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Biomimetic synthesis and properties of cellular SiC

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Abstract

Biomorphous β-SiC ceramics were produced from several species of wood such as ash, wild cherry, black alder, Persian walnut, sessile oak and European hornbeam. The wood was pyrolysed, impregnated with tetraethyl orthosilicate (TEOS) sol in repeated cycles and thermally treated at 1800 °C in vacuum. Four specimen groups included charcoal and three groups with 1, 3 and 5 cycles of impregnation were analyzed. Flexural and compressional strength of charcoal and woodlike SiC ceramics were measured using three-point and compression testing in different directions. Experimental results showed that mechanical properties of woodceramics were improved by repeating of impregnation cycles. Porosity measurement, dilatometric analysis, XRD and SEM analysis were used to study the macroscopical and microscopical properties of the resulting biomorphic SiC ceramics.

Keywords: C. Mechanical properties; D. SiC; Microstructure; Biomorphic ceramics

1. Introduction

Porous ceramics is in use or in development for use in wide variety of applications. Ceramics are known for excellent performances like good friction and wear resistance, electrical properties, corrosion resistance and high specific surface [1]. Ceramics characteristics are interesting for applications such as catalyst support, battery electrodes, hot gas or molten metal filters, heat insulators, ion exchangers, water cleaners and gas sensors [2,3]. Biomorphic ceramics is a new class of structural materials with high potential for different applications. The main advantage of biomimetic preparation process for obtaining ceramic materials is abundant choice of microstructures. Wood tissue, which is usually highly anisotropic and can vary in density, is normally used as bulk template for fast high-temperature conversion into ceramics.

Wood is a natural material with a hard fibrous microstructure, good mechanical properties and good transport of fluids [4]. It is formed by the photosynthesis inside organelles called chloroplasts, which are most abundant in needles or leaves of trees. The photosynthetic process uses light energy of sun to convert carbon dioxide from air and water from soil to organic materials and oxygen. The result of this process is natural composite that has been one of the oldest engineering materials with strongly anisotropic structure. Basic units of its structure are elongated tubular cells aligned with the axis of the tree trunk and growth ring structures [5].

There are two main types of wood with basically different microstructure [6], hardwood or Angiosperms and softwood or Gymnosperms. Softwood trees have simpler microstructure with tracheids – long cells (3–5 mm) with intermediate diameter (30–50 μm) – as the single constituent. Hardwoods contain larger vessel cells – tracheas with 0.1 mm in diameter. Also, there are smaller cells with thick walls – libriform fibers, responsible for imparting mechanical resistance. Cell walls structure in hardwood and softwood is similar, and is consisted mainly of cellulose, hemicellulose and lignin.

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Charcoal is an amorphous carbon material made by pyrolysis from natural wood or wood fiber. Above 600 °C pyrolysis results in complete decomposition of polyaromatic constituents of wood. Microstructure of charcoal is similar to that of tree with carbon atoms instead of organic macromolecules. Charcoal has interesting properties such as good electrical conductivity and self-lubricity, and can be used as friction material and electromagnetic shield material [7].

As carbon preform, charcoal can be used for fabrication of woodceramics. It can be infiltrated with organosilicon compounds in the sol–gel process [8–10,17], or liquid or gaseous silicon bearing precursors such as silicon melt, silicon or silicon monoxide vapor. The result of carbothermal reduction above 1300 °C is a C/SiC or Si/SiC composite that replicates the microstructure of the wood with SiC, while the unreacted carbon remains within, or unreacted silicon fills wood channels [11]. The diversity of wood species provides a wide choice of structures, in which the density and the anisotropy are the main factors of the final microstructure and mechanical properties of the material.

