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Effect of processing on the microstructure and crystalline phase composition of wood derived porous SiC ceramics

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Abstract

Pine (*Pinus silvestris*) wood samples were dried and impregnated with a SiO_2 sol from a sol–gel process. The impregnation involved a two step process in a custom-made apparatus. Impregnated samples were dried and pyrolised at 500 °C under an oxygen-free atmosphere. SiC synthesis was performed in a high-temperature furnace in an argon atmosphere at a temperature of 1600 °C for 2, 4 and 8 h. The samples were investigated with X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The changes in the SiC synthesis time at the maximum temperature lead to changes in the microstructure and crystalline phase composition. An increase in the synthesis time opens up the possibility to produce mainly α-SiC crystalline modification containing porous SiC ceramics.

Keywords: A. Sol–gel process; B. Whiskers; Electron microscopy D. SiC; Wood

1. Introduction

SiC ceramics with a wood-like microstructure, in which wood is used as the carbon precursor, represent a relatively new research area in the 21st century. One of the most promising applications is for solar energy absorbers in volumetric solar receivers that require porous ceramics with open porosity, excellent solar energy absoption and high thermal conductivity. It is well known that SiC ceramics, having larger grain sizes and the addition of α-SiC, produce higher thermal conductivity values.

In the recent years, several technologies have been developed for making porous SiC ceramics with a wood-like microstructure.[1] The evaluation of the previously published research, with attention to the crystalline phase composition of wood-like SiC ceramics, allows summarising the present capabilities. The use of reactive infiltration with Si-containing melts at 1500–1600 °C for 1–2 h only forms the β-SiC crystalline phase[2,3] or β-SiC and a small amount of α-SiC.[4] The reactive silicon vapour infiltration at 1600 °C for 4–8 h only produces the β-SiC crystalline phase.[5,6] However, heating at 1550 °C for 4–16 h forms a small amount of α-SiC that decreases by extending the reaction time.[7] Obtaining wood-like SiC ceramics using SiO_2 sol impregnation with the following carbothermal reactions in the temperature ranges from 1300 to 1600 °C for 30 min to 4 h, β-SiC[8–10] and, as reported in some publications, additionally a small amount of α-SiC[11–16] (somewhere described as stacking faults of cubic lattice[17,14,18]) are detected.

In the synthesis of SiC-containing ceramics via other technologies based on carbothermal reactions, the α-SiC crystalline phase is not determined even at so high-temperature conditions as 1800 °C for 30 min[19] using pulse current sintering and 2000 °C for 30 min[20] using reaction sintering.

In the current research, the possibility of obtaining low-temperature cubic β-SiC crystalline modification, low-temperature cubic β-SiC and high-temperature α-SiC crystalline modification composite, and mainly high-temperature α-SiC crystalline modification containing porous SiC ceramics was shown. Besides the changes in the crystalline modification, also changes in the microstructure of the ceramics and whiskers formed in the pores of the samples were demonstrated. The thickness of the average SiC layer versus time was measured and discussed, comparing to the previous results available in the literature.

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2. Experimental procedure

2.1. Material preparation

Pine wood (*Pinus silvestris*) samples were prepared with dimensions of 20 mm × 20 mm × 5 mm (axial). Wood samples were placed in a self-made impregnation vessel, evacuated for 5 min at 520 mbar, and then showered with a SiO_2 sol and delayed for 5 min before increasing the pressure to atmospheric conditions. Samples with the SiO_2 sol were compressed at 30 MPa for 5 min in a custom-made hydraulic isostatic press, drained and then dried in an oven at 105 °C for 24 h. Impregnation cycles were repeated 3 times to achieve the necessary SiO_2 content in the sample. Pyrolysis was performed in an oxygen-free atmosphere for 30 min at 500 °C with the heating and cooling rate 120 °C/h.

More details are available in the previously published papers.[1,21]

2.2. Synthesis of silicon carbide

The synthesis of SiC was performed in a modified high-temperature furnace (LHT 04/17, Nabertherm (Germany)). To maintain an inert atmosphere during the SiC synthesis, argon was introduced in the furnace. The temperature was raised to 1600 °C at 300 °C/h, and the samples were held for 2, 4 and 8 h.

