# HEMP HURD BASED CARBON TEMPLATE FOR REACTION FORMED SILICON CARBIDE CERAMIC

Z. L. Yan [1, 2*], T. Ma [1, 3], J. C. Zhang [1, 3], H. Zhang [1, 3], H. Wang [1*]

[1] Centre of Excellence in Engineered Fibre Composites, University of Southern Queensland, Toowoomba, Australia, [2] Special High Value Biomass Industry and Technology Innovation Strategic Alliance, Beijing, China, [3] The Research Centre of China-Hemp Materials, Beijing, China

* Corresponding authors (hao.wang@usq.edu.au, yan_zili@sina.com)

**Keywords**: *carbon template, hemp hurd powder, reaction formed silicon carbide ceramic, pore structure*

## 1 Introduction

Reaction formed silicon carbide (RF-SiC) and reaction bonded silicon carbide (RB-SiC) are both fabricated with silicon infiltration as sintering process, in which silicon infiltrated into the porous template and reacted with the carbon in it to form silicon carbide **[1]**. Although RF-SiC has been invented by Hucke for more than 40 years and shows high mechanical properties than RB-SiC, it hasn't been produced in industrial scale due to its high cost and some technical issues whereas RB-SiC has been produced in industrial scale and applied in many different fields **[2-4]**. According to Hucke's method, chemical agents were used to prepare porous polymer pre-template, followed by carbonization to get porous carbon template. The obstacles for the actual application of RF-SiC are the high cost of the synthetic polymer pre-template and the tendency of crack of the pre-template during carbonization. Fabrication of carbon template for RF-SiC with low cost and free from cracking has been a great challenge to materials scientists **[2]**.

Many attempts have been carried out to fabricate RF-SiC with wood blocks as substitute for synthetic polymer pre-template **[5-7]**. The RF-SiC from wood even obtained flexural strengths and elastic moduli comparable to those of commercial RB-SiC ceramics even though it has greatly lower density than the latter, which stimulated wide enthusiasm of researchers on it **[5, 6, 8]**. Compared with Hucke's method, it has advantages of low cost of raw material and simplicity of the process. However, cracking is still inevitable. Other drawbacks of wood blocks include relatively low and uncontrollable density, the wide pore size distribution and so on. To overcome those disadvantages, middle density fibreboard (MDF) and wood powder composites have also been used as pre-templates **[9, 10]**. The structure is still not ideal, such as the high porosity of templates from MDF and the existence of close pores from wood powder composites.

In our previous research **[11]**, a novel method has been developed to achieve wooden pre-templates with controllable density, in which wood powder was hot pressed into blocks with hot pressing. Under optimized processing parameters, the pre-templates could have uniform density cross the whole sample. With this method, hemp hurd, a kind of non-wooden material but with similar component to wood, can also be used as the raw material and has the advantage of high pore connection. In this paper, the carbonization of the pre-templates of hemp hurd powder, the pore structure of the corresponding carbon templates, and the microstructure of the resulted ceramics were studied to evaluate their suitability for the fabrication of RF-SiC.

## 2. Experimental Procedure

Hemp hurd (harvested in Liu'an City, Anhui province) was used to fabricate pre-templates of hemp hurd powder referring process shown in our previous work **[11]**. The pre-templates were carbonized at 1200 $^{o}$C for 2h in a furnace (ZT-100-20, Shanghai Chenrong Electric Furnace Co., Ltd., China) under a nitrogen gas protection. To avoid cracking in the pre-templates during carbonization, the temperature was increased at a rate of 0.5$^{o}$C/min in the range 200–500$^{o}$C. The carbonized plates were cut into blocks of dimensions 50mm×40mm×6mm as carbon templates and then infiltrated with liquid silicon (purity 99.0 wt%, Beijing Yuanchuang Magnesium Co., Ltd., China) at 1550$^{o}$C for 30min under a vacuum (10–30Pa) in a graphite element furnace (EJ-13, General Research Institute for Nonferrous Metals) to yield the Si/SiC ceramics.

