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Porous SiC ceramics fabricated by reactive infiltration of gaseous silicon into charcoal

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Abstract

Basswood has been converted to a porous biocarbon template by carbonizing under vacuum at 1200 °C. Subsequent reactive infiltration of gaseous silicon at 1500–1700 °C for 0.5–8 h in inert atmosphere resulted in the formation of a porous, cellular β-SiC ceramic. X-ray diffraction (XRD) studies show the resulting SiC, obtained at 1600 °C for 6 h in static argon atmosphere, is β-SiC. Scanning electron microscopy (SEM) reveals the resulting SiC ceramic reproduces the biomorphic cellular morphology of basswood tissue with high precision. Gaseous Si diffuses into charcoal through its continuous tracheidal cell channels, and reacts with carbon in the cell wall to form SiC. Growth of SiC layer is dependent of the diffusion of Si vapor through the primary porous SiC layer and further gas–solid reaction of Si(g) and C(s) at C/SiC interface. The densification of SiC strut material may occur at moderate temperatures and holding time.

Keywords: B. Microstructure; D. SiC; Reactive infiltration; Porous ceramics; Biocarbon template

1. Introduction

Design of novel ceramic materials with specific functional properties and structures by mimicking the hierarchical cellular structure of wood has recently attained particular interest [1–3]. Wood is a naturally grown composite material of complex hierarchical cellular structure, and comprised of elongated tubular cells aligned with the axis of the tree trunk and growth ring structures [4]. The tubular cells of wood with a preferential orientation in axial direction offer the possibility to use various infiltration techniques to transform the bioorganic wood structure into an inorganic ceramic material with tailored physical and mechanical properties [2,5]. Wood-derived cellular ceramics might be of interest for high-temperature-resistant exhaust gas filters, catalyst carriers, advanced microreactor systems, immobilization supports for living cells, microbes or enzymes, and waste water treatment, as well as acoustic and heat insulation structures, etc.

Wood has been used to prepare many advanced ceramic materials such as woodceramics, woodceramics/metal composites, porous carbide or oxide ceramics, and biomorphic Si/SiC composites [3,6–11]. Up till now, work converting wood into various SiC-based ceramic materials focuses on infiltration of the pyrolysed biocarbon template with gaseous or liquid silicon bearing precursors such as silicon melt, silicon and silicon monoxide vapors, and organosilicon compounds at high temperatures [2,12–15], and silica sol from tetraethylorthosilicate (TEOS) at low temperature followed by pyrolysis in inert atmosphere [16]. The products obtained by infiltrating molten Si into pyrolyzed wood are always low density Si/SiC-ceramic composites, not pure SiC ceramics, and do not retain the original structure of charcoal very well. TiO_2 or SiO_2 sol can be utilized to prepare pure TiC or SiC ceramic by carbothermal reduction reaction, but this method greatly decreases the thickness of cellular wall, resulting in the decrease in mechanical performance of products. However, the product fabricated by reactive infiltration of gaseous silicon into charcoal is nearly pure SiC ceramic, and reproduces the structure of charcoal with high precision.

The objective of the present work is to prepare porous SiC ceramic with a wood-like microstructure from silicon

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powder and basswood as starting materials by reactive infiltration of silicon vapor into charcoal. The morphology changes and structural conversion of basswood-derived charcoal into SiC ceramic were investigated by SEM and XRD techniques.

2. Experimental procedure

2.1. Material preparation

Basswood, a tilia broad-leaved wood, was purchased from Xi'an Wood Co. Ltd. Basswood was used as the biological template structure (basswood charcoal). Basswood was shaped, dried at 110 °C for 2 days, and subsequently carbonized under vacuum at 1200 °C for 4 h in a graphite heater furnace with a slow heating rate of 2 °C/min up to 600 °C and a higher rate of 5 °C/min up to the peak temperature, resulting in a porous biocarbon template (charcoal). After pyrolysis, the carbon templates were reacted with gaseous silicon produced by melting Si powder in argon atmosphere at 1500–1700 °C for 0.5–8 h in a graphite crucible below the samples. The gaseous Si penetrated into the tubular pore channel system of the carbonized basswood and concurrently facilitated the reaction to form β-SiC. Fig. 1 shows schematically the experimental procedure.

