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The synthesis and microstructure of morphogenetic SiC ceramics

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Highly porous SiC ceramics with a wood like structure were prepared from premineralized wood template through tetraethyl orthosilicate (TEOS) infiltration. The TEOS was first decomposed to SiO_2 and then in situ reaction between silica and carbon template took place in the cellular wall at high sintering temperature. The morphology of resulting porous SiC ceramics have been investigated by scanning electron microscopy (SEM/EDX) and X-ray diffraction (XRD). Experimental results show that the biomorphic cellular morphology of wood is remained in the porous SiC ceramics with high precision that consist of β-SiC phase.

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1. Introduction

A number of manufacturing approaches have been used to fabricate SiC-based ceramics including sintering, hot pressing or hot isostatic pressing, reaction bonding, polymer pyrolysis and chemical vapour deposition [1, 2]. However, all these techniques are both time- and cost intensive. Therefore, there is considerable effort to find and optimize production process for high performance silicon carbide materials. Recently, more attention has been given to biomimetic approach for producing SiC ceramics by transformation of bioorganic wood structure into an inorganic ceramic material with tailored chemical, physical and mechanical properties [3-6].

Wood is natural composite materials composed of biopolimeric constituents such as cellulose, hemicelluloses and lignin [7]. Cellulose is the basic structural component of all wood cell walls. Chemically speaking, it is a long chain linear polysaccharide composed of glucose $(C_6H_{10}O_5)n$. The cellulose superstructure has a matrix of lower molecular weight polysaccharides named hemicelluloses.

Lignin is a three-dimensional polyphenolic molecule of highly branched structure and high molecular weight. Since it permeates cell walls and intercellular region, lignin acts as a glue which bonds all wood cells giving the wood (mechanical strengthening) cells, respectively. The microstructure features of wood tracheidal cells are responded for liquid transportation and they form pore channel system with a preferential orientation in axial direction. However, this feature offers the possibility to use liquid infiltration techniques to transform the hierarchical cellular structure of wood into inorganic materials with preservation of the original cellular structure. Such highly anisotropic cellular structure and carbonous composition can be used as C precursor and a hierarchical template for the synthesis novel non-oxide ceramics with micro, meso and macrostructures [8-10].

In the present study, we demonstrate the possibility of producing porous SiC ceramics by carbothermal reduction of premineralized wood with silica.

2. Experimental method

Linden wood was used as a biological template structure. Linden (*Tilia*) is a deciduous wood which exhibits a monomodual pore distribution with a mean pore diameter of about 20 μm. Tetraethyl orthosilicate, $Si(OC_2H_5)_4$-TEOS was used as a precursor for infiltration. The infiltration/annealing process is described by the schematic diagram in Fig.1. Linden wood was shaped (10 × 5 × 5 mm) and dried at 70 °C for 48 h. Dry wood pieces were soaked in 1 M HCl solution due to leaching lignin out at 60°C for 48 h and again dried at 60°C for 48 h. Pieces of treated wood were soaked into solution of $TEOS/EtOH/H_2O$ with molar ratio = 1:4:12). In these solution a few drops of acetic acid were added due to faster gelation. The gel formation is achieved in five days at room temperature. The wood/silica samples were then dried at 110 °C for 8h and calcinated at 1000°C in Ar atmosphere for 1 h. The final thermal treatment was accomplished in a graphite-heated furnace (Astro, USA) under 0.1 MPa argon atmospheres, at a heating rate of 5 °C/min, at the temperature 1600 °C, for 1 h. The samples were cooled down in room temperature in Ar. Scanning electron microscopy (SEM/EDX) analyses were carried out on untreated surfaces of samples using a JEOL 6300F microscope at 3 kV accelerating voltage. Crystalline phases were identified by X-ray diffraction (XRD) using filtered CuKα radiation (Siemens D5000). For this purpose the carbon from samples were burned of at 700 °C in air.

