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Formation of porous SiC ceramics by pyrolysis of wood impregnated with silica

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ABSTRACT

Biomorphous β -SiC ceramics were produced at 1400°C from pine wood impregnated with silica. This one-step carbothermal reduction process decreases the cost of manufacturing of SiC ceramics compared to siliconization of carbonized wood in silicon vapor. The synthesized sample exhibits 14 m²/g surface area and has a hybrid pore structure with large 5-20 μ m tubular macropores and small (< 50 nm) slit shaped mesopores. SiC whiskers of 20-400 nm in diameter and 5-20 μ m in length formed within the tubular pores. These whiskers are expected to improve the filtration by removing dust particles that could otherwise penetrate through large pores. After ultrasonic milling, the powdered sample showed an average particle size of ~30 nm. The SiC nanopowder produced in this process may be used for manufacturing SiC ceramics for structural, tribological, and other applications.

Introduction

Synthesis of ceramics from natural fibrous and vegetable precursors attracted much interest in recent years [1-4]. The research was mainly driven by economical reasons since natural materials serve as a renewable and relatively inexpensive source of carbon. In addition, biomorphic ceramics templated by cellular biological objects exhibit complex hierarchical microstructures, which are attractive for applications requiring a low specific weight and high stiffness [5, 6]. Synthesis, microstructure and selected properties of biomorphic SiC, Si₃N₄ and oxide ceramics from different types of wood (pine, eucalyptus, fir, aspen, etc.), bast and cereal fibers (rice, jute etc.) have been reported [7-9]. SiC and Si₃N₄ ceramics with cellular structure are usually produced by methods based on a two-step process: (1) a controlled pyrolysis of natural precursors, and (2) high temperature reactive infiltration of the porous carbon preform by molten Si, Si vapor, or SiO in a controlled environment (vacuum, Ar, or N₂) [10-15]. The excellent strength and specific stiffness of the biomorphic ceramics open a wide range of applications for these attractive materials [16, 17].

In this paper we demonstrate a simple synthesis route, in which biomorphic SiC is produced directly from raw wood impregnated with silica (sodium silicate) using waste products of pine wood processing. This method is more economical as it allows eliminating the pyrolysis step and does not require the use of elemental silicon. In addition, the described procedure reduces the temperature and duration of the SiC synthesis and generates SiC nanofibers in the pores.

Experimental

Figure 1 shows the process flow chart for the manufacturing of SiC ceramics. We used pine wood chips mostly consisting of about 5x1x1 mm particles. The chips were dried to a constant weight, and then held in a sodium silicate aqueous solution at 20-50 °C for 3-5

hours. The saturated chips were dried, treated with a hydrochloric acid solution, rinsed with water, and dried again at the temperature of 100 ± 5 °C to a constant weight. The chips impregnated with ~40 wt. % silica were then heated in a graphite reactor under an Ar flow to 1400 °C, held at this temperature for 60 min, cooled down to room temperature and taken out for further analyses. Part of the sample was milled using an UZDM-A (Russia) ultrasonic miller at 22 kHz for 5 min, in 1-wt.% sodium hexametaphosphate aqueous solution.

X-ray diffraction (XRD) of the synthesized products was performed using a DRON-1.5 diffractometer (Burevestnik, Russia) using Cu K_{α} radiation (45kV, 20A, $\lambda=1.54056$ Å) with a Ni filter, step size of 0.25° (2θ) and hold time of 1min. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) was performed using a FEI XL-30 environmental field-emission scanning electron microscope (FEI, The Netherlands) equipped with an EDAX EDS detector. SEM samples were studied without coating and were attached to a metal sample holder using a conductive carbon tape. Accelerating voltage of 5 and 20 kV and a working distance of ~6 and ~11 mm were employed for SEM and EDS analyses, respectively. The semiquantitative analysis of the EDS spectra was done using the Genesis software supplied by EDAX. Gas sorption measurements were performed using an automated micropore gas analyzer Autosorb-1 (Quantachrome Instruments, USA). The Ar sorption isotherms collected at liquid nitrogen temperature (-196 °C) were analyzed using the Brunauer, Emmet, Teller (BET) equation to reveal the specific surface area (SSA) of the produced ceramics. Quantachrome's data reduction software Autosorb v.1.51 was employed for these calculations. Particle size analysis of the grinded sample was done using a Zetasizer 1000 (Malvern Instruments, Ltd., UK).

