Key Engineering Materials Vols. 189-191 (2001) pp 9-15

doi:10.4028/www.scientific.net/KEM.189-191.9

Synthesis and Characterization of SiC from Bamboo

C.R. Rambo and J.R. Martinelli

Brazilian Nuclear Energy Commission, Energy and Nuclear Research Institute,
Cx.P. 11049, CEP 05422-970 São Paulo SP, Brazil

Keywords: Bamboo, Fiber, SiC, Silicon Infiltration

Abstract

Bamboo is a natural composite material where cellulosic vascular fibers are dispersed in a lignin matrix. The present work investigates the transformation of these fibers into silicon carbide. Carbon preforms were prepared by heating bamboo pieces in nitrogen. Samples were treated at 700°C for 30 min to decompose the organic chains to carbon. Carbon preforms were then pyrolyzed in argon at temperatures in the range of 1200°C to 1500°C and time intervals of 5 min to 240 min. Infiltration of molten silicon in the remaining vascular fibers, and its influence on the synthesis of SiC during the pyrolysis was also investigated. Scanning and transmission electron microscopy, X-ray diffraction, X-ray fluorescence, and thermogravimetric analysis were performed to characterize the microstructure of the final materials. It was found out that cellulose was converted to fibers containing silica as a major constituent after processing. Silicon carbide was also obtained after silicon infiltration.

INTRODUCTION

Several biological species show natural composite structures and exhibit high mechanical strength and low density due to their genetic evolution[1]. The search for biological structures that can be used as precursors of biogenetic covalent ceramics is growing[2]. Wood, sea-shells and bamboo are examples of materials that can be used for this purpose. Natural fibers, such as sisal and jute were infiltrated with aluminium and titanium chlorides and transformed in Al_2O_3 and TiO_2 fibers after annealing in air[3,4]. Silicon nitrited coated-cotton fibers were transformed into SiC fibers after annealing in argon at 1200-1600°C[5]. Synthesis of ceramic materials from biomaterials requires the control of the microstructure during the processing to reproduce the original structure. The high open porosity of biomorphic products allows the use of liquid metal infiltration techniques to promote high temperature reactions and to form composite materials[6]. Infiltration of molten Si and Al-Mg alloys into ceramic preforms has been investigated[7,8].
During the liquid metal infiltration, some chemical reactions may occur in the interface of the matrix. The reaction product of Al-Mg alloys with carbon preforms is aluminum carbide if the temperature is higher than 650°C, according to the following equation:

$$4Al_{(l)} + 3C_{(s)} \longrightarrow Al_4C_{3\,(s)} \qquad (1)$$

Al_4C_3 drastically reduces the mechanical strength of the composite[9]. SiC is produced by Si infiltration into carbon preforms at temperatures above 1400°C as shown by eq. 2:

$$C_{(s)} + Si_{(l)} \rightarrow \beta\text{-}SiC_{(s)} \quad (2)$$

Bamboo (grass family *bambusoideae*) is a natural composite material in which the basic structure consists of cellulosic vascular fibers dispersed in a lignin matrix. All these cellulosic based fibers are made up of several fibrils, forming a complex layered structure called polylamellate wall structure[10]. The mechanical properties of bamboo are well known. Bamboo has a maximum strength along the fibers, due to the polylamellate wall structure. The distribution of the major chemical constituents of bamboo is typically 61% of cellulose and 32% of lignin and the density varies from 0.6 g/cm^3 to 0.8 g/cm^3 [10].

In the present work, synthesis and characterization of silicon carbide fibers and biomorphic C-SiC preforms from bamboo was investigated. Infiltration of molten silicon in the remaining vascular fibers of the preforms, and its effects on the synthesis of SiC during the pyrolysis was also studied.

