Bull. Mater. Sci., Vol. 27, No. 5, October 2004, pp. 467–470. © Indian Academy of Sciences.

Biomimetic synthesis of cellular SiC based ceramics from plant precursor

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MS received 3 March 2004; revised 19 July 2004

Abstract. A novel biomimetic approach in designing and fabricating engineering ceramic materials has gained much interest in recent times. Following this approach, synthesis has been made of dense Si–SiC duplex ceramic composites and highly porous SiC ceramics in the image of the morphological features inherent in the caudex stem of a local monocotyledonous plant. The process route involves making of a carbonaceous biopreform and its subsequent reaction with an infiltrating silicon melt to yield the biomorphic Si–SiC ceramic composites with flexural strength and Young's modulus of 264 MPa and 247 Gpa, respectively and loss in weight of only ~ 9% during oxidative heating up to 1200°C in flowing air.

The Si–SiC composites were transformed into porous (49 vol.%) SiC ceramics with complete preservation of microcellular anatomy of the parent plant, by depleting residual silicon phase in channel pores through reaction with carbon. SiC based materials so derived can be used in structural applications and in designing high temperature filters and catalyst supports.

Keywords. Biomimetic synthesis; carbonaceous biopreform; biomorphic Si–SiC ceramic composites; porous cellular SiC ceramics.

1. Introduction

In recent years, there has been tremendous development of engineering materials. With this rapid development various problems are also encountered in both design and fabrication processes. To solve these problems, many new approaches are coming up.

Biomimetics is one such novel approach, the purpose of which is to advance man-made engineering materials through the guidance of nature (Srinivasan *et al* 1991; Vincent and Srinivasan 1992). Following biomimetic approach, synthesis of ceramic composites from biologically derived materials like wood or organic fibres has recently attained particular interest (Calvert 1992; Heuer *et al* 1992). Plants often possess natural composite structures and exhibit high mechanical strength, low density, high stiffness, elasticity and damage tolerance. These advantages are because of their genetically built anatomy, developed and matured during different hierarchical stages of a long-term evolutionary process. Development of novel silicon carbide (SiC) materials by replication of plant morphologies, with tailored physical and chemical properties has tremendous potential. Biomorphic SiC ceramics are distinguished by cellular anisotropy of naturally grown plant structures which are very difficult to produce following conventional techniques.

SiC ceramics are commonly utilized for different structural applications. Among the conventional methods of producing SiC ceramics, reaction bonding/reaction sintering (Popper 1960) has been shown to be the cheapest and the most viable. Reaction bonding/reaction sintering is based on the C–Si reaction and is conventionally restricted to synthetic preforms (Popper 1960; Forrest *et al* 1972). Dense SiC ceramics can also be made using plant biostructure derived preforms (Greil *et al* 1998; Shin *et al* 1999; Singh 2000). Biological preforms from various soft woods and hard woods can be used for making different varieties of porous SiC ceramics (Vogil *et al* 2001, 2002). A wide variety of non-wood ingredients of plant origin commonly used in pulp and paper making can also be employed for producing porous SiC ceramics by replication of plant morphologies (Sieber 2000). In view of the variations in dimensions, composition and morphology of the naturally grown plant structures, the shape and composition of the bulk SiC produced will vary significantly. The formation of SiC ceramics using the caudex stem of a local monocotyledonous plant as the precursor is reported here.

2. Experimental

Rectangular (about 60 × 10 × 10 mm) specimens of carbonaceous preforms (biopreform) were prepared by pyrolyzing dried caudex stems of a monocotyledonous plant

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from a local source at 800°C without any structural damage (cracking, loss of integrity etc) in a self-generated atmosphere in an electrically heated furnace. The details of the biopreform making is available elsewhere (Chakrabarti *et al* 2002a); the biopreform was subsequently infiltrated and reacted with molten silicon (purity 99·41 wt.%, Indian Metals and Ferro Alloys, India) under vacuum at a temperature of around 1600°C in a carbon heated furnace (Astro, Model 1000-3560-FP-8204025, Thermal Technologies, Santa Barbara, CA), to yield biomorphic Si/SiC ceramics (Chakrabarti *et al* 2002b). The carbon biopreform and the final product were subjected to X-ray diffraction (PW1710, Philips, Holland), microstructural examination using light microscopy (Zetopan, Reichert, Austria) and scanning electron microscopy (SE-440, Leo-Cambridge, Cambridge, UK), determination of the volumetric phase composition by point count method from light photomicrograph, thermal analysis (TGA) using a thermo-balance (STA490C, Netzsch-Geratebau GmbH, Germany) up to 1200°C in flowing air (70 ml/min) at a rate of 10°C/min, determination of density by water displacement method and porosity by boiling water method. Three-point bending strength and Young's modulus of Si/SiC ceramic material (specimens of 45 × 3·5 × 2·5 mm ground and polished up to 1 μm finish) were determined at room temperature using an Instron Universal Testing Machine and the deflection was monitored through a LVDT with a resolution of 0·05% of the full scale deflection. Five tests were conducted and an average value was reported.