Results and discussion

Powder X-ray diffraction

XRD analysis of the synthesized and milled material allowed us to determine the minimal temperature of the SiC synthesis as ~ 1400 °C. Below this temperature (1350 °C) the main phases formed are α -cristobalite (diffraction peaks at $2\theta \sim 31.1^\circ$, corresponding to (102) planes, and 35.8° - (200)) and graphite ((002) peak at $2\theta \sim 26.6^\circ$). Figure 2 shows the XRD pattern of the sample produced at 1400 °C during the 60 min annealing. The position of the observed peaks indicated the formation of cubic β -SiC. The SiC synthesis proceeding through the carbothermal reduction reaction [18] is almost completed, and no substantial amount of crystalline SiO₂ phase can be detected. A weak peak at $\sim 26.6^\circ$, visible in the diffraction pattern (Fig. 2), indicates the presence of graphitic carbon in the sample and can be explained by the excess of carbon in the pyrolysis products of the wood/SiO₂ composite. The remaining carbon can be removed from the sample by oxidation at $\sim 600^\circ$ C in air (data not shown).

Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Figure 3 shows SEM micrographs of the SiC sample synthesized at 1400 °C. Large tubular pores of about 5-20 μm in diameter, observed in most of the samples, are believed to originate from the biological vessels existing in wood. The cross-section shape of these macro-channels varies from round/elliptical (Fig. 3a) to nearly rectangular (Fig.3c). The wall thickness is generally in the 1-5 μm range. These walls demonstrate a porous nano-crystalline structure with the grain size of 20-200 nm (Fig.3b).

The EDS analysis showed up to 17 at. % of oxygen and a slight excess of carbon in the SiC samples (Fig. 3f), confirming the presence of graphite detected by XRD (Fig. 2). Oxygen is believed to be in the form of amorphous silicon oxycarbide, since no crystalline SiO₂ was detected by XRD (Fig. 2). The composition of the material is somewhat similar to SiC produced from polymeric precursors, in which nano-sized grains of SiC are surrounded by silicon oxycarbide and carbon (Tyranno fibers). The yield of SiC is expected to increase at

higher temperatures or longer annealing time, but this may increase the grain size of SiC and the overall cost of the process.

Roughly half of the pores in the sample studied by SEM showed the presence of SiC whiskers grown on the walls inside the macro-channels (Figs. 3 c,d,e). The diameter and the length of the whiskers ranged from ~20 to ~400 nm and ~5 to ~20 μm , respectively. Larger SiC fibers with the diameter of ~1 μm were also occasionally observed (Fig. 3e). Formation of SiC whiskers during the synthesis of biomorphic SiC ceramics from mineralized wood was reported in several recent publications [19, 20]. The growth of SiC whiskers is believed to proceed via the vapor-liquid-solid (VLS) mechanism where the chemical reaction between gaseous SiO and CO provides transport of carbon and silicon needed for the whisker growth [18]. Impurities coming from wood or sodium silicate might have acted as nucleation sites. Silica deposited on the carbon surface is known to promote the growth of SiC whiskers [21].

Particle size analysis

Preliminary particle size measurements performed on the ultrasonically milled sample showed the formation of ultra-fine particles (Figs. 4 a,b) with an average particle size of ~30 nm (Figs. 4 b). The relatively small grain size in the synthesized SiC ceramics could be due to the relatively low synthesis temperature which impedes re-crystallization and grain growth. In addition silicon acid gel precipitated onto the wood sample surface is known to consist of SiO₂ (cristobalite) nanocrystals [22] which may determine the size of SiC crystallites formed during the carbothermal synthesis process. A network of small pores existing in wood and transferred to the produced SiC ceramics make milling and separation into small grains relatively easy. Pine wood is a light-weight wood with relatively low carbon content, producing a loose and open pore structure.

Argon sorption

Figure 5 shows Ar sorption on the surface of the synthesized sample. The shape of the adsorption isotherm (Type II according to the Brunauer classification) is typical for macroporous (>50 nm) solids with unrestricted multilayer adsorption [23]. However, the presence of adsorption-desorption hysteresis and the shape of the desorption isotherm indicate the formation of slit-shaped mesopores (2-50 nm) [23], presumably within the walls of the macropores (Fig. 3b). The BET SSA was found to be $\sim 14 \text{ m}^2/\text{g}$, which is typical for biomorphic SiC ceramics.

Thus, the material produced in our one-step process is similar to ceramics made by silicon infiltration of carbonized wood. It has a high surface area and well-developed pore structure, including macropores and mesopores. Since the produced material looks both robust and porous enough for making high-temperature filters, we were satisfied with the achieved yield and did not pursue the synthesis at higher temperatures. A detailed characterization of mechanical properties and gas permeation should be conducted to evaluate potential applications, but it is outside the scope of this study, which mainly reports on the composition and structure of the synthesis products.

