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Research Article

A facile method to fabricate $Al_4B_2O_9$ whiskers on porous SiC substrates for gas–solid separation

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Abstract: $Al_4B_2O_9$ whiskers on the surface of porous SiC substrates were fabricated by chemical reactions between $Al(NO_3)_3$ and H_3BO_3, which is a facile method to prepare cilia-like microstructure for gas–solid separation. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy were employed to investigate the structural morphology and phase compositions. $Al_4B_2O_9$ whiskers with nanometer-sized diameters and micrometer-sized lengths grew on the surface of SiC substrates, and a self-catalytic mechanism was used to explain $Al_4B_2O_9$ whisker growth.

Keywords: ceramics; sol–gel process; microstructure; scanning electron microscopy (SEM)

1 Introduction

Porous silicon carbide is a well-suited candidate for diesel particulate filter (DPF) field in vehicle exhaust treatment due to its excellent properties like high temperature stability, low thermal expansion coefficient, high corrosion resistance, high thermal conductivity, and excellent mechanical strength [1–3]. The literatures of the Society of Automotive Engineers (SAE) have shown that the wall-flow SiC filter is the mainstream technique to decrease particulate emission [3]. The vehicle exhaust is a complex mixture of nonvolatile and semi-volatile components. The nonvolatile components are composed of fractal-like carbonaceous agglomerates also known as the accumulation (soot) mode in the size range of 30–500 nm [4,5]. Many investigations indicate that ultrafine particles are airborne and penetrate deep into the lungs when breathed in, which makes them more hazardous to human health than larger particles [6,7]. Thus, a serious problem has been caused that porous SiC ceramic filter manufactured by the traditional processes could not efficiently separate ultrafine particles from hot exhausts, like the separation of nano-particles is a great trouble when the diameter of particles is much less than the diameter of filter holes [8].

Nature is the greatest and most successful laboratory ever exists. Through evolution, nature experiments with various solutions to its challenges and selects the successful ones, which provide ready answers to scientific and technical problems and inspire us with a series of novel designs and high-performance structures [9–11]. The human respiratory tract is a sophisticated filtration system: the dust or bacteria could be filtered when the air flows through the bronchial surface, and only the clean air enters the

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lungs for breathing (Fig. 1). A large number of the ciliated cells grow on the surface of bronchial wall, and every ciliated cell has about 300 cilia with the length of 6 μm [12,13]. The harmful substance, such as dust and bacteria, could be filtered by these cilia. Inspired by the bronchial microstructure, we have proposed a new strategy to trap ultrafine particles more efficiently using molten salt reaction synthesis of mullite whishers on the porous SiC substrates [8]. However, molten salt synthesis requests the specific utensil which can endure molten salt corruption at high temperature, and the synthesis process is somewhat complicate for industrial manufacture. Thus, our research group looks forward to finding a facile method to fabricate whiskers on porous SiC substrates. In the present paper, $Al_4B_2O_9$ whiskers have been prepared on the porous SiC surface by sol–gel technology.

2 Experimental

2. 1 Reagents and apparatus

The porous SiC substrates (Xi'an Powder Co., Ltd., 46% open porosity for the porous SiC), aluminum nitride hydrate ($Al(NO_3)_3 \cdot 9H_2O$, AR, Xi'an Chemical Reagent Co.), and boric acid (H_3BO_3, AR, Xi'an Chemical Reagent Co.) were used as raw materials in the present study. Crystalline phase of the samples was examined by using X-ray diffractometer (XRD, D/MAX-RA), and monochromated Cu Kα radiation was used. Scanning electronic microscope (SEM, S-4800) was used to characterize and analyze the microstructure, which was operated at 20 kV and 20 mA. The Fourier transform infrared (FTIR) spectrum was recorded with an infrared spectrometer (AVATAR 360) in the wavenumber range of 4000–400 cm^{-1}.

2. 2 Preparation of $Al_4B_2O_9$ whiskers on porous SiC substrates

$Al(NO_3)_3$, H_3BO_3, and citric acid were weighted accurately according to molar ratio of 1:3:2, and these reagents were dissolved in deionized water. Then, these three kinds of solutions were mixed under continuously stirring to form a transparent sol system. Porous SiC substrates were weighted with the same mol quantity of H_3BO_3 in the sol, and immersed into the mixture sol for the diffusion of chemical ingredient. The mixture sol and SiC substrates were evaporated in an electric oven for expelling the extra water. Subsequently, the samples were placed in the alumina crucible and heated to 800 ℃ and 900 ℃ for 2 h, and then cooled down to room temperature in a muffle furnace under air atmosphere. Finally, the modified SiC substrate with aluminium borate whiskers was obtained through the sol infiltration and sintering.