2. Material and methods

2.1. Material preparation

Samples were prepared from pear, field elm, ash, wild cherry, black alder, Persian walnut, sessile oak and European hornbeam. Wood was machined into rectangular specimens with dimensions of ca. 70 mm × 5 mm × 5 mm. The wood was cut in two directions. One direction was parallel with growth direction of wood – axial, and the other was perpendicular – radial/tangential. After cutting to final shape, the specimens were stored for fifteen days at the same conditions (room temperature and humidity) in order to equalize humidity levels in wood. After densities calculation, five species were selected for pyrolysis (ash, wild cherry, black alder, Persian walnut and sessile oak). Samples were pyrolyzed at 850 °C in nitrogen flow with heating rate of 1 °C/min and 2 h of holding time. Slow heating rate was used for decomposing processes of hydrocarbon polymers (cellulose, hemicelluloses and lignin) to carbon with intact microstructure. Silica sol was prepared using tetraethyl orthosilicate (TEOS), ethyl alcohol and distilled water at a suitable molar ratio of 1:4:12 with addition of small amount of acetic acid to obtain pH=4, optimal for increasing gelation rate. In the sol–gel process samples of pyrolyzed wood were placed at sol in a glass vessel in vacuum at room temperature. After treatment with TEOS, samples were calcinated in nitrogen flow at 950 °C with heating rate of 2 °C/min and 2 h of holding time to obtain transformation of sol to silica. Repeating impregnation cycles up to 5 times produced four specimen groups (charcoal without impregnation, 1, 3 and 5 cycles). Carbothermal reduction of prepared samples was carried out in vacuum in a heater furnace at 1800 °C to form porous C/SiC ceramic. Graphite crucibles were used to hold samples of reactant silica–charcoal. Furnace temperature was raised up to the desired temperature with a rate of 30 °C/min, and then held for 1 h to allow complete reaction of silica with carbon structure. The temperature was measured with Pt – 10% Rh termocouple (±5 °C). The scheme of whole experimental procedure is given in Fig. 1.

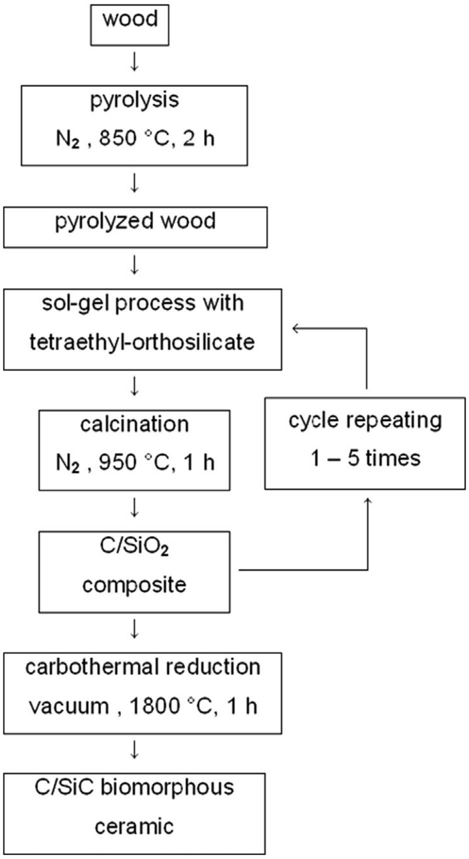


Fig. 1. Processing scheme of manufacturing woodlike SiC from wood.

2.2. Characterization

Specimens dimensions before and after carbonization were measured using a digital slide caliper. Mass changes were measured by analytical balance Mettler and used in density calculation. Pore-size distribution was determined by the Carlo Erba Series 2000 mercury intrusion porosimeter. Flexural and compressional strength of charcoal and woodlike SiC ceramics were characterized using three-point and compression testing at Instron M 1185 universal testing machine. Tests were conducted using Instron test fixtures at room temperature with five to twelve specimens of each group. Crosshead speed was 1 mm/min for all testing.

The XRD patterns of charcoal and biomimetic SiC were recorded using X-ray diffractometer Rigaku Ultima IV with nickel filtered Cu K_α radiation. Morphological changes of starting material during transformation of charcoal/silica material into SiC ceramic were observed by scanning electron microscope Jeol JSM 5800LV operated at 5 kV. Thermal expansion of the biomimetic ceramic materials produced under different conditions was examined using a dilatometer Bähr RHT 08/17. Heating rate was 10 °C/min to maximum temperature of 1400 °C with 1 h holding time in vacuum. Samples

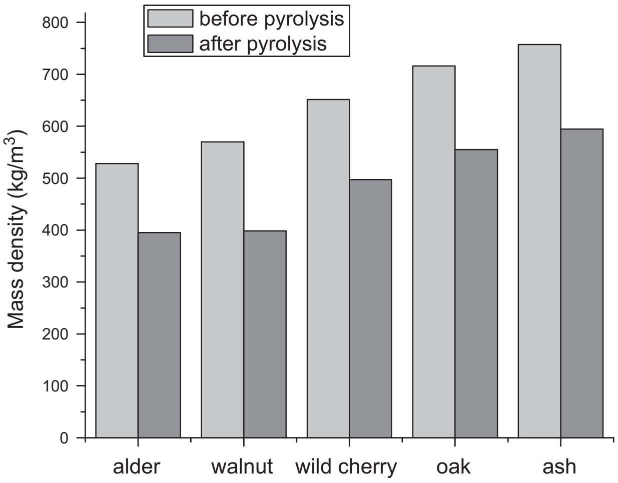


Fig. 2. Mass density before and after pyrolysis at 850 °C in nitrogen.