Summary

Porous β -SiC ceramics have been synthesized at 1400 °C from pine wood infiltrated with silica gel. SEM and gas sorption techniques revealed the presence of both long cylindrically-shaped macropores and slit-shaped mesopores, with the accessible specific surface area of $\sim 14 \text{ m}^2/\text{g}$. SEM has also detected formation of SiC whiskers with a diameter of 20-400 nm and a length of 5-20 μm inside the macropores. The simplicity and relatively low cost of the suggested process may be attractive for industrial production of high-temperature filters, catalytic converters for exhaust gas purification, and heat exchangers, as well as fillers for composites with metallic, polymer, or ceramic matrices. Ultrasonic milling

of the produced ceramics produced SiC nanopowders with an average particles size of ~30 nm.

Acknowledgement

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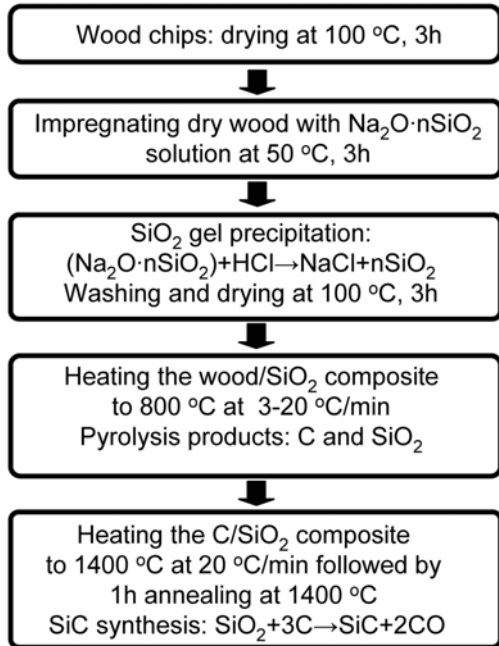


Fig. 1. Process flow used for the fabrication of porous SiC ceramics from wood.

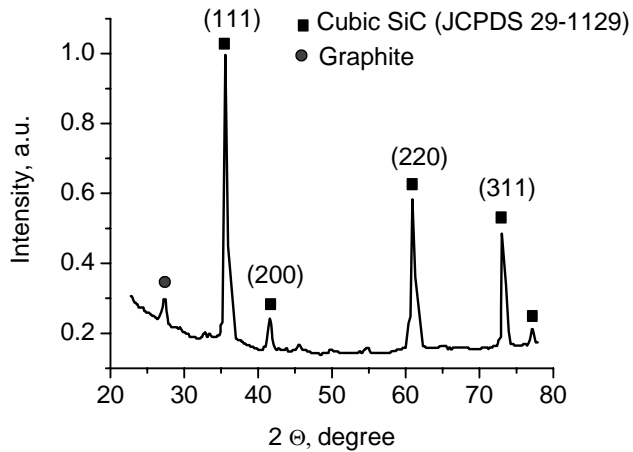


Fig. 2. XRD pattern of the sample produced at 1400°C. Cubic β -SiC crystal phase has been identified. The peak at $\sim 26^\circ$ corresponds to (002) planes of graphite. All other peaks originate from β -SiC.

