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Replication of jute stem for porous cellular ceramics/composites in the SiO_2–SiC–C System☆

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Abstract

The present work demonstrates that carbonaceous template preforms derived from jute stem by thermal and microwave processing can be infiltrated at room temperature under vacuum with silica sol, obtained by acid catalyzed hydrolysis of tetra ethyl orthosilicate (TEOS). The microwave processed carbon-preforms are better suited for exercising control of SiO_2 infiltration. The oven-dried hybrid C/SiO_2 material accumulates silica as $SiO_2{\cdot}nH_2O$ (n lying approximately between 1 and 3) and may be suitably converted, depending on the modes of processing, into macroporous cellular SiO_2 or SiC ceramics or SiC/SiO_2/C or SiC/C or SiC/SiO_2 composites with tailored composition and microstructures. The processes for synthesis of the specific products have been developed and their phase compositions and microstructures have been examined through characterization by bulk density measurements, X-ray diffraction and scanning electron microscopy.

Keywords: Jute; Cellular; Porous; SiC-SiO_2-C Ceramic/Composite

1. Introduction

Ceramics with high volume fraction of porosities and specific orientation of macro- and micro-pores have been of immense active interest to researchers because of their potential special applications requiring differential high temperature corrosion resistance, differential low thermal and electrical conductivities, controlled permeability, specific strength, wear resistance and surface area. Consequently they are attractive materials for appliances like high temperature gas filters, insulator systems, catalytic supports, chemical sensors, biomedical devices and many more.

The routes to their synthesis are varied and many as reviewed by Studart et al. [1]. One of them involves replication of natural cellular precursors such as plants. Plant precursors, on their part, are also of diverse structures and are capable of yielding carbonaceous preforms of different bulk densities and porosities both in extent and in asymmetric distribution. The carbon cellular precursor from plants may be used for fabrication of dense or porous composite ceramics such as Si/SiC [2], porous SiC [3] and others [4]. The process routes involve simultaneous melt infiltration and reaction [2–4] or sol/solution infiltrations followed by treatment for reaction [5,6] or complete oxidation of the carbonaceous precursor [7].

Jute stem is a unique plant precursor and porous Si/SiC cellular composites [4] and ultraporous alumina ceramic [7] have been realized from them following the carbon template route.

Plant derived C-preforms infiltrated with silica sols or their organo-alkoxide precursors can yield C/SiO_2 hybrid precursors with morphological and structural features of the parent plant and can constitute a special route of synthesizing/fabricating SiC based ceramics/composites [5,8–10].

The present article deals with preparation of macroporous cellular ceramics/composites in the SiO_2–SiC–C system from jute stem via the sequential processing for making C-preform, C/SiO_2 hybrid precursor and ceramics/composites with tailored composition and microstructure. The modalities for development of the specific products, their phase and pore compositions and microstructures have been explored, established and discussed.

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2. Experimental

2.1. *Thermal and microwave processing of jute stem into C-preform*

Sun-dried jute stem (JS) after winning the outer cover of textile fibers were collected from various local sources, cut into small lengths (0.02–0.06 m) and were oven-dried at 338 K for 24–72 h. The elemental and molecular compositions of the JS were very similar to those already reported [4].

Pieces of oven-dried JS were thermally treated by controlled heating in an electrically heated muffle furnace under self-generated atmosphere. The gases and volatiles generated were allowed to escape through a cold trap to condense the tarry materials. Temperature was raised at different rates in segments: 2 K min^{-1} up to 493 K, 1 K min^{-1} and 3K min^{-1} in the ranges of 493–773 and 773–1073 K, respectively. The furnace was allowed to cool and the C-preform products were recovered. Dimensional shrinkages and weight losses for drying and for thermal processing were measured.

Samples of jute stem were also microwave treated for preparing C-preforms in a laboratory single mode MW oven (24.5 GHz) under vacuum. The samples were placed in a special borosilicate glass chamber fitted with a cover connected to a vacuum pump outside to help remove the volatiles as they evolved. Although microwave processing of plant materials into carbonaceous products are known [11], the optimum conditions of MW power input, vacuum level and duration of treatment for this work were found out by preliminary trials. It was established that the oven operating at full power (800 W) under vacuum suction of 400–500 mm mercury and microwave showering time of 10–15 min yielded workable preforms with various degrees of carbonization (on the basis of the degree of weight loss). Embedding the samples in SiC powder (acting as MW energy susceptor [12]) was helpful towards uniform carbonization of the samples.

2.2. *Preparation silica sol*

The technique of acid catalyzed hydrolysis of TEOS was followed [13]. A mixture of 4 ml TEOS, 1 ml of ethyl alcohol and 0.3–0.4 ml of 1(N) HCl was maintained at 55–60 °C for ~4 h in a water bath. Silica (SiO_2) content in sol was measured by weighing the residual mass obtained by first drying a known volume of the sol at 110 °C and then heating the residue at 400 °C for 1 h.

2.3. *Infiltration into C-preform*

The C-preform was primarily soaked with silica sol held in a small glass trough and then mild vacuum (300–500 mm mercury) was applied for few minutes (8–10 min) for maximum weight gain (measured after oven drying of the sample at ~80 °C for 24 h). Freshly prepared transparent sol was used for infiltration into C-preform.

The vacuum level and the time for maximum gain in weight were established by trials. The sol-infiltrated C-preforms were

Table 1
Processing of jute stem (JS) into carbon-preform.