2.2. Characterization

The morphological changes of the starting material during the transformation of basswood charcoal into SiC ceramic were observed and analyzed by scanning electron microscopy (SEM, Hitachi, S-2700) operated at 20 kV and 20 mA. X-ray diffraction (XRD) was measured on a D/MAX-RA X-ray diffractometer to determine the crystalline phases formed during the reactive infiltration process, using nickel filtered Cu Kα radiation produced at 35 kV and 20 mA. The samples were pasted on a stub and then metallized with gold.

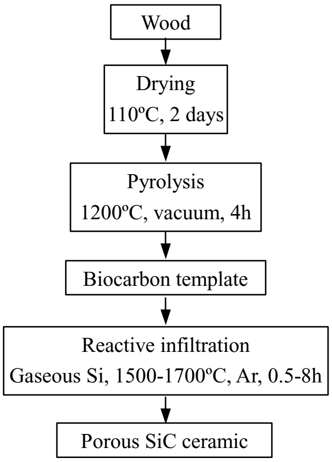

Fig. 1. Flow chart for the fabrication process of porous SiC ceramic from basswood.

The degree of conversion from charcoal to SiC reaction product, α, was derived from the weight increase $\Delta W = W_{\text{Final}} - W_{\text{C}}$ of the reaction product, W_{Final}, compared with the initial weight of charcoal, W_{C}:

$$\alpha = \frac{\Delta W}{W_{\text{C}}}\left(\frac{M_{\text{SiC}}}{M_{\text{C}}} - 1\right)^{-1} = \frac{\Delta W}{2.33 W_{\text{C}}} \tag{1}$$

where M_{SiC} and M_{C} are the molecular weights of SiC (40 g/mol) and C (12 g/mol), respectively. Thus, for $\alpha = 1$ the theoretical weight gain attains 233%.

3. Results and discussion

3.1. Phase identification

The XRD patterns of charcoal and porous SiC ceramics obtained at 1600 °C for different times are shown in Fig. 2. It can be seen that two broad peaks centered at around 22 and 44° in Fig. 2a suggest that charcoal is amorphous. Peaks due to β-SiC (cubic type) phases are observed together with the broad peaks due to charcoal after 0.5 h of reaction time (Fig. 2b), indicating that the formation of β-SiC has taken place. The intensity of peaks due to β-SiC phases in the XRD patterns increases significantly with increasing the reaction time, whereas the peaks (0 0 0 2) and (0 0 0 4) due to residual free carbon gradually disappear (Fig. 2c). When re-

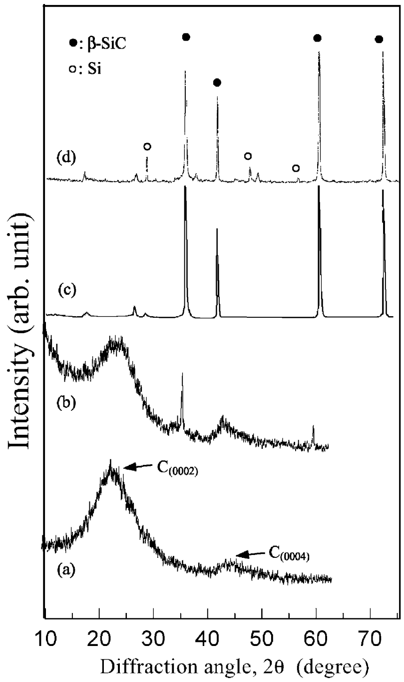

Fig. 2. XRD patterns of samples obtained at 1600 °C for different reaction times during basswood-derived charcoal-to-SiC ceramic conversion. (a) 0 h, (b) 0.5 h, (c) 6 h, (d) 8 h.

