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An ultralight porous alumina ceramic in the image of jute stem

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A carbonaceous preform (C-preform) was prepared by thermal and microwave (MW) processing of short lengths (0.02-0.06 m) of dry stems of jute (Corchorus capsularis L). Infiltration of an Al_2O_3-sol into the C-preforms and a subsequent oxidising heat treatment (1273-1723 K) resulted in the formation of an ultralight monophasic Al_2O_3 ceramic (bulk density ~200 kg·m^{-3}) with perfect replication of the pore structure of the starting C-preforms derived from the jute stems (JS). The cellular porous alumina ceramics derived from JS having special morphologies with a long, large and oriented growth of alpha alumina grains are likely to be suitable for devices such as high temperature insulators, catalyst supports, permeators for gas phase reactions at elevated temperatures, and biomaterials such as for controlled drug release devices.

Key words: Jute stem, Cellular carbonaceous preform, Ultralight cellular alumina.

Introduction

Alumina is the most versatile engineering ceramic and porous alumina structures have come to occupy a special position. Porous alumina is widely used as a biomaterial, in prosthetic implants, dental implants, as devices for controlled drug release, etc [1, 2]. Other areas of application of porous alumina include adsorption, gas permeability and catalytic support [3, 4]. In porous alumina ceramics the proportion, size, shape, distribution, orientation and connectivity of pores are all important in determining their applicability in a particular field. One of the most common methods of pore generation is to use different pore formers such as expanded polystyrene beads [2], wheat particles [5], substances used for the preparation of cakes [6] and even via the combined techniques of foaming and sol-gel technology [7]. An extrusion method using a plastic substance as a pore former has been described for the preparation of porous alumina ceramics with unidirectionally oriented pores [3]. A hydrothermal synthesis method has been reported for producing nano-porous (100-1000 Å) alumina ceramic from amorphous alumina [4].

Ceramic materials with tailored morphologies and structures derived by replicating those of plants have been synthesized. They include dense bulk and porous oxide and non-oxide ceramics [8-14]. Endowed with unique combinations of anisotropic structures and physical and chemical properties, they hold tremendous application prospects.

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It is recognized that, subject to appropriate processing to retain parent plant micro-cellular anatomical features and macro-structural integrity, carbon preforms made from suitable plant precursors could constitute a special substrate for fabrication of porous ceramics [11, 15]. Recently we have reported the use of carbonaceous preform (C-preform) made from stems of jute (JS) as a unique bio-template for fabrication of porous Si/SiC composites [16]. The present communication deals with the fabrication of ultralight porous alumina with cellular structures with the image of pores in the C-preform made from JS. Fibrous alumina was earlier synthesized using jute fibers [10].

The present study incorporates a) conversion of dry JS to active C-preforms retaining the morphological and macro- and micro-structural features of the plant precursor, b) exploring processes for infiltration of alumina sol into the C-preforms, and c) burning out the skeletal carbon of the sol-infiltrated body to yield an alumina ceramic with oriented grains and channels.

Experimental

Thermal and Microwave Processing of Jute Stem for Conversion into C-preform

Sun-dried stems of jute (JS) after removing the outer cover of textile fibers were cut into short lengths (0.02 -0.06 m) and were oven-dried at < 338 K overnight. Oven-dried JS samples were converted into C-preforms by controlled thermal processing. Pieces of oven-dried JS were heated in an electrically heated muffle furnace under self-generated atmosphere allowing the gases and volatiles to escape through a cold trap where tarry materials condensed. Temperature was raised at different

rates in segments: ~2 K·minute^{-1} up to 493 K, ~1 K·minute^{-1} and ~3 K·minute^{-1} in the ranges of 493-773 K and 773-1073 K respectively. The active C-preform products, thus prepared, were recovered after cooling the furnace. Similar short lengths of dry raw JS samples were also microwave (MW) processed into C-preforms. MW processing into C-preforms was carried out in a single mode oven (2.45 GHz). The samples were placed in a borosilicate glass jar fitted with an outlet glass tube under a vacuum of about 26.7 to 40 kPa (200-300 mm Hg) to remove the evolved matters under suction, the whole set-up rotating on a turntable.

The dimensional shrinkages and weight losses by drying and those for thermal and MW processing into C-prefroms were measured.