JS	Wt of dry JS (g)	Pre-carbonization dimension				Proc. mode[a]	%Wt loss	Dimensional shrinkage (%)				Wt of C-preform (g)	Product Id
		L (cm)	OD (cm)	ID (cm)	Vol (cm^3)			*L*	OD	ID	Vol		
JS-1–JS-5	0.89–1.32	4.04–6.26	1.05–1.59	0.28–0.36	3.31–10.2	T	75.1–75.7	21.3–22.3	26.2–32.1	51.8–61.8	56.6–62.1	0.218–0.329	C-1-C-5
JS-6–JS-11	0.22–0.57	2.80–4.85	0.67–1.57	0.29–0.44	0.93–5.95	M	65.5– 72.0	14.9–20.0	17.6–25.2	22.3–31.9	37.9–50.5	0.070–0.171	C-6-C-11

[a] T: thermal processing, M: microwave processing.

then allowed to dry in air oven at ~80 °C for 8–24 h to constant dry weight. The cycle of infiltration and drying was repeated several times (up to four cycles), in some samples, to achieve maximum weight gain of the C-preform.

2.4. Conversion of sol-infiltrated C-preform into ceramics

The sol-infiltrated C-preforms were then treated for conversion into ceramic:

(i) by heating in an inert atmosphere (N_2 gas flowing at a constant rate of ~100 ml/min) at desired treatment temperatures, and/or
(ii) by heating in a furnace in air at an appropriate temperature for burning out residual carbon.

In all cases the materials were held for 1 h at the highest processing temperature.

2.5. Characterization of samples

Samples of C-preform, before and after silicic sol infiltration and ceramics developed were characterized by photographic imaging, measurement of bulk density (BD) and porosity, by X-ray diffractometry (XRD) [Rigaku MINIFLEX] on powdered samples and by scanning electron microscopy (SEM) [S-3400N, Hitachi] of fractured surfaces.

3. Results and discussion

Table 1 summarizes the processing of JS precursors into corresponding C-preforms identified as C-1 to C-11 by thermal and microwave processing. In both cases the dimensional shrinkages are highly anisotropic. The losses in weight by thermal processing are seen to be higher compared to those in MW processing. In fact, attempts at achieving higher loss in weight by MW processing were mostly met with products' disintegration may be due to near complete loss of dipoles in the substrate.

Extent of silica (hydrated) accumulated in different C-preforms is presented in Table 2. Sol prepared in the manner described previously was almost transparent and stable. Left at room temperature, it gradually turns viscous and sets into a gel in about 72 h. Solid content of sol was found to be 0.22 g/ml of sol.

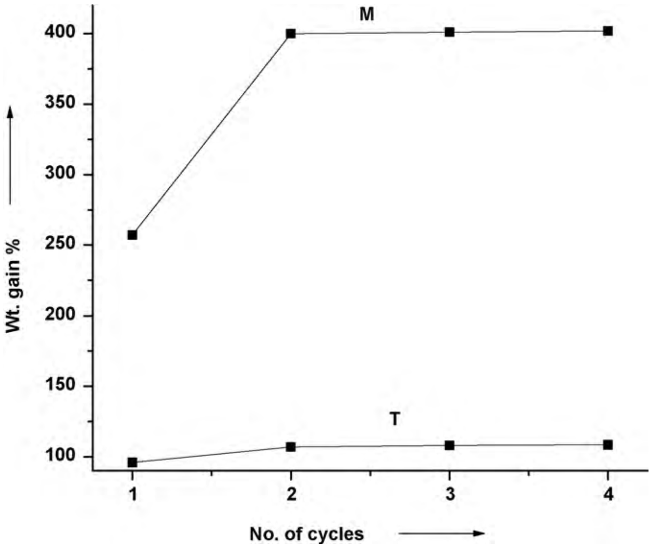

Fig. 1. Weight gain (per cent increase in dry weight) as a function of number of cycles of sol infiltration by thermal and by MW processed C-preforms [T = thermally processed (C-3), M = MW processed (C-8)].

After infiltration, however, the sol adhering to the surfaces and pore interiors gels quickly. It is seen (Table 2) that the uptake is fast and almost peaks in one–two cycles.

It is found that thermally processed C-preforms take up much less sol compared with those processed by MW. It is possible that in the latter cases due to incomplete decomposition of the biopolymer materials in the JS, there are some residual O–H linkages that help quicker infiltration [14] and gelation and the pick-up is also considerably higher. The microwave processed C-preforms are thus better suited for enhanced and controlled SiO_2-sol infiltration. The end products of C/SiO_2 hybrid precursors (C-preforms with accumulated hydrated silica) are identified as CS-1, CS-2, etc. (Table 2). Fig. 1 depicts the difference in sol uptake behavior of two typical C-preforms – C-3 and C-8, the former being thermally processed and the latter MW processed.

C/SiO_2 hybrid precursors (CS) were subsequently processed to yield ceramics; the processing conditions and other details are summarized in Table 3. Derived ceramics/composites from the corresponding CS-precursors are designated as CC-1, CC-2, etc. Of the samples included in Table 3, only CS-3 was given a two-stage heat treatment in nitrogen: the first at 1000 °C (1 h) followed by the second at 1450 °C (1 h). All the other samples

Table 2
C-SiO_2 hybrid precursor from C-preform by sol infiltration.

C-preform	Initial wt. (g)	BD of C-preform (calculated, approx.) (g cm^{-3})	Uptake (oven dried) (%)				Final wt. (g)	Product Id	Comment
			1st cy	2nd cy	3rd cy	4th cy			
C-3	0.225	0.17	96	107	108	108	0.466	CS-3	Volumes of dry CS closely matched those of C-vols
C-6	0.083	0.12	214	277	–	–	0.313	CS-6	
C-7	0.070	0.12	132	282	567	–	0.397	CS-7	
C-8	0.083	0.17	257	400	401	402	0.420	CS-8	
C-9	0.089	0.12	265	409	581	–	0.593	CS-9	
C-11	0.171	0.14	137	–	–	–	0.467	CS-11	

Table 3
Ceramization of carbon-silica (CS) hybrid precursors.