2.3. Characterisation

X-ray diffraction (XRD) was applied to identify the crystalline phases over a 2θ range of 15–75 in a powder X-ray diffractometer (PANalytical X'Pert Pro, The Netherlands), using Cu Kα radiation at 40 kV and 30 mA.

The morphology of the microstructure was observed from the fracture surface of the samples using a field emission scanning electron microscope (FE-SEM) (Tescan Mira/LMU, Czech Republic) at 25 kV and a distance of 7 mm.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows XRD patterns of pine wood, impregnated 3 times, and held heated at 1600 °C. Holding the samples for 2 h at 1600 °C (Fig. 1a), mainly a *3C-SiC* crystalline modification is formed, with maxima at 2θ 35.84°, 41.85°, 60.23° and 72.00°. The maximum at 2θ 33.85° (marked with *) is characteristic for the stacking faults in the *3C-SiC* crystalline lattice. The maximum at 2θ 22.16° represents SiO_2 cristobalite and suggests an incomplete reaction between SiO_2 and biocarbon (C_B) at 1600 °C for 2 h. Cristobalite is no longer present after heating at 1600 °C for 4 h (Fig. 1b), and the sample represents a *3C-SiC* crystalline phase. A small amount of *2H-SiC* is present, as is revealed by the diffraction peaks at 2θ 38.45° and 64.85°. Upon the heating for 8 h, the *12R-SiC* crystalline phase begins to form (Fig. 1c). Then the phase composition includes *3C-SiC*, *2H-SiC* and *12R-SiC*. The maxima characteristic for the *12R-SiC* crystalline phase are located at 2θ 35.84°, 41.73°, 44.70°, 60.39°, and 72.17°. The diffraction peaks from the different phases overlap and are difficult to differentiate. It can be concluded that the main components are *2H-SiC* and *12R-SiC* as can be seen from the 80% intensity of the 2θ 38.45° and the 50% intensity of the 2θ 64.85° diffraction maxima for *2H-SiC*, and from the 10% intensity of the 2θ 44.70° diffraction maximum for *12R-SiC*. The amount of *3C-SiC* decreases with time as shown by the shift of the diffraction maximum from 2θ 33.85° to 33.96° to form *2H-SiC*. In all cases, the broad maxima indicate the formation of fine crystals.

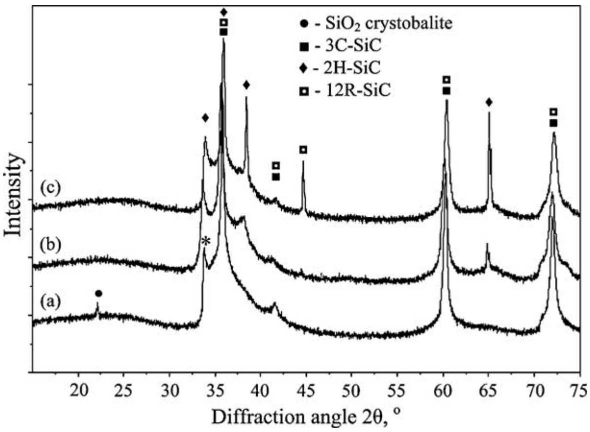

Fig. 1. XRD diffraction patterns of samples heated to 1600 °C for (a) 2 h, (b) 4 h and (c) 8 h.

A great amount of *2H-SiC* and *12R-SiC* is formed from the SiO_2 sol impregnation into the wood, as compared to the results reported in other publications.[8–18] This can be explained by the close contact between the SiO_2 and biocarbon (C_B) in the pore walls from the vacuum/pressure impregnation, followed by the pyrolysis of the obtained SiO_2 gel/wood composite.[21] In this case, a significant amount of SiO_2 was introduced into the wood cell wall, and SiO_2 was enclosed in the amorphous C_B matrix during pyrolysis. The formation of the high-temperature SiC crystalline phase at 1600 °C can be facilitated also by the presence of different impurities (e.g. Na, K, Ca, etc.) in the C_B matrix, which are retained in the wood derived SiC ceramics.[22]

3.2. FE-SEM analysis

FE-SEM micrographs show the effect of holding time at 1600 °C on the microstructure. The samples held at 1600 °C for 2 h show a SiC layer on the pore walls (Fig. 2b). The non-reacted C_B is found deeper in the pore walls, between the SiC layers. The transverse direction shows a tubular SiC structure (Fig. 2c) and porous walls (Fig. 2d) with interconnected pores.