action time is further lengthened, some additional lines in the XRD patterns of porous SiC ceramic are detected (Fig. 2d), which are characteristic of free silicon. Diffraction peak near the (1 1 1) line of the cubic structure of the silicon carbide at $2\theta = 35.64^\circ$ for hexagonal polytypes (α-SiC phase) is never observed. It can be inferred that the highly localized exothermic reaction between gaseous Si and carbon does not lead to higher temperatures than 2000 °C, because the $\beta \rightarrow \alpha$ transformation does not take place. The results show that the resulting porous products are essentially constituted of SiC of cubic type (β-SiC). This would suggest that the C/SiC composites with various carbon contents can also be produced by controlling reaction time on the basis of this procedure.

3.2. Microstructure evolution

Fig. 3 shows the SEM micrographs of basswood-derived biocarbon template and resulting porous SiC ceramics. As seen in Fig. 3a, the microstructure of the as-prepared basswood charcoal shows hollow channels of various diameters that originate from tracheidal cells that are parallel to the axis of the tree. The channels can be classified into two groups, depending on their cross-sectional area (as shown in Fig. 3b): large channels (noted by “A”) and small channels (noted by “B”) that are in the vicinity of the larger channels and form a honeycomb structure. The average diameter of each group of cells is 50 μm for the large cells and 10 μm for the small cells, respectively. Most of the cellular pores show a round or elliptic shape. The topologically uniform arrangement of cells in early wood is interrupted by growth ring patterns.

It can be seen from Fig. 3d–h that the resulting SiC material has a microstructure pseudomorphous to biocarbon template derived from basswood. For SiC ceramic obtained at 1500 °C for 8 h, its struts are composed of SiC grains with typical diameter of less than 10 μm. The crystalline texture of the as-formed SiC may be related to the initial microfibril orientation in the cell walls of wood [17], which indicates that the crystallization of SiC is the result of the reaction between carbon and silicon. From SEM observations it is concluded that SiC forming the cell wall material between the cells is highly porous in the initial state of reaction, making rapid gas transport possible. The diffusion of Si via grain boundaries and micropores makes the reaction proceed at the SiC/C interface [18]. When the reactive infiltration is conducted at 1700 °C for 8 h, the densification of the strut material is observed (Fig. 3g and h), which is caused probably by the sintering of SiC grains and/or the strengthening action of excessive free silicon on the surface of SiC grains on the connection between SiC grains. At the same time, it becomes increasingly difficult to transport Si vapor to the carbon reaction sites and reaction rate decreases. It can be seen from Fig. 4 that degree of advancement of reaction (α) markedly increases to 80% after 4 h of Si vapor infiltration at 1700 °C, and then increases slowly as reaction time is further lengthened. After 8 h of reaction time, α increases up to about 96%.

Thus, tailoring of the strut microstructure by suitable processing techniques seems to play a key role for improving the mechanical properties of biomorphous low density silicon carbide ceramics. It is also shown that increasing the strut thickness and density may result in an improvement of mechanical strength of highly porous material by selecting original wood.

3.3. Conversion mechanism of charcoal to SiC ceramic

The diffusion of Si vapor into porous charcoal is one of decisive factors for the formation of SiC ceramic, and is dependent of pore channel diameter. A value of lower critical pore channel diameter for gaseous phase infiltration of Si at temperatures of 1400–1600 °C was estimated to be 1 μm [19], above which effective gas phase transport can occur within reasonable time. Thus, for the infiltration of gaseous media into charcoal, pore diameters larger than 1 μm are required to obtain reasonable infiltration rates. From SEM micrographs of basswood charcoal, it is known that the pores in basswood charcoal are large enough to infiltrate gaseous Si.