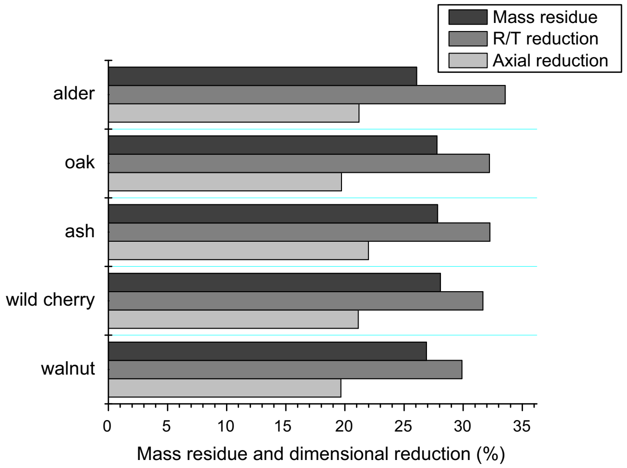


Fig. 3. Mass residue and dimensional reduction of five wood species during pyrolysis.

dimensions were checked by digital caliper before and after heating.

3. Results and discussion

3.1. Weight change

After pyrolysis, specimens were measured and analyzed. Five species of wood were chosen from eight by criteria of densities dispersion. Density was calculated from dimensional and mass measurements. The lowest density was measured in pieces of alder (528 kg/m^3), whereas the density of Persian walnut, wild cherry, sessile oak and ash were 570, 652, 716 and 758 kg/m^3 respectively. During transformation from wood to charcoal changes in density occurred and it was shown in Fig. 2.

Fig. 2 shows that alder was the lowest density wood before pyrolysis (528 kg/m^3), and the lowest density charcoal (395 kg/m^3) after pyrolysis. Also, despite 8% difference before, after pyrolysis densities of alder and walnut were almost the same, 395 and 398 kg/m^3.

Beside the change in density, there is also the change in mass and dimensions of pieces after pyrolysis. Mass and dimensions reduction results are shown in Fig. 3.

Average shrinkage was more than 10% higher in radial/tangential direction than in axial (31.9% to 20.7%). Percentage of residual mass after pyrolysis was almost the same in all five species (between 26.1% of alder and 28.1% of cherry).