The grain size in the walls ranges from 100 to 200 nm.

The porous SiC ceramics formed at 1600 °C for 4 h have rounded tubular parallel pores, corresponding to the tracheids in the wood structure (Fig. 3(a)).

The microstructure of the ceramics has characteristics, similar to those of the wood microstructure. Openings are seen at some sites of the pore walls, formed from the pits present in pine wood.[23] The longitudinal pore size in SiC is 10–20 μm,

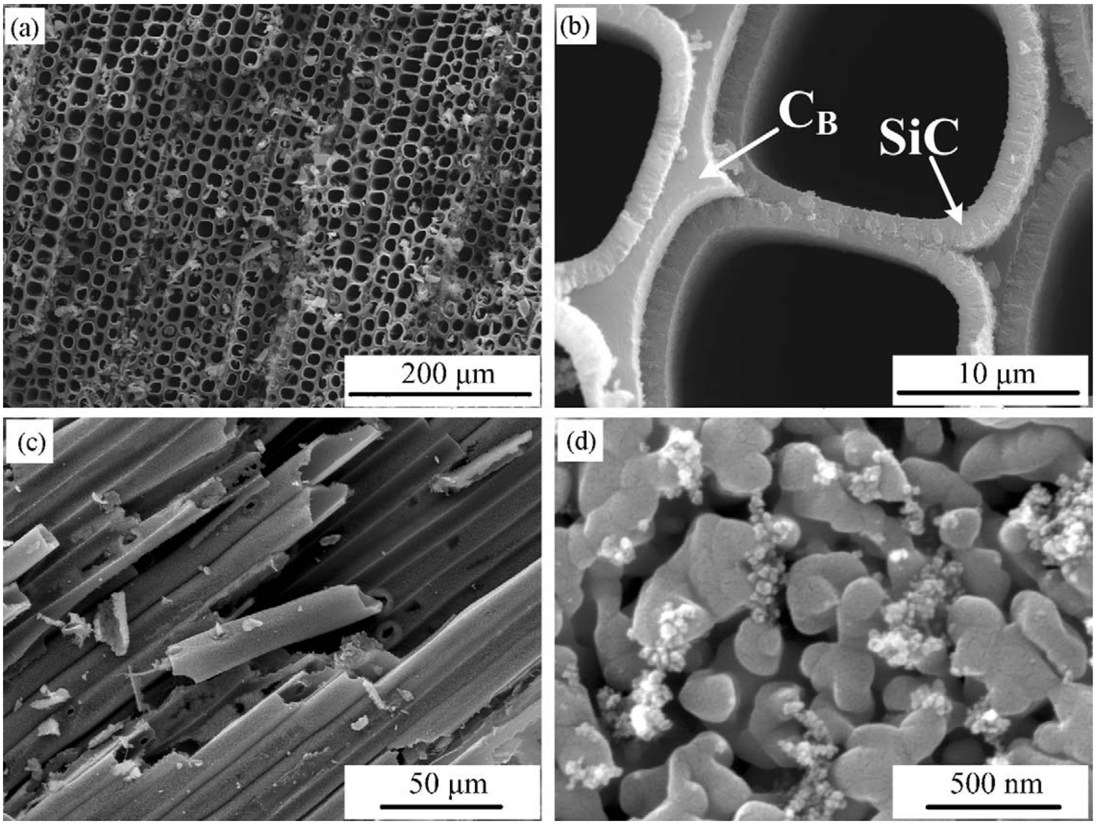

Fig. 2. Cross-section (a) and (b), and transverse (c) and (d) FE-SEM microphotographs of the samples treated at 1600 °C for 2 h.