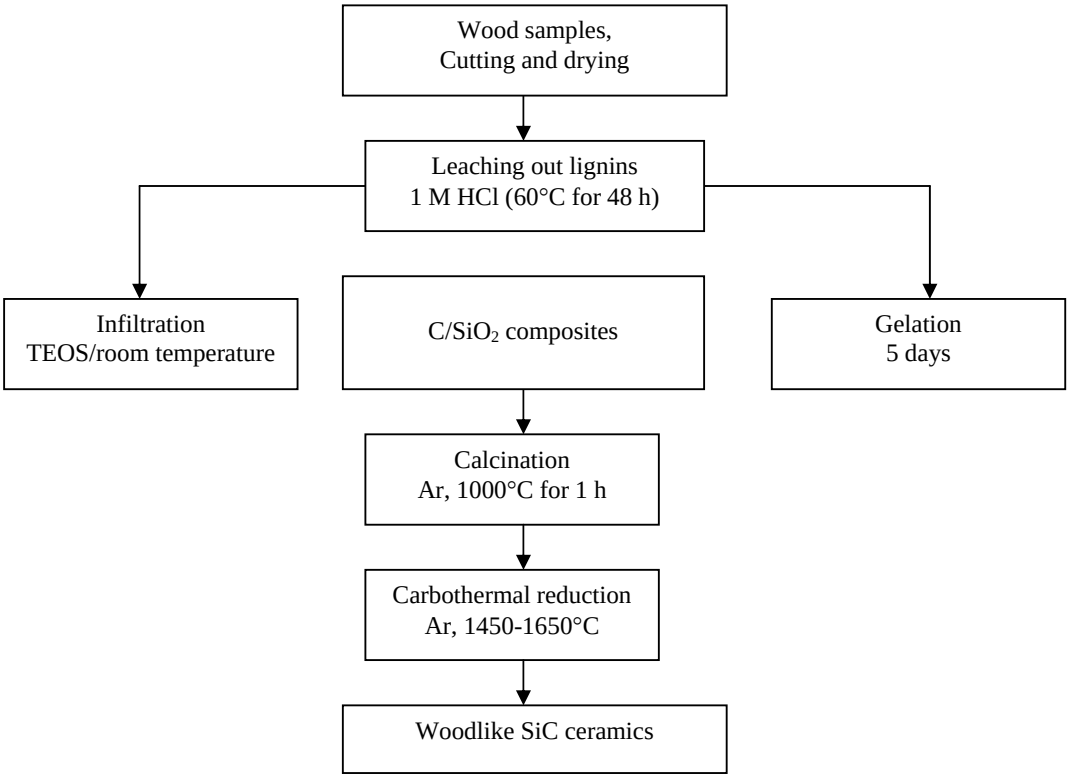


Fig. 1. Flow chart for the manufacturing of biomorphic SiC ceramics.

3. Results and discussions

3.1. Mineralization of wood

The morphology properties of the linden-wood after leaching out lignin as well as after TEOS infiltration and calcination are shown in Fig. 1 and Fig. 2, respectively. It could be noticed that microstructure features of wood samples such as tracheidal pore channels and pits are very well visible. Thus, microstructure after chemical treatment remained the same as as-received samples, in spite of high weight loss (about 19%). In case of TEOS infiltrated wood sample after calcination, the microstructure exhibits the homogeneously distributed a very thin layer through wood cellular network. However, the sample remained completely intact and retained the original microstructure. The energy dispersive spectroscopy (EDS) analysis of this layer confirms only the present of silicon and oxygen (Fig. 3).

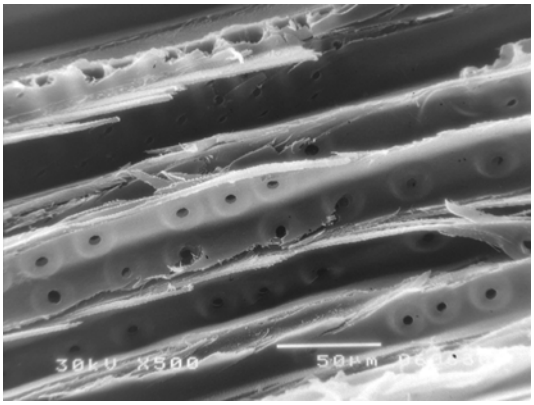


Fig. 1. Photomicrograph of leached wood sample. Radial direction of sample.

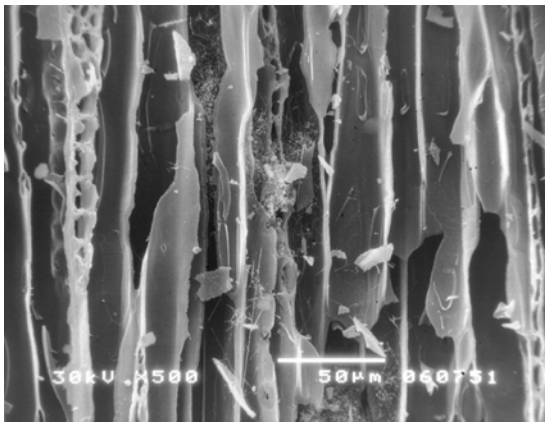


Fig. 2. Photomicrograph of the microstructure of as infiltrated wood sample after calcinations.