3.2. Mechanical properties

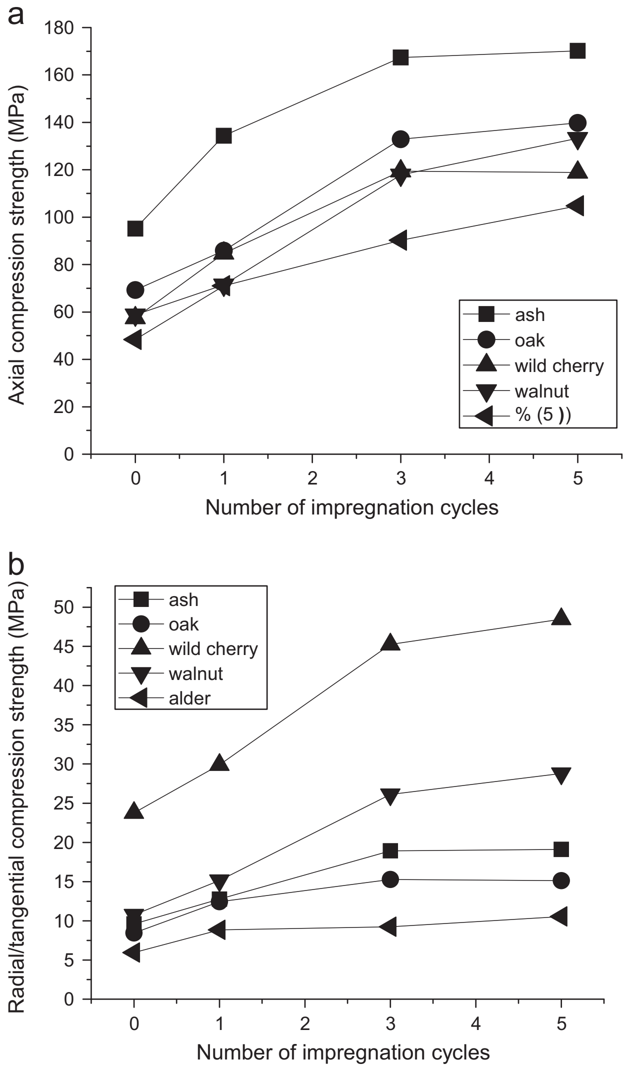


Fig. 4. Compression strengths of different wood species in (a) axial and (b) radial-tangential direction.

Mechanical properties of biomimetic ceramics were characterized by bending and compression testing in two directions, axial and radial/tangential. Charcoal as starting material shows the highest strength in axial compression, averagely 65.8 MPa. Array of wood species in axial compression is the same as in density, except for walnut and wild cherry with similar values (57 ± 6 MPa and 59 ± 4 MPa). Average charcoal radial/tangential compression strength is 11.7 MPa, axial bending 7.6 MPa and radial/tangential bending 6.0 MPa. All types of strength increase with number of impregnation cycles. Both compression strengths showed higher overall increase – 106% axial and 105% radial/tangential, than bending (86% and 73% respectively). Axial

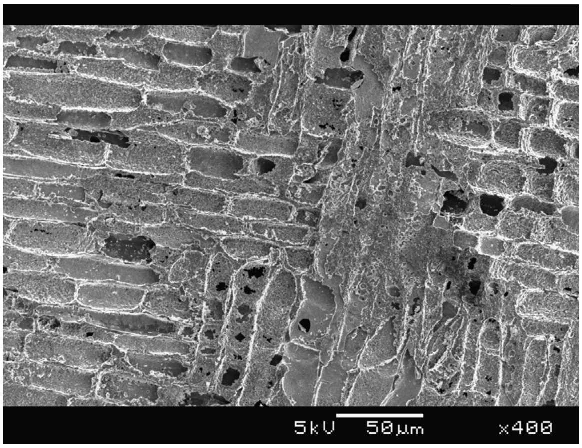


Fig. 5. Closed pores of wild cherry after five impregnation cycles.

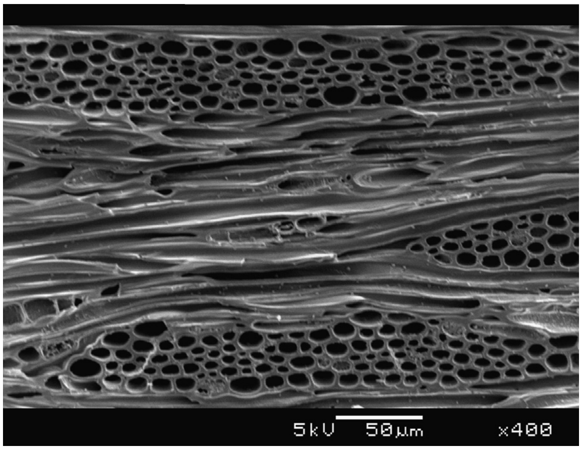


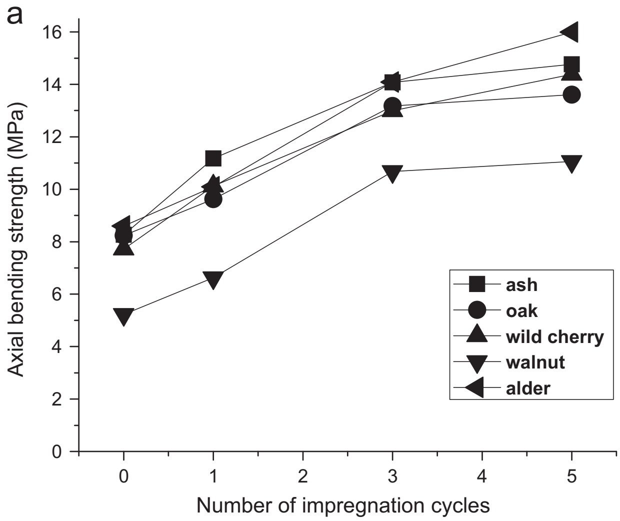
Fig. 6. Cross-sectioned woodcells in wild cherry.

compression of oak reaches value of 170 ± 13 MPa after five cycles of tetraethyl-orthosilicate impregnation. Fig. 4. shows crushing strengths for both directions.