In a separate set of experiments, the dense biomorphic Si–SiC ceramic sample was reacted with powdered carbon (ash content 0·68%, Assam Carbon Products Ltd., India) under vacuum at a temperature of around 1600°C in the carbon heated furnace (Chakrabarti *et al* 2003); this procedure ensured the removal of free silicon phase from biomorphic Si–SiC ceramic to yield porous cellular SiC ceramics. After reaction, the sample was polished and the microstructure was observed using scanning electron microscopy; density and porosity were determined by boiling water method and phase constitution by XRD.

3. Results and discussion

3.1 *Carbon biopreform*

The transformation to the carbon preform was found to be associated with anisotropic shrinkages in different directions (axial, radial and tangential) with an overall change in linear dimensions of around 29%. Despite such a vast change, the structural integrity and the microscopic structural features were almost perfectly preserved. The microstructure of carbon preform shows retention of tubular elongated cell structures of the precursor plant that are aligned with the axis of the tree (figure 1a). Hollow channels of varying diameters originating from the tracheidal pores are seen to be distributed in the cross-section (figure 1b). The transformed preform contained 35·7 vol.% solid, which is essentially amorphous carbon.

3.2 *Biomorphic Si–SiC ceramic*

Infiltration of molten Si into the biocarbon preforms was found to be spontaneous when the tracheidal pore system had contact with melt. The specimens got fully infiltrated and reacted throughout into dense structures with complete retention of the macroscopical structural integrity. A marginal change in the overall linear dimension (around 1%) was noticed. The density and porosity of the final ceramic were found to be 2·7 g/cm^3 and 2·3 vol.%, respectively. The XRD analysis of the material shows the presence of *b*-SiC and Si. After reaction the carbonaceous pore wall is converted to *b*-SiC and the pores are filled with unreacted Si; the composition of the final ceramic was found to be 48·0 vol.% SiC and 49·7 vol.% Si. The diameter of the Si-filled pores was found to vary widely. This may be because of the variation of the pore diameter in the native wood tissue (from large diameter vascular channels to moderate diameter tracheidal cells) (Vogil *et al*

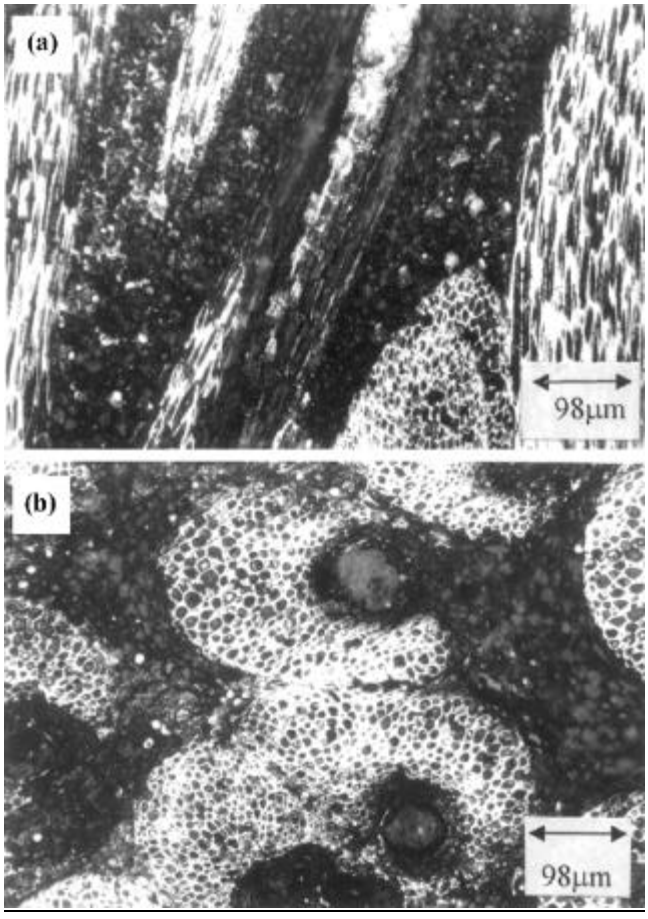

Figure 1. Light photomicrographs of the carbon preform: (**a**) longitudinal view and (**b**) cross-sectional view.