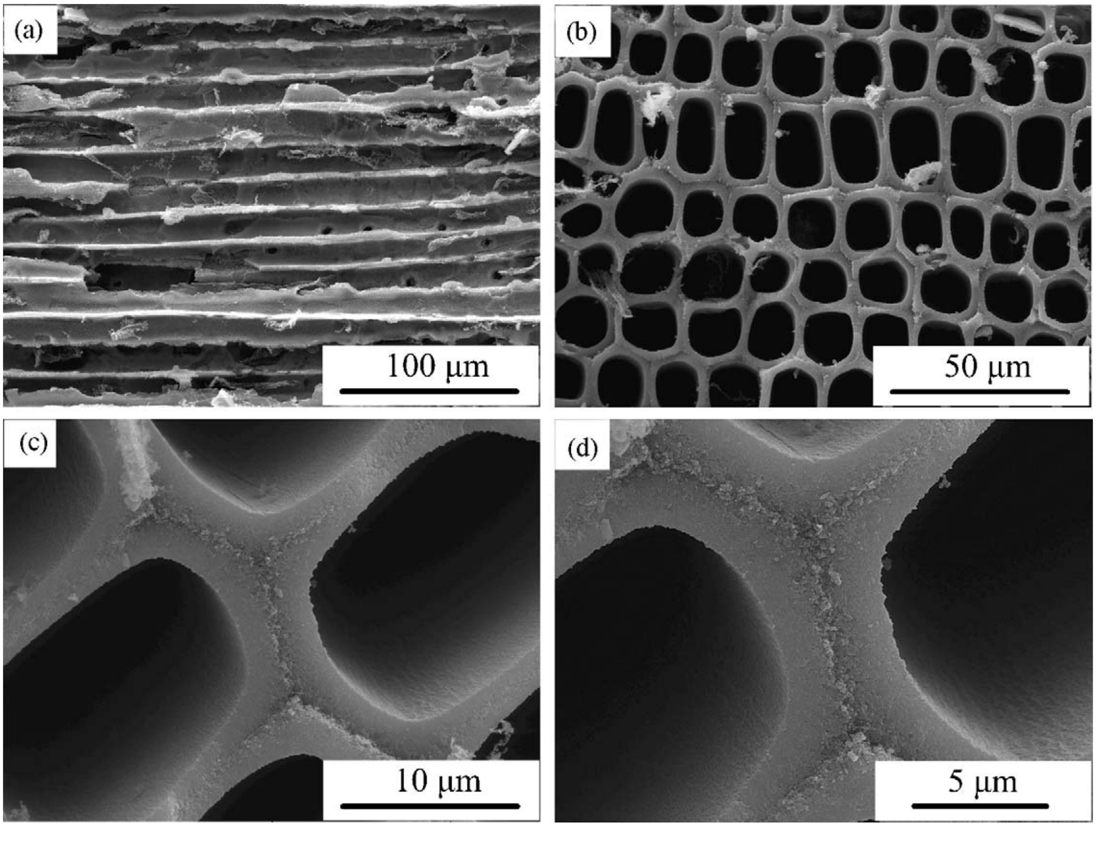

Fig. 3. Transverse (a) and cross-section (b–d) FE-SEM microphotographs of the samples treated at 1600 °C for 4 h.

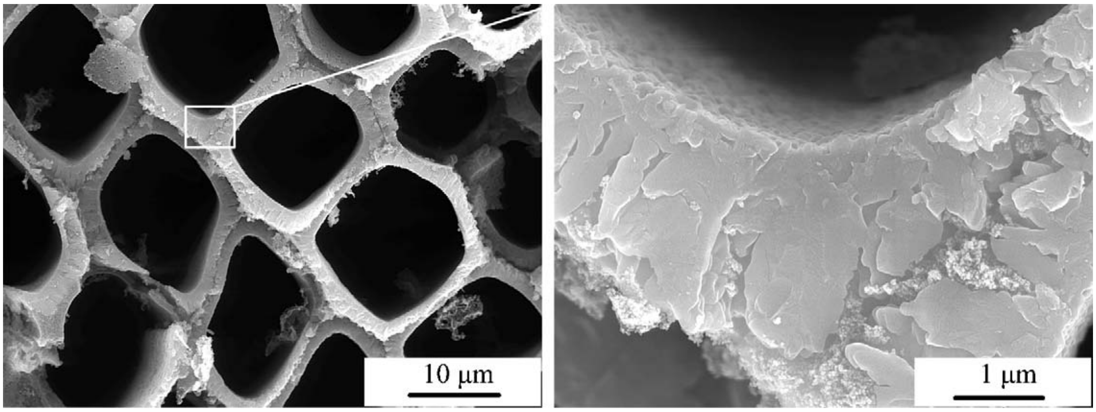

Fig. 4. Cross-section FE-SEM microphotographs of the samples treated at 1600 °C for 8 h.