The increase of mechanical properties is the highest after the first impregnation, 35% and 36% in axial and r/t direction respectively. Contribution of next two impregnations combined is 40% and 45%, and of the last two is only 6.3% for both directions. This happens due to closing of the charcoal pores with silica after repeated impregnations, which is clearly visible at SEM micrographs (Fig. 5). Wild cherry exhibits unusually high radial/tangential compression strength as it is shown in Fig. 4b. This can be attributed to high amount of cross-sectioned woodcells in r/t plane (Fig. 6.).

Fig. 7. shows bending strength for biomimetic ceramic with axial (a) and radial/tangential (b) orientation of longest specimen axis. Improvement of average r/t bending strength between three and five impregnation cycles is lower than that of compression strength.

Walnut shows the best improvement of mechanical properties, 128% average for all four types of strength. Ash exhibits the lowest overall properties improvement, only 76% averagely, and oak is slightly better with 78%. Changing of mechanical properties is attributed to formation of SiC layer at inner cell walls. Infiltrated sol leaves SiO_2 after reaction with water [12]:



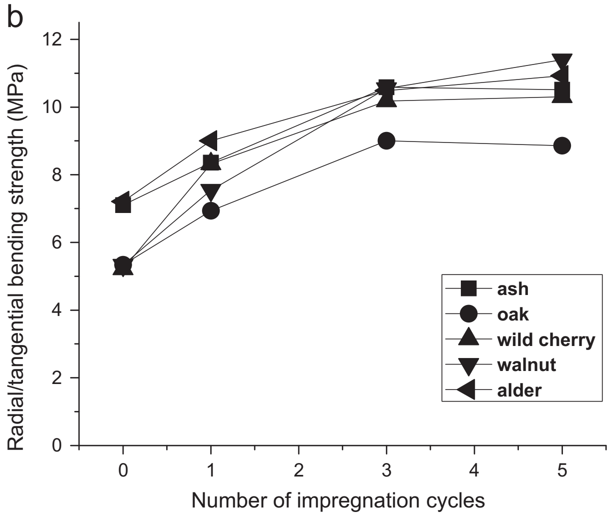


Fig. 7. Bending strengths of different wood species in (a) axial and (b) radial-tangential direction.

$$Si(OC_2H_5)_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4C_2H_5OH \quad (1)$$

Repeated infiltration increases the amount of residual silica, which is transformed to SiC during carbothermal reduction by reaction [13]:

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(v)$$

In reality this reaction proceeds through two stages with gaseous intermediate SiO [14]:

$$SiO_2(s) + C(s) \rightarrow SiO(v) + CO(v)$$

Silicon monoxide can be produced with carbon monoxide according to reaction

$$SiO_2(s) + CO(v) \rightarrow SiO(v) + CO_2(v)$$

Obtained silicon monoxide reacts with carbon

$$SiO(v) + 2C(s) \rightarrow SiC(s) + CO(v)$$

or reacts with carbon monoxide [15]

$$\mathrm{SiO(v)+3CO(v)\rightarrow SiC(s)+2CO_2(v)}$$

Under very high SiO partial pressure, gaseous SiO converts

$$\mathrm{2SiO(v)\rightarrow Si(l)+SiO_2(s)}$$

And resulting Si reacts with carbon [16]

$$\mathrm{Si(l)+C(s)\rightarrow SiC(s)}$$

Since the shape of woodcells is elongated cylindric, than newly created SiC layer at inner surface is tubular. The wall thickness of the tubes can range from hundreds of nanometers to several microns [17]. Thus, resulting biomimetic ceramic can be considered as porous composite material with amorphous carbon matrix reinforced with SiC tubes.

