

Preparation of Silicon Carbide Ceramics from Bamboo Charcoal by High-Temperature Silicon Infiltration

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Abstract

Bamboo charcoal, silica, and phenol-formaldehyde resin were mixed powders that were heated at temperatures from 1,500°C to 1,800°C in an argon atmosphere to produce a silicon carbide (SiC) ceramic. Differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray analysis (EDXA) were used to monitor heat flow and physical, chemical, and structural changes during the formation of the ceramic. The DSC results indicated that during firing, endothermic reactions occurred below 800°C, after which exothermic reactions dominated. FTIR study suggested conversion of Si-O bonds to Si-C bonds at temperatures above 1,500°C. SEM and EDXA showed that the microstructure of the bamboo charcoal was observable in the ceramic structure and that the surface of the ceramic material contained a high proportion of Si. X-ray diffractometry analysis indicated that the ceramics obtained by firing above 1,650°C mainly consisted of SiC with trace amounts of elemental carbon and silicon.

Recently, a new technique has been developed to prepare silicon carbide (SiC) ceramic products from natural wood, bamboo, and man-made wood (wood-based panels or paper) by C-Si reaction at high temperature (Qiao et al. 2002a, 2002b). Preparing ceramics with these materials is advantageous because of their microstructure characteristics. These materials are also renewable, and they reduce costs (Nagase et al. 2005). Bamboo charcoal SiC ceramic was also synthesized by reaction sintering between bamboo charcoal and a Si/SiO₂ powder mixture; the samples were characterized according to their crystallinity, morphology, microstructures, and pore structures (Zhu et al. 2009). X-ray diffractometry (XRD) analysis indicated that the SiC ceramic prepared by this technique was multiphase solid, composed of β-SiC and free silicon; the experiment results showed that this technique is a suitable new method to prepare ceramics with a bionics structure (Qiao et al. 2002a, 2002b).

Wood and bamboo are important renewable resources and can be used as base materials for the preparation of biomorphic SiC ceramics (Kang 1998, Huang and Gao 2004). Such biomorphic ceramics have advantages for various industrial applications of low density, with their high mechanical strength, good conductivity, absorption of gases, and chemical and thermal stability (Vogli et al. 2001, Singh and Salem 2002). Biomorphic SiC ceramics have been prepared from different species of wood such as pine

and oak by techniques including infiltration of molten silicon, sol-gel, and thermal reduction processing (González et al. 2003, Sun et al. 2004). However, there have been few reports of porous SiC ceramics made from bamboo.

Bamboo is a fast-growing woody plant that matures in 3 to 5 years. The species is an important source for biomass because it is easy to establish and regenerate, has a high rate of fiber production, and requires little maintenance. It has been estimated that there are 3.6 million hectares of bamboo forest in China, which amounts to about one-quarter of the world's bamboo forests, producing 20 to 30 million tons of culms annually (Yang and Xue 1998). The anatomical structure of bamboo culms is different from pine and oak timber, in that the mechanical strength of the culm is provided by scattered vesicular bundles embedded in a large volume of extremely porous tissue. Therefore, it is to be expected that SiC ceramics made from bamboo culms may

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Forest Prod. J. 60(6):522–526.

have significantly different characteristics than that prepared using timber.

In the present study, bamboo charcoal and silicon powders were compression molded into pellets bonded with a phenol-formaldehyde resin followed by sintering the pellets at temperatures ranging from 1,500°C to 1,800°C. The resulting SiC ceramics were analyzed with differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray analysis (EDXA) to monitor heat flow and physical, chemical, and structural changes during the formation of the ceramic.

Materials and Methods

Bamboo charcoal, obtained by pyrolysis at 800°C, was ground into a powder diameter of no more than 150 µm. One part by weight bamboo charcoal and three parts Si powder (120 mesh) were mixed with four parts phenol-formaldehyde (PF) resin binder (resol, 30% solids), and the mixture was compression molded at 180°C for 5 minutes into 2-cm-diameter cylindrical pellets (density, approximately 1.2 g/cm³). Then, the bamboo charcoal/Si pellets were sintered in an argon atmosphere at 1,500°C, 1,650°C, and 1,800°C for 30 minutes to obtain the SiC ceramic.

DSC

The bamboo charcoal/SiO₂ pellets were ground into particles sieved through a 0.071-mm mesh and analyzed with a Shimadzu model 60A DSC using Al₂O₃ as a reference. Samples were scanned from room temperature to 1,500°C at a rate of 15°C/min.