2001). The retention of the tubular elongated cell structures is clearly seen in the converted specimen (figure 2), where the diameter of Si-filled pores was found to be around 8 μm and likely to be originated from the tracheidal cells. Also, the thickness of the *b*-SiC layer was found to vary within 5–13 μm in the converted specimen. Converted *b*-SiC structures and the Si-filled channel pores are fibrous in shape. When viewed under SEM, the preservation of the cellular ring morphology is more distinctly evident (figure 3); formation of around 5 μm thick SiC cellular ring around a Si-filled pore of around 53 μm diameter (likely to be originated from large vascular channels) is visible.

The bend test results and other properties have been presented in figure 4. The biomorphic Si/SiC ceramics contained more silicon than conventional reaction-bonded SiC (RBSC), a duplex ceramics also containing Si- and SiC-phases (Chakrabarti *et al* 1994). The strength and elastic modulus data are comparable to those of the conventional RBSC ceramics (figure 4, see also Chakrabarti *et al* 1994). The presence of fibrous structures is presumed to be contributing to the significant anisotropic strength of the final material. Thermogravimetry of the composite ceramic (figure 5) exhibited a small decrease in weight (~ 9%), indicating sufficient resistance of the final ceramic in high temperature oxidative environment. Most of the decrease in weight occurs between 580 and 680°C region probably due to the unreacted carbon getting oxidized.

3.3 *Porous cellular SiC ceramics*

Outward movement and reaction of residual Si-phase of biomorphic Si–SiC ceramic specimens occurred when they were positioned in the axial direction in intimate contact with powdered carbon during heating. The density and porosity of the Si-depleted material were found to be around 1·62 g/cc and 48·6 vol.%, respectively. XRD reveals *b*-SiC as the major phase present in the cellular SiC product thus formed with no detectable residual Si-peak (table 1). Figure 6 shows the cellular microstructure of Si-depleted porous *b*-SiC ceramic. As may be seen, the initial cellular anatomy was reproduced in the ceramic product. The SiC forming the cell wall material (e.g. struts) between the cells, is seen to be more or less sintered, resulting in densification of the strut material. The strut thickness was found to be 5–10 μm. Cellular SiC-ceramics have directed pores of diameter up to around 60 μm. Anisotropic cellular SiC ceramics may be suitable for applications as heat insulation structures, filters, catalyst carriers at high temperatures and thermally and mechanically loaded lightweight structures.

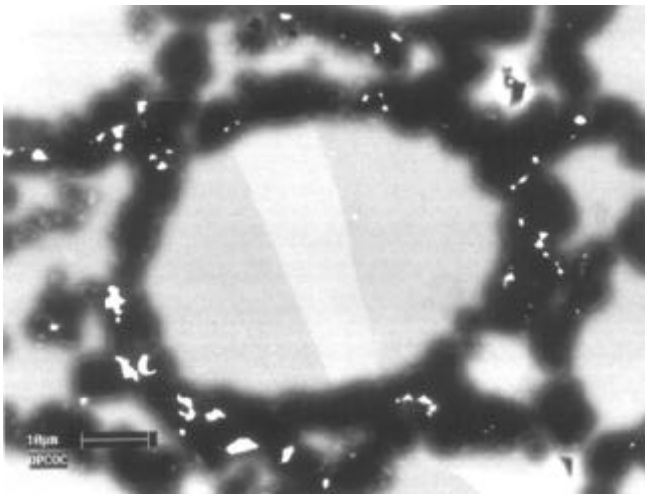

Figure 3. SEM of duplex Si/SiC showing formation of *b*-SiC cellular ring structure around Si-filled pore.

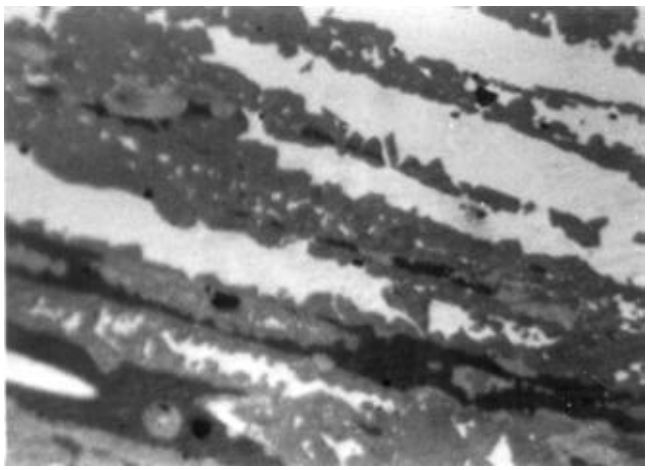

Figure 2. Light photomicrograph of duplex Si/SiC showing near-isomorphism with precursor plant.