3.3. XRD analysis

XRD patterns of walnut charcoal and biomimetic ceramics with 1, 3 and 5 infiltration cycles are shown in Fig. 8. It can be seen at charcoals pattern (Fig. 8a) that two broad peaks are positioned around 26° and 43°. They are attributed to diffraction from the {002} plane and the overlapping {101} and {100} planes of carbon [18]. Peaks shapes suggest that charcoal is in partly graphitized amorphous state. In infiltrated samples (Fig. 8b, c and d) sharp β-SiC peaks are observed. Major peak is at Braggs angle of 35.6° (diffraction from the {111} plane of β-SiC), with other peaks at 41.4° {200}, 60.0° {220}, 71.8° {311} and 75.5° {222}. An additional peak at $2\theta=33.7°$ is characteristic for stacking faults of {111} plane in 3C SiC [19]. From XRD patterns it is obvious that carbothermal reduction temperature (1800 °C) was not sufficiently high for formation of α-SiC. Also, peaks of crystobalite (crystalline SiO_2) are absent, which suggests that silica was completely consumed by the reaction. Amount of SiC is increasing with number of infiltration cycles. Resulting material after five impregnation cycles is evidently composed of amorphous carbon and β-SiC.

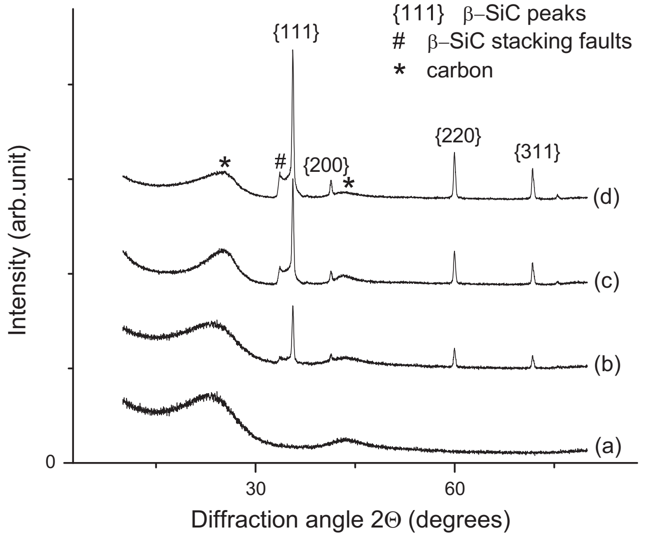


Fig. 8. XRD patterns of walnut charcoal (a) and biomimetic ceramics with 1 (b), 3 (c) and 5 (d) infiltration cycles.

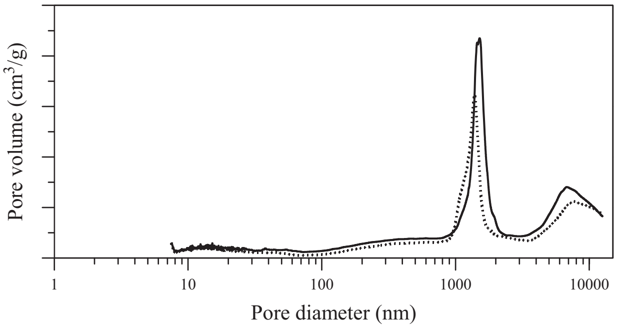


Fig. 9. Pore size distributions of ash charcoal (solid line) and bioceramic (dash line).

3.4. Pore size distribution

Pore size distributions of the carbon template and resulting bioceramics is shown in Fig. 9.

It can be seen that the carbon template and final SiC ceramics possess multimodal pore size distributions with two characteristic peaks around 1 μm and 10 μm. Total pore volume of the material decreased after impregnation cycles and carbothermal reduction due to introduction of the new silica phase and its transformation into SiC. BioSiC obtained from ash tree has an average pore diameter of 1.34 μm and the lowest porosity of all wood species (53%). Alder wood has the highest woodceramics porosity of all species (70%) with average pore size of 1.08 μm. These two species also have the largest span in the total open pore volume, 712 mm^3/g for ash and 1422 mm^3/g for alder.

3.5. Thermal expansion

Thermal expansion of bioSiC was observed in temperature range 20 °C–1400 °C. Fig. 10a shows the dilatometric curve of the investigated bioSiC. Dilatometric curve exhibits nearly linear behavior of the material with no obvious structure transformations observed during heating. Thermal expansion coefficient were calculated by equation $\alpha=\Delta L/(L_o\Delta T)$. At lower range of temperatures samples thermal expansions coefficient were $5.07^{*}10^{-6}\,K^{-1}$, at middle range $8.19^{*}10^{-6}\,K^{-1}$, and at higher range $5.51^{*}10^{-6}\,K^{-1}$. Linear dimension hysteresis can be seen in Fig. 10b.

