

Fabrication of Biomorphic Silicon Carbide from Agriculture Waste Powders

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Abstract—Biomorphic Silicon Carbide (SiC) has been widely used in industries due to its unique biological structure produced by natural wood. SiC exhibits excellent strength at low density. Besides, using agricultural waste residues such as woods as the starting material can lower the manufacturing cost. In this study, the agriculture waste which was Dark Red Meranti wood powders were chosen as the precursor. The synthesis of biomorphic SiC involved two important stages which are pyrolysis and silicon infiltration. The wood powders were compacted at 160 °C for 20 minutes to form a dense pre-template. The compacted wood powders were then experienced pyrolysis process to be converted into a carbon template. Pyrolysis process was conducted at 850 °C in argon atmosphere to decompose the wood's aromatic constituents including cellulose, hemicellulose and lignin. The carbon template was then transformed into biomorphic SiC through Silicon (Si) infiltration process at 1500 °C. The study aims to investigate the effect of infiltration holding time on the formation of SiC, four different holding times of 1 to 4 hours were used. Thermogravimetric analysis (TGA) was conducted to study the wood decomposition behaviour during carbonization process. Scanning electron microscopy (SEM) were used to characterize the microstructure of SiC ceramic. The density and porosity of the sample were determined. Using wood powders as the starting material produced a dense SiC having average pore diameter around 1µm. Due to low porosity and small pore size, the conversion into SiC at early stage was difficult. Better Si infiltration and more SiC formation were found as the holding time was increased. Besides, the density of the biomorphic SiC was increased. On the other hand, the porosity was decreased as more SiC were formed.

Index Terms—biomorphic, SiC, wood powders, dense

I. INTRODUCTION

Silicon Carbide (SiC) has been synthesized since 1892 using Acheson process involving reaction between silica and petroleum coke. Since then, the technology has grown and there are many methods to produce SiC including carbothermal reduction reaction, Chemical

Vapour Deposition (CVD), sol-gel and reaction bonded process. However, there are environmental and economic issues associated with processes that has been highlighted. Most of the methods use high working temperature more than 2000 °C, which increasing the production cost. Besides, they also produce liquid and gaseous chemical by-products that are harmful to the environment [1].

Production of SiC from natural-based precursors has been attracting great interest in producing ecoceramic material. Furthermore, processing biomorphic SiC from natural precursors can be considered as low cost as the starting material can be found abundantly as agriculture waste residues. Past study also reported that biomorphic SiC require lower manufacturing temperature than the conventional methods, thus reduced the production cost [1].

Biomorphic silicon carbide (SiC) can be derived from wood, sawdust, fibreboard and papers. The unique characteristic of biomorphic SiC has attained interest. The biological structure of wood exhibits excellent strength at low density and inherits microstructure of the original woods. Past researchers used natural wood blocks as precursors and produced porous SiC that can be used in many applications such as filters and separation, heat exchangers and catalyst supports [1]. Using wood powders in contrast, a denser SiC ceramic is produced and the SiC is more homogenous.

The biomorphic SiC formation process was usually initiated by pyrolysis process. The pyrolysis changed the natural wood into carbon template. The subsequent process involved the conversion of carbon template into SiC ceramic. There are several methods have been done by previous studies such as carbo-thermal reduction reaction [2], Liquid Silicon Infiltration (LSI) [3] and chemical vapour infiltration (CVI) [4]. LSI is a type of reactive melt infiltration using chemical reaction between liquid infiltrant and porous template. In order to fabricate SiC ceramic, carbon template is converted into SiC by infiltrate Si into the carbon template. During LSI process, there are several factors should be taken into consideration such as carbon template's porosity, pore size and density of the carbon template. Besides, the

infiltration temperature and time play important role in affecting the infiltration rate of Si into carbon template. Thus, the aim of this paper is to explore the feasibility of natural wood powders to be converted into SiC using LSI process at different infiltration times.

II. EXPERIMENTAL WORKS

A. Sample Preparation

Biomorphic SiC sample was fabricated using Dark Red Meranti (DRM) wood powders as the starting precursors. The powders were collected from the agriculture waste. The wood chips were crushed and sieved to obtain wood powders having average particle size of 0.08 mm. The powders were then compacted by hot pressing process without any adhesive at 160 °C and hold for 20 minutes. The pre-template was ready for pyrolyzed in a flowing argon gas atmosphere. The pyrolysis process converted the wood precursors into carbon template at 850 °C.

The carbon template was placed in an alumina crucible and covered by silicon powders. The silicon powders have average particle size of 45 μm. The Si infiltration proceeded at 1500 °C at four different holding times from 1 to 4 hours. To ensure the full conversion of carbon, Si/C weight ratio of 3 to 2 was used. This ratio was higher than the stoichiometry needed because the silicon may loss at high temperature due to high vapour pressure of silicon.