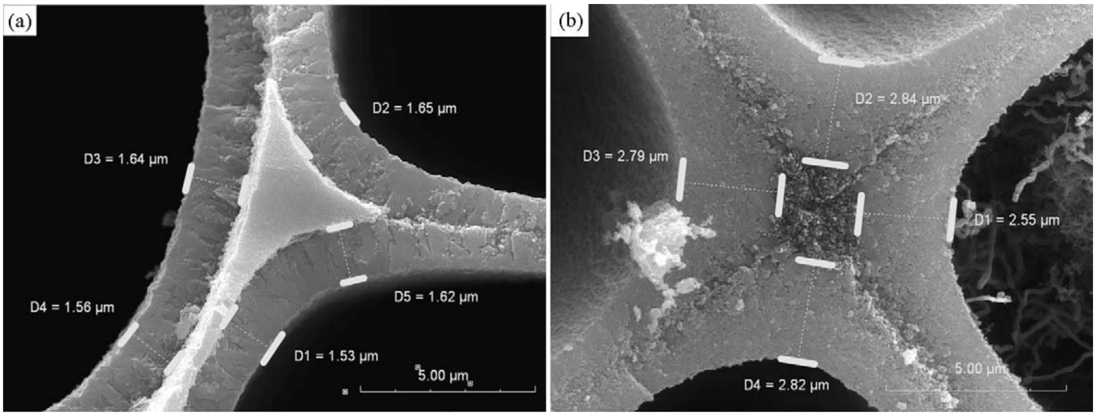

Fig. 5. Cross-section FE-SEM microphotographs of the sample treated at 1600 °C for (a) 2 h and (b) 4 h.

and the wall thickness is 3–5 μm (Fig. 3(b and c)). The analysis of the pore wall microstructure reveals that the porosity varies throughout the volume. The walls' outer layer is denser than the inner zone. The grain size in the walls is 50–200 nm (Fig. 3(d)).

Heat treatment for 8 h leads to a more variable microstructure with grains 1 μm in size. A similar observation can be made for the samples held for 4 h. The outside of the pore walls is denser than the middle part (Fig. 4). Such changes in the microstructure occur under the action of temperature and time that lead to grain recrystallisation and phase change, as confirmed by XRD patterns (Fig. 1).

The growth of the SiC layer begins at the pore wall surface and continues into the wall at the SiC–C_B interface.

Treating the samples for 2 h at 1600 °C, non-reacted carbon is retained in the pore walls. Treating the samples for 4 h, nearly all the carbon is consumed. Only small regions remain non-reacted (Fig. 5).

Measurement of the layer thickness formed within 2 and 4 h allows the determination of the average SiC layer thick-

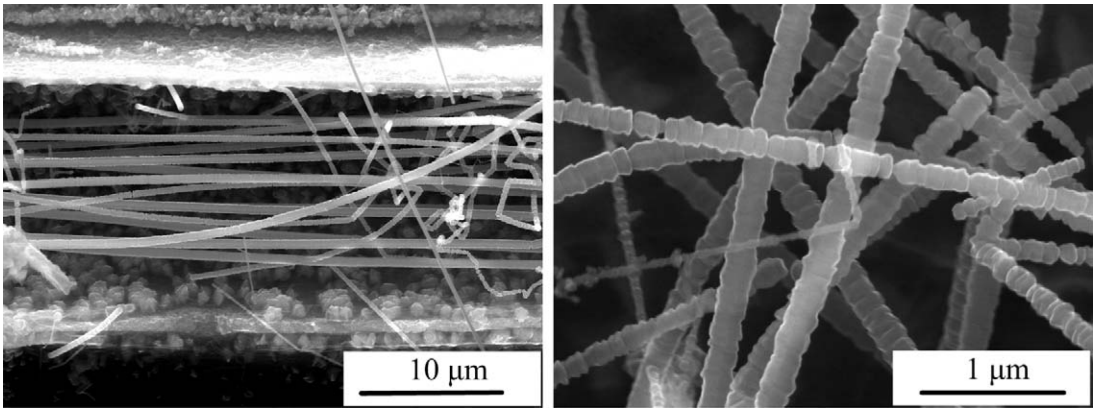

Fig. 6. FE-SEM microphotographs of the whiskers formed in the samples treated for 2 h.

ness versus time. With increasing time, the wall growth rate decreases, which is explained by an increase in the layer thickness that requires a longer migration time of the reaction raw materials and products. The experimentally obtained growth rate of 0.7–0.8 μm/h (at 1600 °C) is higher than the theoretically calculated 0.3 μm/h at the temperature 2000 °C,[24] when the reaction products diffuse throughout the SiC volume. The fact that the growth rate is higher than the theoretical growth rate can be explained by the porous SiC layer, which facilitates the migration of the reaction raw materials and end products.