After infiltration of gaseous Si into carbon template, Si vapor reacts through the continuous tubular pore channels with solid carbon on the pore channel wall surface to form β-SiC ceramic. It can be expressed as

$$\mathrm{C_B\text{-}template(s)} + \mathrm{Si(g)} \rightarrow \beta\text{-}\mathrm{SiC(s)} \tag{2}$$

The heterogeneous nucleation and growth of SiC leads to the formation of a continuous two-dimensional SiC layer. The formation of this initial continuous SiC layer is very fast. The primary SiC layer separates the gaseous Si from the carbon and therefore, prevents further reaction. The further growth of SiC layer is attributed to the diffusion of gaseous Si through the SiC layer. Thus, the siliconizing process involves two steps, namely, the infiltration of gaseous Si into charcoal, and the heterogeneous gas/solid reaction between gaseous Si and carbon to form SiC. The first step is a period of rapid growth corresponding to a mechanism of heterogeneous nucleation and subsequent growth on the carbon surface. Once the continuous SiC layer has been built, the following growth is ensured by the diffusion of gaseous Si through the SiC layer, thereby considerably reducing the reaction rate, due to small diffusion coefficient value of Si through SiC layer. However, the conversion of carbon into SiC induces an important volume increase of the solids and the formation of micropores in the SiC layer. SEM observations also permit us to conclude that the SiC forming the cell wall material (e.g., struts) between the cells is highly porous in the initial state of reaction. These new pore channels provide a supplementary pathway for the gaseous Si diffusion. The gaseous Si penetrates the already formed microporous SiC layer and reacts with the inner carbon to form SiC at the SiC–C interface. When excessive silicon vapor