FTIR

Bamboo charcoal/SiO₂ pellets and SiC ceramics prepared at 1,500°C, 1,650°C, and 1,800°C separately were ground into particles sieved through a 0.071-mm mesh. From each powdered sample, 2.0 mg was reground with 500 mg KBr (potassium bromide) and pressed into KBr pellets for

examination with a Nicolet model 170SFT FTIR spectrometer.

SEM and SEM-EDXA

Ground samples as described above were examined with a Philips/FEI Quanta 200 environmental SEM equipped with an Oxford INCAx-act analytical silicon drift detector.

XRD

Powdered samples of bamboo charcoal and SiC ceramics prepared at 1,500°C, 1,650°C, and 1,800°C were examined with a Shimadzu model S-7000 XRD operated at 30 mA and 40 kV of Cu Ka radiation and scanned at 2°/min.

Adsorption tests

One gram of each sample was weighed to 0.0001-g accuracy and then exposed to fumes of either formaldehyde, benzene, or ammonia in a chamber at 20°C for 24 hours and then reweighed. Total volatile organic content was also measured.

Results and Discussion

Figure 1 is a typical DSC curve of bamboo charcoal/Si bonded with PF resin, showing a major phase transition at about 800°C and another phase transition before reaching 1,500°C. Endothermic decomposition of the resin binder and residual organics in bamboo charcoal occurred below 800°C, followed by exothermic carbon crystallization at temperatures above 800°C. The second phase transition seen just below 1,500°C may indicate the onset of Si melting.

In the FTIR analyses, broad peaks at 3,430/cm and 1,640/cm for O-H stretching in the control samples (unsintered charcoal/Si), shown in Figure 2, diminished when the charcoal/Si substrate was exposed to high temperatures. The absorption peak at 1,050/cm for Si-O bonds disappeared after sintering the substrate at 1,650°C and 1,800°C. The absorption band at 825/cm can be attributed to Si-C stretching (Preiss et al. 1995) and is absent in the control and 1,500°C samples but reappears in the 1,650°C and

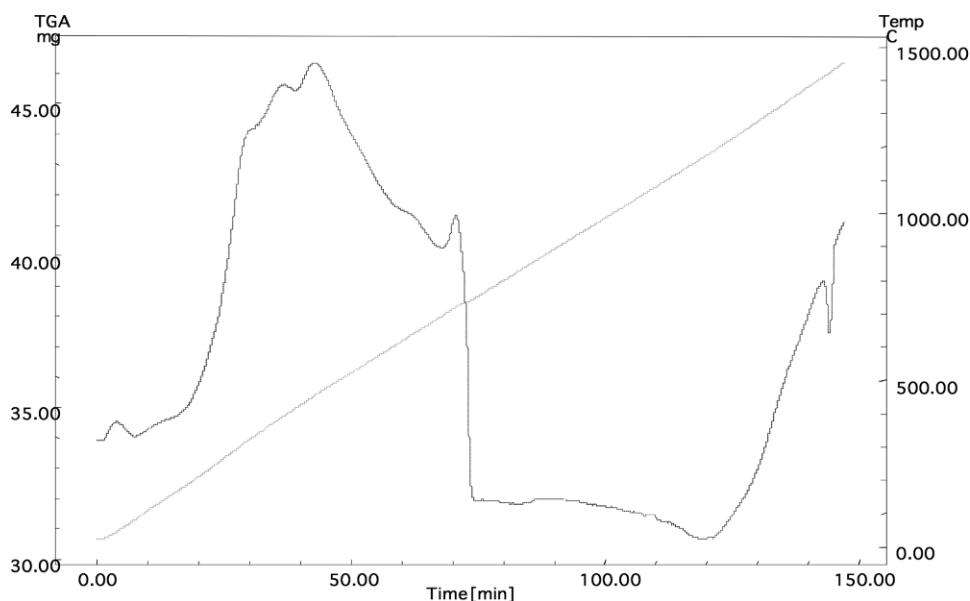


Figure 1.—DSC curves of bamboo charcoal/Si bonded with phenol-formaldehyde resin.

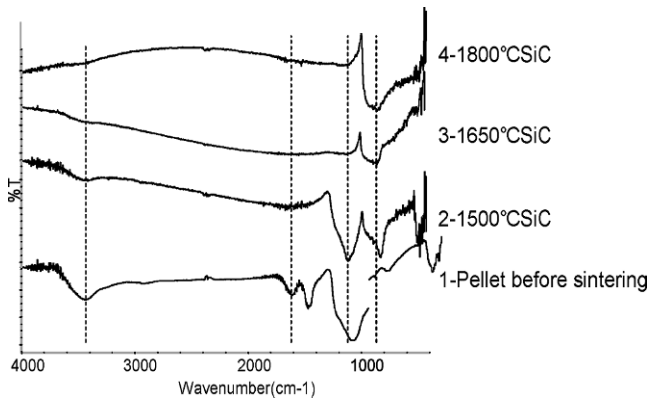


Figure 2.—FTIR spectra of powders of bamboo/SiC pellet and SiC ceramics.

