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Original scientific paper

## Synthesis of biomorphic SiC and SiO<sub>2</sub> ceramics

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**Abstract:** Coniferous wood (fir) was transformed by pyrolysis into carbon preforms, which were subsequently converted into biomorphic ceramics by the pressure infiltration technique with colloidal silica. An *in situ* reaction between the silica and the carbon template occurred in the cellular wall at a high sintering temperature. Depending on the employed atmosphere, non-oxide (SiC) or oxide (SiO<sub>2</sub>) ceramics were obtained. The morphology of the resulting porous ceramics and their phase composition were investigated by scanning electron microscopy (SEM/EDX) and X-ray diffraction (XRD). The experimental results showed that the biomorphic cellular morphology of the wood maintained in both the SiC and silica ceramics, which consisted of only the  $\beta$ -SiC phase and SiO<sub>2</sub>, respectively.

**Keywords:** biomimetic synthesis; cellular SiC; porous ceramics.

### INTRODUCTION

The term "ecoceramics" denotes a class of ceramics made of wood-based products. Wood is a natural composite material composed of biopolymeric constituents, such as cellulose, hemicellulose and lignin.<sup>1</sup> Cellulose is the basic structural component of all wood cell walls.<sup>2</sup> Chemically speaking, it is a long chain linear polysaccharide composed of glucose (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>. The cellulose superstructure has a matrix of lower molecular weight polysaccharides, named hemicelluloses. Lignin is a three-dimensional polyphenolic molecule with a highly branched structure and high molecular weight. Since it permeates cell walls and the intercellular region, lignin acts as glue, which bonds all wood cells giving the wood its hardness. Wood exhibits a hierarchical architecture with a cellular microstructure of high porosity due to specific functions of living cells, transportation (tracheidal), storage (parenchymal) and mechanical strengthening (libriformal) cells, respectively. The microstructural features of wood are tracheidal cells which are responsible for liquid transportation and they form a pore channel system with a pre-

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ferential orientation in the axial direction. This feature offers the possibility to use liquid infiltration techniques to transform the hierarchical cellular structure of wood into inorganic materials with the preservation of the original cellular structure.<sup>3–6</sup>

Single phase, porous biomorphic SiC ceramics were manufactured using Si-containing vapors as reactants. The Si-containing vapors were forced to penetrate the pores of the carbon template and react with the biocarbon to form SiC. Different reactive Si vapor sources, such as Si,<sup>7</sup> SiO<sup>8</sup> and CH<sub>3</sub>SiCl<sub>3</sub> (methyltrichlorosilane)<sup>9</sup> were applied. Also, Si-melt<sup>10</sup> and TEOS (tetraethyl orthosilicate)<sup>11–13</sup> were used, resulting in biomorphous SiC ceramics. In the other hand, there are only a few investigations about biomorphous oxide-based ceramics. SiO<sub>2</sub>-, Al<sub>2</sub>O<sub>3</sub>-, TiO<sub>2</sub>- and ZrO<sub>2</sub>- ceramics were prepared from pine wood, as well as from cellulose fiber performs, *via* a sol–gel process with metal-alkoxides.<sup>14–16</sup> However, it seems that no work has been performed to-date on the synthesis of biomorphic ceramics using colloidal silica. Hence, the present work was focused on the synthesis of porous SiC and SiO<sub>2</sub> ceramics by the annealing of premineralized wood with colloidal silica under an argon or ambient atmosphere, respectively.

#### EXPERIMENTAL

Fir wood was used as the biological template structure. Fir is a coniferous wood which exhibits a monomodal pore distribution with a mean pore diameter of about 20 μm. Colloidal silica was used as the precursor for infiltration. The infiltration/annealing process is described by the schematic diagram in Fig. 1. The fir wood was shaped (10×5×5 mm<sup>3</sup>) and dried at 70 °C