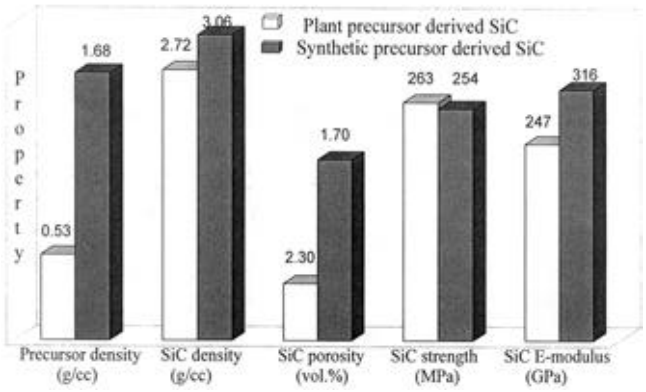

Figure 4. Comparative property diagram of plant precursor derived biomorphic SiC and synthetic precursor derived reaction bonded SiC (RBSC).

Table 1. Characteristics of biomorphic Si–SiC and porous cellular SiC ceramics synthesized from plant precursor.

Specimen	Density (g/cm^3)	Porosity (% vol.)	Major phases present
1. Biomorphic Si–SiC ceramic	2·70	2·26	*b*-SiC, Si
2. Porous cellular SiC ceramic	1·62	48·6	*b*-SiC

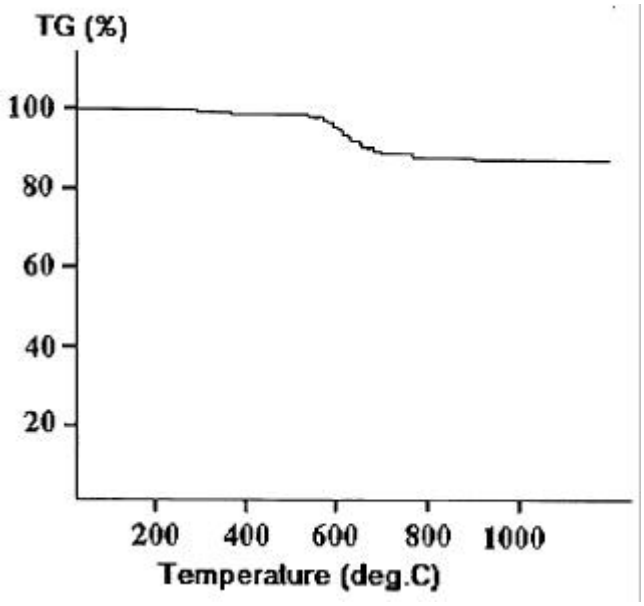

Figure 5. TGA scans during heating up to 1200°C of Si/SiC showing slow and low weight loss.

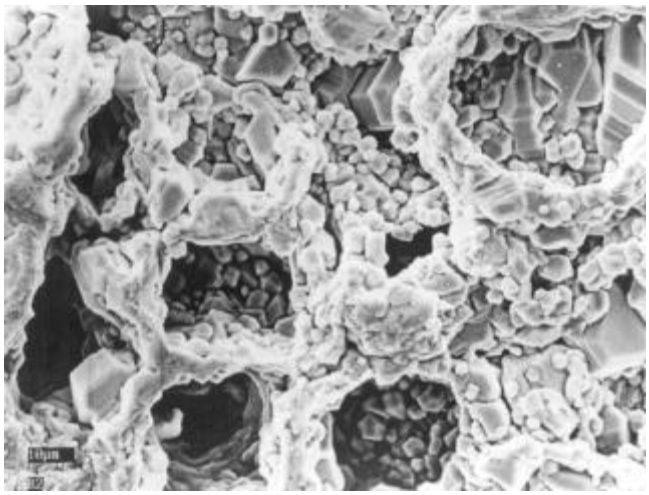

Figure 6. SEM of cellular porous SiC showing formation of *b*-SiC cellular strut structure around pores depleted in Si.

4. Conclusions

The present study demonstrates the possibility of producing novel Si/SiC duplex dense composite as well as cellular porous SiC ceramic retaining the morphological and structural features of the caudex stem of a monocotyledonous plant of local and renewable source. The dense biomorphic Si/SiC ceramic has little porosity, exhibits room temperature flexural strength and Young's modulus of 264 MPa and 247 Gpa, respectively, comparable to those of conventionally manufactured RBSC and also shows high oxidation resistance during heating up to 1200°C in flowing air. The cellular porous SiC ceramics has a porosity of around 49 vol.%. The pore size ranges up to around 60 μm in diameter. The materials are suitable for high temperature filters, catalyst support structures and such other applications.

Acknowledgements

The authors wish to thank Mr S K Dalui for measuring the flexural strength and Young's modulus, Mr S Das for XRD analysis and Mr T K Chatterjee for TGA work. They also wish to thank the staff-members of Non-Oxide Ceramic Division, CGCRI, for their cooperation and help.

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