The lack of reproducibility in the length after heating can be attributed to thermal expansion anisotropy stresses, caused by differences in strains between the carbon and SiC phases. Overall samples shrinkage of 0.22% was calculated from compared initial and final length at room temperature.

3.6. SEM analysis

The morphology of charcoal and bioSiC ceramic are shown in Figs. 11–13. From those figures can be seen that charcoal and bioceramic have complex porous microstructure.

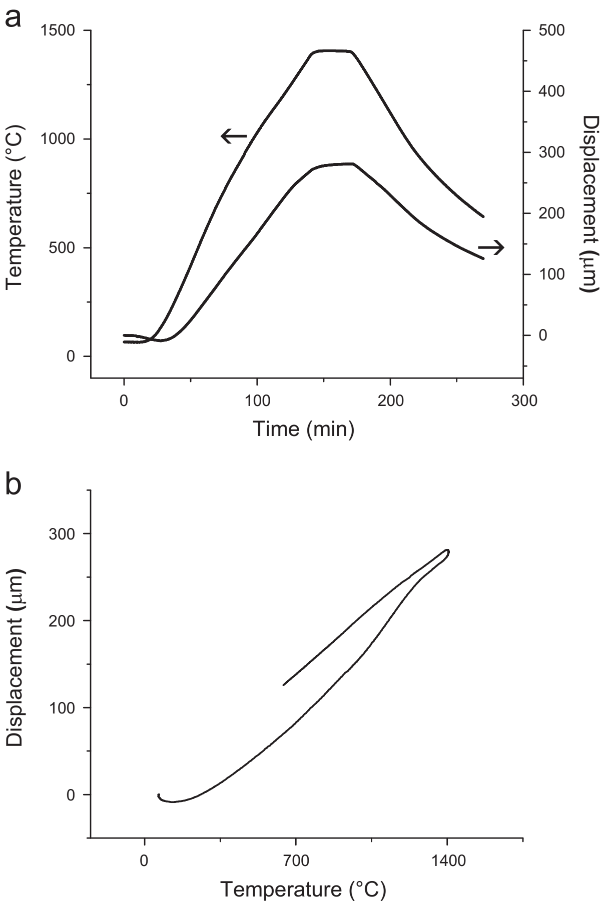


Fig. 10. Thermal expansion of biomimetic SiC ceramic.

Fig. 11a shows the heterogeneous pore size distribution in which the large pores are vessels (large circles) and the small pores are fibers (small circles) and rays (horizontal cells). Fig. 11b shows latewood of oak tree, fibers of unequal radii with thick cell walls.

During the impregnation process, silica sol infiltrates through the pores and channels of the pyrolized wood structure. After gelation and calcination, residual silica rests in pores of the charcoal structure. After high temperature reaction of carbon and silica, SiC layer is formed on the pore surfaces. At the initial impregnations, silica is uniformly dispersed in samples. Fig. 12 shows smooth SiC layer on the inner surfaces.

After repeated impregnations pores are partly clogged and distribution of silica becomes unequal. After carbothermal reduction (at outer samples surfaces) a porous β-SiC layer with medium particle size about 1 μm is formed on the outer surfaces of the samples (Fig. 13.).