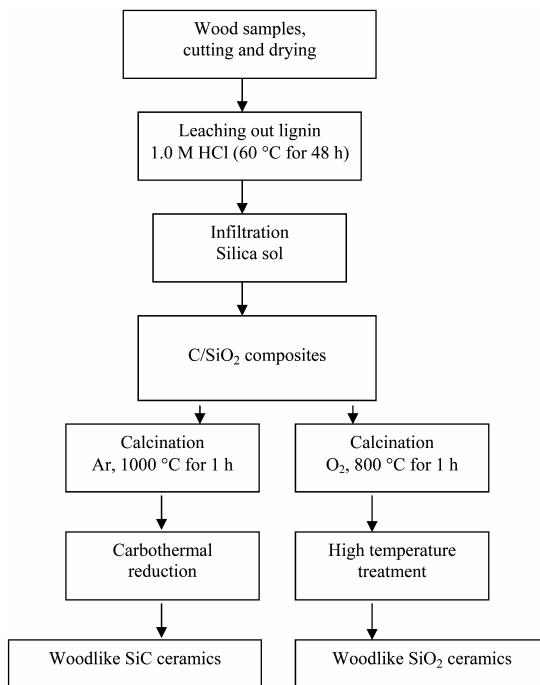


Fig. 1. Flow chart for the manufacture of biomorphic SiC and SiO<sub>2</sub> ceramics.

for 48 h. The dry wood pieces were soaked at 60 °C for 48 h in 1.0 M HCl solution to leach out the lignin and again dried at 60 °C for 48 h. Pieces of treated wood were placed in an infiltration vessel and then backfilled with silica sol, followed by raising the pressure in the vessel up to 5.0 bar. The wood/silica samples were then dried at 110 °C for 8 h.

Two types of experiments were performed. In the first ones, samples were calcinated at 1000 °C under an Ar atmosphere for 1 h. The final thermal treatment was accomplished in a graphite-heated furnace (Astro, USA) under a 0.10 MPa Ar atmosphere at a heating rate of 10 °C min<sup>-1</sup> to 1450 °C and maintained at this temperature. The samples were cooled down to room temperature under Ar. In the second experiments, the samples were calcinated under ambient atmosphere up to 1300 °C.

Scanning electron microscopy (SEM/EDX) analyses were performed on the "as obtained" surfaces using a JEOL 6300F microscope at 3.0 kV accelerating voltage.

The crystalline phases were identified by X-ray diffraction (XRD) analysis using filtered CuK $\alpha$  radiation (Siemens D5000). For this purpose, the carbon from the samples of experiment one was burnt out at 700 °C in air.

#### RESULTS AND DISCUSSION

The XRD pattern of the infiltrated wood sample after calcination at 1000 °C for 1 h shows that the obtained C/SiO<sub>2</sub> composite was amorphous (Fig. 2). Two broad peaks centered at around 25 and 44° correspond to the (002) and (004) peaks of carbon.<sup>17</sup>

The phase evolution of the C/SiO<sub>2</sub> composite during heat treatment under an argon atmosphere is depicted in Fig. 3. At 1250 °C there was no evidence of SiC peaks but many weak peaks of SiO<sub>2</sub> (cristobalite) appeared, suggesting that the amorphous silica recrystallized at this temperature. Simultaneously, the baseline line was still high, indicating a rather large amount of amorphous carbon and silica. At 1350 °C, the peaks of the  $\beta$ -SiC phase at  $2\theta = 35.68$  and  $60.00^\circ$  were observed, suggesting that carbothermal reduction of silica occurred with the formation of SiC. This was confirmed at 1450 °C, when the high baseline line and the peaks of cristobalite nearly completely disappeared and only the  $\beta$ -SiC peaks existed. Thus, the carbothermal reduction reaction was nearly completed after annealing at 1450 °C for 4 h.

The SEM micrographs of a composite prepared from fir charcoal impregnated with SiO<sub>2</sub> sol and calcinated at 1000 °C as well as the corresponding SiC ceramics obtained at 1450 °C are shown in Fig. 4. In both cases, the porous morphology retains the same structural features as those of fir wood. It was found that the thickness of the SiC-cell wall material, *i.e.*, struts, were less than 1  $\mu\text{m}$ . Cellular SiC ceramic has preferentially oriented pores of diameter up to 5  $\mu\text{m}$ . Energy dispersive spectroscopy (EDS) analysis of the obtained SiC material revealed the peak of Si without O, confirming the results of the measurements. Thus, the porous C/SiO<sub>2</sub> composite was completely converted into SiC ceramic with a similar microstructure.