Thus, during calcination the wood is converted into charcoal [11] and TEOS into silica making the C/SiO_2 composite. The XRD analysis of these composite shows that it is in amorphous state.

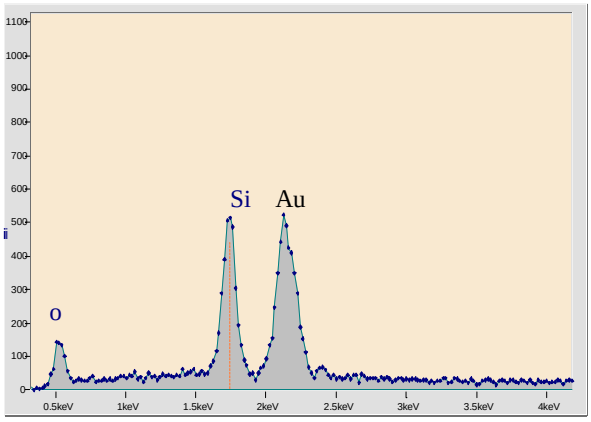


Fig. 3. EDS of coated of C/SiO_2 composite.

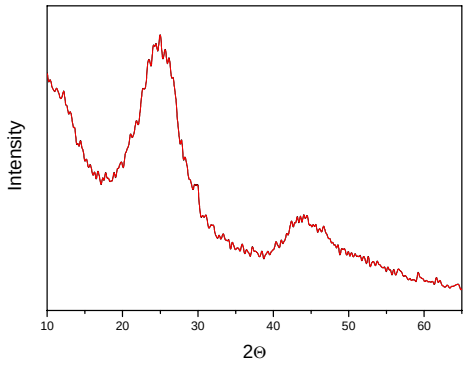


Fig. 4. XRD pattern of C/SiO_2 composite.

3.2. Conversion of C/SiO_2 composite into SiC ceramic

XRD pattern of the as-synthesized SiC from C/silica composite prepared at 1600°C in Ar revealed mainly cubic type β-SiC phase as shown in Fig. 5. The additional diffraction peak was detected at $2\theta = 33.671^{o}$, which represents stacking faults on the ⟨111⟩ planes in cubic SiC whiskers [12]. The intensity ratio of the peaks at 33.6 and 41.4 (2θ) can be used to evaluate the stacking faults density in the SiC crystal. When the intensity ratio is higher than 1, the stacking faults are significant [13, 14]. Since the observed ratio is 1.5, this result suggests the density of crystal lattice defects is very high. This is confirmed by whiskers with length (5-10 µm) and radius (1-0.2 µm) which are observed by SEM in the edges of sample (Fig. 6d).

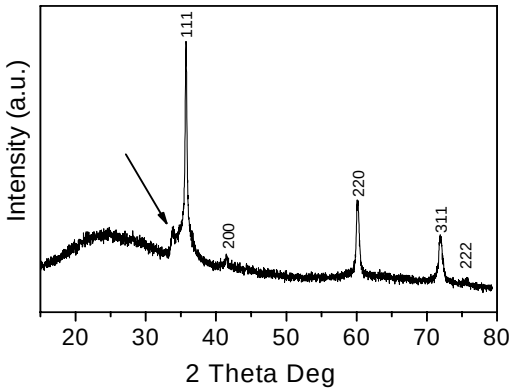


Fig. 5. X-ray diffraction pattern of SiC material prepared from wood/TEOS composite at 1600 °C for 2 h. The arrow indicates stacking faults on the octahedral planes in cubic SiC whiskers.

It has been shown that under the experimental condition of the present work, reaction for producing silicon carbide involves reduction of silica (SiO_2) thin layer by reducing agent – carbon wall under an inert protective atmosphere. This treatment liberates Si or SiO in gaseous form, which further reacts with carbon to form SiC following the general reaction:

$$SiO_2(s) + 3\,C(s) \Rightarrow SiC(s) + 2\,CO(g) \qquad (1)$$

Formation of final product is more complex than above equation shows, since the formation of SiC requires a series of solid-solid, solid-gas and gas-gas reactions [15-17]:

