Synthesis of biomorphic Si-based ceramics[#]

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Abstract

Tilia wood was transformed by pyrolysis into carbon preform. This porous carbon preform was infiltrated with TEOS ($Si(OC_2H_5)_4$), as a source of silica. In situ reaction between the silica and the carbon template occurred in the cellular wall at a hight temperature. Depending on the applied atmosphere, non-oxide (SiC) or oxide (SiO_2) ceramics were obtained. Scanning electron microscopy (SEM), X-ray diffraction (XRD), infrared (IR) spectroscopy, mercury porosimetry and BET measurements were employed to characterize the phases and crystal structure of biomorphic ceramics. The experimental results showed that the biomorphic cellular morphology of the wood maintained in both the SiC and SiO_2 ceramics, wich consisted of β-SiC with trace of α-SiC and SiO_2, respectively.

***Keywords**: biomorphic SiC and SiO_2,, porous ceramic, wood, sol-gel process*

I. Introduction

Biomorphic porous ceramics prepared from wood is a novel kind of porous ceramics that cannot be prepared by the traditional technologies [1].

Wood is a natural composite material of complex hierarchical cellular structure that consists of biopolymers such as cellulose, hemicellulose and lignin which form a porous microstructure [2]. Anisotropy in wood is the result of the orientation and alignment of cells and cell walls, as well as variation in density. The highly anisotropic cellular structure of wood may serve as a hierarchical template to generate novel cellular ceramics with a micro-, meso- and macrostructures [3–5].

The morphology and arrangement of the different cells may vary in a wide range between the different kind of wood with large vessel cells dominating in hardwood and tracheids dominating in softwood. The diameter of the vessels and tracheids (named as pores) varies between 5 and 50 μm in softwood and between 1 and 300 μm in hardwood. These cells with a preferential orientation in the axial direction offer the possibility of using various infiltration techniques to transform the bioorganic wood structure into an inorganic ceramic material with tailored physical and mechanical properties. Among them, the sol-gel procedure with carbothermal reduction or high temperature treatment at ambient atmosphere has some advantages such as low cost, easy procedure and allowing lower synthesis temperatures and high pure resultant, and can retain the structure and morphology of starting material [1,2,5].

The objective of this work was to prepare porous ceramics with wood-like microstructure from Tilia wood and TEOS in argon, in case of SiC ceramic, and in ambient atmosphere, in case of SiO_2 ceramic.

II. Experimental

Starting materials were linden (Tilia) wood that was used as a biological template structure and tethraethylortosilicate ($(Si(OC_2H_5)_4$ TEOS) as a precursor for infitration. Linden wood was shaped into pieces with 10 mm in axial direction and 5 mm in tangential and radial direction (10×5×5 mm) and dried at 343 K for 48 h. Carbon preforms were prepared by carbonizing the dried wood at 1273 K in argon atmosphere for 2 hour with a heating rate of 5 K/min. These carbon preform specimens were then soaked in an ethanol solution of tethraethylorthosilicate (molar ratio TEOS : EtOH = 1 : 4)

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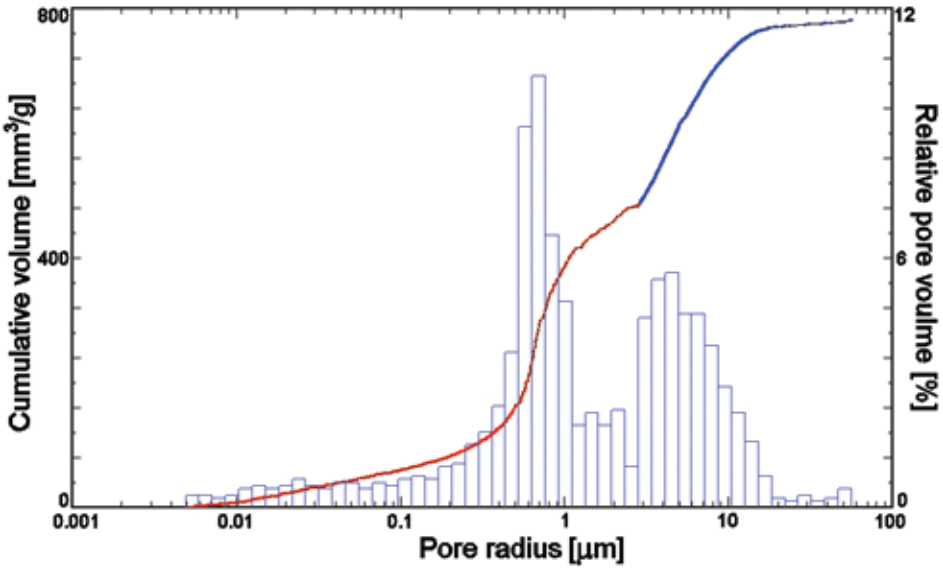

