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Mechanical Properties of Biomorphic Silicon Carbide Ceramics

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Abstract:

Biomorphous β-SiC ceramics were produced from linden wood by impregnation with tetraethyl orthosilicate (TEOS), followed pyrolysis and high temperature treatment at 1580 °C. Six specimen groups included charcoal and five groups with different number of impregnation were analyzed. Flexural and compressional strength of charcoal and woodlike SiC ceramic were characterized using three-point and compression testing. Mechanicall properties increased slightly with number of impregnation cycles. Ultrasonic pulse velocity testing (UPVT) was used to determine dynamic young modulus of elasticity. Laser surface modification was studied by interaction with Nd:YAG laser, operating at 1064 or 532 nm wavelengthss and pulse duration of 150 ps.

Keywords: *SiC, Mechanical properties, Microstructure, Biomorphic ceramic*

1. Introduction

Woodlike ceramics are new class of structural materials with excellent performances like good friction and wear resistance, electrical properties, corrosion resistance and high specific surface [1]. These characteristics are interesting for applications such as in catalyst supports, battery electrodes, hot gas or molten metal filters, heat insulators, ion exchangers, water cleaners and gas sensors [2,3]. Woodlike ceramics are prepared by the biotemplating technique, where wood (or woody material) is used as bulk template for fast high-temperature conversion into ceramics.

Wood is a natural material with a complex microstructure, highly anisotropic mechanical properties and good transport of fluids [4]. It is formed by the photosynthesis - reaction within the needles or leaves of trees. The photosynthetic process uses sunlight to take carbon dioxide from air and convert it into oxygen and organic materials. The result of this process is natural composite that has been one of the best and most intricate 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].

Microstructure differs basically at two main types of wood [6]. Trees are classified in Angiosperms (hardwood) and Gymnosperms (softwood). Hardwoods are consisted of larger vessel cells – tracheas, large as 0.1 mm in diameter. Among them, there are smaller cells with thick walls - libriform fibers. That cells are responsible for imparting mechanical resistance. Softwood trees have a less complicated microstructure. Vessels are absent and tracheids -

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long cells (3-5 mm) with intermediate diameter (30-50 μm) - are the single constituent. The diameter of the tracheids in gymnosperms changes in relation to the mesostructure of the wood, that in both categories includes notably seasonal rings. Structure of cell walls is similar in hardwood and softwood, and is consisted of cellulose, hemicelluloses and lignin.

Charcoal is a material made by pyrolysis from natural wood or wood fiber. Charcoal has interesting properties such as high electric conductivity and self-lubricity, and can be used as friction material and electromagnetic shield material [7]. Structurally, charcoal is similar as tree with carbon atoms instead of organic macromolecules. After pyrolysis, charcoal can be infiltrated with gaseous or liquid silicon bearing precursors such as silicon melt, silicon or silicon monoxide vapor, or organosilicon compounds [8-11].

After carbothermal reduction result is a Si/SiC composite that replicates the highly interconnected microstructure of the wood with SiC, while the remaining unreacted Si fills most of the wood channels [12]. The diversity of wood species provides a wide choice of structures, in which the density and the anisotropy are the critical factors of the final microstructure and hence of the mechanical properties of the material.

2. Experimental procedures

2.1. Material preparation

Samples were prepared from linden wood (*Tilia amurensis* L.). Wood was shaped in dimensions 63 mm × 16 mm × 16 mm. Control samples were used to record dimensional changes during pyrolysis. After pyrolysis dimensions of charcoal samples were approximately 50 mm × 10 mm × 10 mm. The cutting direction was selected to make the long edge of specimen to be parallel with the fiber and growth direction of wood. Samples were pyrolysed at 850 °C with heating rate of 1 °C/min and 2 h of holding time. Silica sol was prepared using tetraethyl orthosilicate – TEOS, ethyl alcohol and distilled water at a suitable molar ratio of 1:4:12 with few drops of acetic acid. Samples of wood were placed in a glass vessel at normal pressure.

