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Cellular silica-based ceramics prepared by direct foaming at high temperature

Changming Xu [a,b,*], Shiwei Wang [a], Katarina Flodström [b], Xiaojian Mao [a], Jingkun Guo [a]

[a] *Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China*
[b] *Department of Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden*

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Abstract

Cellular silica-based ceramics, including Si_3N_4/SiO_2 composite ceramics and monolithic silica ceramics, with dense shell and closed cells with dense and crack-free cell wall inside was prepared by the direct foaming of the green-compacts at 1310–1370 °C. The influences of the heat-treatment temperature on the relative density as well as the mechanism of the cell formation were investigated. The porosity of the obtained cellular silica and Si_3N_4/SiO_2 ceramics was within 60.0–84.0%, the cell size distribution was in the range of 10–120 μm, and the flexural strength was 9.7–16.3 MPa.

Keywords: Cellular; Silica-based ceramics; Direct foaming

1. Introduction

Silica ceramics as well as its composite ceramics reinforced with Si_3N_4 [1–3], AlN [4], BN [5] particle and silica fiber [6,7] have excellent dielectric properties and thermal-shock resistance, low thermal conductivity and thermal expansion coefficient, making them promising candidates for high-temperature dielectric and thermal-shielding application in aero craft in the recent decades. In order to expand their application under more rigorous conditions, the introduction of cells into the silica-based ceramics is desirable, owing to the fact that the existence of cells in ceramics can effectively decrease the dielectric constant, thermal conductivity, and specific weight [8–11].

By far, cellular ceramics with adjustable cell size, shape, and porosity can be prepared by the processing techniques of replica, sacrificial template, and direct foaming techniques [9]. However, organic templates for the cellular structure formation or agents for the generation of gas and/or liquid are usually required for the fabrication of cellular ceramics, which brings impurities into the products or does harm to the mechanical properties. In addition, open cell silica-based structure can absorb moisture, which is detrimental for the dielectric constant [12,13].

To the best of our knowledge, studies on the preparation of cellular ceramics with high porosity and closed cell have been reported only very recently [14,15]. In this study, we report the preparation of cellular silica-based ceramics, including Si_3N_4/SiO_2 composite ceramics and monolithic silica ceramics with high porosity and high mechanical properties such as flexural strength by the direct foaming of green-compact at high temperature. The influence of the heat-treatment temperature on the porosity of the resultant sintered-body was studied and the cell formation mechanism was investigated.

2. Experimental procedure

Silica powders and Si_3N_4/SiO_2 composite powders were prepared with sol–gel method. All of the chemicals used in present study were in chemical purity. α-Si_3N_4 powders (UBE-10, UBE Industry Co., Ltd., Japan), with an average diameter of 0.5 μm were also used to prepare Si_3N_4/SiO_2 composite powders. The processing route for Si_3N_4/SiO_2 composite powders as well as monolithic silica gel powders was illustrated in Fig. 1. Firstly, silica sol was prepared by mixing

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[*] Corresponding author at: Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China.
E-mail address: charmingxu@hotmail.com (C. Xu).

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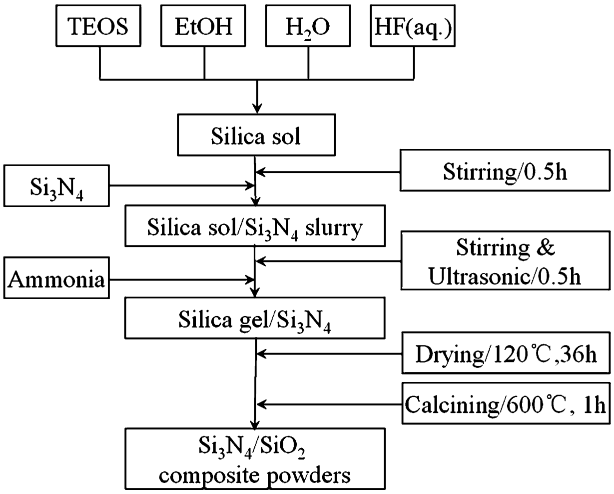

Fig. 1. Sol–gel processing route for the Si_3N_4/SiO_2 composite powder. Silica monolithic gel powders can also be prepared with this method without adding Si_3N_4 powders.

tetraethoxysilane (TEOS), ethanol (EtOH), deioned-water, and HF aqueous solution with the molar ratio of TEOS:EtOH:H_2O:HF = 1:5:3:0.03 together. After stirred at room temperature for 0.5 h, the Si_3N_4 powders with 10 wt.% based on solids, was added into the mixture solutions. After ultrasonic treatment with simultaneously and vigorously stirring for another 0.5 h, the mixture was then added rapidly with sufficient ammonia till the complete accomplishment of the gellization. Silica gel with Si_3N_4 powder uniformly dispersed inside was therefore quickly formed. The composite gel was dried at 120 °C for 36 h and then calcined at 600 °C for 1 h. Silica gel without adding Si_3N_4 powder was also prepared by this method at the same time.

