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The role of carbon biotemplate density in mechanical properties of biomorphic SiC

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Abstract

Biomorphic SiC was prepared from four types of Mediterranean wood as carbon precursor. Carbon biotemplates were obtained by pyrolysis and carbonization up to 1400 °C and they were infiltrated with liquid silicon in two different directions. A linear correlation between bending strength and bioSiC density for different types of softwood and hardwood has been found. Mechanical properties were modelled according to the MSA (minimum solid area) approach. Fairly good correlation was found when biomorphic SiC is treated as porous solid. Moreover, the fabrication of bioSiC from carbon biotemplates heat-treated up to 2500 °C has been additionally studied. An improvement up to 56% in flexural strength has been reached by densification of bioC at such high temperature.
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1. Introduction

Recently, ceramics mimicking the biological structure of natural developed tissues have attracted increasing interest.[1–3] The lightweight and open porosity of these materials make them great candidates for structural applications in biomedicine[4] and also at high temperature.[5] Several research groups have developed biotemplating high temperature techniques to convert biological structures into ceramic materials. Thus, different kinds of wood have been converted into Si/SiC composites by reactive infiltration with liquid silicon[6–10] whereas Si-vapour phase infiltration[11–13] and carbothermal reduction reaction[14] have been used to make different porous SiC ceramics. Detailed mechanical tests and microstructural characterization have shown some outstanding mechanical properties of biomorphic SiC.[6,8–10,15–20] However, high scatter of results is found in SiC properties produced from natural substrates. This fact is commonly attributed to the different pore structure and anisotropy of each precursor, the term pore structure being generally admitted to be in this case the shape, size and distribution of tracheidal cells (in softwood) and vessels (in hardwood).

The aim of this work is to demonstrate that SiC mechanical properties produced from wood follow a general trend which is mainly a function of SiC density and not so dependent on precursor pore structure. Therefore, four wood species with different pore morphology and covering a wide range of porosity were selected as carbon precursors to produce SiC ceramics by reactive infiltration with liquid silicon. The effect of high temperature treatment on carbon substrate and its influence on ceramic properties was additionally studied.

2. Experimental procedure

2.1. Precursor materials

Four different kinds of wood, two softwood and two hardwood, covering a range of density and pore structure were selected to produce bioSiC. Typical Mediterranean species from local sources were used due to their availability and low cost. Chosen wood species were: pine (*Pinus pinea*), cedar (*Cedrela odorata*), almond (*Prunus amygdalus*) and olive (*Olea europaea*) wood, in increasing order of density and hardness. Wood materials were cut into 10 mm × 10 mm × 50 mm rectangular bars parallel to the axial direction. A minimum of five

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preforms of each type of wood were processed for each set of experimental conditions.

2.2. Fabrication method

Wood preforms were dried for 24 h at 100 °C in an oven and then pyrolyzed under nitrogen at 1 MPa in a pressurized stainless steel reactor, heated by a sand-fluidized bed furnace. A slow heating rate of 1 °C/min was applied up to 520 °C. Thereafter, pyrolyzed wood preforms were further carbonized in a horizontal furnace up to 1400 °C during 60 min, using an argon flow of 60 ml/min and a heating rate of 1 °C/min up to the peak temperature. Some of the carbonized preforms were further heat-treated up to 2500 °C into a high temperature furnace using an argon flow and a heating rate of 10 °C/min (at Schunk Kohlenstofftechnik GmbH in Heuchelheim, Germany). The final carbon preforms were ready to be used directly as template structures to produce bioSiC with tailored porosity. Ceramization was performed in a horizontal furnace by reactive infiltration with liquid silicon (Silicon lumps, Aldrich, purity 98.5 wt%) at 1450 °C for 180 min using an argon flow of 60 ml/min.