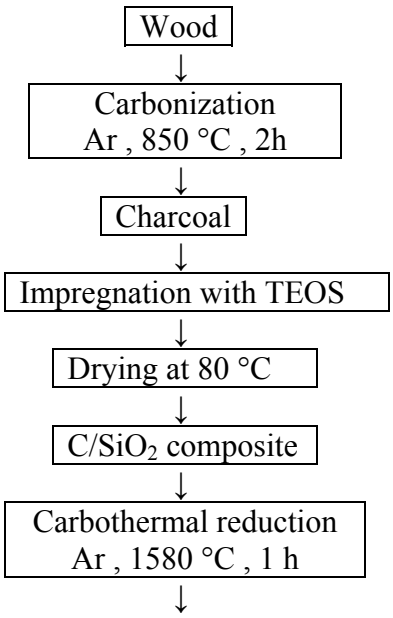

Fig. 1. Processing scheme of manufacturing wood like SiC from wood

After treatment with TEOS, samples were drained and placed in a drying oven applying increasing temperature up to 80 °C temperature with the hold time of 5 h at the maximum temperature. Repeating impregnation cycles up to 5 times produced six specimen groups (one without impregnation). Carbothermal reduction of prepared samples was carried out in argon flow in a heater furnace at 1580 °C to form porous 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 employed Ar gas contained less than 5 ppm O_2 . Flow meter controlled Ar flow of 0.5 l/min was used in all experiments. The temperature was measured with Pt - 10%Rh thermocouple (±5 °C). The Ar flow was maintained during cooling till 200 °C.

2.2. Characterization

Flexural and compressional strength of charcoal and wood like SiC ceramic were characterized using three-point and compression testing at Instron M 1185. Tests were conducted at room temperature with four or more specimens of each group.

The weight change of the sample was measured before and after pyrolysis at 650 °C in presence of O_2. Residual content after pyrolysis is stable SiC. During carbothermal reduction, silica is reacting with charcoal [13] for producing silicon carbide:

$SiO_2 + 3C \rightarrow SiC + 2CO$

This reaction, in fact, proceeds through two stages with gaseous intermediate silicon monoxide [14]:

$SiO_2 + C \rightarrow SiO + CO$

When carbon monoxide is formed, silicon monoxide can be produced according to reaction:

$SiO_2 + CO \rightarrow SiO + CO_2$

Silicon monoxide then reacts with carbon:

$SiO + 2C \rightarrow SiC + CO$

or reacts with carbon monoxide [15]:

$SiO + 3CO \rightarrow SiC + 2CO_2$

Under very high SiO partial pressure, reaction of gaseous SiO is:

$2SiO \rightarrow Si + SiO_2$

And resulting Si reacts with carbon [16]:

$Si + C \rightarrow SiC$

Ultrasonic pulse velocity testing (UPVT) [17] was used to determine dynamic young modulus of elasticity. Pulses of longitudinal stress waves with frequency of 1 MHz were generated by electro-acoustical transducer and, after traveling through material, received and converted into electric pulses by a second transducer. Velocity is calculated from distance between the two transducers and transit time of the pulse as:

$$v\ (\mathrm{m/s}) = L / t$$

where L is path length, and t is transit time. Dynamic modulus of elasticity is calculated [18] using the equation:

$$E_{dyn} = v^2 \rho \left(\frac{(1+\mu_{dyn})(1-2\mu_{dyn})}{1-\mu_{dyn}} \right)$$

where v is pulse velocity (m/s), ρ is the bulk density (kg/m^3), and μ_{dyn} the dynamic Poisson ratio. The dynamic Poisson ratio was obtained from relation:

$\mu_{dyn} = (2\alpha^2 - 1) / (2\alpha^2 - 2)$

where α is ratio of longitudinal velocity v_p and transversal velocity v_s:

$\alpha = v_p / v_s$

Measurements are performed using the OYO 5210 equipment according to JUS. D. B8. 121. testing procedure.

Samples were irradiated by focusing the laser beam with a quartz lens of 12 cm focal length. During irradiation, the laser was operating in the fundamental transverse mode. The angle of incidence of the beam and the sample surface was near 90°. Irradiation was carried out in air at standard pressure and relative humidity. The laser was an active-passive mode locked Nd:YAG system which includes a laser oscillator, amplifier and non-linear crystal (KD*P). Pulse duration of about 150 ps was obtained using a saturable absorber dye and an acousto-optic standing wave modulator. Laser was operating in the TEM_{oo} mode with a typical repetition rate of 10 Hz at wavelengths of 1064 nm and 532 nm.

The phases present in the samples were determined using X-ray diffraction.