The densities of pre-templates and carbon templates were determined by the weight and dimensions of the samples. The densities of the finial Si/SiC ceramics were measured using the Archimedes' method. The microstructures of the carbon templates and ceramics were observed by scanning electron microscopy (SSX-550, Shimadzu Corp., Japan) and light microscopy (KH–1 000, Shanghai Hirox Instrument Technology Co., Ltd., China), respectively. The porosity distributions of the carbon templates were determined using a mercury porosimeter (Autopore-9220, Micromeritics Instrument Corp., USA).

## 3. Results and discussion

### 3.1 The linear shrinkage and weight residual while carbonization

The linear shrinkages and weight residual of pre-templates of hemp hurd powder are shown in **Fig. 1**. There is negligible difference in the linear shrinkages when the density of the pre-templates varies in the range of 0.85-1.02g/cm$^3$. The shrinkages in length direction and width direction are 25.4±0.1% and 25.4±0.3%, almost same with each other. The shrinkage in height direction is 38.3±0.7%. The relevant weight residual is 31.8±0.3%. It should be noted that when wood blocks are directly carbonized, the shrinkages and weight loss vary greatly from sample to sample because of their variation in chemical composition and physical structure **[12, 13]**. Because of the homogeneity of pre-templates of hemp hurd powder, cracking is avoidable at optimized carbonization condition.

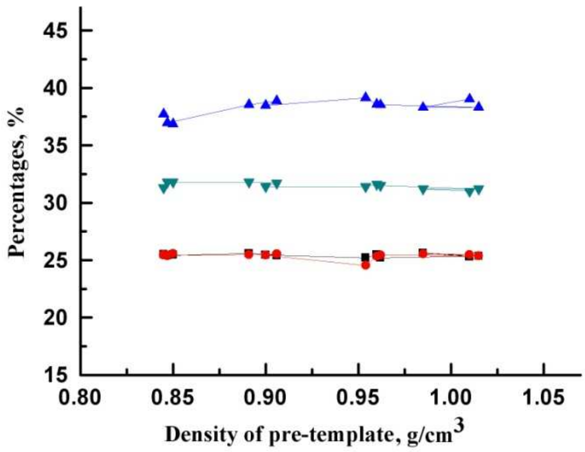


**Fig. 1** The linear shrinkages and weight residual of pre-templates of hem hurd powder when carbonization

■—shrinkage in length; ●—shrinkage in width; ▲—shrinkage in height; ▼—weight residual

**Fig. 2** shows relationship between the densities of the pre-templates of hemp hurd powder and the corresponding carbon templates. A good linear relationship exists in those two densities, which indicates that the density of carbon templates is controllable by adjusting the density of the pre-templates of hemp hurd powder.

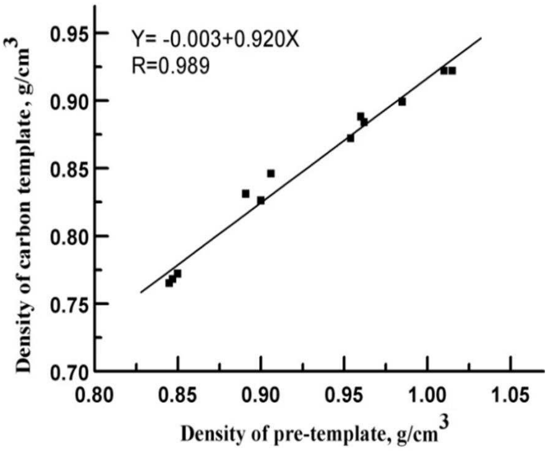


**Fig. 2** The linear relationship between the densities of pre-templates of hemp hurd powder and of the corresponding carbon templates

