °C, the thermal conductivity started to increase. According to the evolution of pores structure of the samples, the increase in wall thickness should be responsible for the increase in the thermal conductivity.

The relationship between sintering temperature and compressive strength is also plotted in Figure 4, which has a similar trend to that of thermal conductivity. Over the sintering temperature range of 1120-1200 °C, compressive strength of the foam ceramics is in the range of 17.5-10.9 MPa, which is much higher than the standard requirements of the foam ceramics for external wall insulation of buildings [14]. The decreasing trend in compressive strength is closely related to the porosity and bulk density of the foam ceramics. In addition, duo to the dispersion strengthened effect of crystals in matrix [15], the decline of crystal content in the samples exacerbated this trend.

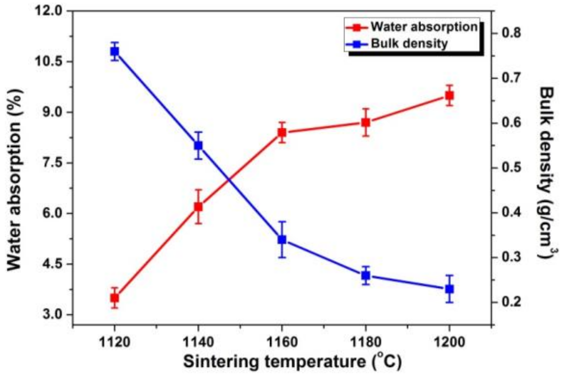

Figure 4. Thermal conductivity and compressive strength of the foam ceramics as a function of sintering temperature.

4. CONCLUSIONS

In the present study, rare earth tailings has been used as the main raw material to develop closed-pore structured foam ceramics with excellent physical properties and performances by using the direct foaming method, together with SiC abrasive waste. It was found that the pore size, bulk density, thermal conductivity, and compressive strength were all decreased, while the water absorption was increased, with increasing sintering temperature over the range of 1120-1120 °C. Sintering temperature can be solely used to optimize thermal conductivity and mechanical strength of the foam ceramics. After sintering at 1180 °C, a foam ceramic material possessed a bulk density of 0.37 g/cm^3, thermal conductivity of 0.021 W/m·K and compressive strength of 11.2 MPa. These performances fully satisfy the national standards of foam ceramics for building exterior walls. Therefore, we have demonstrated that rare earth tailing is an ideal raw material to fabricated foam ceramics, with high performances and low costs. It is believed to be beneficial to the reduction of the environmental pollution caused by the rare earth tailings.

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