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# Studies on formation and siliconization of carbon template of coir fibreboard precursor to SiC ceramics

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## Abstract

Formation reaction of carbon template of coir fibreboard samples via pyrolytic decomposition was studied by methods of thermogravimetric, derivative thermogravimetric and differential thermal analysis using different heating rates (5–20 K $\text{min}^{-1}$). The major decomposition reaction at 250–500 °C had activation energy and frequency parameter of $121.84 \pm 8.78$ kJ $\text{mol}^{-1}$ and $3.2 \times 10^9$–$2.1 \times 10^{11}$ $\text{min}^{-1}$, respectively, supporting a free radical mechanism. Siliconization reaction of the carbon template was also studied by non-isothermal DTA technique using varying heating rates (5–20 K $\text{min}^{-1}$); exothermic C-Si reaction was preceded by endothermic melting of Si and it had activation energy of $2793.09 \pm 187.65$ kJ $\text{mol}^{-1}$; diffusion through solid reaction product was found to control the heterogeneous chemical reaction process. On the basis of these experimental results separate experiments were conducted for preparation of carbon templates and their subsequent siliconization. The correlations between the properties of the coir fibreboard precursor, the carbon template and the siliconized product (SiC) were explained.

*Keywords:* Coir fibreboard; Bio-precursor; Carbon template; Siliconization; SiC ceramics

## 1. Introduction

Reaction bonded SiC ceramics (RBSC) – the well known structural ceramic materials – are produced by infiltration of liquid Si in to a porous SiC/C powder compact.[1–4] During infiltration Si reacts with carbon to form newer SiC that binds the existing SiC and any remaining pores are ultimately filled with residual Si. The product is a composite, also known as SiSiC, and it contains both the SiC and the Si phases. Different carbonaceous precursors like C-fibre preforms, C-felts, C-fibre/C-matrix composite preforms, C-powder compacts, etc. are also used for production of SiSiC for various application purposes.[5–9] SiSiC can also be produced by replication of naturally occurring plant bio-structures (bio-precursors) like woods.[10–15] The obvious aim is to mimic the biological cellular morphology in a ceramic microstructure. The processing technique consists of two steps – the bio-precursors are first pyrolyzed to carbonaceous preforms (carbon templates) which are subsequently converted to biomorphic SiC by infiltration and reaction with liquid Si. Compared to technically manufactured ceramic materials, the biomorphic SiC ceramics are expected to provide superior combination of properties. Natural precursors like woods exhibit structural fluctuations which are reflected in the microstructure of the ceramics and their properties show marked changes between different kinds of woods and even different trees of same kinds of species used as the precursors.[16] Such variations of properties make biomorphic SiC unreliable in widespread applications as structural ceramics. Artificial precursors can be made using reproducible processing techniques and the biomorphic SiC ceramics synthesized from such precursors are expected to exhibit reliable properties. Different processed precursors, such as, fibreboards, papers, pressed wood powder-resin composite boards, cast bamboo pulp fibreboards, etc. were used for this purpose.[16–19] Coir fibre, an agricultural waste material of immense economic importance in the Indian subcontinent, is

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another potential raw material that can be processed to prepare artificial precursors to biomorphic SiC. The present research group has successfully converted coir fibre based precursors to biomorphic SiC ceramics.[20] The success of bio-mimicking primarily depends on how perfectly the cellular structures of the biological precursors are retained in the morphologies of carbon templates as also in the microstructure of the ceramics. For this purpose complete understanding of kinetics of the thermal degradation reactions occurring during formation of carbon templates becomes necessary. Examination of the reaction of Si with the carbon template is another important issue. The parameters that control the properties of carbon templates need to be understood very clearly; knowledge on how the properties of the carbon templates control the properties of the end ceramics is also required. This paper reports the results of processing of biomorphic SiC ceramics using coir fibre as the precursor material with an aim to address all the issues. Results of similar investigations on processing of biomorphic SiC from pine wood as a natural precursor are also incorporated for comparison.