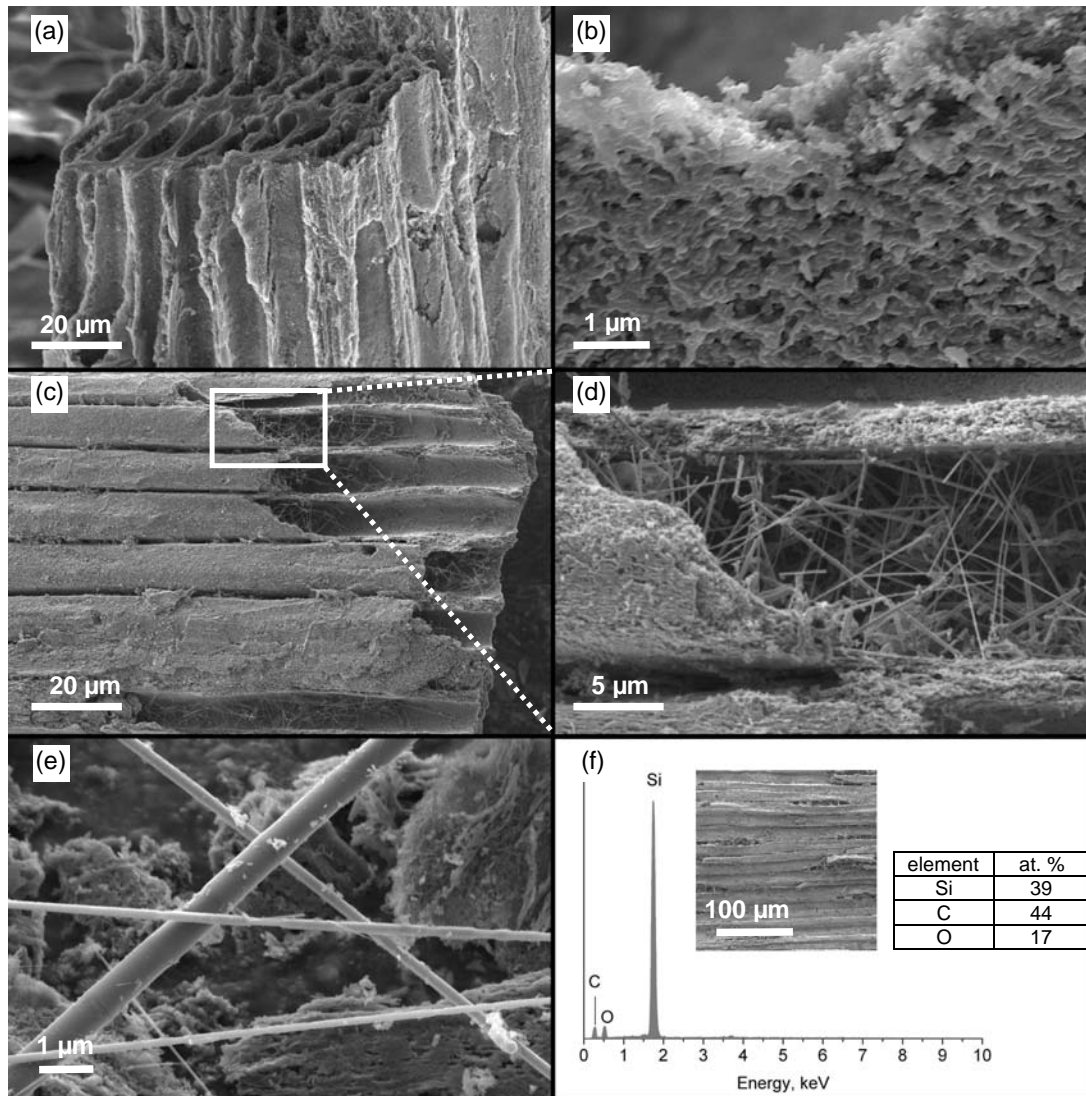


Fig. 3. SEM micrographs (a-e) and EDS spectrum (f) of the SiC samples produced from pine wood at 1400°C. The macro-channels of 5-20 μm observed in the produced ceramics mimics the biological vessels in wood. The 1-5 μm walls show a porous nanocrystalline structure. SiC whiskers and fibers of 0.05-1 μm in diameter are clearly seen in most of the channels.

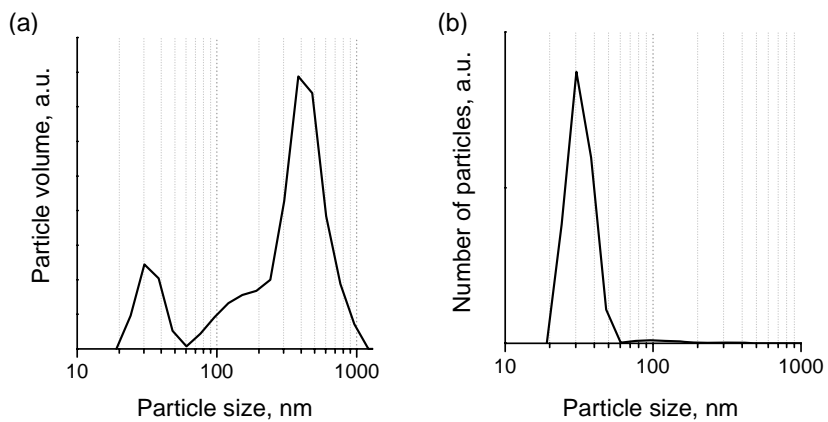


Fig. 4. Particle size distribution by volume (a) and number (b) of the ultrasonically milled SiC samples produced from wood at 1400°C.

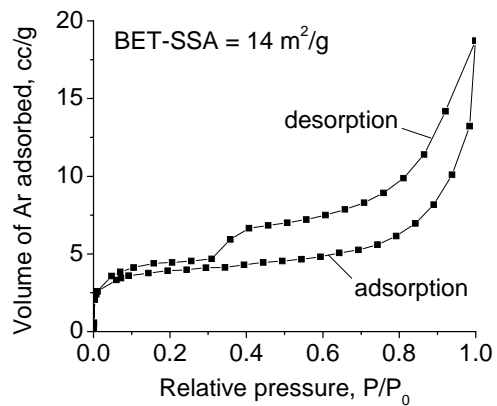


Fig. 5. Argon sorption isotherm recorded at 77 K.