Alumina sol infiltration into JS C-preform

C-preforms derived through thermal and MW processing methods were infiltrated with alumina sol (5 wt% Alumina, aqueous sol, Chemat Technology, USA, A9211) under a vacuum. The samples, taken in a small beaker, were placed in a vacuum glass chamber fitted with a conical flask containing the alumina sol. After the vacuum steadied, the alumina sol was allowed on to the samples drop by drop. As bubbling ceased the vacuum was released and the samples were taken out and were wiped free of any loose sol adhering to the exterior surfaces followed by drying in air and in an oven (353 K) and the cycle was repeated. Four cycles of infiltration treatment was carried out on each specimen.

Conversion into porous alumina ceramic

Alumina sol infiltrated C-preforms, oven dried and weighed, were heated slowly (2-3 K·minute^{-1}) in a muffle furnace in air up to temperatures of 1273-1723 K.

The materials were allowed to stay for 30-60 minutes at the peak temperatures to allow for complete oxidation of carbon and to sinter the ceramic. Cooling down to 1073 K was controlled at ~2 K·minute^{-1} followed by furnace cooling to room temperature.

Characterization of Jute stems, C-preforms and end-ceramics

The jute stems, C-preforms and the end-ceramics were characterized by measuring their bulk densities (BD), phase-analyses by X-ray diffraction (XRD) and by examining their morphology and microstructures by optical microscopy (Reflected Light Microscopy, RLM) [Leitz (Germany)] and/or by scanning electron microscopy (SEM) [LIKA S440] and FESEM [SUPRA^{TM} 35 VP; Gemini Column (Carl Zeiss SMT)].

Results and Discussion

Characteristics of plant precursors and of C-preforms

As reported earlier [16] JS precursors are comprised elementally of 47.85% carbon and 5.79% hydrogen and the rest oxygen. Defatted and dry JS were analyzed to contain 24.48% lignin, 37.07% alpha cellulose and 32.17% hemicellulose that, together, constitute the woven fibrous soft woody tissues of fibers/fiber-bundles surrounding the vascular channels (xylem and phloem).

Physically, most of the thermal C-preform samples were observed to maintain their shapes and were found to be free from any visible cracks. MW processing tends to disintegrate the samples and only ~30% could be recovered without any deformity or crack.

For thermally processed C-preforms dimensional shrinkages are markedly anisotropic in both drying and carbonization (Table 1), the mean BDs of C-preforms are quite low (120 kg·m^{-3}) indicating their highly porous structure (Table 2). XRD profiles of the C-perform indicate the presence of amorphous carbon and scanning electron micrographs reveal the perfect retention of the characteristic anisotropic plant biostructures [16].

Microwave processing into C-preforms could be achieved in just 12-20 minutes. Carbonization weight loss and anisotropic dimensional shrinkages were of the same order of magnitude as for thermal processing (Table 1). The XRD profiles and SEM images of MW processed C-preforms were identical with those of thermal C-preforms.

Table 1. Shrinkage and weight loss of JS precursors on drying and carbonization

Drying		Carbonization			
		Thermal		Microwave	
Shrinkage(%)	Wt. Loss (%)	Shrinkage (%)	Wt. Loss (%)	Shrinkage (%)	Wt. Loss (%)
L : 0.37 OD : 4.11 ID : 9.72	10.58	L : 20.36 OD : 25.13 ID : 30.42	75.2	L : 18.82 OD : 23.33 ID : 29.10	70.0

Table 2. Bulk densities (kg.m^{-3}) of dry JS precursors, C-preform and derived Alumina ceramics

Precursor[a]	C-preform[a]		Alumina Ceramic[b]	
	Thermal	Microwave	From Thermal C-preform	From MW C-preform
390	120	150	200	185

[a]Mercury displacement method; [b]Based on sample dimensions

Table 3. Al_2O_3 sol infiltration and oxidative sintering of infiltrated C-preforms

JS C-preform		% Wt. gain after each infiltration cycle				Alumina ceramic derived
		1st Cycle	2nd Cycle	3rd Cycle	4th Cycle	
Thermal	Wt: 0.210×10^{-3} kg BD: 120 kg·m^{-3}	49.5	68.1	122.8	134.0	Wt: 0.184×10^{-3} kg (Wt loss: 62.5%) Vol: ~ 0.92×10^{-6} m^3 BD: 200 kg·m^{-3}
MW	Wt: 0.355×10^{-3} kg BD: 150 kg·m^{-3}	53.1	75.2	101.7	111.5	Wt: 0.260×10^{-3} kg (Wt. loss: 65.5%) Vol: 1.40×10^{-6} m^3 BD: 185 kg·m^{-3}

The mean BD of MW C-preform was a little higher, 150 kg·m^{-3}, but comparable to those of thermally-processed C-preform (Tables 2, 3).