3. Results and discussion

3.1. Weight change

The weight change of specimens is dependent of increasing numbers of impregnations with TEOS. This process can be explained by accumulation of silica sol at the inner cell walls of the large vessels.

Residue after pyrolysis is stable SiC:

$m_{SiC} = m_{sample} - m_C$

$\delta m\ (\%) = (m_{sample} - m_C) / m_{sample}$

Fig. 2 shows the weight change before and after pyrolysis at 650 °C in presence of O_2.

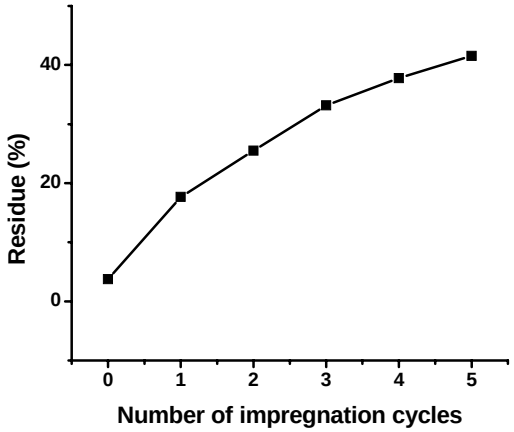

Fig. 2. Effect of impregnation cycles number on residual weight

3.2. Mechanical properties

Mechanical properties of wood like ceramics were characterized by bending and compression testing.

3.2.1. Bending strength

Bending strength testing was conducted by using three-point flexure tests with 40 mm support spans at room temperature. Tests were conducted on specimens at stroke rate of 1

mm/min. Results of flexural strength tests are shown in Fig. 3. It is shown that bending strength increases with number of impregnation cycles, also as content of SiC in samples.

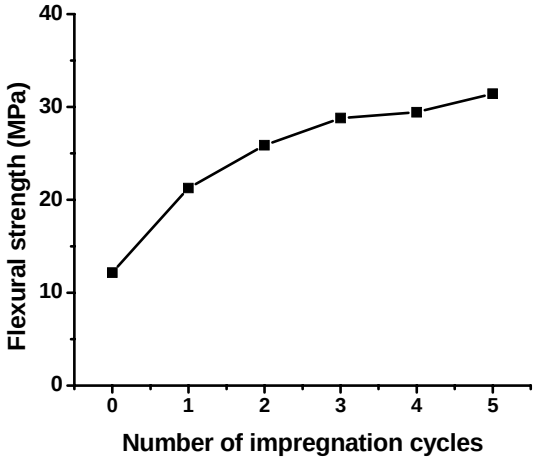

Fig. 3. Effect of impregnation cycles number on flexural strength

As can be seen, the bending strength is 12.2 MPa for charcoal sample. After one impregnation procedure, bending strength of the resulting porous SiC ceramic is 21.3 MPa. Compared with charcoal, bending strength increases because carbonaceous tubular pore struts of charcoal were converted into SiC struts and new SiC foams formed in the tubular pores, respectively. Bending strength further increases and after five impregnation cycles reaches 31.4 MPa. It can be clearly seen that bending strength increases with SiC content.

3.2.2. Compression strength

Compression strength tests were realized by using Instron fixture for compression tests. Specimens were used with stroke rate of 1 mm/min at room temperature. Results of compression strength tests are shown in Fig. 4.

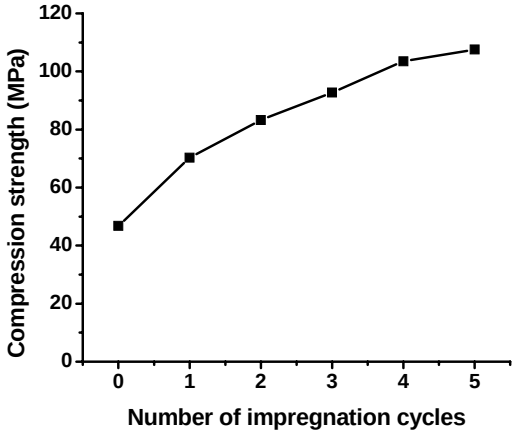

Fig. 4. Effect of impregnation cycles number on compressional strength

Compression strength for charcoal is 46.8 MPa, but after one impregnation and carbothermal reduction increases to 70.3 MPa. After five impregnation cycles, compression strength reaches value of 107.6 MPa.

