Ceramics International 42 (2016) 11270–11274

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Microstructure and property of porous mullites with a whiskers framework obtained by a sol–gel process

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ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form
17 March 2016
Accepted 9 April 2016
Available online 19 April 2016

Keywords:
A. Sol–gel process
B. Whiskers
C. Strength
D. Mullite

ABSTRACT

Porous mullites with a whiskers framework and high porosities were fabricated by the reaction sintering (1100 to 1600 °C, 1 h, in an airtight container) of an aerogel block shaped by the sol–gel transition of a mullite precursor composed of SiO_2 sol, Al_2O_3 and AlF_3 powders (as reaction catalyst). The effect of heating temperatures on porosity, whisker formation, microstructure feature and compressive strength of the porous mullites was determined by XRD, SEM and compressive test. The results indicate that after heating at temperatures from 1100 to 1600 °C, the porosities of the mullites varied within the range of 84.1–80.2%. The whiskers in the framework well lap-jointed each other to form the large space and became elongated and smooth at high temperatures due to the accelerated vapor–solid reaction rate. A maximum compressive strength of 16.1 MPa was obtained for the whiskers framework heated at 1600 °C; this strength was attributed to the strong bonding among the smooth whiskers.

1. Introduction

Porous mullites ($3Al_2O_3 \cdot 2SiO_2$) possess high temperature stability, high corrosion resistance, chemical stability and a low thermal expansion coefficient at elevated temperatures [1,2]. Consequently, the applications of these materials include high-temperature sealing, hot-gas separation and diesel particulate filters [3–5]. High porosities are often required for thermal insulation and sufficient permeability in these applications [4]. However, low strengths at the high porosities limit practical applications [6].

Whiskers as a reinforcement or framework in porous mullite ceramics have attracted extensive attentions to improve the strength of the porous mullites because of their nearly perfect structure and high strength. Zhu [7] and Li [8] prepared porous mullites with whiskers as reinforcement; mechanical strengths of 81.2 ± 3.2 and 100 MPa were obtained at porosities of only 48.6 ± 0.5% and 50% due to the sintering densification of equiaxed particles, respectively. As the whiskers as reinforcement can't retain high porosities during the sintering of the equiaxed particles, whiskers frameworks gradually attracted more attentions due to their lap-joint structure with a high porosity. Liu [6] produced a mullite fiber/whiskers framework with a porosity of approximately 82% by slurry-filtration and heat-treating; the product had a compressive strength of approximately 1 MPa due to the presence of polycrystalline fibers. Li [9] synthesized a framework of single crystalline aluminum borate whiskers, which resulted in a porosity of 85% and a flexural strength of 2.2 MPa. Xu [10,11] prepared a mullite whiskers framework in porous ceramics with a compressive strength of 4.98 MPa at a porosity of 83%. Although the high strength was obtained at the high porosity, the weak bonding by solid sintering limited the advantage of the mullite whisker framework to improve its strength. Hence, the fabrication of a whiskers framework with a strong bond is meaningful to enhance the strength of porous mullites.

Vapor–solid methods can enhance whisker growth [12,13], and several methods have been reported for the preparation of mullite whiskers. Choi [14] synthesized mullite whiskers by heating a mixture of SiO_2 and silicon in an alumina tube reactor under a flow of H_2 and CF_4. Okada [15,16] synthesized mullite whiskers by firing AlF_3 as a catalyst and using tetraethoxysilane (TEOS) and Al $(NO_3)_3 \cdot 9H_2O$ as the starting materials in an airtight container. In these methods, Al_2O_3 and SiO_2 are converted to AlOF and SiF_4 vapors catalyzed by F ions, followed by the formation of intermediates $Al_2SiO_4F_x(OH)_{2-x}$(topaz, $x=0$–1) with an acicular morphology. Preferential growth of mullite whiskers along the (001) direction finally occurs with release of F. Zhu [7] and Li [8] fabricated porous mullites with whiskers as reinforcement with the addition of AlF_3 as a whisker-forming agent. However, no one fabricated porous mullites with a whiskers framework by Okada's method.

In order to form high porosities of mullites, sol–gel methods have been widely used due to the gel network structure with a high porosity. Guo [17] and Ding [18] prepared porous mullites

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http://dx.doi.org/10.1016/j.ceramint.2016.04.043
0272-8842/

with a 42% porosity by sol–gel and a 92.9% porosity by gel freeze drying, respectively. Compared with adding pore-forming agent [11], foaming method [19] and so on, the sol–gel method in this paper removes the process to burn out sacrificing templates because TEOS as SiO_2 source could allow green bodies form a high porosity through its intrinsic sol–gel transition. As cracks often occur during gel drying, freeze [18] and supercritical drying [20] were used to solve it. But, the dependence on equipments and freeze intermediates limits their operations to a certain extent. A method by gel slowly drying could simplify the operation and also avoid obvious cracks via reducing the evaporation rate of solvents, where the shrinkage of gel networks could compensate the cracks [21]. To our best knowledge, there are few reports that gel slowly drying was employed to fabricate porous mullites.

In this paper, we report a novel approach to fabricate porous mullites with a whiskers framework by the vapor–solid reaction sintering of a slowly dried aerogel block shaped by the SiO_2 sol with nanosized α-Al_2O_3 and AlF_3 powders. The effect of heating temperatures on porosity, whisker formation, microstructure, compressive strength and fracture morphology was characterized and are discussed.