Sample Id	Wt. of CS samples before processing (g)	Heat treatment details, temp (°C), ambient atmosphere	Wt. of products (g)	Loss in wt. (%)	Volume shrinkage (w.r.t. original JS vol) (%)	BD (Exptl.) ($g\ cm^{-3}$)	Product Id
CS-3	0.466	1600, N_2	0.195	57.60	63.0	0.20	CC-3
CS-6	0.313	1000, N_2/1450, N_2	0.153	51.10	74.8	0.53	CC-6
CC-6	0.153	1200, O_2	0.143	06.50	76.1	0.49	CC-6A
CS-7	0.397	1200, O_2	0.270	61.00	NM	1.81	CC-7A
CS-8	0.420	1450, N_2	0.292	30.50	73.6	0.89	CC-8
CS-9	0.593	1450, N_2	0.370	37.60	NM	0.57	CC-9
CC-9	0.370	1200, O_2	0.341	07.80	75.4	1.59	CC-9A
CS-11	0.467	1600, N_2	0.240	48.60	75.0	0.41	CC-11

NM: not measured.

were subjected to one stage heat treatment in nitrogen or in air (oxygen). The ceramized products CC-6 and CC-9 derived from CS-6 and CS-9, respectively, were further heat treated (1200 °C, 1 h) in air to yield products identified as CC-6A and CC-9A, respectively. CC-7A, however, is the product derived by heating CS-7 at 1200 °C in air. It was expected that this heat treatment in air would burn off any retained carbon in CC and CS.

Bulk densities of the end-ceramics/composites have also been presented in Table 3 along with volume shrinkages (with respect to the volumes of starting JS precursors). BD of CC-3 ($0.20\ g\ cm^{-3}$) shows a small increment over that of C-3 ($0.17\ g\ cm^{-3}$) (cf. Table 2) and this is the only sample that undergoes very little shrinkage during ceramization (cf. Tables 1 and 3). But, for all other samples in Table 3 the shrinkages during ceramization are considerably higher. The increased BD's of these samples are partly due to shrinkages and partly due to enhanced silica content in them.

Calculated phase compositions (by weight and by volume) of five different ceramics/composites (CC-3, CC-6, CC-9, CC-6A and CC-9A) are shown in Table 4.

Photographs of some of the CC and CC-A products are reproduced in Fig. 2. X-ray diffraction profiles and SEM images (back scattered) of some of the selected samples enlisted in Table 4 are shown in Figs. 3–6. The XRD profiles indicate that the composites derived comprise of SiC/C (Fig. 3a for CC-3), SiC/SiO_2/C (Figs. 4a and 5a for CC-6 and CC-9, respectively) or SiC/SiO_2 (Fig. 6a for CC-9A). The CS hybrid precursors, such as CS-7, could be heat treated at 1200 °C in air into cellular porous SiO_2 ceramic (CC-7A, Table 3, Fig. 2b) and the SiC/C composite (e.g. CC-3, Fig. 3) could be similarly treated to oxidize carbon to yield cellular porous SiC ceramic.

Calculated phase compositions, including pores, by weight and by volume, of different ceramics/composites are as presented in Table 4 and were based on, *inter alia*, following observations and arguments.

3.1. Conversion into SiC and possible ceramics/composites

Assuming that the overall reaction between carbon and silica to form silicon carbide is represented as [5,15,16]

$$3C + SiO_2 = SiC + 2CO \tag{1}$$

it could be easily calculated that C-preforms (C-1, etc. of Table 1) comprising essentially of elemental carbon, must pick-up at least 1.667 g silica for each gram of C-preform for stoichiometric conversion to SiC. It can be presumed, under appropriate conditions (proper temperature, sufficient duration and non-oxidizing atmosphere such as nitrogen), reaction (1) would run to completion and CS-precursors having less than this threshold accumulation of silica, would lead to CC materials having un-reacted residual carbon and those accumulating more are likely to have residual SiO_2 in the end-ceramics. It is presumed that in the C/SiO_2 hybrid precursors silica is present in the hydrated form ($SiO_2{\cdot}nH_2O$). Since thermally derived C-preforms do not accumulate enough silica (cf. Table 2, Fig. 1) for complete conversion of carbon into SiC, the end-ceramics are likely to lead to composites with residual carbon. Accumulations of silica by repeated infiltration of commercial silica sol in thermally processed wood-carbons

Table 4
Phases and their compositions in the final ceramics/composites.

Product ceramic Id	Phases-weight composition						Phases-volume fraction			
	Weight (g)			Weight fraction						
	SiC	C	SiO_2	SiC	C	SiO_2	V_{SiC}	V_C	V_{SiO_2}	V_{pore}
CC-3	0.085	0.110	0.0000	0.436	0.564	0.000	0.059	0.006	0.000	0.936
CC-6	0.069	0.010	0.074	0.451	0.065	0.484	0.076	0.017	0.110	0.797
CC-6A	0.069	0.000	0.074	0.483	0.000	0.517	0.083	0.000	0.096	0.821
CC-9	0.045	0.029	0.296	0.122	0.078	0.800	0.022	0.023	0.196	0.759
CC-9A	0.045	0.000	0.296	0.132	0.000	0.868	0.066	0.000	0.592	0.342