3.3. Ultrasonic testing

Transducers for ultrasonic testing were placed on two parallel faces of cubic samples with sides of app. 1 cm, using vaseline grease as the coupling medium.
Pulses of longitudinal stress waves were traveling through material in three directions: axial, tangential and radial. Results for the monitoring changes of the dynamic modulus of elasticity versus number of impregnation cycles are shown in Fig. 5.

Axial dynamic Young modulus of elasticity is cca. 50% higher than tangential and radial. After one impregnation with TEOS and carbothermal reduction dynamic modulus in all directions increase 30-40%. After repeated cycles of impregnation, modulus slightly increases and reaches 1.004 GPa in axial direction (0.799 GPa and 0.753 GPa in tangential and radial directions respectively).

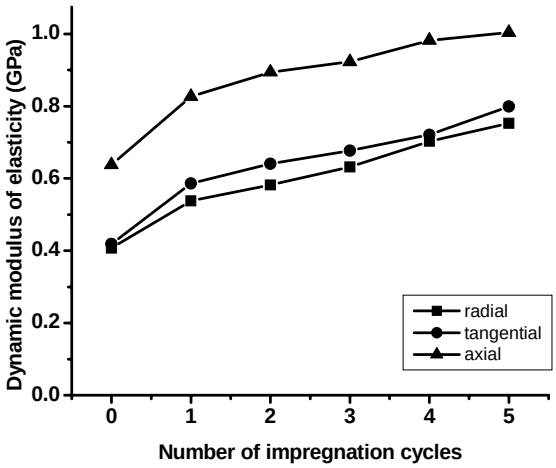

Fig. 5. Effect of impregnation cycles number on dynamic modulus of elasticity

3.4. Laser surface modification

Laser on charcoal and biomorphic SiC induced morphological changes. Intensity of effects depended on laser beam characteristics - fluency/energy density, peak power density, number of accumulated pulses, wavelength, etc. Duration of radiation was 2 – 25 s with 10 Hz frequency of 150 ps laser impulses. Energy of impulses was 35 – 45 mJ for radiation with wavelength of 532 nm and 15 mJ for 1064 nm.

Charcoal specimen produced 5 mm long white-yellow plasma in front of the target during irradiation with 1064 nm, and 1 mm yellow-orange plasma with 532 nm light. Shapes were conical in both cases. With increasing number of impregnations, biomorphic SiC produced shorter plasma (to 0.5 mm for specimen with 5 impregnation cycles). Laser at 1064 nm produced craters with diameter up to 750 μm, and at 532 nm up to 200 μm. There was no damage threshold at these laser irradiations. No hydrodynamic features have perceived and no periodic surface structures.