Figure 1. Pore size distribution of carbonized samples determined with Hg porosimetry

and stirred for two hour at room temperature. Distilled water (12 part per one part of TEOS) and few drops of acetic acid were added to obtain the maximum gelling rate (pH = 4). The silica sol contained in carbon preform was gelled at room temperature for two days and dried at 373 K for 8 hours to remove other solvents [6,7]. After that two experiments were performed.

In the first one C/SiO_2 composite samples were then heat treated at 1273 K in Ar atmosphere for 1 h. The treatment procedure of impregnation, gelling, drying and 1273 K treatments were repeated several times, to increase the silica content in C/SiO_2 composites. Carbothermal reduction reaction of the C/SiO_2 composite was carried out at 1873 K in flowing Ar atmosphere in a furnace with graphitic heating element for 1 hour with a heating rate of 40 K/min to form a porous SiC ceramic [6,7]. In the second experiment C/SiO_2 composite samples were heat treated at 1073 K in ambient atmosphere for 1 h. For this heat treatment a low heating rate (1 K/min) was adopted to avoid damage of the wood cell walls due to gas release. The treatment procedure of impregnation, gelling, drying and heating on 1073 K were repeated three times to increase the ceramic content in biomorphic samples. The final thermal treatment was accomplished in horizontal tube furnace in air atmosphere at 1573 K for 1 hour.

The pore size distribution of carbonized samples were determined by mercury porosimetry (type PASCAL 240/140 with working pressure of 1–200 MPa and with minimal poresize detection of 3.7 nm) and by BET method. Specific surface area (S_{sp}), mezo- and microporous area (S_{mezo}, S_{mic}) as well as microporous volume (V_{mic}) also were determined with BET method.

Crystalline phases obtained biomorpic SiC and SiO_2 were identified by X-ray diffraction (XRD) using CuKα radiation (Siemens D5000). Additional, crystalline phases of biomorphic SiO_2 were investigated with IR spectroscopy (Perkin-Elmer 782).

The morphology changes and transformation of the C/SiO_2 composite into SiC and SiO_2 ceramics were investigated by scanning electron microscopy (SEM/EDS - JEOL JSM-5300F).

III. Results and discussion

Pore size distribution of carbonized samples, determinated with Hg porosimetry is shown in Fig. 1. There are two peaks, first one between 50 and 60 μm and the second one between 70 and 80 μm, which means that these samples are mostly macroporous according to IUPAC classification (micropores ≤ 2 nm, mesopores 2–50 nm and macropores ≥ 50 nm). This is in a good agreement with SEM investigation, which will be discussed later.

Nitrogen adsorption isotherms of carbonized samples as a function of relative pressure at 77 K are shown in Fig. 2. According to the IUPAC classification isotherms are of type-IV with hysteresis loop which is associated with mesoporous materials.

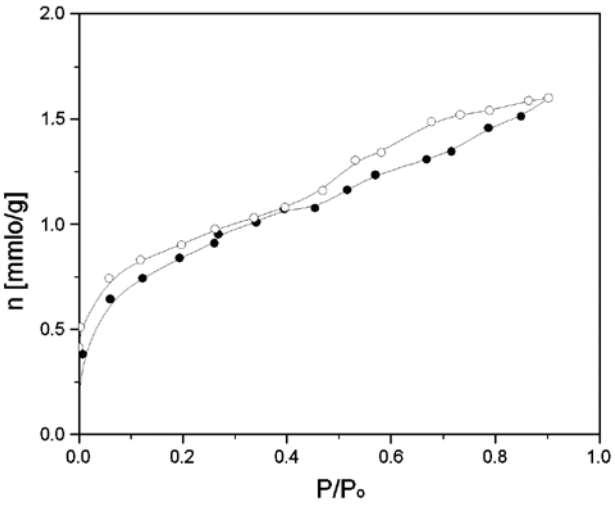

Figure 2. Nitrogen adsorption isotherms of carbonized samples as a function of relative pressure on temperature of 77K