3 Results and discussion

The XRD patterns of the modified SiC ceramics fabricated by the sol infiltration and sintering are shown in Fig. 2(a). SiC, $Al_4B_2O_9$, and $Al_7Si_3BO_{13}$ crystalline phases are observed in the sintered specimens (800 ℃ and 900 ℃), indicating that $Al_4B_2O_9$ whiskers could be formed at lower temperature, which is in agreement with the published literature [14]. The strong diffraction peaks of SiC are observed, which originate from porous ceramic substrates, indicating that the main chemical composition could not be changed in low temperature calcinations, and the products are essentially constituted of SiC with a minor amount of $Al_4B_2O_9$ and

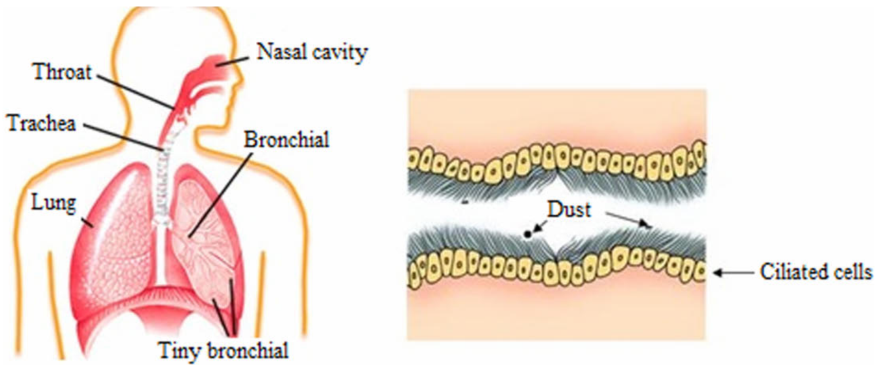

Fig. 1 Schematics of the human respiratory organization (left) and the bronchial microstructure (right).

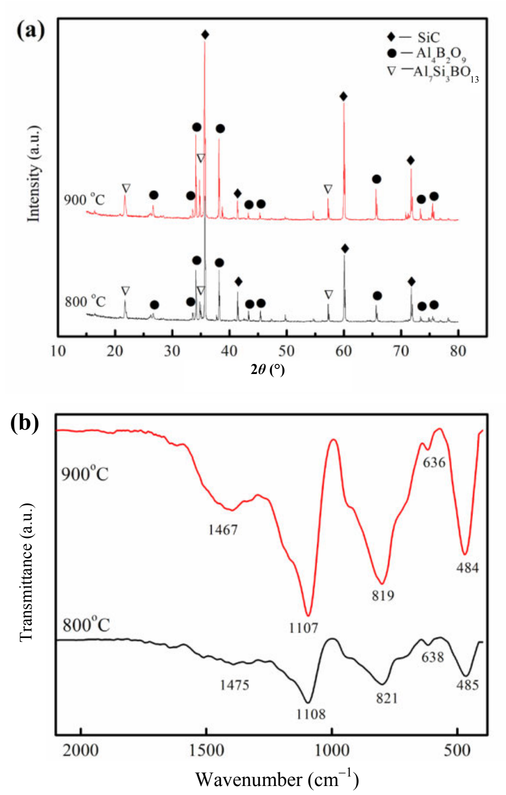

Fig. 2 (a) XRD patterns and (b) FTIR spectra of the modified SiC ceramics.

$Al_7Si_3BO_{13}$. The phase of $Al_7Si_3BO_{13}$ would be formed through the intricate reactions among $Al(NO_3)_3$, H_3BO_3, and SiO_2, where SiO_2 comes from the SiC substrates.

Figure 2(b) shows the FTIR spectra of the resulting products with different sintering temperatures. Absorption band at 819 cm^{-1} is attributed to the Si–C fundamental stretching vibration in 900 ℃ sample, and the same characteristic absorption appears at 821 cm^{-1} in 800 ℃ sample. The characteristic antisymmetric stretching bands of the BO_4 tetrahedron vibration region at 1107 cm^{-1} is assigned to $Al_4B_2O_9$ [15]. The absorption peak at 1467 cm^{-1} is attributed to the antisymmetric stretching vibrations of the BO_3 group, and 636 m^{-1} and 484 m^{-1} are ascribed to the vibrations of the AlO_x polyhedral and lattice vibrations contained in the complex coordination of Al–O–B bonds [15]. In comparison with the 900 ℃ sintering, the characteristic adsorption peaks of each chemical bond appear at similar wavenumbers of 800 ℃ sintered specimen.