$$SiO_2(s) + C(s) \Rightarrow SiO(g) + CO(g) \qquad (2)$$

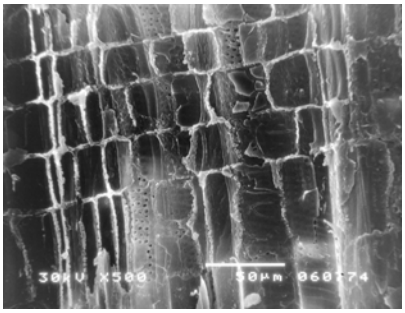
$$C(s) + SiO(g) \Rightarrow SiC(s) + CO(g) \qquad (3)$$

$$SiO_2(s) + CO(g) \Rightarrow SiO(g) + CO_2(g) \qquad (4)$$

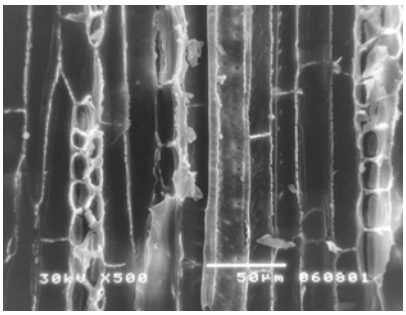
$$C(s) + CO_2(g) \Rightarrow 2\,CO(g) \qquad (5)$$

The SiO vapor from Eqs.(2) and (4) react with carbon to yield SiC nuclei heterogeneously on the surfaces of carbon through Eq.(3), which is commonly accepted mechanism of bulk SiC formation [18]. As soon as SiC forms on carbon walls, the growth process via Eg.(3) can be hindered by either the solid diffusion of carbon or the diffusion of SiO gas molecules through SiC layer. However, the present work shows that SiC formation continues due to porous struts after initial carbothermal reduction reaction (Fig. 6c), which provides the path for diffusion of SiO gas molecules into carbonaceous cell wall, allowing Eq.(4) to proceed.

Fig. 6. shows respectively the SEM photographs of morph-genetic SiC ceramic in two different directions (a,b). In both, it is shown that the cellular texture of wood sample is retained after thermal treatment with heterogeneous pore size. The cell size ranges from 20 to 100 μm. It exhibits a relatively homogeneous strut. Some whiskers are also formed (d) with very high aspect ratio.



a



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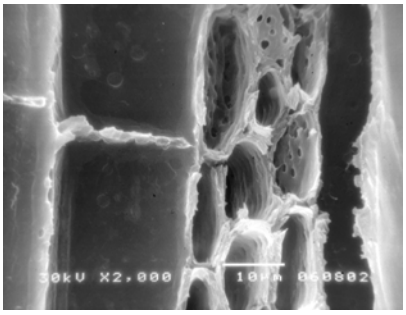
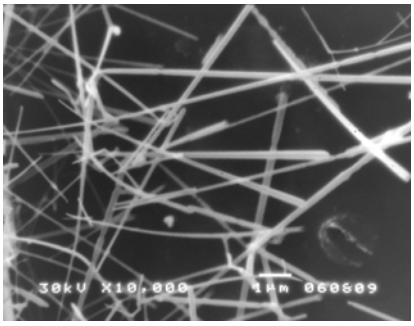


c



d

Fig. 6. SEM images of thermal treated C/SiO_2 precursors.

The energy dispersive spectroscopy (EDS) analysis of SiC material after the removal of residual carbon confirms the present of silicon and without oxygen. Thus, all infiltrated silica was reacted with carbon forming SiC.

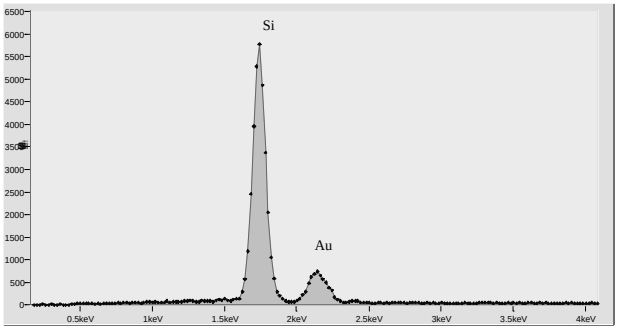


Fig. 7. EDS of final SiC ceramic.

These SiC materials have a possibility for using as a high temperature filters, catalyst support structures and similar applications.

4. Conclusions

The current results demonstrated the conversion of biological cellular tissues structure into porous ceramics. This porous SiC ceramic with woodlike microstructure was prepared at 1600 °C for 2 h in an argon atmosphere by sol-gel and carbothermal reduction techniques using TEOS and linden wood as the starting materials. XRD reveals β-SiC as the only phase present in the cellular SiC product. This technique provides a promising future application for advanced materials design.

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