Alumina Sol infiltration, Conversion into porous alumina ceramics and Characterization of Alumina ceramics

The progress of accumulation (after oven drying) of hydrous alumina by typical C-preforms, thermal and microwave, over four cycles of sol-infiltration are presented in Table 3. An ultralight alumina body with a bulk density of about 200 kg·m^{-3} was derived (1723 K, 30 minutes) from a thermal C-preform of BD 120 kg·m^{-3}. The BD of the alumina ceramic derived is only about 5% of the density of alpha-alumina implying a nominal porosity of 95%. The starting C-preform derived by MW processing (BD 150 kg·m^{-3}) yielded, under the same conditions, an alumina ceramic with a BD of 185 kg·m^{-3} with a nominal porosity of 95.4%. Both the final alumina ceramic bodies were, however, too weak to be subjected to strength measurements.

An optical image of the cross section of an alumina ceramic obtained from a thermal C-preform at 1723 K is shown in Fig. 1. An SEM image of the axial wall of the same, presented in Fig. 2, shows the tubular cellular walls and the exposed elongated channel pores covered by them. X-Ray Diffraction of the same ceramic (Fig. 3) exhibited the signature peaks of alpha-alumina.

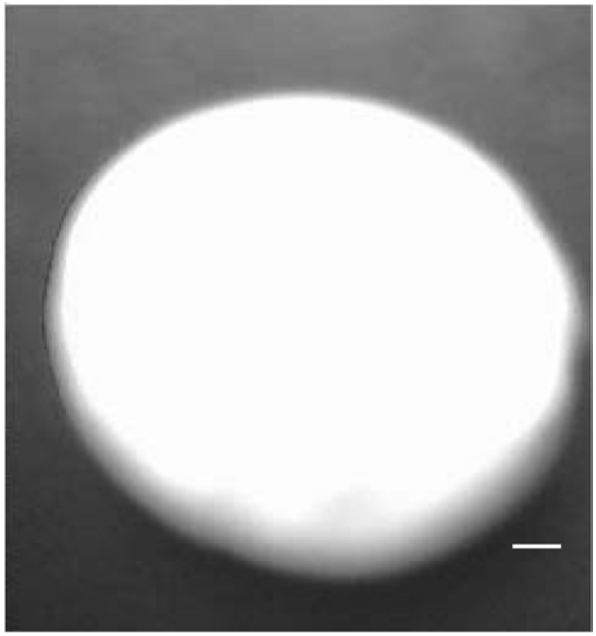

Fig. 1. Cross section of the Al_2O_3 ceramic (bag leagth : 500 μm) derived from alumina sol-infiltrated C-preform (thermal).

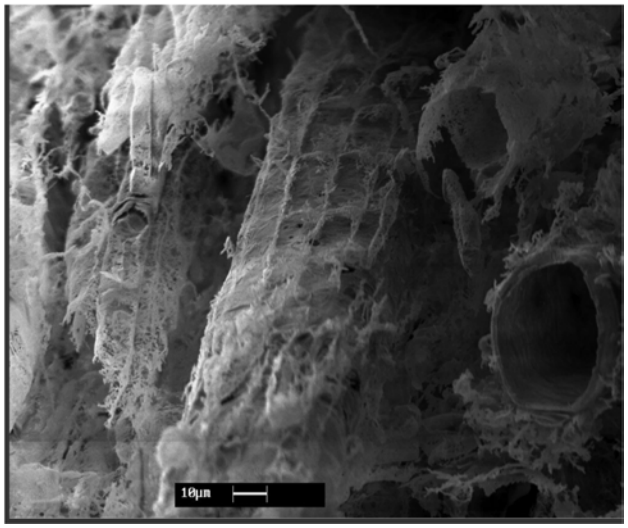

Fig. 2. SEM image of cellular porous alumina ceramic replicating pores in JS.