The treatment of the samples at 1600 °C produces SiC whiskers as by-products of the porous SiC ceramics. With increasing treatment time, whiskers change their shape and

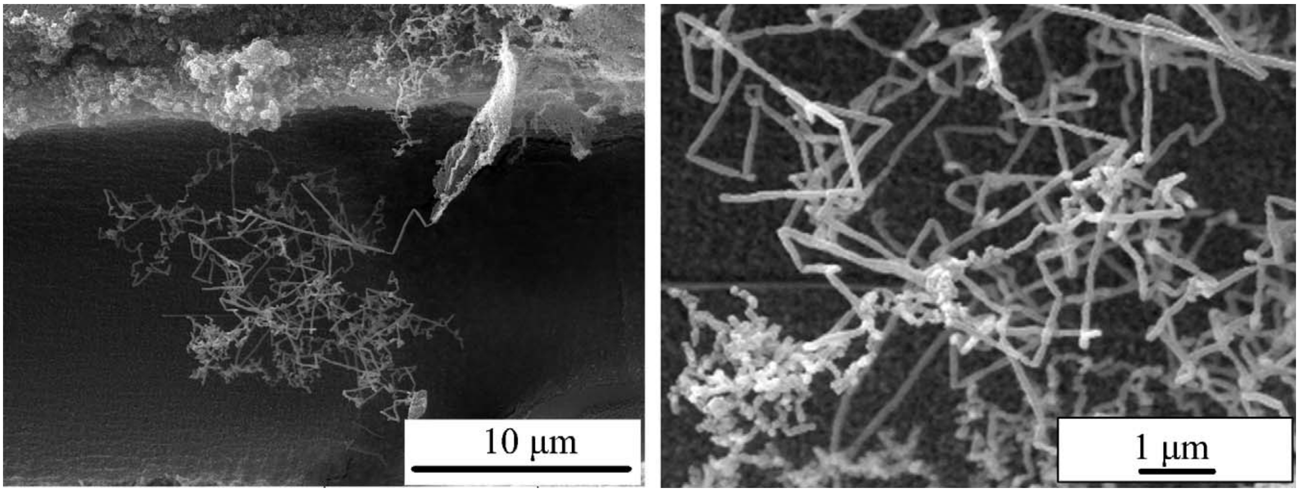

Fig. 7. FE-SEM microphotographs of the whiskers formed in the samples treated for 4 h.

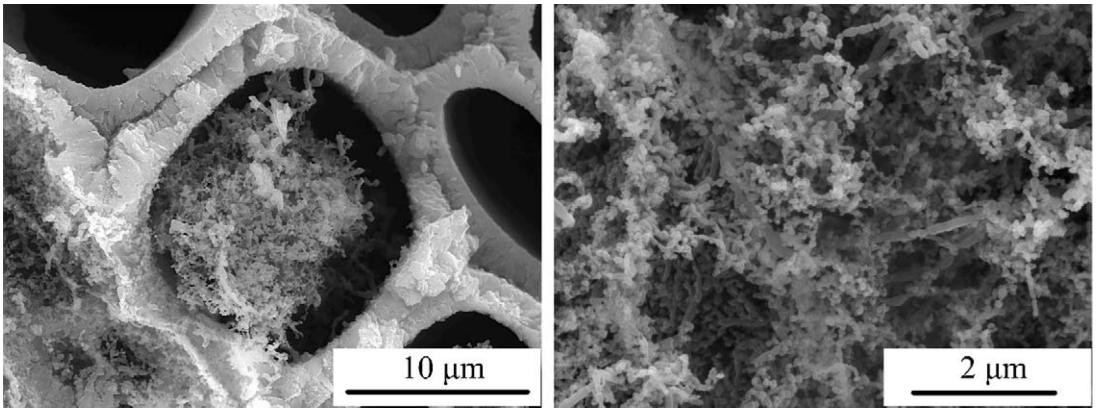

Fig. 8. FE-SEM microphotographs of the whiskers formed in the samples treated for 8 h.