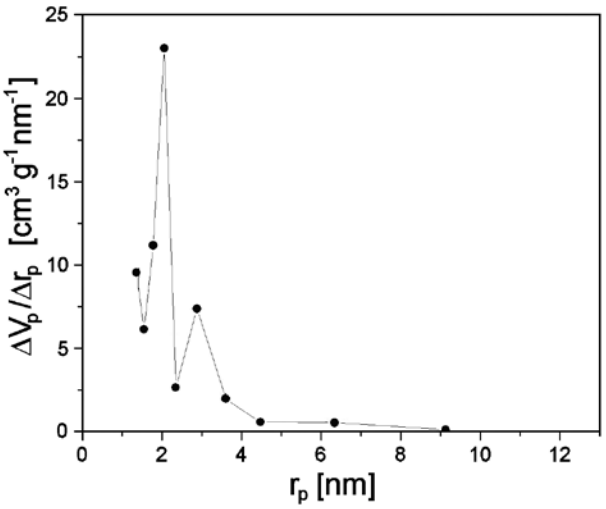

Figure 3. Pore size distribution of carbonized samples determined with BET method

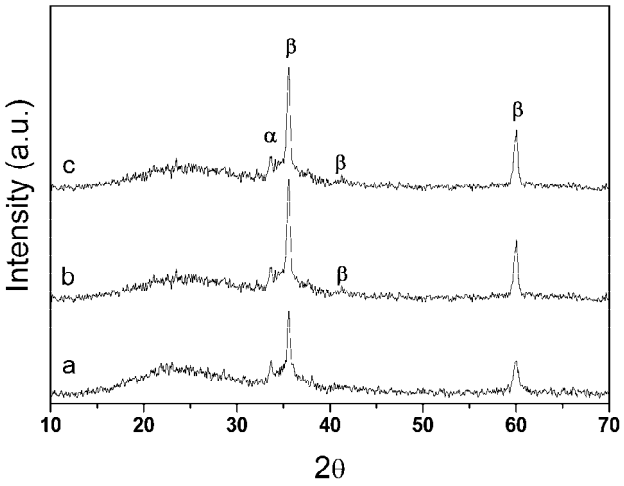

Figure 4. XRD patterns of samples treated at 1873K after: a) one infiltration, b) two infiltrations, c) three infitrations

Specific surface area (S_{BET}) of carbonized samples was determined from isotherms of N_2 by BET method. From the isotherms mesoporous area (S_{mezo}), microporous area (S_{mic}) and micropore volume (V_{mic}) also were calculated. These porosimetry parameters are given in Table 1.

Pore size distribution, estimated by applying BJH method, is shown in Fig. 3. Pore size radius varies between 2 and 10 nm, with sharp peak around 2 nm, which indicate that these samples are mostly mesoporous according to IUPAC classification. Although, these samples were mostly macroporous, their walls show significant presence of mesoporosity.

The XRD patterns of samples after carbothermal reduction are shown in Fig. 4. The obtained SiC ceramics consists of β-SiC with traces of α-SiC. The amount of β-SiC increases with increasing number of infiltrations.

The SEM micrographs (Fig. 5) show the preserved biomorphic cellular structure of the resulting SiC ceramics. Fig. 5a shows channels that originate from tracheids cells that are parallel to the axis of the tree. Cross-section perpendicular to axial direction is presented in Fig. 5b, showing pore structure.

Corresponding EDS spectra are presented in Fig. 6, showing that this phase is mainly composed of Si and small amounts of O, Ca and K. Unfortunately, carbon cannot be detected due to instrument limitations.