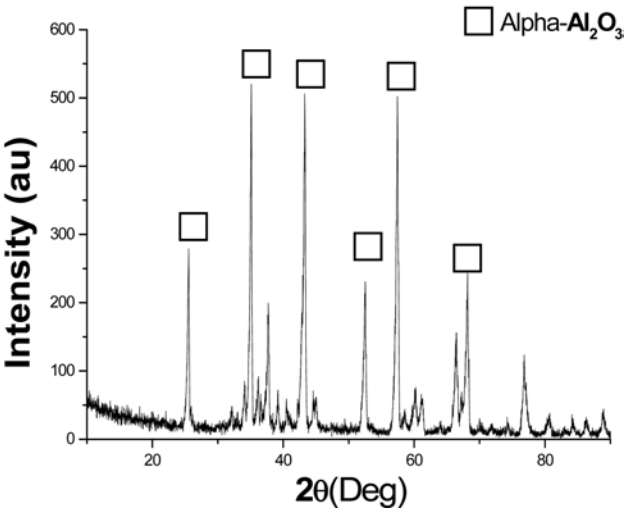

Fig. 3. XRD pattern of Al_2O_3 ceramic from alumina sol-infiltrated C-preform.

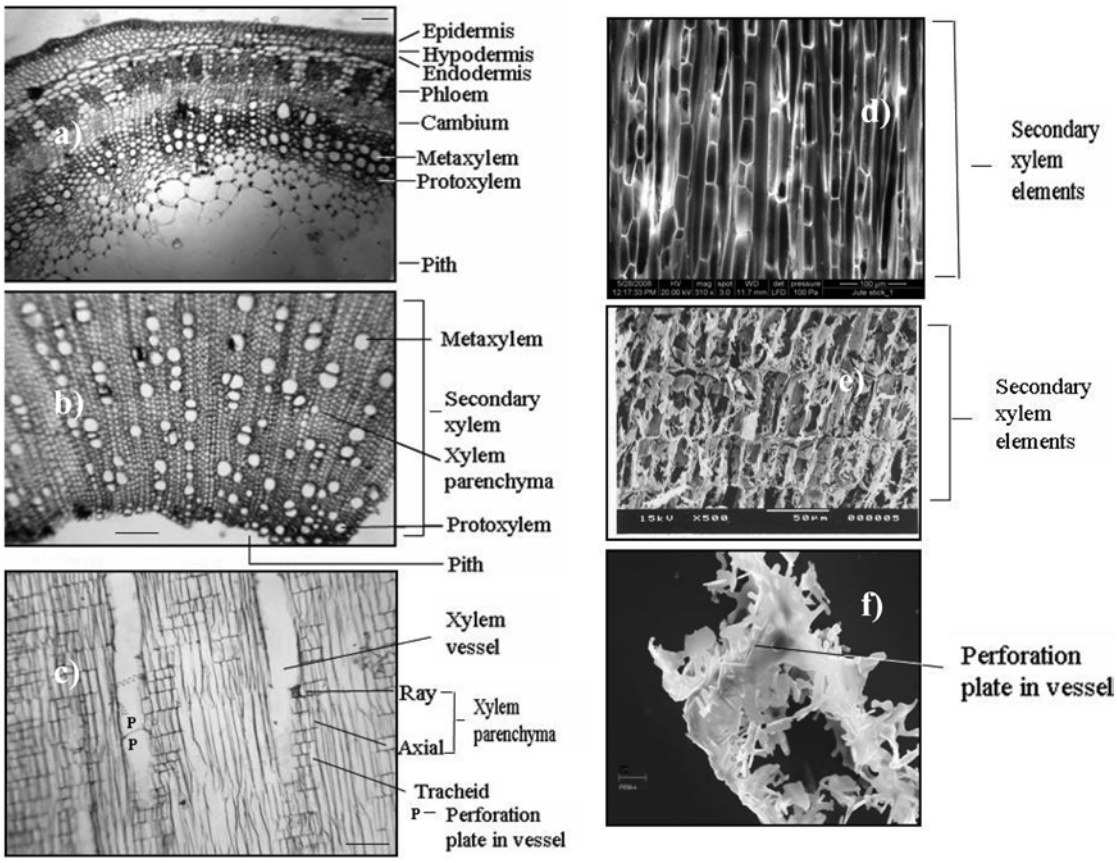

Fig. 4. Optical micrographs of cellular structure of (a) a young JS (transverse section), (b) mature JS (transverse section), (c) mature JS (Longitudinal section), (bar length in a, b and c: 100 μm), (d) SEM of secondary xylem elements in longitudinal section, (e) SEM of alumina ceramic, longitudinal view and (f) FESEM image of Alumina Ceramic showing detail structures in vessel segment of (e).