EXPERIMENTAL PROCEDURE

Bamboo pieces were dried in an oven at 110°C for 24 h. Carbon preforms were prepared by heating these materials in nitrogen and cutted in rectangular shapes 8.5 x 7.5 x 6.5 mm^3 . A low heating rate was used (3°C/min) to avoid damages in the fibers due to the gas release. Samples were treated at 700°C for 1h to decompose the organic chains (cellulose and lignin) to carbon. Carbon preforms were then pyrolyzed in argon at temperatures in the range of 1200°C to 1500°C and time intervals of 1h to 4h in an electric tubular furnace. Molten silicon was infiltrated in the preforms by heating the material at 1500°C for 1.5 h. Scanning electron microscopy (*PHILLIPS XL30*) were performed to provide a full microstructural characterization. Elemental distribution was determined by EDS. X-ray diffraction (*RIGAKU DMAX100*) was used to determine the crystalline phases of the products. The main constituents and impurities of the samples were evaluated by semi-quantitative analysis by x-ray fluorescence (*RIGAKU RIX3000*). Thermogravimetric analyses (*NETZSCH STA409C*) were performed to determine the mass loss during the bamboo pyrolysis in air. Densities were measured by helium pycnometry (*MICROMERITICS 1305*) and by the Archimed's method. Compression strength was determined from compression strain-stress curves (*INSTRON 4400R*). Fig. 1 shows schematically the processing steps for the synthesis of SiC from bamboo.

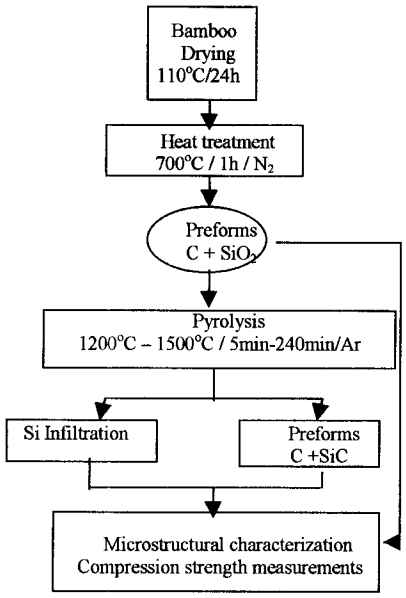


Fig 1 - Processing steps for synthesis of SiC from bamboo.

RESULTS AND DISCUSSION

Table 1 shows the composition of a carbonized bamboo preform after calcining it in air at 700° for 1h determined by a semi-quantitative analysis by x-ray fluorescence. The mass loss was 69.5%.

Table 1: composition of a carbonized bamboo preform after calcining it in air at 700 °C for 1h.

Compound	(wt%)
SiO_2	79.90
CaO	6.73
SO_3	6.27
MgO	2.71
P_2O_5	1.74
Al, K, Cl and Na	< 2.5

It is noticed that silica (80wt%) is the major constituent of the residue. The basic composition of the preform before firing is approximately 70wt% of carbon, 25wt% of silica and 5wt% of other compounds.

A carbonized bamboo preform was calcined in air at 450°C for 10min in order to reveal the silica skeleton. Fig. 2 shows SEM micrographies of these preforms after this heat treatment.

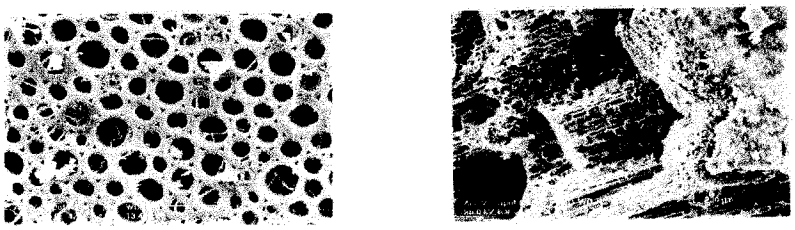
a) ____2μm b) _____20μm

Fig. 2 – SEM micrographies of the residual silica obtained by calcination of a carbonized preform in air at 450°C for 10min.

It is observed that silica is in the fiber-like shape with a triangular cross section (fig. 2a) having a mean edge length of 5μm. Fig. 2b) shows that these fibers are longer than 20μm and distributed around the pores of the preform.