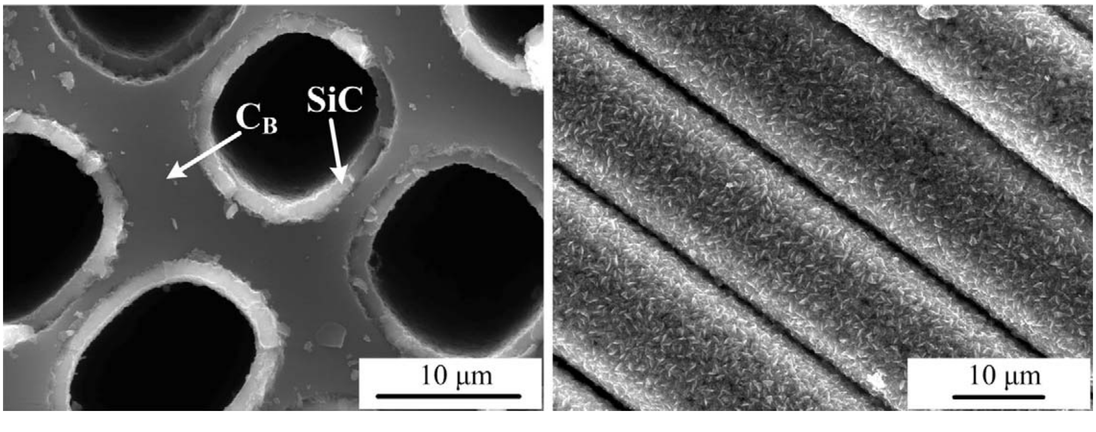

Fig. 9. FE-SEM microphotographs of SiC tubes formed in the samples treated for 4 h.

develop a complex three-dimensional randomly stepped structure. After 2 h, the whiskers have a diameter of 200–600 nm and a length of 100–300 μm (Fig. 6). After 4 h, the diameter is reduced to 200–400 nm, and the whiskers begin to show steps in the shape (Fig. 7). A three-dimensional net-like structure is formed after 8 h as whiskers reduce their diameter to 150–400 nm for providing the extra length in the crooked whiskers (Fig. 8).

A lower amount of SiO_2 in the samples will create SiC/C_B composites. The oxidation of the remaining C_B can produce SiC tubes (Fig. 9). The dimension of SiC tubes is determined by the microstructure of the raw material. The wall thickness of the tubes can range from hundreds of nanometres to several microns. Samples with a higher SiO_2 content can produce tubes with thicker walls. Such SiC tubes may find future application in microreactors or as microreagent injection tubes in high-temperature and chemically aggressive media.

4. Conclusions

It is possible to manufacture porous SiC ceramics with various structures and compositions. High-temperature crystalline modifications can be obtained at temperatures as low as 1600 °C by heating for 8 h. The microstructure of the SiC ceramics changes with time. The SiC whiskers develop a smaller diameter and enlarge the three-dimensional net-like structure. The control of the SiO_2 content provides the option to produce SiC tubes.