2. Experiments

2.1. Raw materials and process

Porous mullite ceramics were prepared by a sol–gel process, as shown in Fig. 1. An ethanol slurry of 2 mol/L distilled H_2O and 0.5 mol/L TEOS (AR, Sinopharm Chemical Reagent, China) was stirred for 3 days to form a SiO_2 sol. α-Al_2O_3 (20 nm, 99% purity, Chaowei Technology Co. Ltd., China) and AlF_3 powders (AR, Sinopharm Chemical Reagent, China) were used as sources of Al and a whisker-forming agent, respectively. Another ethanol slurry containing 0.6 mol/L Al_2O_3, 0.3 mol/L AlF_3 and 1 mol/L $NH_3 \cdot H_2O$ was prepared by ball milling for 24 h. Then, the two slurries were mixed by magnetic stirring with a volume ratio of 1:1, and the molar ratio of Al to Si corresponded to the stoichiometry of mullite for all samples. The mullite precursor slurry gradually gelled in a columned beaker due to the condensation of the SiO_2 sol catalyzed by $NH_3 \cdot H_2O$. The wet gel block with a paper cover was naturally dried at room temperature for 25 days to avoid cracking, followed by heating at 80 °C for 24 h to evaporate all liquid. Although certain shrinkage occurred, no obvious cracks were found at the surface of the aerogel block. Finally, the green bodies were placed in an airtight alumina container prepared by polishing the contact parts of a cover plate and the rim of a crucible to prevent vapors extravasation by F ions, followed by heat treatment at 1100, 1300, 1500 or 1600 °C for 1 h with a heating rate of 2 °C/min in a muffle furnace.

2.2. Characterization methods

The weight loss of samples before and after sintering was measured using a precision electric balance, and linear shrinkage was determined by the height change measured with a Vernier caliper. The porosity and bulk density were measured by the Archimedes method using distilled water as the immersion liquid. Samples were machined into approximately Φ16 mm × 10 mm with two parallel end surfaces. A compression test was performed using a universal testing machine (Instron 5943, Instron Int. Ltd., USA), with a cross-head speed of 0.5 mm/min. Scanning electron microscopy (SEM, S-4800, HITACHI, Japan) was used to observe the fracture surface after the compression test, and the diameter of the mullite whiskers was measured from the micrograph. More than 400 grains were measured for each sample to obtain an average value. The composition of the sintered samples was analyzed by energy dispersive X-ray spectroscopy (EDS). Phase composition was identified by X-ray diffraction (XRD, Empyrean, PANalytical, Netherlands) using ground powders in the 2θ range of 10–70° with Cu K_α radiation.

3. Results and discussion

The variations of the weight loss, linear shrinkage and porosity of the samples before and after heat treatment are presented in Table 1. Due to the low solid content (6.6%) of the wet gel precursor, the green body occupied a high porosity of 76.2% and a low density of 0.64 g/cm^3. The weight loss after heat treatment was very high due to the presence of AlF_3, and the formation of mullite was accompanied by the vapors leaking of AlF_3, AlOF and SiF_4. Weight losses of 28.4% and 28.9% were measured after heat treatment at 1500 and 1600 °C, whereas weight losses of 22.5% and 24.0% were measured after heat treatment at 1100 and 1300 °C; the increase in weight loss at higher temperature may be due to greater AlOF and SiF_4 formation. The linear shrinkage of samples varied with heating temperatures and was 6.8% and 8.7% after heat treatment at 1500 and 1600 °C but only 1.4% and 1.5% after heat treatment at 1100 and 1300 °C; the increase in the linear shrinkage at higher temperature is attributable to enhanced particle rearrangement. The apparent porosity of the samples further increased from that of the green body after heat treatment due to the large weight loss but decreased from 84.1% to 80.2% as the temperature increased from 1100 to 1600 °C, corresponding to a slight increase in the apparent density from 0.51 to 0.64 g/cm^3. These results indicate that the high porosity was maintained in the porous ceramics even after heat treatment at 1600 °C.

The X-ray diffraction patterns of the samples after heating at temperatures up to 1600 °C are presented in Fig. 2. The phase compositions of all samples were nearly identical, with a main phase of mullite ($3Al_2O_3 \cdot 2SiO_2$, PDF#00-015-0776) and a small amount of corundum (Al_2O_3, PDF#01-074-0323). Most studies have suggested that the synthesis of the mullite by heating a mixture of Al_2O_3 and SiO_2 powders with catalysis by F ions occurs via a vapor–solid mechanism [14–16], which will be described in detail in a next paragraph. The remaining Al_2O_3 phase may be attributable to the high loss of SiF_4 due to its high partial pressure [15].

SEM images of the fracture surfaces of the samples after heat treatment at 1100, 1300, 1500 and 1600 °C are shown in Fig. 3. In addition to a few equiaxed particles, a large number of rod-like whiskers were observed. The results of EDX analysis at spots A1–

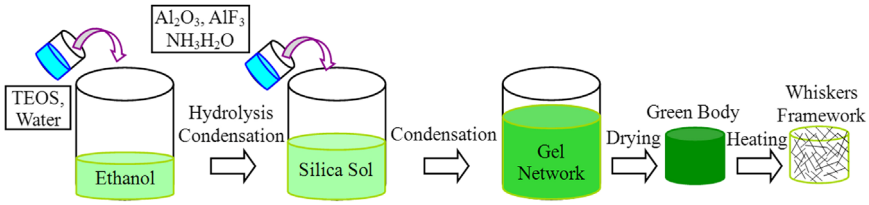

Fig. 1. The process flow sheet for the preparation of the porous mullite with a whiskers framework.