Fig. 3 shows SEM micrographies of a carbonized preform obtained by calcining bamboo in nitrogen at 700°C for 1h.

It is noticed that the preform has a mean pore diameter of 20μm with 6 or 7 triangular silica fibers surrounding them (fig.3a). Fig. 3b) shows the pore distribution along the fibers.

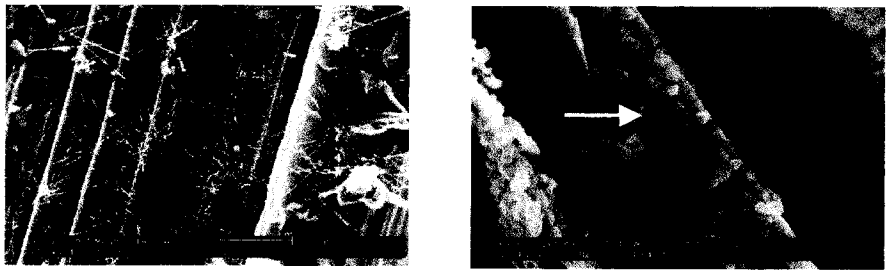


a) _____50μm b) _____200μm

Fig. 3 – SEM micrographies of a carbonized preform obtained by calcining bamboo in N_2 at 700°C for 1h. a) transversal section; b) longitudinal section.

Fig. 4 shows microstructural features of two preforms pyrolyzed at 1500°C for 1h and 4h in argon. It is seen that after 1h at 1500°C SiC whiskers were formed by the reduction of silica (fig. 4a). In fact carbon reduces silica to form SiC whiskers at temperatures above 1200°C[11]. These whiskers have an average lenght of 3μm and are distributed along the fibers. In fig.4b) it is observed that after 4h at 1500°C, SiC particles were formed due to the whisker's coagulative recrystallization. A similar result has been observed elsewhere[12]. SiC particles are also distributed along the fibers varying from 0.5μm to 1μm in length.

Fig. 5 presents the EDS spectrum taken from the region indicated by an arrow in fig. 4b). C and Si are the major elements in the particles but a small amount of K is also detected.



a) _____10μm b) _____2μm

Fig. 4 – SEM micrographies of pyrolyzed preforms in argon at 1500°C for: a) 1h; b) 4h.

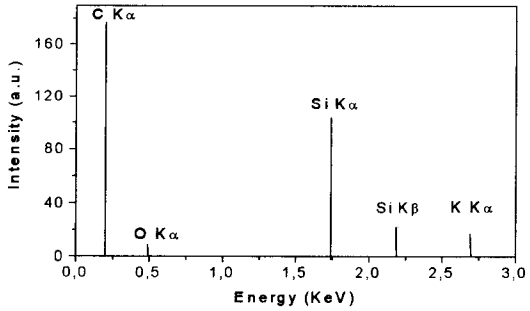


Fig. 5 – EDS spectrum taken from the region indicated by an arrow in fig.4b).

Fig. 6 shows the XRD pattern of a previously carbonized preform pyrolyzed at 1500°C for 4h in argon. XRD peaks related to crystalline β-SiC and a halo around $2\theta=20^{\circ}$ related to an amorphous silica phase can be seen. This result indicates that particles shown in figure 4b) are β–Si.

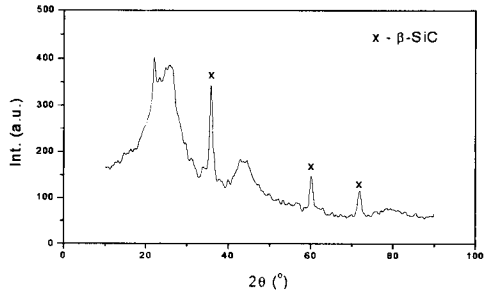


Fig. 6 - XRD pattern of a carbonized preform pyrolyzed at 1500°C for 4h in argon.