2.3. Density and porosity measurement

Geometrical density of bioC and bioSiC was determined by measuring weight and volume of the specimens. Bulk density and open porosity were measured by Archimedes' method in water (standard DIN 51918), employing an AG204 delta range analytical balance and the Density Kit AG from Mettler Toledo. Skeleton and powder densities were measured by helium pycnometry (AccuPyc 1330TC, Micromeritics). Powder materials were obtained from preforms by grinding in a ball mill (S100, Retsch). Open and closed porosity values were obtained from the relationship between geometrical, skeleton and powder density of the materials.

2.4. Crystal structure

Crystal structure of reaction products was determined by X-ray diffraction (XRD) employing an X-ray diffractometer Bruker model D8 advance, fitted with a Cu cathode and Ni filter, using Bragg–Brentano geometry and monochromated Cu Kα₁ radiation ($\lambda = 1.5406$ Å). The device operated at 40 kV and 40 mA, and for measurements a step of 0.1° and a preset time of 3 s were used in the angular scanning from 10° to 80°. To overcome the non-planarity of samples, and work properly with parallel optical beam, a Göbel mirror was used.

2.5. Microstructure

Microstructure of both bioC and bioSiC was analyzed by scanning electron microscopy (SEM) using a Hitachi microscope model S-3000N. Energy dispersive X-ray analysis (EDX) Link QK 200 was used to identify the chemical composition of different phases of the materials. Samples were coated with a gold thin layer to enhance the electronic conductivity.

2.6. Thermogravimetric analysis

Simultaneous thermogravimetric differential analysis was carried out on a SDT 2960 simultaneous DSC–TGA from TA Instruments. Pure α-alumina powder (10 mg) was used as reference and 10-mg wood pieces were placed in the open alumina cell. TGA–DTA measurements were carried out using a heating rate of 5 °C/min up to 900 °C with a nitrogen flow of 100 ml/min.

2.7. Mechanical properties

Three-point bending strength of bioSiC was determined at room temperature using an Instron 4411 universal testing machine. Mechanical tests were carried out following standard DIN IEC 413 using specimens of 4 mm × 8 mm × 32 mm, 26 mm of span length and a crosshead displacement rate of 0.1 mm/min. Young's modulus and strain-to-failure values were calculated from the linear zone of stress–strain curves.

2.8. Thermal properties

The coefficient of thermal expansion (CTE) for bioSiC was calculated from the expansion curves of the material following the ASTME 831-86 standard. The device employed was a TMA 2940 thermomechanical analyzer from TA Instruments. Specimen size was 5 mm × 5 mm × 10 mm. Samples were submitted to four cycles of heating up to 500 °C and cooling down to 50 °C, at 3 °C/min rate, and isothermal stages of 5 min at maximum and minimum temperatures. Applied force was 0.05 N and a nitrogen flow of 150 ml/min was supplied.

3. Results and discussion

3.1. Carbon biotemplates

3.1.1. Thermogravimetric analysis

Characterization of the thermal degradation of wood under nitrogen was performed using thermogravimetric analysis (TG) at atmospheric pressure. TG curves for the different woods are plotted on the same graph for comparison and shown in Fig. 1. In general terms, there is an initial weight loss at 50–150 °C (a), where moisture is removed. Second step in the weight loss process occurs between 150 and 300 °C (b), which can be assigned to the decomposition of hemicellulose and release of small molecules such as CO, CO_2 and volatile components. At higher temperature range, 300–350 °C (c) weight loss occurs due to the decomposition of cellulose and lignin, which are higher molecular weight components, leaving behind the carbon structure.[7] Between 350 and 900 °C (d) weight loss occurs due to carbonization process, where carbon polymeric chains are cracked and graphene layers formed. As can be seen, some differences exist in the thermal behaviour of the four woods. These can be attributed to the different cell wall structure of each type of wood which limits the transformation rate of the reactions described above.[9] Carbon yield obtained from the different wood samples by TG at 900 °C ranged from 13 wt% (for pine) to 30 wt% (for olive), the data for 520 °C – the temperature