XRD analysis after heat treatment under an ambient atmosphere at 1073 K shows that samples are still amorphous (Fig. 7). However, a weak peaks of SiO_2 (tridimite) appeared, indicating crystallization of samples. The XRD pattern of the sample treated at higher temperature (1573 K), also under ambient atmosphere, exhibits sharp peaks of crystalobalite (SiO_2) and small ones of tridimite (SiO_2) (Fig. 7). Thus, this XRD analysis of infiltrated wood samples, after calcination in ambient

Table 1. Porosimetry parameters of carbonized samples calculated by BET method

S_{BET} [m^2 g^{-1}]	S_{meso} [m^2 g^{-1}]	S_{mic} [m^2 g^{-1}]	V_{mic} [cm^3 g^{-1}]
67	57	10	0.0042

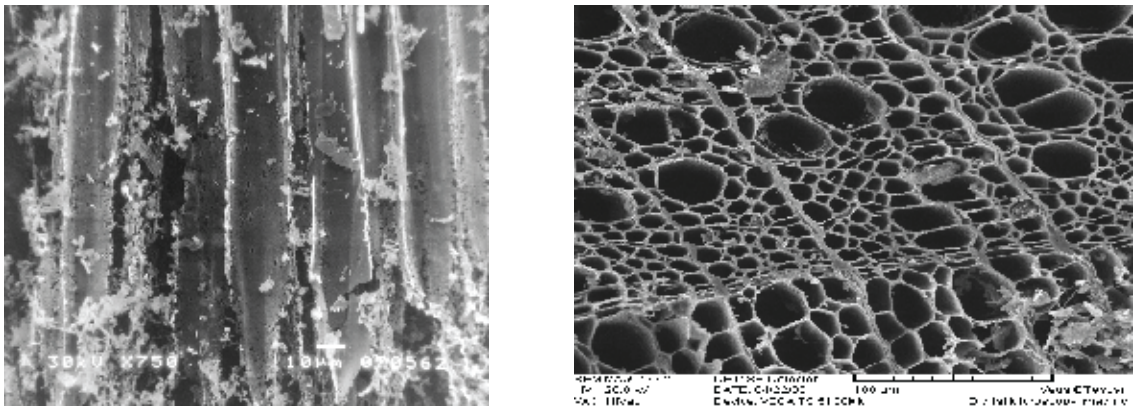

Figure 5. SEM mocrograph of woodlike SiC ceramic structures

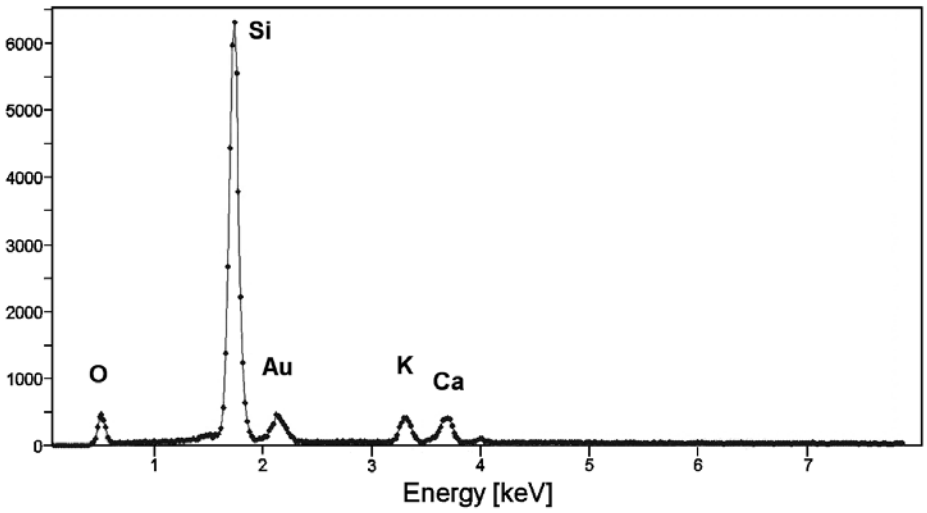

Figure 6. EDS spectra of woodlike SiC ceramic structure

atmosphere, shows that carbon is removed and amorphous SiO_2 is transformed into crystalline phases.

The SEM micrographs of the resulting SiO_2 ceramics are shown in Fig. 8. The morphology in the tangential direction (Fig. 8a) depicts a structure similar to the starting wood sample. At some points along the channels replica (Fig. 8b) small pits with 2–3 μm in diametar are noticed. They were formed during carbon removal in form of CO/CO_2.