At the end of infiltration process, the end product of SiC and excess solid silicon was formed on the surface of the sample. The excess silicon was removed by chemical leaching process using a mixture of HF/NH₃ at ratio of 1 to 1. The flow chart in Fig. 1 shows the process used to synthesize biomorphic SiC from wood powder precursor.

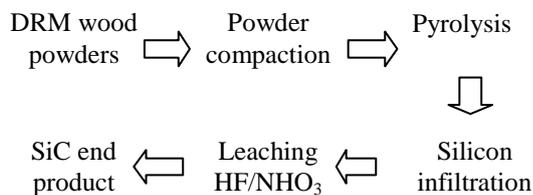


Figure 1. Flow chart to form biomorphic SiC

B. Sample Characterization

The decomposition of the wood during the carbonization process was characterized using Thermogravimetric Analysis (TGA) at heating rate of 10 °C/min in Argon atmosphere. Hitachi TM3030Plus model of Scanning Electron Microscopy (SEM) was used to analyse the microstructure of the carbon template and SiC ceramic. The density of pre-template, carbon template and SiC samples were investigated using Archimedes principle. The pore size distribution and porosity of all samples were characterized using mercury porosimetry (Micrometrics, Autopore IV).

III. RESULTS AND DISCUSSION

Fig. 2 shows the Thermogravimetric Analysis (TGA) and Differential Thermogravimetric (DTG) behaviour of Dark Red Meranti wood during pyrolysis process.

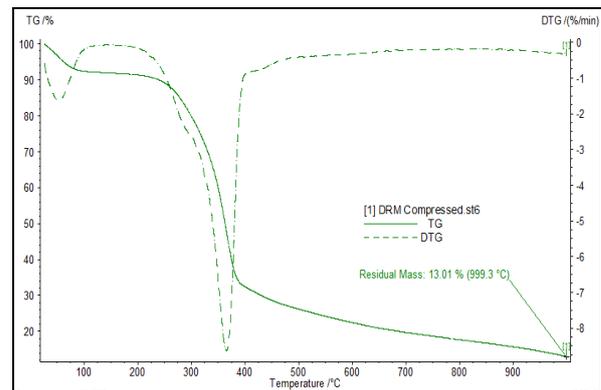


Figure 2. TGA-DTG thermograms of Dark Red Meranti

During pyrolysis process, the pre-template experienced thermo-chemical decomposition of its aromatic constituents including cellulose, hemicellulose and lignin. TGA thermogram shows the pattern of weight loss during the pyrolysis process. The sample experienced 3 stages of weight loss, where a slight weight loss of 5 % recorded at temperature range of 30 °C to 100 °C. The wood was in dehydrocellulose condition in which the moisture in the wood was removed. The latter weight loss was found at temperature about 120 °C to 330 °C and another major weight loss reaches maximum rate at 411 °C, causes almost 70% of weight loss.

From DTG thermogram, the peak at 285 °C accounted for the degradation of hemicellulose and later peak of 360 °C was mainly due to decomposition of cellulose. This has been supported by Lukas Gasparovic et al. [5] that stated hemicellulose and cellulose decompose at temperature range of 176 °C to 344 °C, while lignin is a slow and longer decomposition process that took place at high temperature up to 900 °C. The weight loss process almost completed at 600 °C. The graphitic carbon started to form at temperature above 600 °C. The formation of carbon template is crucial for the silicon infiltration process.

Table 1 shows the density and porosity of Dark Red Meranti carbon template before and after pyrolysis process. The wood original pores structure was still retained. The weight loss about 21.4 % was not only caused by the decomposition but also the moisture evaporation during the pyrolysis.

The density of the carbon template was reduced after pyrolysis due to decomposition of wood aromatic constituents such as lignin, hemicellulose, cellulose and volatile [5]. The density of the carbon template is below the critical value of 0.96g/cm³. Hence, it is possible for the carbon template to be transformed into SiC ceramic. In contrast, if the density is greater than the critical value, the end product will have excess carbon due to lack of Si per unit volume [6].

The porosity was increased after the void formation due to the decomposition of wood constituents. The porosity percentage of the carbon template is acceptable

for Si infiltration process to take place. In fact, the carbon template must have porosity higher than 37.9% to allow full conversion of SiC[7].

TABLE I. DENSITY AND POROSITY OF CARBON TEMPLATE BEFORE AND AFTER PYROLYSIS PROCESS

Density (g/cm ³)		Porosity (%)		Weight loss (%)
Pre-template	Pyrolysis	Pre-template	Pyrolysis	
1.23	0.86	34.89	38.76	21.4

Fig. 3 shows the SEM images of carbon template and SiC samples. The carbon template has homogenous microstructure that retained original structure with no visible pores. Based on mercury porosimetry analysis, average pore diameter of the carbon template was 1.0226 μm. The carbon template was transformed into SiC after infiltrated with Si.