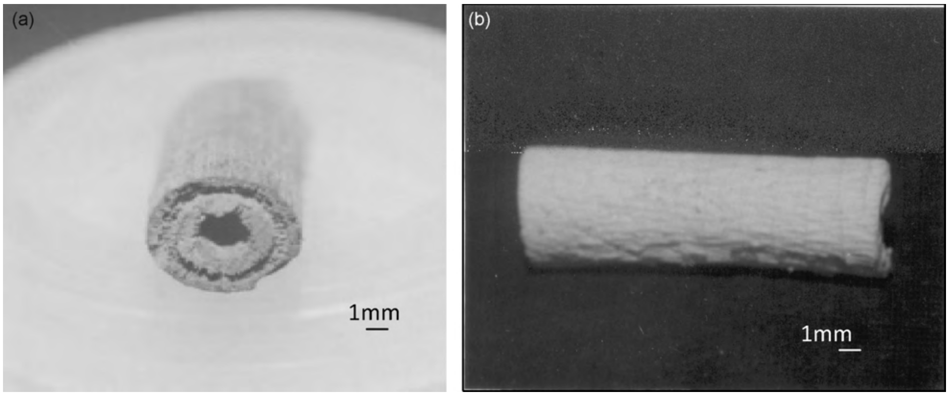

Fig. 2. Photograph of (a) sample CC-3 (1600 °C/N_2) and (b) CC-7A (1200 °C/O_2).

are reported [5,16] to be lower than the stoichiometric requirement for full conversion into SiC.

On the contrary, C-preforms derived by MW processing are capable of accumulating more than enough silica required for stoichiometric formation of SiC. Infiltration and accumulation of silica in these samples can be controlled and can be stopped at either side of the threshold (cf. Table 2, Fig. 1) to lead to products with either excess carbon or excess silica. However, incomplete reactions also may lead to residual carbon or residual silica. Any carbon-excess ceramic can be further heat treated in air to burn the carbon off.

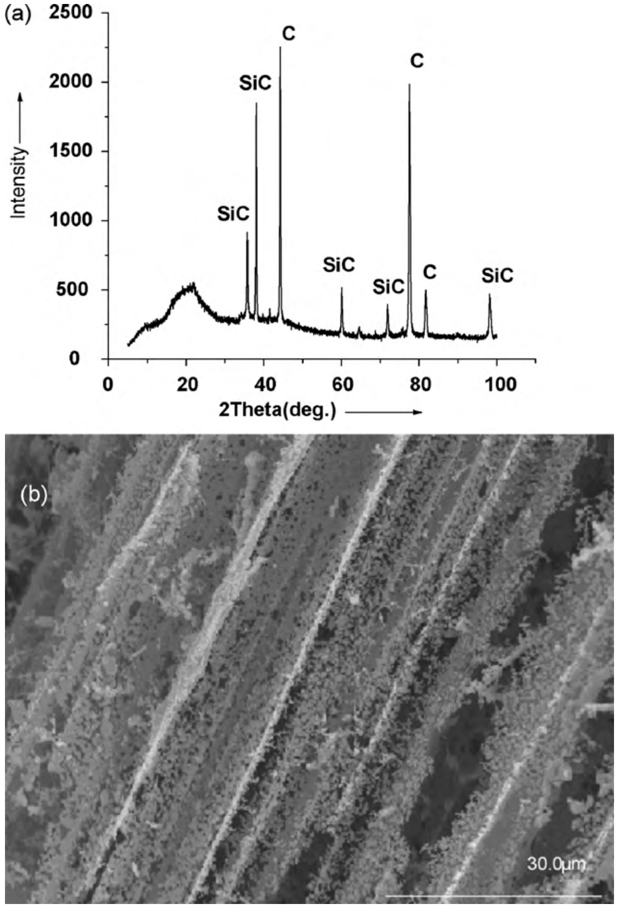

Fig. 3. Product ceramic CC-3 (a) XRD profile and (b) SEM image.

XRD profile of CC-3 (Fig. 3a) shows the presence of SiC and C phases only. Since CS-3 gained only 108% of C-3 (less than stoichiometric requirement of SiO_2, accumulated as $SiO_2 \cdot nH_2O$; n was calculated to be about 3 in this case), it could be presumed that the SiO_2 introduced reacted completely leaving some un-reacted carbon.

XRD profile of CC-6 (Fig. 4a) and of CC-9 (Fig. 5a) reveal the presence of SiC, SiO_2 (β-cristobalite) and C caused either by stoichiometric inadequacy of any of the reactants or by