1,800°C samples in increasing intensity. This suggests that conversion of Si-O bonds to Si-C bonds occurred at temperatures beyond 1,500°C. The pure carborundum shows a main Si-C peak at 840/cm and a shoulder at 950/cm, but it has also been reported that the main Si-C absorption is located between 789/cm and 794/cm and that its exact location varies with different SiC crystalline structures (Preiss et al. 1995).

Figures 3a through 3d show SEM microphotographs of fractured surfaces of bamboo charcoal samples and ceramic materials sintered at 1,500°C, 1,650°C, and 1,800°C, respectively. The porous structure of bamboo remained in all the samples, offering passageways for infiltration of molten material. Figure 3 also shows the development of amorphous grains on bamboo charcoal surfaces after sintering at high temperatures and growth of grain size with increasing sintering temperature.

Results of the SEM-EDXA analysis shown in Table 1 indicate that bamboo charcoal contained (by weight) 79.87

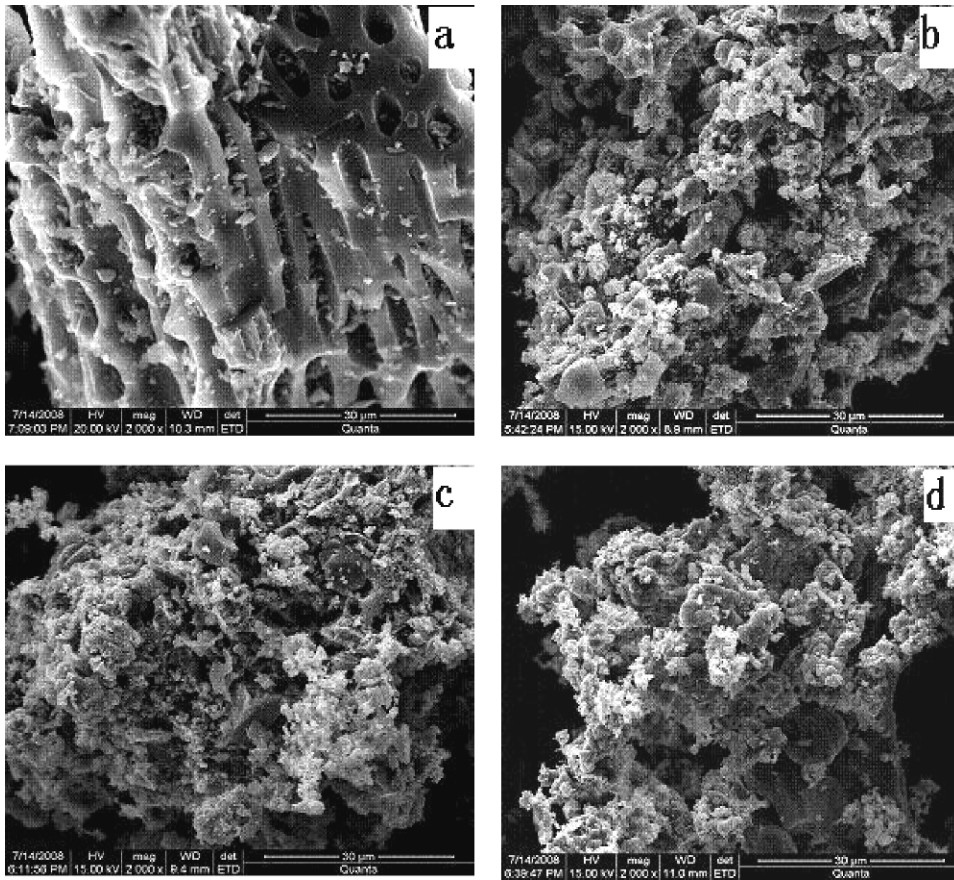


Figure 3.—SEM microphotographs of bamboo charcoal and SiC ceramics: (a) bamboo charcoal, (b) 1,500°C SiC (0.5 h), (c) 1,650°C SiC (0.5 h), and (d) 1,800°C SiC (0.5 h).

Table 1.—Elemental analysis of bamboo charcoal and SiC ceramics.

