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

J. Locs [a,*], L. Berzina-Cimdina [a], A. Zhurinsh [b], D. Loca [a]

[a] *Riga Technical University, Riga Biomaterials Innovation and Development Center, 3/3 Pulka Street, LV-1007, Riga, Latvia*
[b] *Latvian State Institute of Wood Chemistry, 27 Dzerbenes Street, LV-1006, Riga, Latvia*

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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.

* Corresponding author. Tel.: +371 67089605; fax: +371 67089619.
E-mail address: janis.locs@rtu.lv (J. Locs).

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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.

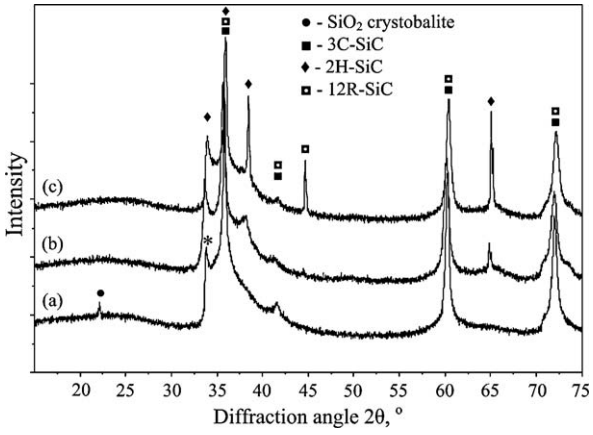

Fig. 1. XRD diffraction patterns of samples heated to 1600 °C for (a) 2 h, (b) 4 h and (c) 8 h.

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,