The SEM image of the porous SiC substrate is shown in Fig. 3(a). SiC grains randomly stack to form irregular pores and some additives are used for monolith formation; the smooth surface is formed owing to the glass phase formation. The microstructure has huge change after the sol infiltration and sintering treatment, and numerous $Al_4B_2O_9$ whiskers grow on the surfaces of the porous SiC ceramics (Figs. 3(b)–3(d), here the surfaces involve the outer surface of the porous ceramic substrates and the inner surface of the pores). The whiskers display nanometer-sized diameters and micrometer-sized lengths, and the surface roughness of SiC ceramics increases clearly as the $Al_4B_2O_9$ whiskers growing. This unique microstructure simulates the human bronchial surface

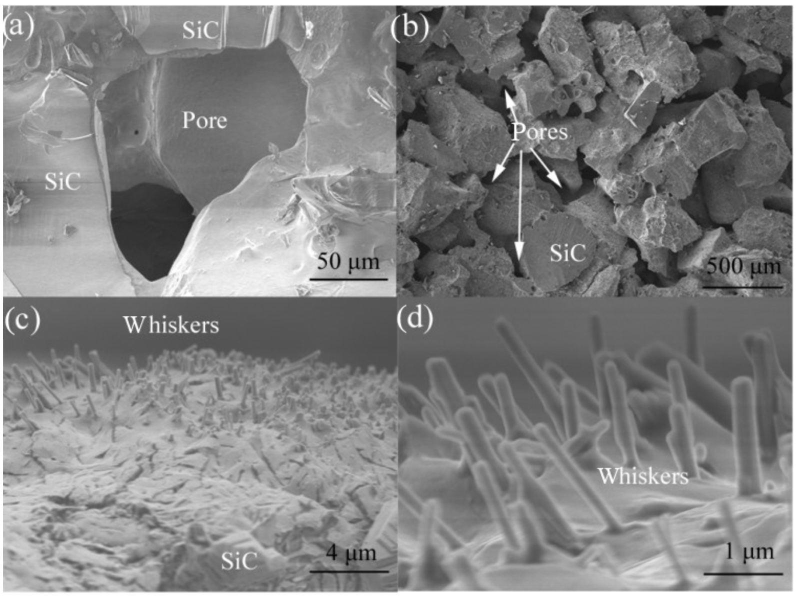

Fig. 3 SEM morphologies of (a) unmodified SiC substrate and (b)–(d) modified SiC substrates, where (c) and (d) are high-magnification SEM images of the surface of SiC pores.

and has potential application in hot gas filtration field, for example, diesel particulate filter (DPF) [8].

The mechanism of $Al_4B_2O_9$ whisker growth on the surface of porous SiC substrates is different from the vapor–liquid–solid (VLS) explanation [16,17]. The VLS mechanism is suitable for the growth of the whiskers which possess tips as the starting growth points. Therefore, the self-catalytic mechanism can be used to explain the growth of aluminum borate whiskers as that described elsewhere [18–20]. The chemical reactions between $Al(NO_3)_3$ and H_3BO_3 for producing $Al_4B_2O_9$ whiskers can be described in Eqs. (1)–(4). During the process, H_3BO_3 decomposes into B_2O_3 at about 250 ℃, and then B_2O_3 melts at about 450 ℃. With the increase of temperature, $Al(NO_3)_3$ decomposes into Al_2O_3 grains at about 500 ℃. Subsequently, small Al_2O_3 grains dissolve into molten droplets of B_2O_3, and all these small Al_2O_3 grains serve as nuclei for the growth of $Al_4B_2O_9$ according to the reaction (4).

$$4H_3BO_3 \rightarrow 2B_2O_3 \text{ (solid)} + 6H_2O \text{ (gas)} \quad (1)$$

$$B_2O_3 \text{ (solid)} \rightarrow B_2O_3 \text{ (liquid)} \quad (2)$$

$$2Al(NO_3)_3 \rightarrow Al_2O_3 \text{ (solid)} + 6NO_2 \text{ (gas)} \quad (3)$$

$$2Al_2O_3 + B_2O_3 \rightarrow Al_4B_2O_9 \text{ (solid)} \quad (4)$$

Citric acid is added to serve as ferment, which plays an important role in the synthesis of aluminum borate whiskers. In the sol precursor fabrication, the viscosity of these solutions can be adjusted through citric acid quantity. And the total mixture of $Al(NO_3)_3$ and H_3BO_3 is converted in a short period under these conditions especially when they are intrinsic mixed in a colloidal level, which will shorten the diffusion paths so that the reaction kinetics need not to be considered in the whole process. In comparison with mullite whiskers prepared on porous SiC ceramics using molten salt synthesis [21], the sol infiltration is a facile method to fabricate cilia-like microstructure on porous SiC substrates, which has potential applications for gas filtration.

4 Conclusions

$Al_4B_2O_9$ whiskers have been successfully grown on porous SiC substrates by the sol infiltration and sintering, which have potential applications for ultrafine particle filtration. XRD and SEM analyses showed that $Al_4B_2O_9$ whiskers are formed when the precursor is calcined at 800 ℃ in air for 2 h. The self-catalytic mechanism was used to explain the growth mechanism of $Al_4B_2O_9$ whiskers on the porous SiC substrates.

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