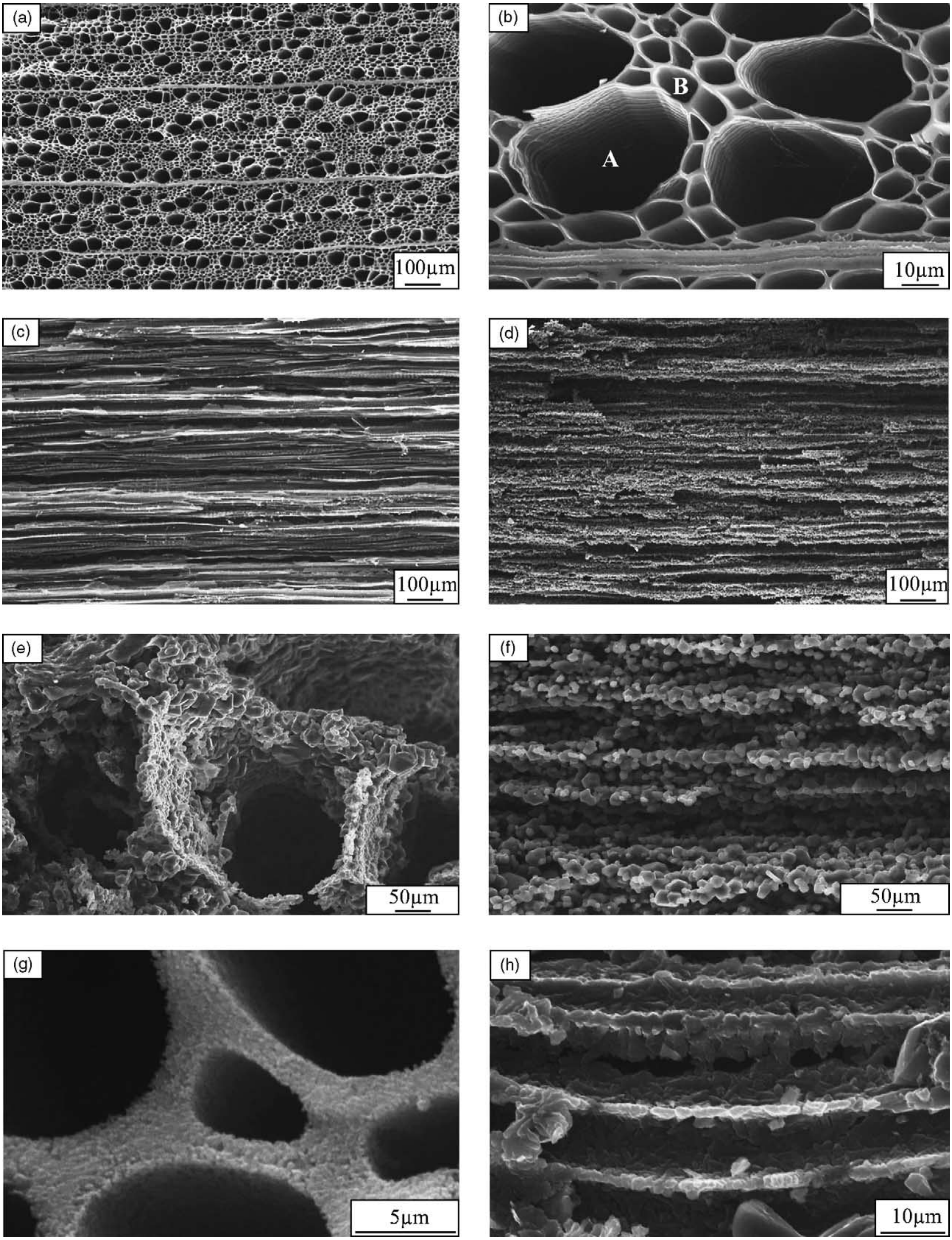

Fig. 3. SEM micrographs of basswood charcoal (a)–(c) and resulting SiC ceramics (d)–(h) at different conditions. (d), (e) and (f) 1500 °C, 8 h; (g) and (h) 1700 °C, 8 h; (a), (b), (e) and (g) cross-section perpendicular to axial direction; (c), (d), (f) and (h) cross-section parallel to axial direction.

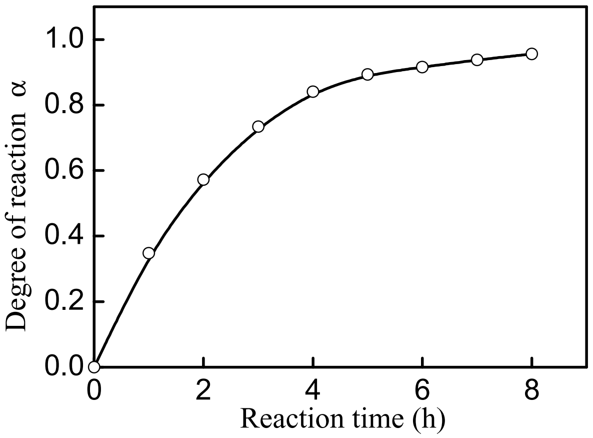

Fig. 4. Degree of reaction α as a function of reaction time t at 1700 °C.

is introduced into charcoal, free silicon may exist on the surface of SiC grains, make the sintering of SiC easy, and strengthen the connection between SiC grains. In a word, the diffusion of gaseous Si is the preferred transport mechanism and the rate controlling step (and not the diffusion of carbon through the primary SiC layer). The carbon is constantly converted into SiC with the infiltration/reaction time.

4. Conclusions

Biomorphic porous silicon carbide ceramic was prepared by the reactive infiltration of gaseous Si into basswood charcoal. XRD and SEM studies indicate that the final SiC ceramic is composed of β-SiC, and retains the microstructure and morphology of basswood charcoal with high precision. The sintering of resulting cellular SiC ceramic may occur at moderate temperatures and holding time. The siliconizing process of basswood charcoal is described as a heterogeneous gas/solid reaction followed by a mechanism of diffusion of gaseous Si. Conversion of wood into ceramic materials with microstructures pseudomorphous to the bioorganic template anatomy offers a great potential for designing novel ceramics with anisotropic cellular morphologies.

Acknowledgements

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