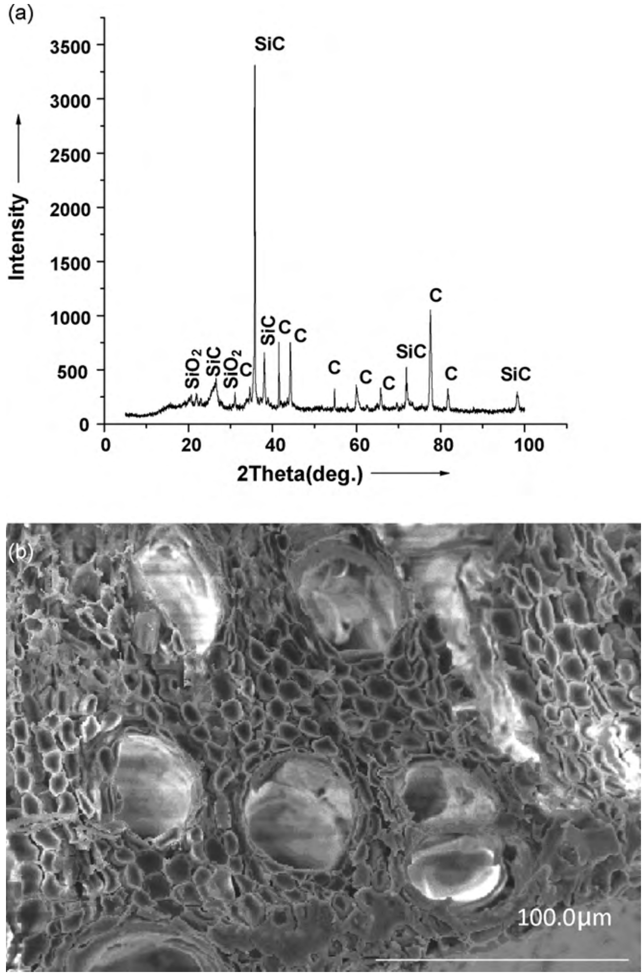

Fig. 4. Product ceramic CC-6 (a) XRD profile and (b) SEM image.

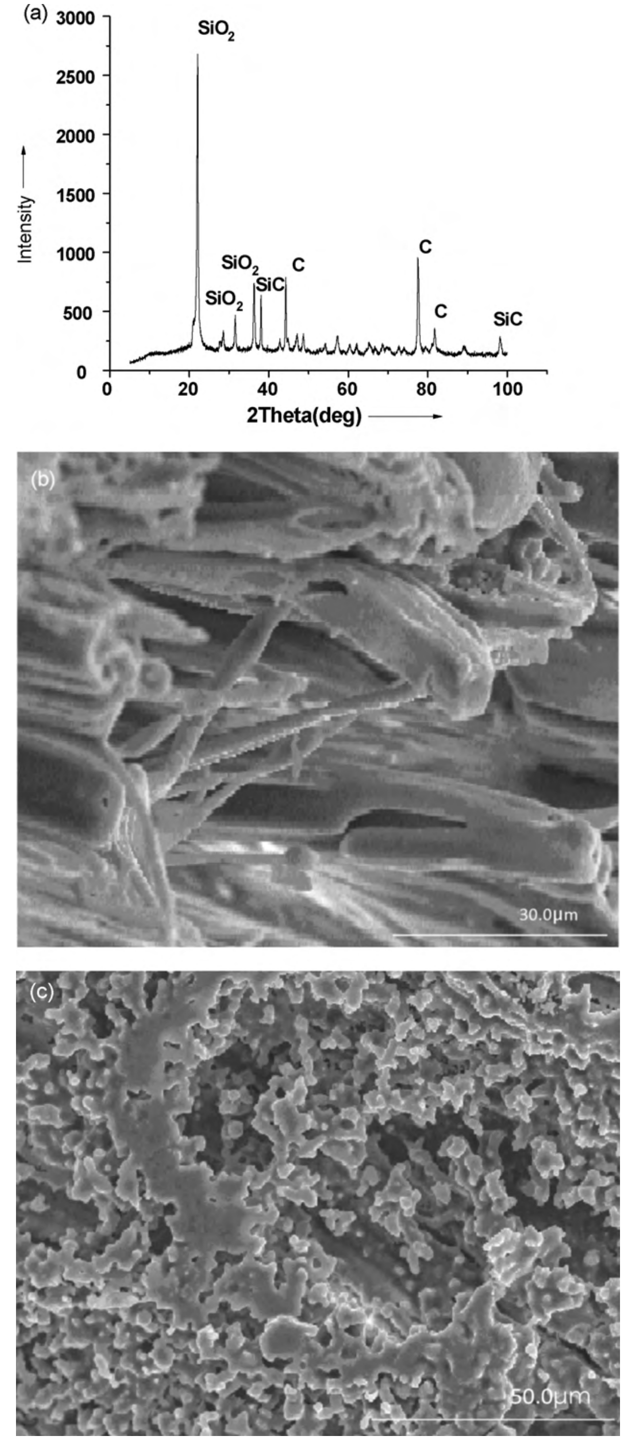

Fig. 5. Product ceramic CC-9 (a) XRD profile and SEM images (b) longitudinal section and (c) cross section.

incomplete reaction. Carbon could not be detected in CC-9A (XRD profile, Fig. 6a), presumably due to its loss by oxidation.

3.2. *Volume fraction of SiC can be directly calculated using bulk density of C-preform*

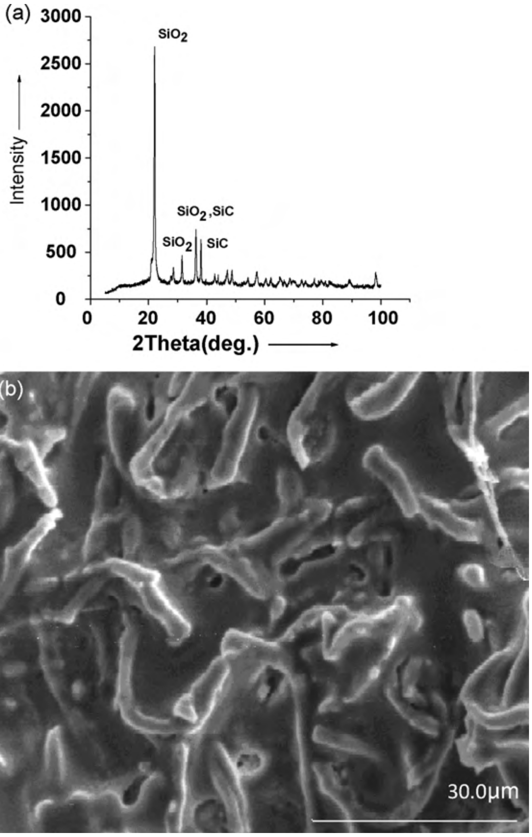

Fig. 6. Product ceramic CC-9A (a) XRD profile and (b) SEM image (longitudinal section).