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References

1. Locs J, Berzina-Cimdina L, Zhurinsh A, Loca D. Optimized vacuum/pressure sol impregnation processing of wood for the synthesis of porous, biomorphic SiC ceramics. *J Eur Ceram Soc* 2009;**29**:1513–9.
2. Zollfrank C, Siebera H. Microstructure and phase morphology of wood derived biomorphous SiSiC-ceramics. *J Eur Ceram Soc* 2004;**24**: 495–506.
3. Esposito L, Sciti D, Pinacastelli A, Bellosi A. Microstructure and properties of porous β-SiC template from soft woods. *J Eur Ceram Soc* 2004;**24**:533–40.
4. Ha J-S, Lim BG, Doh GH, Kang I-A. Properties of porous cellular SiC ceramics derived from three kinds of wood by embedding process using Si/SiO_2 powder mixture. In: *Proc. 10th ECerS Conf.*. 2007. p. 2032–5.
5. Qian J-M, Wang J-P, Jin Z-H. Preparation and properties of porous microcellular SiC ceramics by reactive infiltration of Si vapor into carbonized brasswood. *Mater Chem Phys* 2003;**82**:648–53.
6. Vogli E, Sieber H, Greil P. Biomorphic SiC-ceramic perpetrated by Si-vapor phase infiltration of wood. *J Eur Ceram Soc* 2002;**22**:2663–8.
7. Vogli E, Mukerji J, Hoffmann C, Klandy R, Sieber H, Greil P. Conversion of oak to cellular silicon carbide ceramic by gas-phase reaction with silicon monoxide. *J Am Ceram Soc* 2001;**84**:1236–40.
8. Herzog A, Klingner R, Vogt U, Graule T. Wood-derived porous SiC ceramics by sol infiltration and carbothermal reduction. *J Am Ceram Soc* 2004;**87**:784–93.
9. Furuno T, Fujitsawa M. Carbonization of wood–silica composites and formation of silicon carbide in the cell wall. *Wood Fiber Sci* 2004;**36**(2):269–77.
10. Hata T, Castro V, Fujisawa M, Imamura Y. Formation of silicon carbide nanorods from wood-based carbons. *Fullerenes, Nanotubes, Carbon Nanostruct* 2005;**13**:107–13.
11. Shin Y, Wang C, Exarhos GJ. Synthesis of SiC ceramics by the carbothermal reduction of mineralized wood with silica. *Adv Mater* 2005;**17**:73–7.
12. Egelja A, Gulickovski J, Devecerski A, Ninic M, Radoslavljevic-Mihaljovic A, Matovic B. Synthesis of biomorphic SiC ceramics. *J Optoelectron Adv Mater* 2008;**10**(12):3447–9.
13. Qian J-M, Jin Z-H. Preparation and characterization of porous, biomorphic SiC ceramic with hybrid pore structure. *J Eur Ceram Soc* 2006;**24**:1311–6.
14. Qian J-M, Wang J-P, Qiao G-J, Jin Z-H. Preparation of porous SiC ceramic with a woodlike microstructure by sol–gel and carbothermal reduction processing. *J Eur Ceram Soc* 2004;**24**:3251–9.
15. Greil P, Vogli E, Fey T, Bezold A, Popovska N, Gerhard H, et al. Effect of microstructure on the fracture behaviour of biomorphous silicon carbide ceramics. *J Eur Ceram Soc* 2002;**22**:2697–707.
16. Sieber H. Biomimetic synthesis of ceramics and ceramic composites. *Mater Sci Eng A* 2005;**412**:43–7.
17. Qian J, Wang J, Jin Z. Preparation of biomorphic SiC ceramic by carbothermal reduction of oakwood charcoal. *Mater Sci Eng A* 2004;**371**:229–35.
18. Klinger R, Sell J, Zimmermann T, Herzog A, Vogt U, Graule T, et al. Wood-delivered porous ceramics via infiltration of SiO_2–sol and carbothermal reduction. *Holzforschung* 2003;**57**:440–6.
19. Fujitsawa M, Hata T, Bronsveld P, Castro V, Tanaka F, Kikuchi H, et al. SiC/C composites prepared from wood-based carbons by pulse current sintering with SiO_2: electrical and thermal properties. *J Eur Ceram Soc* 2004;**24**:3575–80.
20. Basu H, Godkhindi MM, Mukunda PG. Investigation on the reaction sintering of porous silicon carbide. *J Mater Sci Lett* 1999;**18**:389–92.
21. Zhurinsh A, Locs J, Berzina-Cimdina L. Investigation of the feasibility of pyrolytic obtaining of porous biomorphic SiC ceramics. *J Anal Appl Pyrol* 2009;**85**:544–8.
22. Cano Pavon JM, Vereda Alonso E, Siles Cordero MT, Garcia de Torresa A, Lopez-Cepero JM. Use of spectroscopic techniques for the chemical analysis of biomorphic silicon carbide ceramics. *Anal Chim Acta* 2005;**528**:129–34.
23. Gross KA, Ezerietis E. Juniper wood as a possible implant material. *J Biomed Mater Res Part A* 2003;**64A**(4):672–83.
24. Vogli E, Mukerji J, Hoffmann C. Conversion of oak to cellular silicon carbide ceramic by gas-phase reaction with silicon monoxide. *J Am Ceram Soc* 2001;**84**:1236–40.