On the other hand, the C/SiO<sub>2</sub> composite heat treated under an ambient atmosphere at 800 °C was shown by XRD analysis to be still amorphous. How-

ever, weak peaks of SiO<sub>2</sub> (tridimite) appeared, indicating crystallization of the amorphous material. The XRD pattern of the composite treated at higher temperatures exhibited sharp peaks of crystalobalite (SiO<sub>2</sub>) and small ones of tridimite (SiO<sub>2</sub>). Thus, the XRD analysis showed that after calcination of the infiltrated wood sample under an ambient atmosphere, the carbon was evaporated and the amorphous SiO<sub>2</sub> was transformed into crystalline phases (Fig. 5).

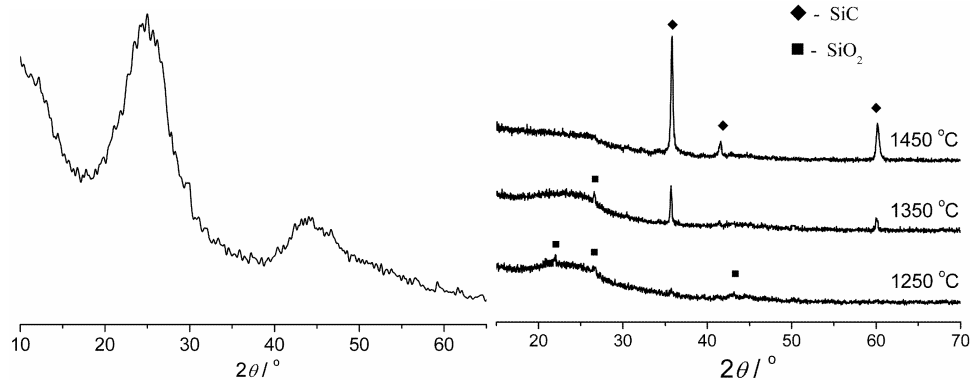


Fig. 2. XRD Pattern of the C/SiO<sub>2</sub> composite.

Fig. 3. XRD Patterns of the products obtained from C/SiO<sub>2</sub> composites under an argon atmosphere at different temperatures for 4 h.

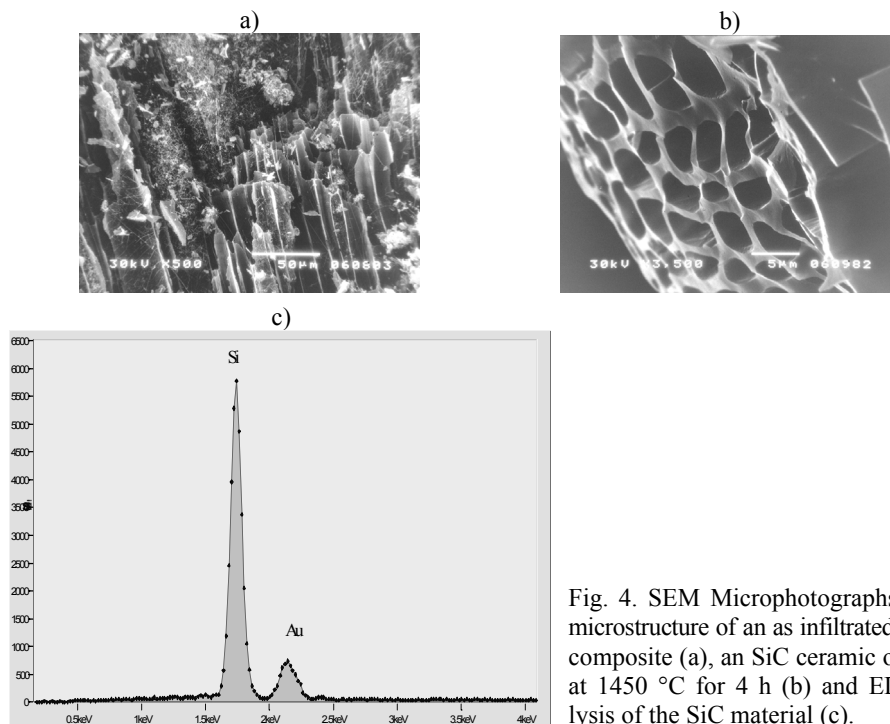


Fig. 4. SEM Microphotographs of the microstructure of an as infiltrated C/SiO<sub>2</sub> composite (a), an SiC ceramic obtained at 1450 °C for 4 h (b) and EDS analysis of the SiC material (c).