The carbonization behavior of the pre-template from hemp hurd powder and the improvement on the density controllability of the resulted carbon template can be attributed to the homogeneity in chemical composition and physical structure of the pre-template of hemp hurd powder. Wood is a typical composite with evident anisotropic characteristics, which leads to the different shrinkages in three directions while carbonization. The chemical composition and the physical structure vary between different trees even in a same tree, which results in the great variation of shrinkages while wood is carbonized **[12]**. For the pre-templates of hemp hurd powder, the milling and hot pressing eliminated the difference in physical structure and chemical composition in pre-templates. Therefore the pre-templates of hemp hurd powder can be looked as a homogeneous material, which is the reason why the pre-templates of hemp hurd powder have small deviation in shrinkages and weight residual. **Fig. 3** shows the appearance of the hemp hurd powder. They mainly exist in the shape of small sheet. The direction with bigger size should be parallel with the axial direction of hemp hurd because of its higher strength in this direction. In hot pressing, these powders in sheet shape have a tendency to lie down in any direction which is perpendicular to the pressing force. Therefore, the structural difference only exists between the height direction and length/width direction and the pre-template has same shrinkages in both length and width directions but different shrinkage in height direction.

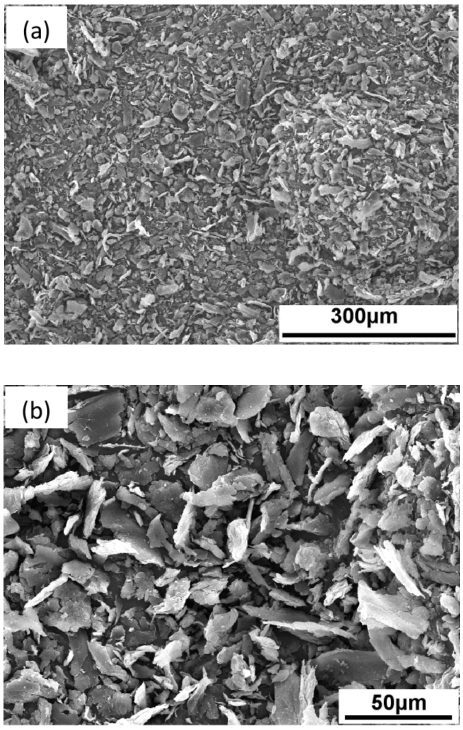


**Fig. 3** The scanning electronic microscopy photos of hemp hurd powder

### 3.2 Pore structure of carbon templates

In the carbonization process, the pore structure of pre-templates can be inherited to the carbon template **[5]**. **Fig. 4** shows the SEM photos of carbon templates from hemp hurd and hemp hurd power. It can be seen from **Fig. 4(a)** that there are two types of pores with very different pore size in carbon template from hemp hurd. The pores with diameters of about 120 μm are inherited from vascular vessels, while the smaller pores at 15 μm are from tracheidal channels. On the contrast, the carbon template from hemp hurd powder has invisible difference in pore size (**Fig. 4 (b)**). It can be seen from **Fig. 4 (c)** that there are some pores from the interval between the powders.