Assuming that during infiltration–accumulation of sol and reaction leading to formation of SiC, the volume of C-preform remains unchanged and SiC forms *in situ* by one-third of the carbons present in the preform [as per reaction (1)], 3 mol of carbon in the preform has a volume $3M_C/dC_B$ (dC_B is the bulk density of C-preform) in which one mole of SiC would occupy a volume of M_{SiC}/d_{SiC} [M_C and M_{SiC} are the molecular weights of carbon and SiC (viz., 12 and 40), respectively]; so, the volume fraction of SiC would be given by (molar volume of SiC/volume of C-preform containing 3 mol of carbon), i.e. $(M_{SiC}/d_{SiC})/(3M_C/dC_B)$.

Putting the values of M_{SiC}, M_C and d_{SiC} (3.20 g cm^{-3}, the density of beta silicon carbide)

$$V_{SiC} = \left(\frac{1.038}{3}\right) dC_B; \quad \text{or,} \quad V_{SiC} = 0.346 dC_B \tag{2}$$

For volume fractions of phases present, the general equation is

$$d_{Cer} = V_{SiC} \cdot d_{SiC} + V_C \cdot d_C + V_{SiO_2} \cdot d_{SiO_2} + V_{pore} \cdot d_{pore} \tag{3}$$

where V_x represents volume fractions of respective phases, the sum of which must be 1 and d_{Cer}, d_{SiC}, d_C, d_{SiO_2} and d_{pore} are the bulk density of the ceramic (single/composite), true densities of SiC, C (amorphous), SiO_2 (β-cristobalite) and pore, respectively.

As $d_{pore} = 0$,

$$d_{Cer} = V_{SiC} \cdot d_{SiC} + V_C \cdot d_C + V_{SiO_2} \cdot d_{SiO_2} \tag{4}$$

3.3. Corrections for full decomposition of MW processed samples

In calculating the weight and volume fractions of phases in ceramics derived from the MW processed C-preform, BD of C-preform (dC_B) was corrected for full decomposition and for full shrinkage. It is seen (Table 3) that all ceramics/composites derived from MW processed C-preforms undergo volume shrinkages of ~75% of the starting JS precursor presumably due to completion of decomposition that took place during processing for ceramization. It is also to be noted that thermally processed JS samples undergo ~75% weight loss during processing of the C-preform itself, compared to lower weight losses in MW processing (Table 1). The BD of C-preform used for making CC-6 (and CC-9) was thus corrected on the basis of 75% weight loss and 75% volume shrinkage of the corresponding JS precursors. Despite such shrinkages the ceramics/composites maintain their cellular features and integrity as revealed by the photographs (Fig. 2) and SEM images (Figs. 3–6) of them.

So, for example, the weight and the volume of C-6 that are involved in the process of ceramization should be 0.298 g (wt. of JS) $\times$ 0.25 = 0.0745 g and 1.26 cm^3 (volume of JS) $\times$ 0.25 = 0.315 cm^3, respectively.

Corrected BD (dC_B) of C-6 that should be considered reasonable for calculation of volume fraction of SiC (V_{SiC}) in CC-6/CC-6A using Eq. (2) is thus

$$\left(\frac{0.0745}{0.315}\right)\,\mathrm{g\,cm^{-3}} \approx 0.24\,\mathrm{g\,cm^{-3}}.$$

The details of calculations of the weight and volume fractions of phases in ceramics/composites presented in Table 4 are shown in Annexure.

It is noteworthy that in CC-6/CC-6A the conversion of carbon into SiC has been much higher compared to that in CC-9/CC-9A although in both cases the maximum temperature of treatment is 1450 °C and the duration at that temperature is the same (Table 3). The higher conversion in CC-6/CC-6A is possibly due to the two-stage heat treatment (1000 and 1450 °C in N_2) given to CS-6 in contrast with the single stage heat treatment given to CS-9. These results indicate, further, that carbothermal reduction of silica into silicon carbide by C-preforms derived from plants can be achieved through ceramization treatment at as low temperature as 1450 °C compared to higher temperatures reported [5,16].

A relatively high BD of 1.59 g cm^{-3} of CC-9A compared to that of CC-9 (BD: 0.57 g cm^{-3}) is indicative of considerable shrinkage during the formation of CC-9A at 1200 °C/air. The SEM of CC-9A (Fig. 6b) reveals that the silica phase has started fusing on the surfaces, but the cellular structure has not collapsed. The SEM image of CC-9 (Fig. 5b) clearly indicates preservation of cellular structure and this is also true for CC-3 (Fig. 3b) and for CC-6 (Fig. 4b).

Some approximations are involved in calculating the phase compositions; for example, carbon in the samples may not be totally amorphous as they exhibit characteristic sharp XRD peaks. But they were amorphous to start with and were so during most part of processing [4]. Bulk density of silica rich samples such as CC-9A (Table 4) is relatively high indicating considerable shrinkage and so the dC_B values as calculated may not be strictly applicable in calculating volume fraction of SiC using Eq. (2). Nevertheless, the phase compositions, weight and volume fractions of phases as presented in Table 4, are reasonably realistic and clearly indicate that different porous cellular ceramics/composites with wide range of porosities (34–94%) can be fabricated in the SiO_2/SiC/C system from a single plant precursor. The possibilities are schematically shown in Fig. 7.