The obtained silica-based powders were dry-pressed into 40 mm × 60 mm green-compacts with ~60 MPa pressure without any binder added, and followed by cold isostatic pressing with ~200 MPa pressure, respectively. The green-compacts were then heat-treated at 1100–1370 °C for 2 h in an air atmosphere at a rate of 10 °C min^{-1}.

The morphology of the Si_3N_4/SiO_2 composite powders was observed by transmission electron microscopy (TEM, JEM2100F, JEOL, Tokyo, Japan). The phase composition of the sintered compacts was identified by X-ray diffraction (XRD, D/max 2550 V, Rigaku Co., Tokyo, Japan). The microstructure of the resultant ceramics was observed by scanning electron microscopy (SEM, JSM6700F, JEOL, Tokyo, Japan). Flexural strength was measured using an Instron-1195 universal testing machine (Satec Co., Port Monmouth, USA) with a cross head speed of 1 mm s^{-1}. The inner fraction of the samples was cut into test pieces with a dimension of 5 mm × 5 mm × 40 mm. The cross-sectional area of the samples and the maximum failure load were used to calculate the fracture stress. The density of the whole sintered-body was measured by the Archimedes' method. After the measurement, the outer part of the samples was cut-off so that the density of the inner part of the sample can be measured by the same method. The Fourier transform infrared (FTIR) spectra were obtained using a Nicolet NEXUS 7000-C spectrometer with a 4 cm^{-1} resolution.

3. Results and discussion

3.1. Composite powders characterization

The morphology of the Si_3N_4/SiO_2 composite powders was shown in Fig. 2. Without serious hard agglomeration, the Si_3N_4 particles generally disperse well in the silica gel and most of the Si_3N_4 particles were surrounded by silica gel particles with a much less average particle diameter.

3.2. Sintering behavior, phase composition, and microstructure observation

Fig. 3 shows the relationships between the shrinkage of the relative density and XRD pattern (lower-left inset) of the Si_3N_4/SiO_2 ceramics and sintering temperature. The relative density of the samples was about 96.0% when heat-treated below 1200 °C for 2 h, however, decreased considerably to 33.0–40.0% and then kept stable when the temperature was increased above 1200 °C, which indicates a cell formation in the Si_3N_4/SiO_2 ceramics when heat-treated at increasing temperature.

From the XRD pattern, it can be observed that, although the Si_3N_4/SiO_2 green-compacts were subjected to an oxidative atmosphere at high temperature, α-Si_3N_4 diffraction peaks were found from the XRD patterns, which demonstrated the existence of α-Si_3N_4 phase in the resultant ceramics. Besides, trace cristobalite was detected as well in the ceramics when the heat-treatment temperature reached up to 1370 °C, which can be ascribed to the crystallization of the silica matrix at the temperature usually higher than 1350 °C [16] or partially from the oxidation of the α-Si_3N_4 particles [2].

The fact that the Si_3N_4/SiO_2 sample heat-treated at 1340 °C can float on water (see upper-right inset of Fig. 3) demonstrates the microstructure of the Si_3N_4/SiO_2 ceramics with a cellular inner fraction and dense outer shell. The apparent porosity of this sample was calculated to be 60.0% and the porosity of the

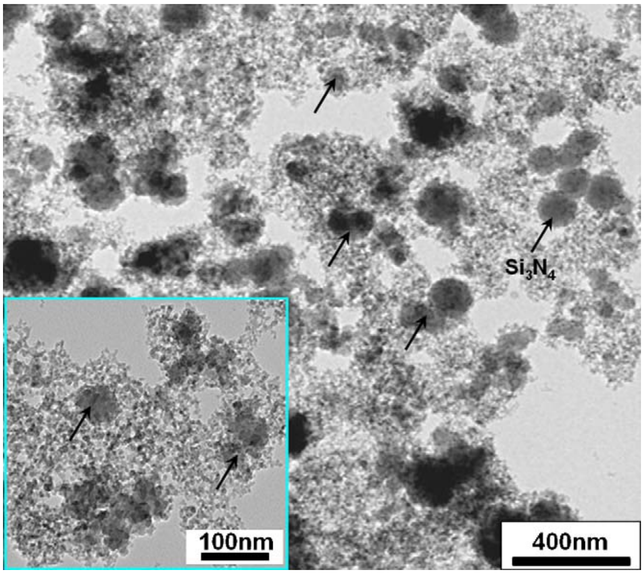

Fig. 2. TEM image of the Si_3N_4/SiO_2 composite powder.