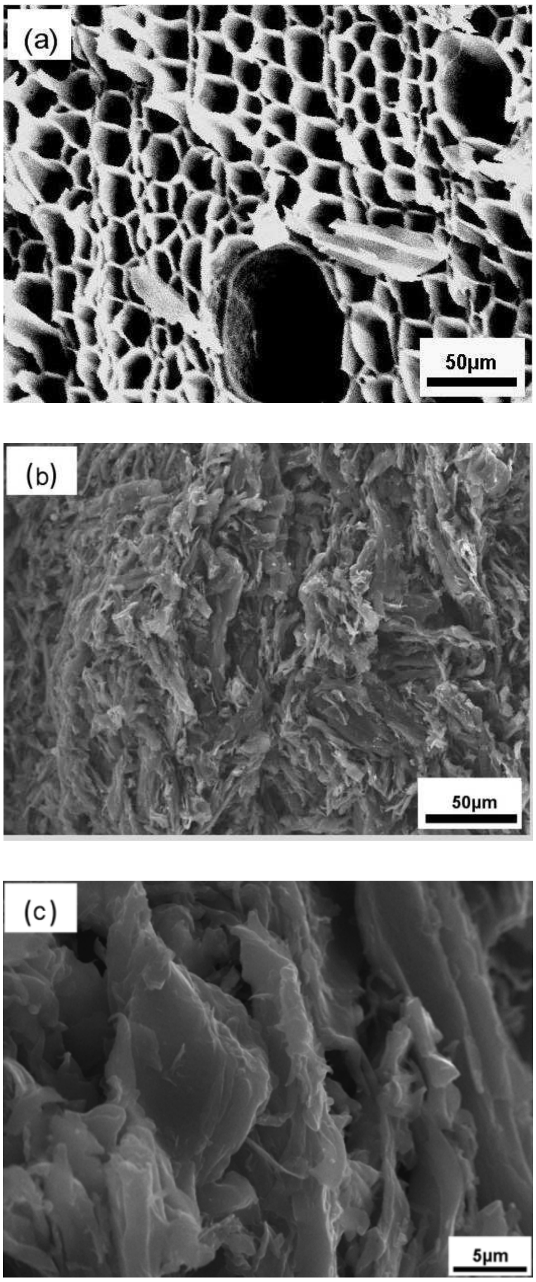


**Fig. 4** Scanning electronic microscopy photos of carbon templates from hemp hurd (a) and hemp hurd powder (b) and (c)

The mercury intrusion measurement is an effective method to test pore size distribution of porous materials. **Fig. 5** shows the pore size distribution of carbon template from hemp hurd powder. There is only one peak in the differential curve, being similar with the pore size distribution of carbon template from the tradition sythetic method **[2, 3]**. This characteristic is beneficial to get high density silicon carbide ceramic because the existence of huge pores will result in high content of silicon in the resulted ceramics, which means less silicon carbide content and low mechanical properties. The cumulative pore volume percentages of pores with diameter larger than 4.5 μm and with diameter smaller than 0.5 μm are about 1.4% and 11.0%, respectively. Thus, about 87.6% of the pore volume is attributed to pores with diameters between 0.5 μm and 4.5 μm.

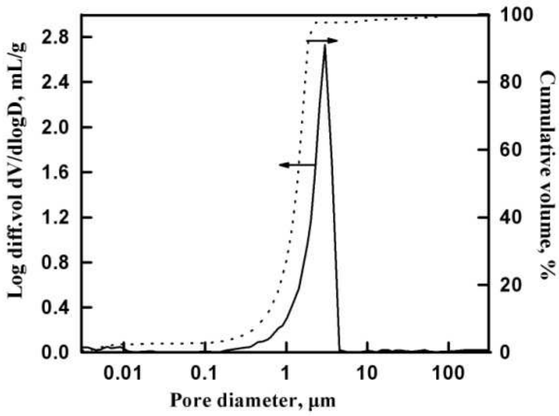


**Fig. 5** Pore size distributions of carbon templates from pre-template of hemp hurd powder (The sample density: 0.78g/cm$^3$)

### 3.3 Ceramic microstructure

The microstructure of RF-SiC ceramic from hemp hurd powder is shown in **Fig. 6**. The light grey area represents free silicon and the dark grey area represents silicon carbide. The free silicon is uniformly distributed in the ceramic from hemp hurd powder, similar with RF-SiC by Hucke’s method and totally different from that of ceramics from wood blocks **[2, 5]**. There are no visible pores in the ceramics shown in **Fig.6 (a) and (b)**, which means the pores in the carbon template from hemp hurd powder are mainly connective pores which leads to a complete infiltration of silicon into the carbon template. Compared with the ceramic in **Fig. 6 (b)**, the ceramic in **Fig. 6 (a)** has higher silicon content due to the lower density of the carbon template. However, higher density of carbon template didn’t always do good to the microstructure. In **Fig. 6 (c)**, the density of the carbon template is 0.83g/cm$^3$, the resulted ceramic is not as dense as the ceramics in **Fig. 6 (a) and (b)**.