From the morphology, the grey region represents SiC; white region is silicon and black region is unreacted carbon. Once the Si melted and in contact with the carbon template, reaction between them occurred instantaneously. However, not all Si can diffuse into the template. The pores were too small and were clogging easily during the SiC. Past study showed that the optimum pore diameter should not less than 1 μm, otherwise volume expansion associated to formation of SiC can lead to pore closure and early termination of infiltration occurs [6]. Porosity of the carbon template plays important roles during silicon infiltration process. This is because the sample experienced volume expansion during the process and carbon template with porosity lower than 37.9% will have the possibilities of flow chocking as there is not enough volume for the conversion to occurs.

The Si was incapable to infiltrate deep into the template due to “pore-chocking” phenomenon. The early formation of SiC layer hindered further direct contact of Si and carbon. However, by extending the holding time of the Si infiltration process, there were more SiC formed and enhance the SiC layer. Table 2 shows the thickness of SiC layer at various holding times. At 1 hour holding time, the SiC layer was formed at 546 μm thickness. As the holding time prolongs, a stable and thicker layer of SiC were formed. The Si had more time to diffuse through SiC layer formed earlier before reacted with the carbon underneath the early-formed SiC layer. This finding was supported by A. Ciftja [8] stated that SiC layer can be thicken and more stable as the reaction time was increased.

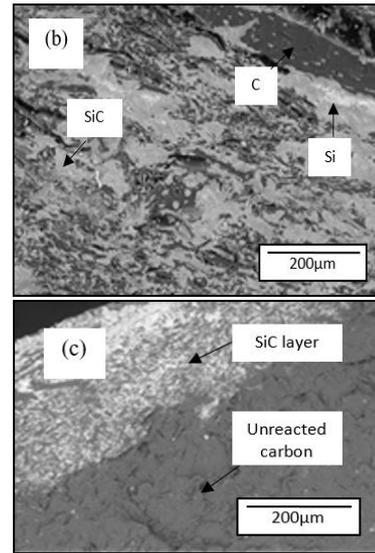
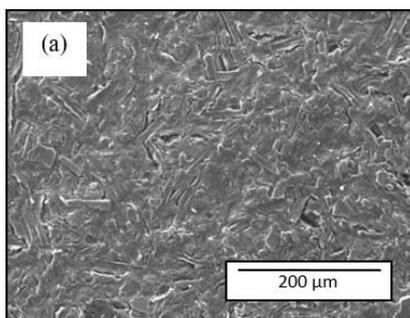


Figure 3. SEM images of (a) carbon template, (b) surface and (c) cross-section of biomorphic SiC

TABLE II. SiC LAYER THICKNESS AFTER INFILTRATION

	Infiltration Holding Time (hrs)			
	1	2	3	4
SiC layer thickness (μm)	546	749	805	818

The density and porosity of the biomorphic SiC were recorded in Fig. 4. After infiltrated with Si, the samples became denser compared to carbon template (0.86 g/cm³) due to the reaction between the silicon and carbon. The infiltration rate of silicon into carbon template has been enhanced when the holding time prolongs. This finding is supported by numerical simulation by Gern and Kochendorfer [9]. They showed that the infiltration time plays an important factor toward the rate of silicon infiltration. However, the density of the SiC ceramic was much lower if compared to the theoretical density of SiC, which is about 3.12 g/cm³. By increasing the holding time, the infiltration rate could be increased to form denser SiC ceramic.

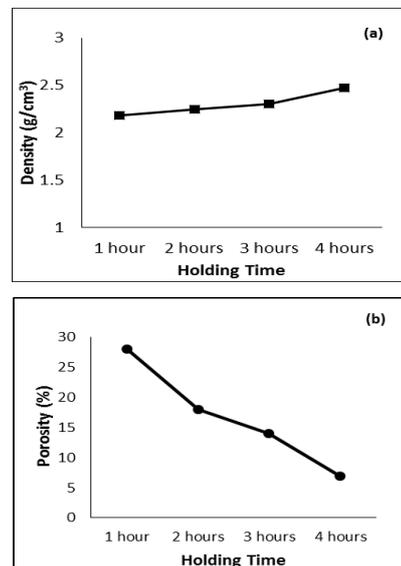


Figure 4. (a) Densities and (b) porosities of biomorphic SiC at various holding times

On the other hand, the porosity of SiC was decreased as the holding time was prolonged. Denser SiC ceramic were then formed due to better diffusion of Si into the carbon template. This finding was similar to the finding found by past literature [10].