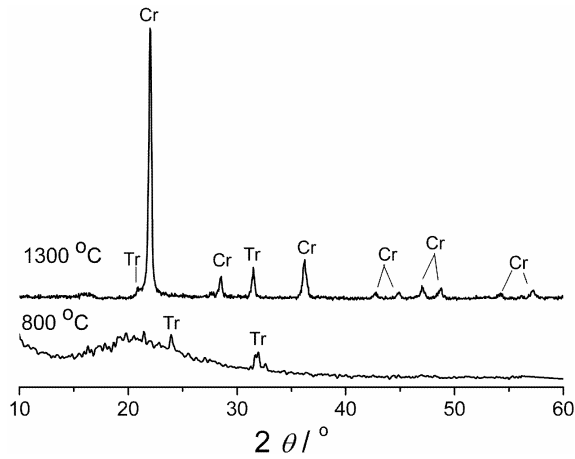


Fig. 5. XRD Patterns of the products obtained from an C/SiO<sub>2</sub> composite under an ambient atmosphere annealed for 4 h (Cr – crystobalite, Tr – tridymite).

The SEM micrographs of the resulting SiO<sub>2</sub> ceramics are shown in Fig. 6. Its morphology in the tangential direction depicts a structure similar to that of the starting wood sample. In comparison with the microstructure of the SiC ceramics, the SiO<sub>2</sub> ceramics possess small pits of 2–3 μm in diameter (Fig. 6b). They were formed during carbon evaporation. The cross sections, perpendicular to the axial direction (Fig. 6c), reveal tracheidal pore channels of diameter up to 10 μm.

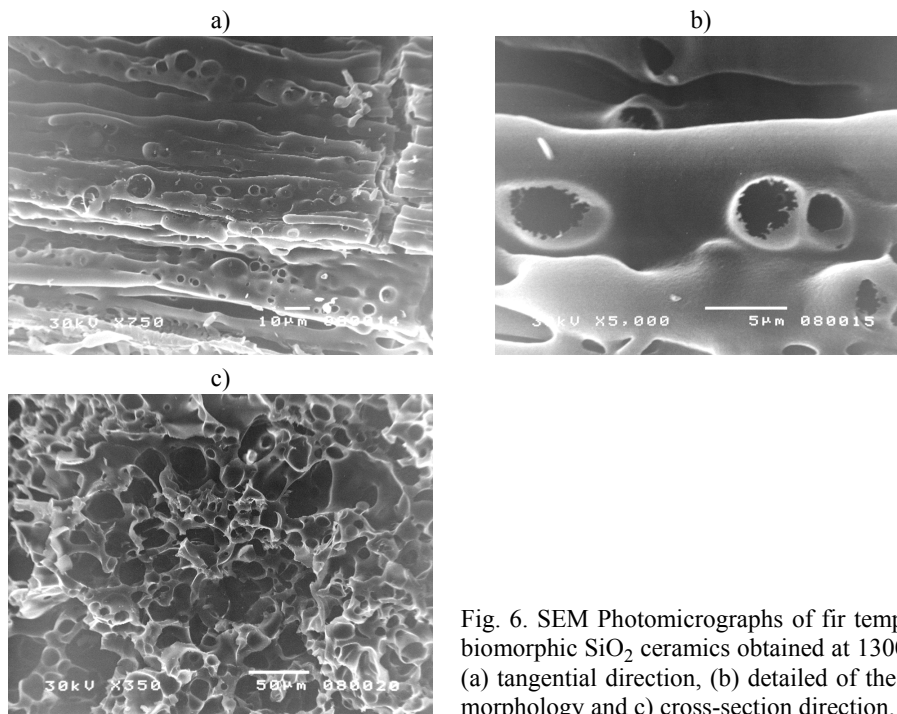


Fig. 6. SEM Photomicrographs of fir template biomorphic SiO<sub>2</sub> ceramics obtained at 1300 °C (a) tangential direction, (b) detailed of the pits morphology and (c) cross-section direction.

The mechanism of SiC ceramics formation can be explained by the reaction of SiO vapor, obtained during the reduction of silica, and the carbon wall under an inert protective atmosphere.<sup>18</sup> In contrast, the SiO<sub>2</sub> ceramics with a wood-like structure depend on stable films of infiltrated colloidal silica onto the carbon template,<sup>19,20</sup> which remain after heat treatment and loss of carbon.