## 2. Experimental

Coir fibres obtained from coconut trees (*Cocos nucifera*) available in the state of Assam, India, were used in the present study. Coir fibreboards – the artificial or processed bio-precursors – were fabricated by mixing in a drum mixer the chopped coir fibres of 1–1.5 cm length with cellulose acetate (Loba Chemicals, India) diluted in acetone for homogenous dispersion of fibres and binding. The mixtures were hot pressed in a metallic mould (30 cm × 30 cm × 10 cm) at a temperature of around 135 °C. The boards were air-cooled and finally removed from the mould. The fabrication details of the coir fibreboards were described in Ref. 20. Wood of a common gymnosperm plant of local origin (pine (*Pinus Sylvcstris* L.)) was used as the natural precursor. The dimension and weight of the well-dried bio-precursor samples were recorded and their microstructure was examined by a scanning electron microscope (Model JSM 5200, JEOL, Japan). Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) of the bio-precursor samples were done in a flow of nitrogen at a rate of 100 ml $\text{min}^{-1}$ using a thermoanalyzer (SDT Q600 V20.9 Build 20, Universal V4.74, TA Instruments, USA). Samples of 7–9 mg were used and tests were conducted at different heating rates (5–20 K $\text{min}^{-1}$) up to 800 °C. Samples were loaded into an alumina pan and the TG, DTG and DTA curves were recorded simultaneously with 0.1 mg sensitivity. The carbon templates of the bio-precursors were produced by pyrolyzing the samples in an electrically heated pyrolysis furnace (Steadfast International, Kolkata, India) at 800 °C under flowing nitrogen using programmed heating and cooling rates. The carbon template samples were characterized by measuring the pyrolytic mass loss and shrinkage, determining the bulk density from mass and dimension data. XRD analysis of the pyrolyzed bio-precursor samples was done by a PW 1710 diffractometer (Philips, Holland, with Cu $K_\alpha$ radiation of wavelength $\lambda = 1.5406$ Å) and microstructure was examined under a scanning electron microscope (SEM) (SE 440, Leo-Cambridge, UK).

The reaction of carbon template with Si (siliconization reaction) was studied using the technique of differential thermal analysis (DTA) (STA 449 F3 Jupiter, NETZSCH Geratbau GmbH, Selb, Germany). Around 30 mg of carbon template sample was taken with Si (98.4%, Johnson Matthey Chemicals India Pvt. Ltd., Alpha Aesar, A.P., India; C: Si mole ratio was maintained at 1: 1.2) in an alumina crucible, heated in a flowing argon stream (BOC India Ltd., Kolkata, India; flow rate of 120 ml $\text{min}^{-1}$) up to 1600 °C using several heating rates (5–20 K $\text{min}^{-1}$) and the DTA curves were recorded simultaneously. The carbon templates were separately infiltrated and reacted with silicon (an excess of silicon to the amount needed for stoichiometric conversion of carbon template was used) at a temperature of 1550 °C for 1 h under vacuum in a graphite resistance furnace (Astro, Thermal Technologies Inc., Santa Barbara, CA, USA). The dimension of the siliconized samples was measured and any un-reacted silicon adhered to the surfaces was removed by grinding. Bulk density were determined by water immersion method, the product phases were identified by XRD technique (X-ray diffractometer, PW1710, Philips, Holland; using Ni-filtered Cu $K_\alpha$ radiation of wave length $\lambda = 1.5406$ Å) and microstructure was examined using scanning electron microscopy.

## 3. Results and discussion

### 3.1. Kinetic studies of thermal degradation reaction of bio-precursor

The molecular compositions of the bio-precursor samples are shown in Table 1. Both the natural and the artificial or processed bio-precursors contained cellulose, hemicellulose and lignin as the major bio-polymers. The coir fibreboard precursor samples contained more lignin and less combined cellulose and hemicellulose than the pine wood samples. The thermal decomposition behaviour of bio-precursors was studied by determination of kinetics of thermal degradation reactions. The rate of thermal degradation reaction under non-isothermal conditions is given by[21–23]:

$$\frac{d\alpha}{dt} = q\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (1)$$

where $\beta$, the degree of conversion, is expressed as:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \qquad (2)$$

$m_i$, $m_f$ and $m_t$ represent the initial and final sample mass and the sample mass at time $t$, respectively, $q$ (= $dT/dt$) is the rate of heating, $A$ and $E$ are the pre-exponential factor and activation energy, $T$ is the absolute temperature, $R$ is the universal gas constant (= 8.314 J $\text{mol}^{-1}$ $\text{K}^{-1}$) and $f(\alpha)$ is the differential conversion function expressed as[24]:

$$f(\alpha) = a^m(1-\alpha)^n[-\ln(1-\alpha)^p] \qquad (3)$$

where $m$, $n$ and $p$ are exponent factors (different values of $m$, $n$ and $p$ make it possible to describe different reaction mechanisms). The algebraic expression of conversion function, $f(\alpha)$ for