Element	Bamboo charcoal		1,500°C sample		1,650°C sample		1,800°C sample	
	Wt%	Atom%	Wt%	Atom%	Wt%	Atom%	Wt%	Atom%
C-K	79.87	84.29	46.91	60.63	45.19	63.57	43.60	63.50
O-K	19.43	15.39	24.00	23.29	7.58	8.01	2.91	3.18
Si-K	0.49	0.22	29.09	16.08	47.23	28.42	53.49	33.32

percent carbon, 19.43 percent oxygen, and 0.49 percent silicon, and the granular surface of samples sintered at 1,500°C contained (by weight) 46.91 percent carbon, 24.00 percent oxygen, and 29.09 percent silicon. Also, Figure 4 shows that the carbon content remained relatively constant for samples sintered at 1,500°C to 1,800°C. When the samples were sintered at higher temperatures, the oxygen content decreased sharply from 24.00 percent in the 1,500°C sample to 7.58 percent in the 1,650°C sample, followed by a smaller drop from 1,650°C to 1,800°C. The decrease in oxygen content was accompanied by a proportional increase in silicon content. These results suggest that conversion of Si-O bonds to Si-C bonds occurred mainly at 1,650°C, although the conversion was still observed occurring at 1,800°C. The result of the SEM-EDXA analysis is in agreement with the appearance of the Si-C absorption band

at 825/cm in the 1,650°C sample (Fig. 4c). This absorption band increased in intensity in the 1,800°C sample (Fig. 4d).

Figures 5a through 5d are XRD spectra of bamboo charcoal and SiC ceramics sintered at various temperatures. The peak at $2\theta = 28^\circ$ in Figures 5a and 5b, respectively, is from the Si element in bamboo charcoal and the remaining Si after the bamboo charcoal/Si pellets were sintered at 1,500°C, which disappeared when the samples were sintered at above 1,650°C. Peaks 47.2, 56.1, 69.0, and 76.4 in the XRD spectrum of the 1,500°C sample (Fig. 5b) are also characteristic of silicon (Poper 1960), and these peaks (except the one at 76.4) disappeared when the samples were sintered at 1,650°C and 1,800°C. Peaks 35.7 and 41.5 in Figures 5c and 5d correspond to the 102 plane and 104 plane of 6H-SiC, and 60.0 and 71.8 are the 220 plane and 311 plane of the 3C-SiC. The XRD analysis indicated that