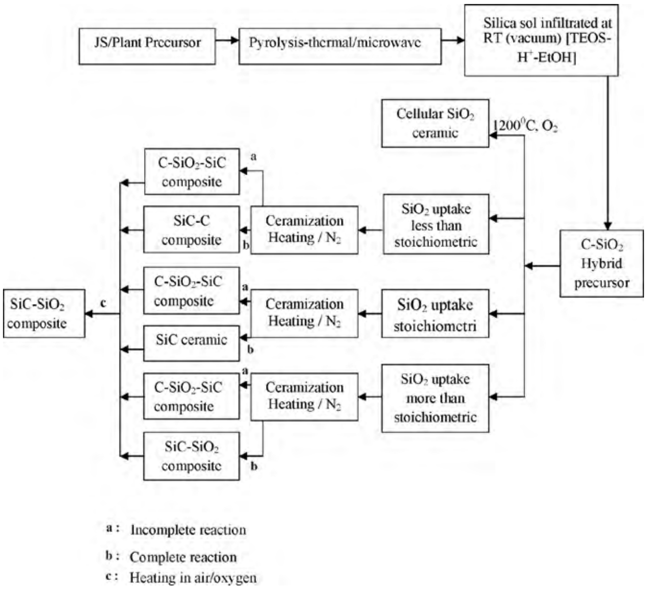

Fig. 7. Schematic showing possible ceramics/composites from plant precursors via silica accumulation by sol infiltration into C-preform and thermal processing for ceramization.

The volume fractions of SiC in the products demonstrated in this work have been rather low (Table 4) as the particular plant precursor (JS) itself is of low bulk density and yields C-preforms that are of high porosity and inherently low in carbon content. By suitable selection of plant precursor, C-preforms with much higher densities may be prepared and the proportion of SiC in the ceramics/composites derived from them may be considerably increased.

4. Conclusion

The following general conclusions may be drawn from the study:

1. Porous cellular ceramics/composites in the SiO_2/SiC/C system with ranges of compositions and porosities can be synthesized/fabricated using Jute stem as plant precursor and processed through the route of carbonization – silica accumulation by sol infiltration – ceramization.
2. It is possible to realize single component silica or silicon carbide ceramics, two component SiC/C, SiC/SiO_2 or three component SiC/SiO_2/C composites from the single plant precursor.

3. Carbon-preforms can be made from the plant precursor both by thermal as well as by microwave processing. In is advantageous to have incompletely carbonized MW processed C-preforms as they are better suited for subsequent silica sol infiltration in terms of rate and control of infiltration and extent of accumulation as hydrated silica ($SiO_2{\cdot}nH_2O$).
4. Although the proportion of SiC in the products made from jute stem is relatively small, it can be considerably increased by selecting denser plant precursors yielding C-preforms of higher bulk densities.

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Appendix A. Annexure

A.1. Calculation of phase compositions of CC and CC-A composites (Table 4).

A.1.1. CC-3: [1600 °C/N_2]

XRD profile: SiC & C (Fig. 3a)
Weight of C-3 = 0.225 g
Weight of CS-3 = 0.446 g
Weight of CC-3 = 0.195 g
Weight of $SiO_2{\cdot}nH_2O$ in CS-3 = 0.446 − 0.225 = 0.241 g
Weight of SiO_2 = 0.241 × (60/60 + 18n) g
Weight of SiC = 0.241 × (60/60 + 18n) × 40/60 g
Weight of C reacted = 0.241 × (60/60 + 18n) × 36/40 g
Weight of C un-reacted = 0.225 − 0.241[(60/60 + 18n) × 36/40] g
Weight of SiC + weight of C un-reacted = weight of CC-3
So, 0.241[(60/60 + 18n) × 40/60] + 0.225 − 0.241[(60/60 + 18n) × 36/40] = 0.195
Or, 14/60 + 18n = 0.124
Or, n = 2.94
So, weight of C un-reacted = 0.225 − 0.241(60 × 36/40 × 113) = 0.110
So, SiC = 0.195 − 0.110 = 0.085 g
Weight fractions: SiC: 0.436, C: 0.564
For volume fractions, from Eq. (4),
$d_{Cer} = V_{SiC}{\cdot}d_{SiC} + V_C{\cdot}d_C$ (as V_{SiO_2} is zero)
Or, $0.201 = V_{SiC}{\cdot}d_{SiC} + V_C{\cdot}d_C$
From Eq. (2), $V_{SiC} = 0.346\ dC_B = 0.346 \times 0.17 = 0.059$
Then, $0.201 = 0.059 \times 3.2 + V_C \times 1.9$ (d_{SiC} and d_C are 3.2 g cm^{-3} and 1.9 g cm^{-3}, respectively)
So, $V_C = 0.0064$; $V_{pore} = 1 - V_{SiC} - V_C = 0.936$.
Thus the volume fractions of the phases in CC-3 are:
$V_{SiC} = 0.059$, $V_C = 0.0064$ and $V_{pore} = 0.936$

A.1.2. CC-6 [1000 °C, N_2/1450 °C, N_2] and CC-6A [CC-6 at 1200 °C, O_2]