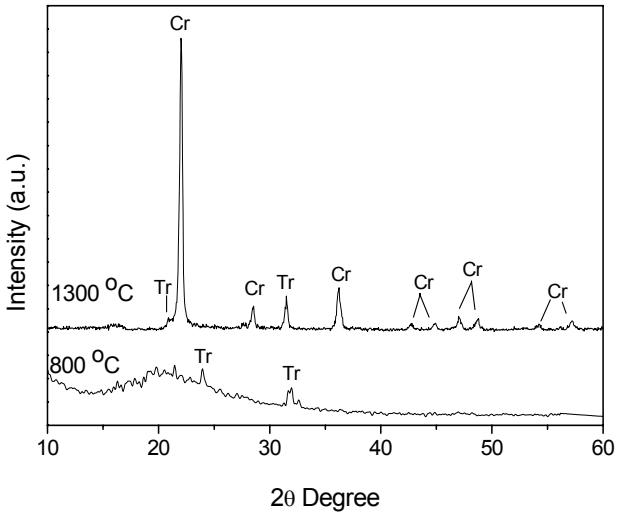

Figure 7. XRD patterns of the products obtained from C/SiO_2 composite under an ambient atmosphere (Cr-crystobalite, Tr-tridymite)

Structural changes of samples after heat treatment at 1573 K in ambient atmosphere also were investigated with IR spectroscopy. The corresponding frequencies of normal vibration are given in Table 2. All these vibrational bands belong to silica polymorphous forms namely crystobalite and tridymite.

IV. Conclusions

This work demonstrated the possibility of obtaining meso- and macroporous biomorphic ceramics from the wood. After carbonization and sol-gel procedure with TEOS, mercury porosimetry and nitrogen adsorption showed that the samples were meso- and macroporous, acording to the IUPAC clasification. A porous SiC ceramics with a woodlike microstructure was obtained by sol infiltration and carbothermal reduction at 1873 K in argon atmosphere. XRD and EDS analysis reveal that β-SiC is the major phase present in the cellular ceramic product. A SiO_2 ceramic was formed at 1573 K in ambient atmosphere, with cristobalite as the principal phase. XRD and IR anal-

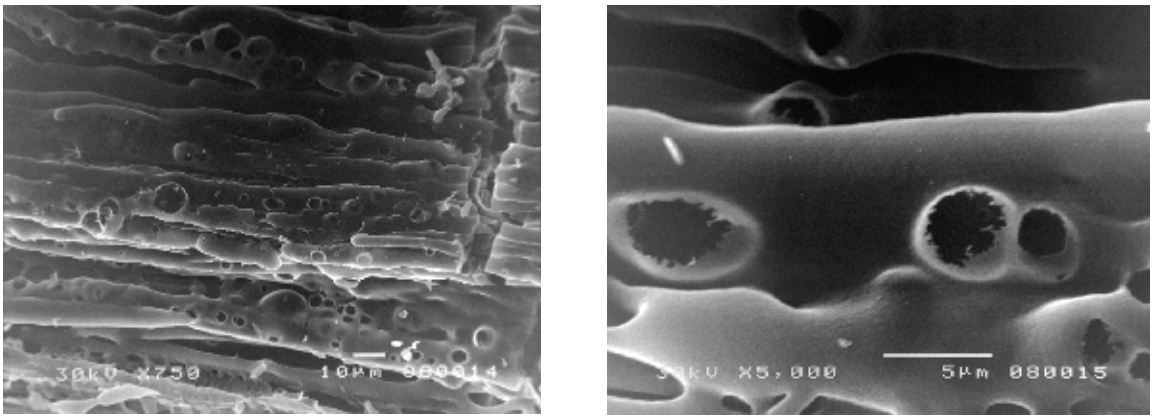

Figure 8. SEM mocrograph of biomorpic SiO_2 ceramics obtained at 1573 K

Table 2. Characteristic band position in spectrum of obtained silica at 1573 K in region between 350 and 1200 cm^{-1}

Band positions [cm^{-1}]	Band positions [cm^{-1}]
1140 1069	Asymmetric stretching bridging Si-O
791 619	Bending vibration of Si-O-Si angles
474	O-Si-O bending vibration
382 239	Lattice vibration

ysis reveal crystobalite and minor amount of tridymite as phases present in these cellular products. These tehniques provide promising future applications for designing advanced materials with low density and high porosity.

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