In Fig. 4 are placed together, for ease of comparison, optical micrographs of the transverse (cross) section of a young green jute stem (Fig. 4(a), those of transverse and longitudinal sections of a mature JS (Fig. 4(b) and (c)) respectively. Figs. 4(d) and (e) are the SEM images of a mature JS and of the alumina ceramic respectively and fig 4(f) is the FESEM image of the alumina ceramic (all longitudinal views).

Along with the jute fiber, the epidermis, hypodermis, endodermis and the phloem elements depicted in the young stem (Fig. 4(a)) are lost and are not to be found in the mature JS used in this study and depicted in Figs. 4(b) and 4(c) which clearly show the secondary xylem elements. The alumina ceramic replicates these secondary xylem elements (fig.4(e)), hydrous alumina being deposited against the walls of carbonaceous remains of those elements only. In a further magnified FESEM image (Fig 4(f)) showing detailed structures in the vessel segment of Fig. 4(e), can be discerned the image of perforation plates in the xylem vessels.

Thus the cellular morphology and structure with a longitudinal disposition of xylem elements, their orientation and interconnectivity are perfectly maintained in the alumina ceramic.

The Scherrer particle size based on the major XRD (Fig. 2) peak was calculated to be 20 nm.

Conclusions

1. Short pieces of dry stems of jute can be converted into carbonaceous shapes (C-preforms) maintaining their morphological and structural features by controlled thermal and microwave processing.
2. C-preforms derived from jute stems are of low bulk density with open longitudinal channels parallel to the stem-axis at the center as well as in the walls. The C-preforms are devoid of crystallinity.
3. Infiltrated with alumina sol under vacuum, C-preform derived from jute stem accumulates enough hydrated alumina that can yield, on controlled oxidation of the carbon, an ultra low density porous alumina ceramic with the image of the pores in the preform and hence in the image of the cellular structures of secondary vascular elements in the JS precursor.

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References

1. K.L. Eckert, M. Mathey, J. Mayer, F.R. Homberger, P.E. Thomann, P. Groscurth and E. Wintermantel, Biomaterials, 21, (2000) 63-69.
2. J. Liu and X. Miao, J. Mat. Sci. 40, (2005) 6145-6150.
3. T. Isobe, Y. Kameshima, A. Nakajima and K. Okada, J. Euro. Ceram. Soc. 27, (2007) 61-66.
4. B.K. Park, K.H. Kim and N.K. Kim, J. Ceram. Procg. Res., 8, (2007) 150-155.
5. K. Pravhakaran, A. Melkeri, N.M. Gokhale and S.C. Sharma, Ceramic Internatl, 33, (2007) 77-81.
6. T. Banno, Y. Yamada, Z. Xie and H. Nagae, J. Ceram. Soc. Japan, 115, (2007) 156-159.
7. Xiang-jin Ding, Ji-Zhou Zhang, Ruo-ding Wang and Chu-de Feng, J. Euro. Ceram. Soc. 22, (2002) 411-414.
8. N.K. Sharma, W.S. Williams and A. Zangvil, J. Am. Ceram. Soc., 67, (1984) 715-720.
9. R.V. Krishnarao and Y.R. Mahajan, J. Mat. Sci. Lett., 15, (1996) 232-235.
10. M. Patel and B.K. Padhi, J. Mat. Sci., 25[2B] (1990) 1335-1343.
11. T. Ota, M. Imaeda, H. Takase, M. Kabayashi, N. Kinoshita, T. Hirashita, H. Miyazaki and Y. Hikichi, J. Am. Ceram. Soc., 83, (2000) 1521-1523.
12. H. Sieber, J. Cao, C.R. Rambo and P. Greil, Ceram. Engg. Sci. Proc., 23 (2002), 175-181.
13. C.R. Rambo, J. Cao and H. Sieber, Mat. Chem. Phys., 87, (2004) 345-352.
14. C.E. Byrne and D.C. Nagle, Mat. Res. Innovat, 1, (1997) 137-145.
15. A. Herzog, R. Klingner, U. Vogt and T. Granle, J. Am. Ceram. Soc., 87, (2004) 784-793.
16. P.K. Mandal, R. Majumdar, K.K. Mukherjee, O.P. Chakrabarti and H.S. Maiti, J. Por. Mat. doi 10.1007/s10934-007-9180-9.