Weight of JS = 0.298 g
Weight of C-preform = 0.083 g (Table 2)
Weight of C and hydrated silica ($SiO_2{\cdot}nH_2O$) = 0.313 g (Table 2)
Weight of hydrated silica ($SiO_2{\cdot}nH_2O$) = 0.313 − 0.083 = 0.230 g
Weight of CC-6 (C + SiC + SiO_2 as per XRD, Fig. 4a) = 0.153 g (Table 3)
Weight of CC-6A (SiC + SiO_2) = 0.143 g (Table 3)
Weight of un-reacted C = 0.153 − 0.143 = 0.01 g
Weight of C from JS = 0.298 × 0.25 = 0.0745 g (25% of the wt of JS)
Weight of C reacted to form SiC = 0.0745 − 0.01 = 0.0645 g
So, weight of SiC formed = 0.0645 × 40/36 = 0.0694 g
So, weight of SiO_2 in the final ceramic = (0.143 − 0.0694) g = 0.0736 g
Weight of SiO_2 reacting to form 0.0694 g SiC = 0.0694 × 60/40 = 0.1041 g
So, total SiO_2 uptake = 0.0736 + 0.1041 = 0.178 g
So, nH_2O = 0.230 − 0.178 = 0.0523 g
SiO_2:H_2O = 0.178/60:0.0523/18 = 1:0.97
So, the weight fractions of phases in CC-6:
SiC: 0.069/0.153 = 0.451, SiO_2: 0.074/0.153 = 0.484, C: 0.010/0.153 = 0.065
And the weight fractions of phases in CC-6A:
SiC: 0.069/0.143 = 0.483; SiO_2: 0.074/0.143 = 0.517
Since the actual weights and volumes of CC-6 and the phases present in it could be derived, the volume fractions of phases were arrived at using the actual volumes of phases and the volume of CC-6.
The actual volume of CC-6 = Wt of CC-6/BD of CC-6 = 0.153/0.53 cm^3, or, 0.289 cm^3.
The actual volume of SiC = Wt of SiC/true density of SiC (β-SiC) = 0.069/3.2 cm^3 = 0.022 cm^3
Actual volume of SiO_2 = (0.074/2.33) cm^3 = 0.032 cm^3 (true density of beta cristobalite, the form of silica as revealed by the XRD profiles, is 2.33 g cm^{-3})
Actual volume of C = 0.010/1.9 cm^3 = 0.005 cm^3
So, the volume fractions in CC-6 are V_{SiC} = 0.022 cm^3/0.289 cm^3 = 0.076, V_{SiO_2} = 0.032 cm^3/0.289 cm^3 = 0.110
And V_C = 0.005 cm^3/0.289 cm^3 = 0.017
So, V_{pore} = 1.000 − (0.076 + 0.110 + 0.017) = 0.797
For volume fractions of phases in CC-6A:
V_{SiC}: 0.346 × dC_B (corrected for full shrinkage during ceramization) = 0.346 × 0.24 = 0.083
$d_{Cer} = V_{SiC}{\cdot}d_{SiC} + V_{SiO_2}{\cdot}d_{SiO_2}$
Or, $0.49 = 0.083 \times 3.2 + V_{SiO_2} \times 2.33$
Or, V_{SiO_2} = 0.096. Hence, V_{pore} = 0.821

A.1.3. CC-9 [CS-9 at 1450 °C, N_2] and CC-9A [CC-9 at 1200 °C, O_2]

For the ceramics CC-9 and CC-9A, the weight and volume fractions of phases were calculated following the same procedures used for CC-6 and CC-6A.
Volume of JS used for C-9: 1.46 cm^3
Wt of CC-9: 0.370 g, BD of CC-9: 0.57 g cm^{-3} (Table 3)
So, volume (corrected) of C-9 should be (1.46 × 0.25) cm^3 = 0.365 cm^3

Volume of CC-9 = Wt of CC-9/BD of CC-9 = (0.370/0.57) $cm^3 = 0.649\ cm^3$

Weight of C-preform = 0.089 g (Table 2)

Weight of C (corrected) = $0.278 \times 0.25 = 0.0695$ g

So, dC_B (corrected) = Wt of C-9/Vol of C-9 = 0.0695 g/0.365 $cm^3 = 0.19\ g\ cm^{-3}$

Weight of C-preform & hydrated silica ($SiO_2 \cdot nH_2O$) = 0.593 g

Weight of hydrated silica ($SiO_2 \cdot nH_2O$) = 0.593-0.089 = 0.504 g

Weight of CC-9 ($C + SiC + SiO_2$, as per XRD, Fig. 5a) = 0.370 g (Table 3)

Weight of CC-9A ($SiC + SiO_2$ as per XRD, Fig. 6a) = 0.341 g (Table 3)

Weight of un-reacted C = $0.370 - 0.341 = 0.029$ g

Weight of C reacted = $0.0695 - 0.029 = 0.0405$ g

0.0405 g C gives 0.045 g SiC

So, SiO_2 in CC-9A = $0.341 - 0.045 = 0.296$ g

0.045 g SiC comes from 0.0675 g SiO_2

So, $nH_2O = 0.504 - (0.0675 + 0.296) = 0.1405$ g

$SiO_2{:}nH_2O = 0.3635/60{:}0.1405/18 = 1{:}1.29$

Thus, the weights of phases in CC-9: SiC: 0.045 g, SiO_2: 0.296 g, C: 0.029 g

The weight fractions in CC-9: SiC: (0.045/0.370) = 0.122, SiO_2: 0.800, C: 0.078

The weight fractions in CC-9A: SiC: (0.045/0.341) = 0.132, SiO_2: 0.868

Volume fractions in CC-9: V_{SiC}: (0.045/3.2/0.649) = 0.022

V_{SiO_2}: (0.296/2.33/0.649) = 0.196, V_C: (0.029/1.9/0.649) = 0.023, V_{pore}: 0.759

Volume fractions in CC-9A:

V_{SiC}: $0.346 \times dC_B = 0.346 \times 0.19 = 0.066$

$d_{Cer} = V_{SiC} \cdot d_{SiC} + V_{SiO_2} \cdot d_{SiO_2} = 1.59\ g\ cm^{-3}$. Putting values, V_{SiO_2}: 0.591

So, $V_{pore} = 0.342$

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