#### CONCLUSIONS

This study demonstrated the conversion of biological cellular tissues structures into a porous ceramic. This porous ceramic with a wood-like microstructure was prepared by sol infiltration and carbothermal reduction techniques using colloidal silica and fir wood as the starting materials. A SiC ceramic was obtained at 1450 °C under an argon atmosphere. XRD Analysis reveals  $\beta$ -SiC as the only phase present in the cellular SiC product. A SiO<sub>2</sub> ceramic was formed at 1300 °C with crystallobalite as the principal phase, after annealing under an ambient atmosphere. This technique provides promising future applications for advanced materials design.

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#### ИЗВОД

#### СИНТЕЗА БИОМОРФНЕ SiC И SiO<sub>2</sub> КЕРАМИКЕ

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Карбонизовано дрво јеле је инфилтрирано под притиском са колоидним SiO<sub>2</sub>, а затим конвертовано у биоморфну SiC и SiO<sub>2</sub> керамику *in situ* реакцијом између Si и C на високој температури. Морфологија и фазни састав резултујуће оксидне/неоксидне керамике испитивани су скенирајућом електронском микроскопијом (SEM/EDX) и рендгено-структурном анализом (XRD). Резултати су показали да се основна ћелијска морфологија дрвета у SiC и SiO<sub>2</sub> керамици очувала и после третмана на високим температурама.

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#### REFERENCES

1. R. A. Parham, R. L. Gray, in *Advances in Chemistry, Series 207*, R. Rowell, Ed., American Chemical Society, Washington, DC, 1984
2. P. Griel, *J. Eur. Ceram. Soc.* **21** (2001) 105
3. J. Shin, C. Wang, G. J. Eharhus, *Adv.Mater.* **17** (2005) 73
4. C. R. Rambo, J. Cao, O. Rusina, H. Sieber, *Carbon* **43** (2005) 1147
5. O. Guanjun, M. Rong, C. Ning, Z. Chunguang, J. Zhihao, *J. Mater. Process. Technol.* **120** (2002) 10
6. T. Ota, M. Takahaski, T. Hibi, M. Ozava, S. Suzuki, Y. Hikicki, H. Suzuki, *J. Am. Ceram. Soc.* **78** (1995) 3409
7. E. Vogli, H. Sieber, P. Greial, *J. Eur. Ceram. Soc.* **22** (2002) 2663

8. E. Vogli, J. Mukerji, C. Hoffmann, R. Kladny, H. Sieber, P. Greial, *J. Am. Ceram. Soc.* **84** (2001) 1236
9. H. Sieber, E. Vogli, F. Muler, P. Greial, N. Popovska, H. Gerhard, G. Eming, *Key. Eng. Mater.* **206–213** (2002) 2013
10. M. Sighn, J. A. Salem, *J. Eur. Ceram. Soc.* **22** (2002) 2709
11. T. Ota, M. Takahashi, T. Hibi, M. Ozava, S. Suzuki, Y. Hikichi, *J. Am. Ceram. Soc.* **78** (1995) 3409
12. B. Matović, A. Egelja, B. Babić, J. Gulicovski, E. Volceanov, S. Bošković, *J. Optoelectron. Adv. M.* **10** (2008) 549
13. H. Sieber, A. Kaindl, D. Schwarze, J. P. Werner, P. Greil, *Efi/Ber. DKG* **77** (2000) 21
14. J. Cao, C. R. Rambo, H. Sieber, *J. Porous Mater.* **87** (2004) 163
15. C. R. Rambo, J. Cao, H. Sieber, *Mater. Chem. Phys.* **11** (2004) 345
16. J. Cao, O. Rusina, H. Sieber, *Ceram. Int.* **30** (2004) 1971
17. C. E. Byrne, D. C. Nagle, *Carbon* **35** (1997) 267
18. H. P. Martin, R. Ecke, E. Muller, *J. Eur. Ceram. Soc.* **18** (1998) 1732
19. H. Sieber, *Mater. Sci. Eng. A* **412** (2005) 43
20. Y. Shin, J. Liu, J. Chang, Z. Nie, G. Exarhos, *Adv. Mater.* **13** (2001) 728.