Fig. 5 shows the pore size distribution of the sample. The carbon template shows a very thin peak for large pore diameter at higher pore volume. The peak however, disappeared once the carbon template was introduced to silicon particle. When the silicon infiltrated into the carbon template, the pores especially the bigger pores were started to fill up and occupied within silicon, leaving only the small pores unreacted. The silicon would have more time to infiltrate deep into the carbon template and form SiC if longer holding time is permitted. There was a big difference of pore volume between 1 hour and 4 hours holding time of SiC. At 1 hour, less pores were filled with Si thus resulted in high pore volume. After 4 hours pyrolysis, the pores reduced dramatically and evident that the SiC formation filling within the pores. Hence, the pores volume become very low.

IV. CONCLUSION

Biomorphic SiC was fabricated from Dark Red Meranti wood powder. Hot pressing process was used to form pre-template and Si infiltration of carbon template to form SiC ceramic. Resulting SiC have homogenous microstructure that retained the original structure with pore diameter around 1 μm . The pore size of the carbon template was too small and intended to block the diffusion of Si and resulted in "pore-chocking" phenomenon. Furthermore, the early SiC formation hindered latter Si from infiltrated deep into carbon underneath the SiC layer. However, prolonged the holding time of infiltration process make the Si able to diffuse through the early formed SiC layer and improved the formation of SiC. Denser SiC ceramic was formed at longer infiltration time resulting in low pores volume.

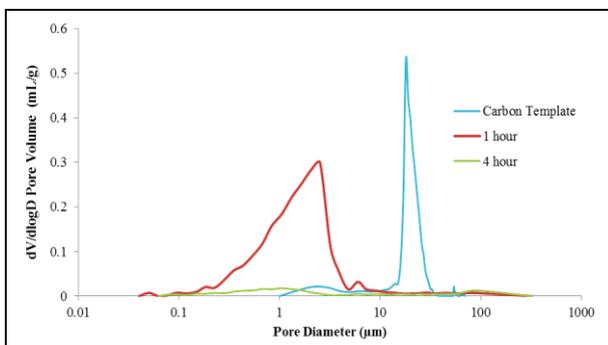


Figure 5. Pore size distribution of carbon template and biomorphic SiC at 1 hour and 4 hour holding time

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REFERENCES

- [1] M. a. Bautista, J. Q. Cancapa, J. M. Fernandez, M. A. Rodríguez, and M. Singh, "Microstructural and mechanical evaluation of porous biomorphic silicon carbide for high temperature filtering applications," *J. Eur. Ceram. Soc.*, vol. 31, no. 7, pp. 1325–1332, Jun. 2011.
- [2] X. Guo, L. Zhu, W. Li, and H. Yang, "Preparation of SiC powders by carbothermal reduction with bamboo charcoal as renewable carbon source," *J. Adv. Ceram.*, vol. 2, no. 2, pp. 128–134, Jun. 2013.
- [3] K. E. Pappacena, S. P. Gentry, T. E. Wilkes, M. T. Johnson, S. Xie, a. Davis, and K. T. Faber, "Effect of pyrolyzation temperature on wood-derived carbon and silicon carbide," *J. Eur. Ceram. Soc.*, vol. 29, no. 14, pp. 3069–3077, Nov. 2009.
- [4] J.-M. Qian, Z.-H. Jin, and X.-W. Wang, "Porous SiC ceramics fabricated by reactive infiltration of gaseous silicon into charcoal," *Ceram. Int.*, vol. 30, no. 6, pp. 947–951, Jan. 2004.
- [5] L. Gašparovi, Z. Kore, and L. Jelemenský, "Kinetic Study of Wood Chips Decomposition by TGA," in *36th International Conference of Slovak Society of Chemical Engineering*, 2009, p. 178 (1-14).
- [6] J. C. Margiotta, D. Zhang, D. C. Nagle, and C. E. Feeser, "Formation of dense silicon carbide by molten silicon infiltration of carbon with tuned structure," *Journal of Materials Research*. 2008.
- [7] E. S. Nelson and P. Colella, "Parametric Study of Reactive Melt Infiltration," pp. 1–11, 1999.
- [8] A. Ciftja, "Wettability of Silicon with Refractory Materials: A Review," no. February, 2008.
- [9] F. H. Gern and R. Kochendörfer, "Liquid silicon infiltration: description of infiltration dynamics and silicon carbide formation," *Compos. Part A Appl. Sci. Manuf.*, vol. 28, no. 4, pp. 355–364, 1997.
- [10] G. Hou, Z. Jin, and J. Qian, "Effect of holding time on the basic properties of biomorphic SiC ceramic derived from beech wood," *Mater. Sci. Eng. A*, vol. 452–453, pp. 278–283, 2007.



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