Fig. 7 shows the compression strength as a function of density for carbonized preforms prepared at 1500°C for different time intervals. The compression strength increases for higher densities. Although the densities do not vary more than 36%, the variation of the compression strength is higher than 400%. This fact can be explained by the different microstructural features of synthesized SiC, changing from whiskers to particles for longer treatment times. Since the density of SiC particles is higher than the one for SiC whiskers, the compression strength of preforms increases as a function of the amount of agglomerate particles along the fibers.

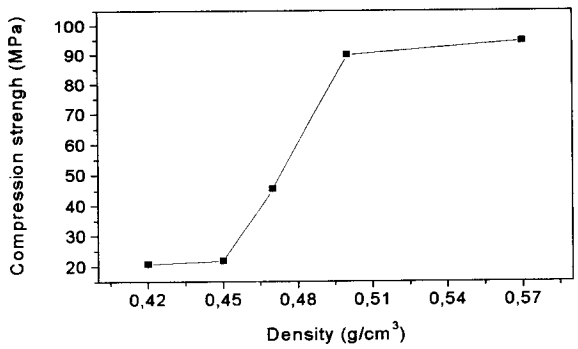


Fig. 7 – Compression strength as a function of density of pyrolyzed preforms.

Fig. 8a) presents the microstructural features of a cross section for a Si infiltrated preform heated at 1600°C for 1.5h in argon. Large pores of 20μm in diameter and small silicon and SiC obstructed pores can be seen. The density of this sample was 2.21g/cm^3 (the excess of Si was not etched out). Fig. 8b) shows the XRD pattern of the same material. XRD peaks related to crystalline β-SiC and a halo around 2θ=20° related to a remaining amorphous silica phase can be observed.

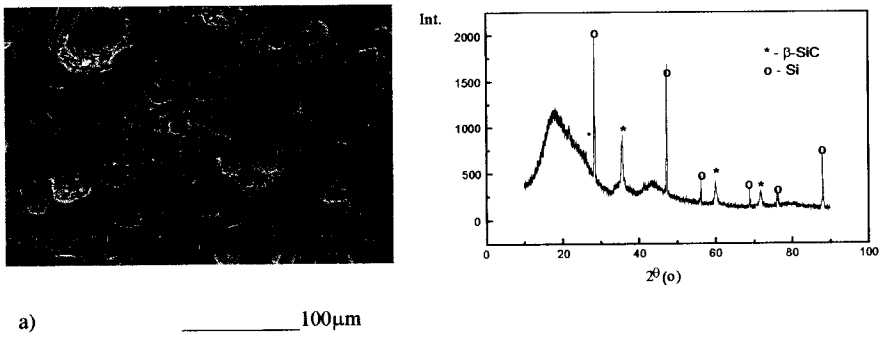


Fig. 8 – a) SEM cross section microcraphy of a Si infiltrated preform heated at 1600°C for 1.5h; b) XRD pattern of the same material.

CONCLUSIONS

SiC fibers and C-SiC-SiO_2 preforms were obtained from bamboo. The microstructural analysis revealed that silica fibers with triangular cross sections were distributed around pores. Therefore it was possible to synthesize SiC whiskers and particles by carbothermal reduction of silica. The densities of the carbonized preforms vary from 0.4g/cm^3 to 0.6g/cm^3 and the compression strength is in the range of 20-100MPa. These results suggest that this material can be used to produce metal matrix composites by liquid infiltration. Porous low density SiC preforms can be infiltrated by Al-Mg alloys to produce metal matrix composite materials.

ACKNOWLEDGEMENTS

The authors thank Prof. Dr. Peter Greil (Erlagen Univ Erlangen Nurnberg, Erlangen, Germany)for the profitable discussion about this work, Mr. Valter Ussui and Cristiane A. Menezes for the technical cooperation. The thermal analyses and the x-ray diffraction analyses were performed on a facility sponsored by FAPESP under contracts #95-5172/4 and #96-9604/9 respectively.
C.R.Rambo thanks CNPq for the scholarship.

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Advanced Powder Technology II
doi:10.4028/www.scientific.net/KEM.189-191

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