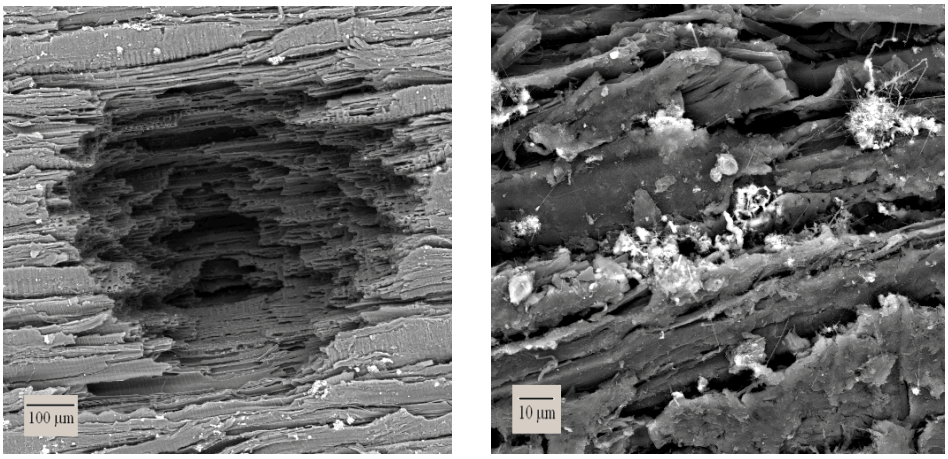

Fig. 6 SEM images of craters created at charcoal surface by the laser beam

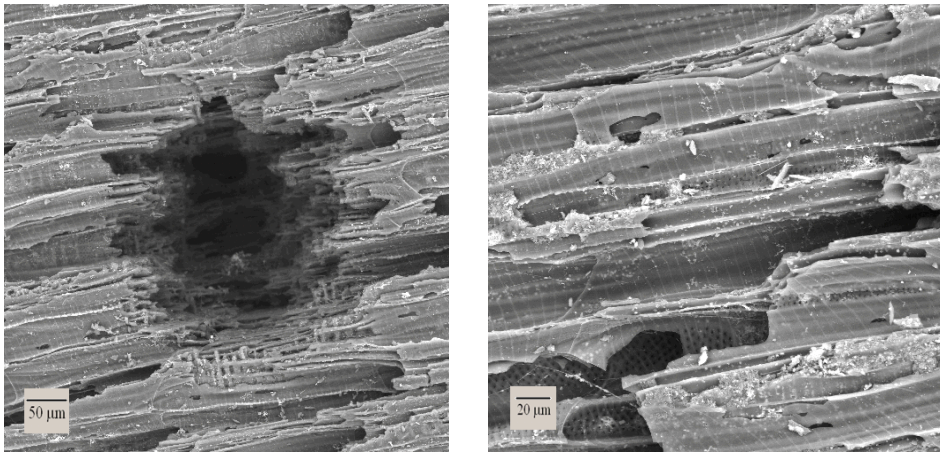

Fig. 7. SEM images of craters created at biomorphic SiC (5 impregnations) surface by the laser beam

3.5. XRD analysis

XRD pattern of obtained silicon carbide wood ceramic at 1580 °C in Ar revealed mainly cubic type β-SiC phase as shown in Fig. 8.

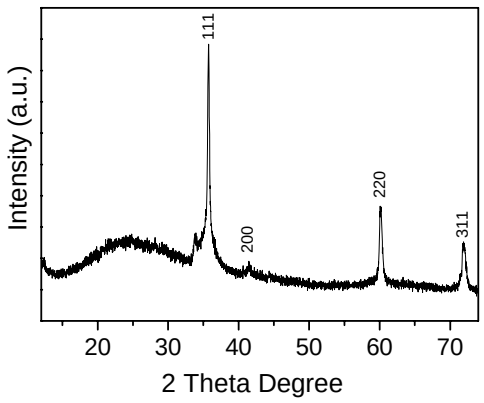

Fig. 8. XRD pattern of manufactured SiC biomorphic ceramic at 1580 °C.

Also the additional diffraction peak was detected at 2θ = 33.671, which represents stacking faults on the ⟨111⟩ planes in cubic SiC.

4. Conclusions

Biomorphic SiC was produced by sol-gel infiltration and carbothermal reduction at 1580 °C. Specimens with increasing content of SiC are produced by repeating impregnation procedures. Measuring of residual weight of biomorphic ceramics after pyrolysis at 650 °C in presence of O_2 showed different SiC fraction. The biomorphic cellular morphology of wood is remained in the porous SiC ceramics with high precision that consist of β-SiC phase. The mechanical properties (strengths, modulus) of biomorphic SiC improved significantly on the basis of charcoal. Ultrasonic pulse velocity testing was employed to determine velocity of longitudinal stress waves and Young's modulus. Both laser wavelengths induce morphological changes at the target. The laser radiation induced surface roughness and formation of conical structures 200 – 750 μm wide in the base.

Acknowledgement

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Садржај: *Биоморфна керамика β-SiC је добијена од карбонизоване липе уз импрегнацију тетраетил ортосиликатом (TEOS), са карботермалном редукцијом на 1580 °C. Испитивано је шест група узорака – карбонизовано дрво и пет група биоморфног SiC са различитим бројем импрегнација. Чврстоће на савијање и компресију карбонизованог дрвета и биоморфног SiC је мерена применом метода савијања у три тачке и тестирања компресије. Механичка својства су се постепено побољшавала са бројем циклуса импрегнације. Одређивање динамичког модула еластичности је вршено помоћу мерења брзине ултразвучних импулса (UPVT). За проучавање површинске интеракције са ласерским зрачењем коришћен је Nd:YAG ласер који је емитовао зрачење на таласним дужинама 1064 і 532 nm и трајањем импулса 150 ps.*

Кључне речи*: SiC, механичка својства, микроструктура, миоморфна керамика*