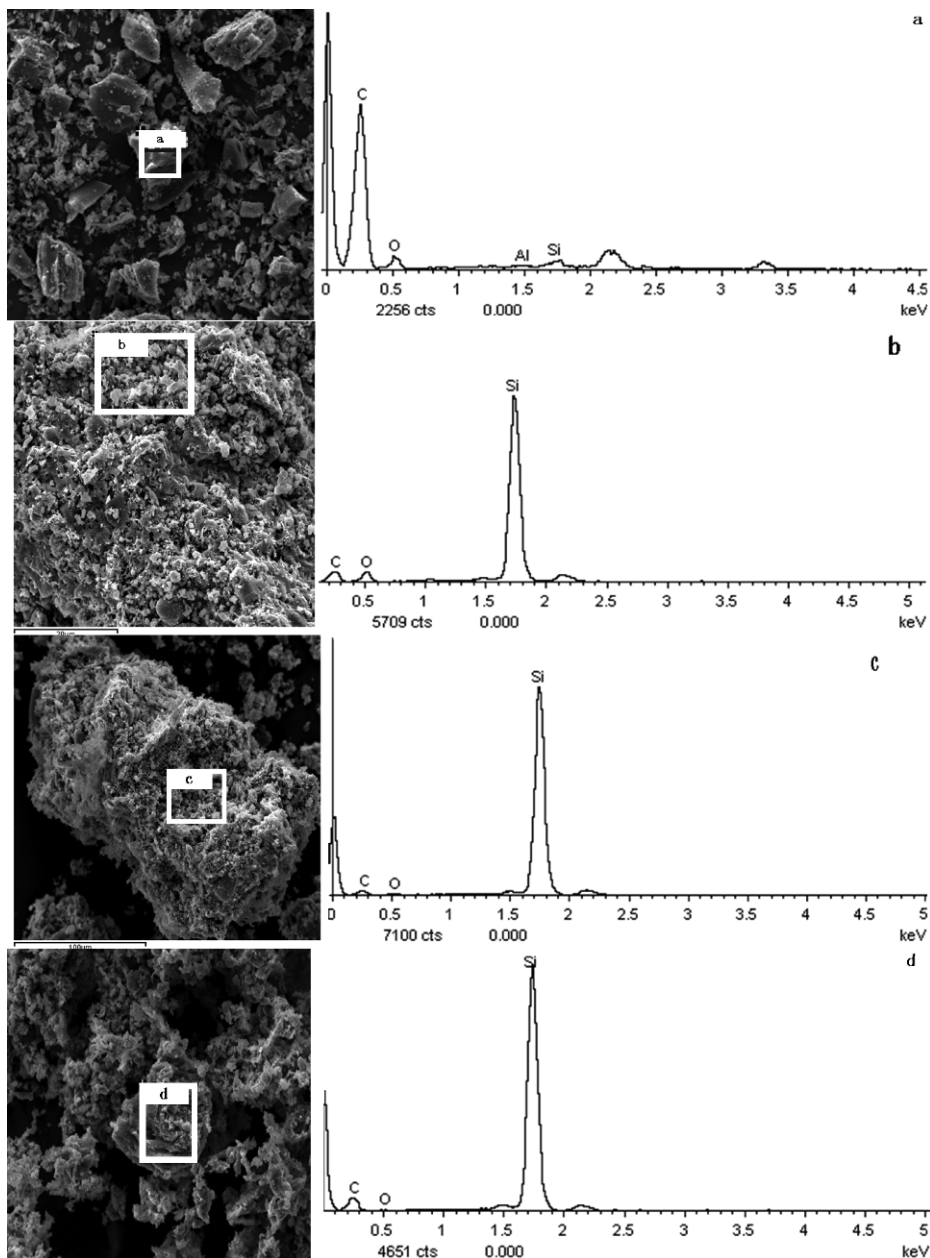


Figure 4.—SEM-EDXA spectra of bamboo charcoal and SiC ceramics: (a) bamboo charcoal, (b) 1,500°C SiC (0.5 h), (c) 1,650°C SiC (0.5 h), and (d) 1,800°C SiC (0.5 h).

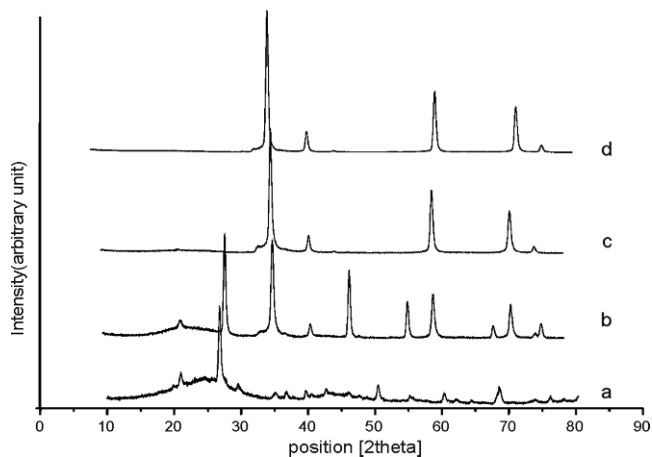


Figure 5.—XRD spectra of bamboo charcoal and SiC ceramics: (a) bamboo charcoal; (b) 1,500°C SiC (0.5 h); (c) 1,650°C SiC (0.5 h), and (d) 1,800°C SiC (0.5 h).

formation of SiC initiated at 1,500°C and completed at 1,650°C with only a trace of unconverted silicon.

The ability of prepared SiC ceramics to absorb various fumes is compared with bamboo charcoal in Table 2. The bamboo charcoal sample was far better at absorbing all the test fumes than the SiC ceramics. However, the ceramic obtained at 1,650°C absorbed more fumes, especially benzene, than those obtained at 1,500°C and 1,800°C. Until now, little work has been done on the fume absorption ability of SiC ceramics, so these test results may indicate a new area of application for SiC ceramics.

Table 2.—Absorption of various fumes by powders of bamboo charcoal and SiC ceramics.

Test samples	Wt%			
	Formaldehyde	Benzene	Ammonia	TVOC ^a
Bamboo charcoal	11.58	11.19	10.80	11.94
SiC ceramic				
1,500°C	0.79	0.78	0.81	0.35
1,650°C	0.83	5.25	1.41	2.38
1,800°C	0.16	1.04	0.20	0.40

^a TVOC = total volatile organic compounds.

Conclusions

Firing the charcoal/silica, grains appeared on the porous carbonaceous surfaces, and they became more numerous and smaller upon firing at higher temperatures. SEM-EDXA analysis showed that the surfaces of granular SiC ceramic obtained at 1,650°C contained about equal amounts of carbon and silicon and less than 10 percent oxygen. Examination of ceramics prepared at 1,650°C and 1,800°C by XRD indicated that they were mainly SiC and SiC with a trace of silicon. Examination of powdered specimens of ceramics obtained at 1,650°C and 1,800°C with FTIR also confirmed the formation of Si-C bonds.

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