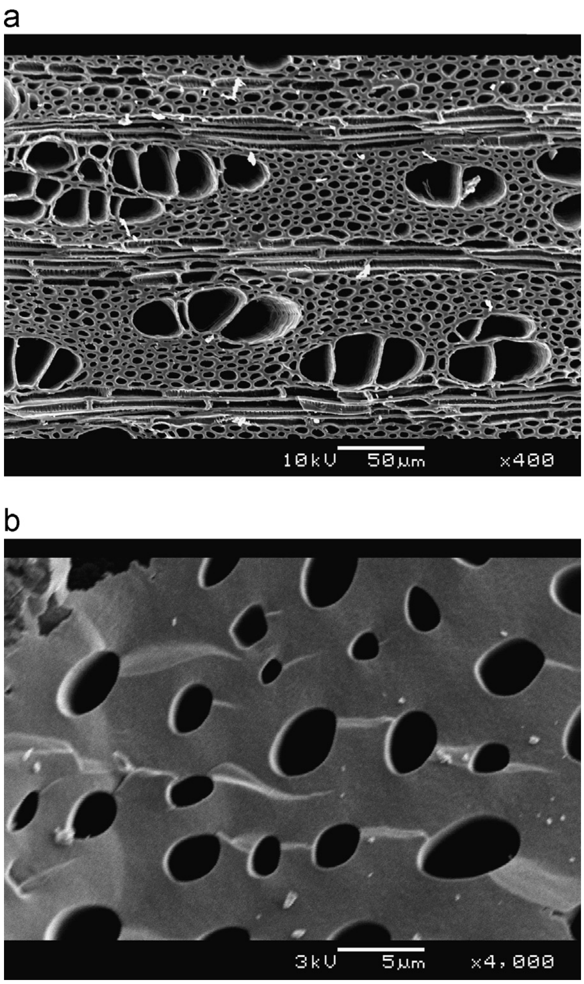


Fig. 11. SEM micrographs of amorphous carbon template of wild cherry (a) and oak (b).

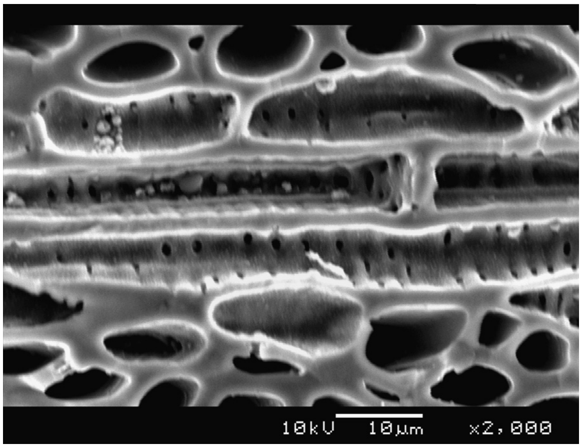


Fig. 12. Smooth SiC surface at inner pores of woodceramic.

4. Conclusions

Biomorphic SiC was produced by the sol–gel infiltration and carbothermal reduction at 1800 °C in vacuum. Repeating impregnation procedures before high temperature reaction produced samples with increasing SiC content. The cellular microstructure of wood remained intact in the porous SiC ceramics. The mechanical properties of biomorphic SiC (bending and compressional strength in two directions) improved significantly on the charcoal basis. Pore size distribution of woodceramics was analyzed and found to be slightly different after the conversion of charcoal into bioceramics. Dilatometric measurement showed nearly linear thermal behavior in the temperature range from room temperature to 1400 °C.

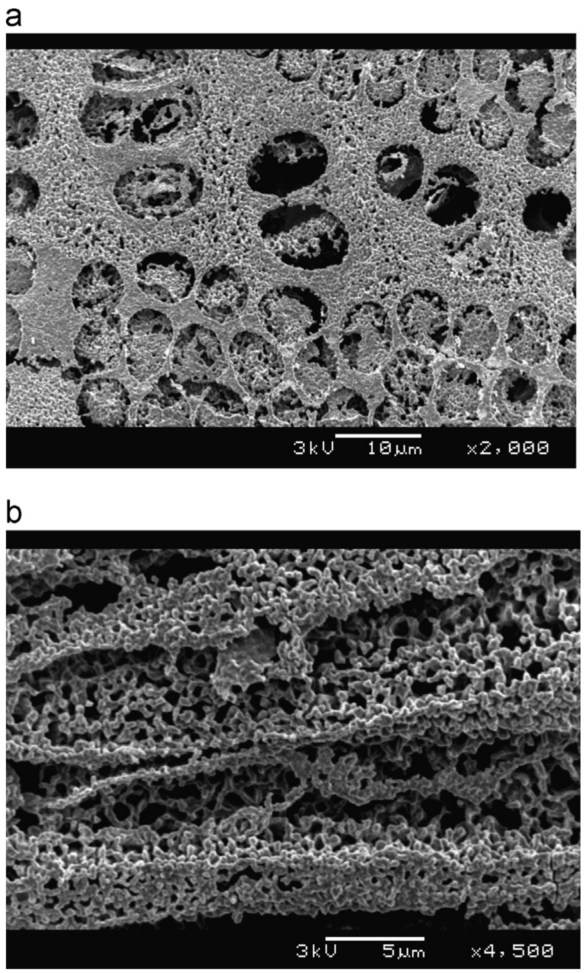


Fig. 13. Porous SiC layer at outer surfaces of samples of woodceramic.

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