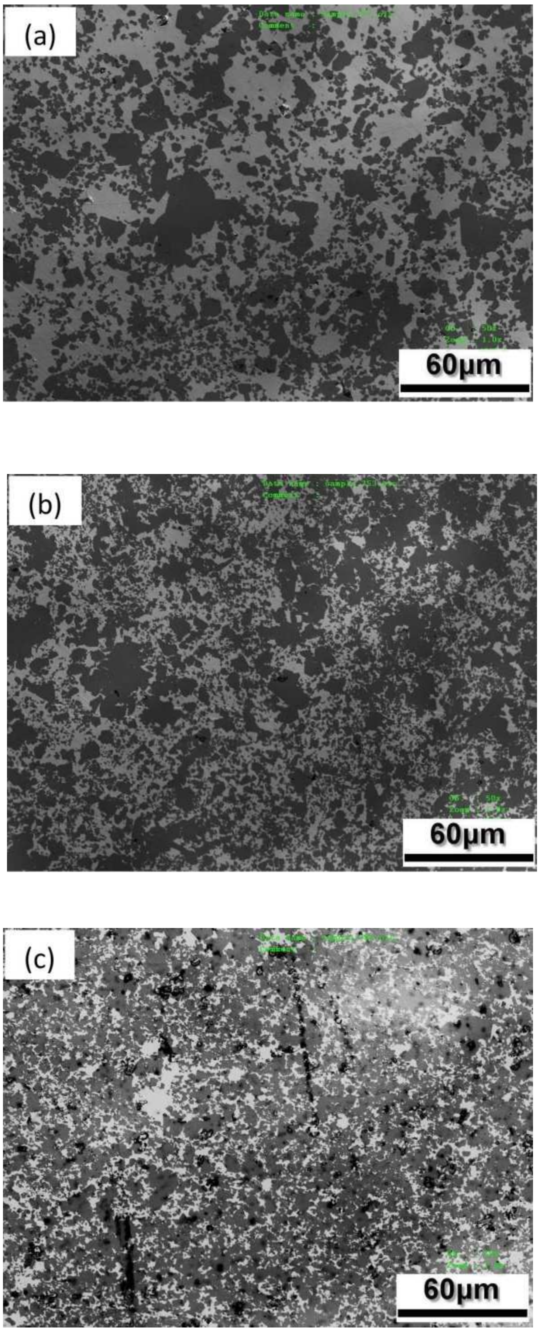


**Fig.6** The microstructure of biomorphic Si/SiC ceramics from hemp hurd powder
(a), (b) and (c) correspond to ceramics with a density of 2.80 g/cm$^3$, 2.94 g/cm$^3$, and 3.01 g/cm$^3$

The influence of carbon template density on the microstructure can be interpreted by the theory of reactive infiltration of silicon. In the infiltration process, silicon melt infiltrated into the porous carbon template and then reacted with the carbon skeleton to from silicon carbide. In this process, the skeleton of carbon transferred into silicon carbide, accompanied with increasing of its thickness, which means the decreasing of pore size and porosity. Bigger pore size is helpful to finish reactive infiltration of silicon and the carbon in the template can transfer into silicon carbide whereas smaller pore size can cause the connective pores being closed and then incomplete infiltration happens.

## 4. Conclusion

Pre-templates of hemp hurd powder fabricated by hot pressing were carbonized to get carbon templates for RF-SiC. The carbonization study shows that the carbon templates from pre-templates of hemp hurd powder have controllable density because the pre-templates have stable linear shrinkages in three directions and weight residual while carbonization. The cracking of pre-templates in carbonization is also evitable. The pore size distribution of the resulted carbon templates is narrow and ideal for the fabrication of RF-SiC. The microstructure of the resulted RF-SiC ceramic testified the suitability for RF-SiC fabrication of pre-templates of hemp hurd powder.

## Acknowledgement

This work has been supported by the Foundation for Returned Scholars, Ministry of Education of China. The authors would like to thank Mr. Weidong Chi and Mr. Ruisheng Xue of Beijing University of Chemical Technology for their help in carrying out the experimental work.

## References

[1] W.L. Liu. Advanced Ceramics Processing, 1st ed., Wuhan University of Technology Press, Wuhan, 2004 (in Chinese).
[2] Y.X. Wang, S.H. Tan, D.L. Jiang, The fabrication of reaction-formed silicon carbide with

controlled microstructure by infiltrating a pure carbon preform with molten Si. Ceramics International, 2004, 30:435-439.
[3] Singh M, Behrendt D R. Microstructure and mechanical properties of reaction-formed silicon carbide (RFSC) ceramics [J]. Materials Science and Engineering A, 1994, 187 (2): 183-187
[4] Xu S J, Qiao G J, Li D C, et al. Reaction forming of silicon carbide ceramic using phenolic resin derived porous carbon preform. Journal of the European Ceramic Society, 2009, 29 (11): 2395-2402
[5] M. Singh, J.A. Salem, Mechanical properties and microstructure of biomorphic silicon carbide ceramics fabricated from wood pre-templates. Journal of the European Ceramic Society, 2002, 22:2709-2717.
[6] D. Mallick, O.P. Chakrabarti, H.S. Maiti, R. Majumadar, Si/SiC ceramics from wood of Indian dicotyledonous mango tree, Ceramics International, 2007, 33 (7): 1217-1222.
[7] C. Zollfrank, H. Sieber, Microstructure and phase morphology of wood derived biomorphous SiSiC–ceramics. Journal of the European Ceramic Society, 2004,24: 495-506.
[8] D. W. Shin, S. S. Park, et al. Si/SiC composites fabricated by infiltration of a Si melt into charcoal. Joural of Amercian Ceramic Society, 1999, 82 (11): 3251-3253.
[9] M.A. Bautista, A.R. de Arellano-Lo´pez, J. Martı´nez-Ferna´ndez, A. Bravo-Leo´n, J.M. Lo´pez-Cepero, Optimization of the fabrication process for medium-density fiberboard (MDF)-based biomimetic SiC. International Journal of Refractory Metals and Hard Materials, 2009, 27:431-437.
[10] A. Hofenauer, O. Treusch, F. Tro¨ger, G. Wegener, J. Fromm, M. Gahr, J.Schmidt, W. Krenkel. Dense reaction infiltrated silicon/silicon carbide ceramics derived from wood-based composites. Advanced Engineering Materials, 2003, 5 (11):794-799.
[11] Z. L. Yan, J. Liu, J. C. Zhang, J. M. Gao, Z. L. Zhou, L. X. Meng. Study on the Vertical Density Profile of Hot-pressed Blocks of Birch Powder. Wood Industry, 2011, 25(2): 11-13.
[12] P. Greil, T. Lifka, A. Kaindl. Biomorphic cellular silicon carbide ceramics from wood: Ⅰ. processing and microstructure. Journal of the European Ceramic Society, 1998, 18 (14): 1961-1973.
[13] P. Greil, T. Lifka, A. Kaindl. Biomorphic cellular silicon carbide ceramics from wood: Ⅱ. Mechanical properties. Journal of the European Ceramic Society, 1998, 18 (14): 1975-1983.
[14] P. Duncker, H. Spiecker. Cross-sectional compression wood distribution and its relation to eccentric radial growth in Picea abies [L.] Karst. Dendrochronologia, 2008, 26 :195-202.