Transformation of Wood Powder Carbon Template into Biomorphic Silicon Carbide

Husna Elias
A. Kalam
Noorleha Abd Rahman
Faculty of Mechanical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

Koay Mei Hyie
Faculty of Mechanical Engineering, Universiti Teknologi MARA (Pulau Pinang), 13500 Permatang Pauh, Pulau Pinang, Malaysia

ABSTRACT

Liquid silicon infiltration (LSI) process is a cost effective process to produce biomorphic silicon carbide (SiC) ceramic. In this study, the production of biomorphic silicon carbide from wood powder precursors was investigated. Two types of wood powders were used which were Kapur and Dark Red Meranti. Wood powders were compacted into cylindrical shaped without any adhesive. Biocarbon template was produced via pyrolysis process at 850°C in controlled atmosphere, subsequently infiltrated with melting silicon at 1500°C. Pyrolysis was conducted using double stage process to avoid any cracks. The compacted sample was carbonized with slow heating rate of 1°C/min at temperature 200°C to 500°C. The heating rate was increased to 2°C/min until the pyrolysis process completed. The infiltration process was done by varying the holding time from 2 to 4 hours. The effect of holding time was analyzed by using density and X-ray diffractometer (XRD analysis). The characteristic of the biocarbon template and biomorphic silicon carbide were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Due to compaction process, the microstructure of biocarbon produced was found homogenous and uniform with pore size less than 2µm. The pore size and porosity reduced after infiltration process but the density increased. By increasing holding time, the density also increased, which indicates better SiC formation. SEM micrograph shows that the thickness of SiC formation increased by prolonging the holding time. Dark Red Meranti was found to be denser and exhibited better formation of SiC compared to Kapur.

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Introduction

Biomorphic ceramics have been attracting attention among industries for the past decades due to the availability of natural resources such as rice husk, plants, woods and sawdust [1]. The novelty of complex microstructure that inherited from the original precursors is one of the advantages of biomorphic ceramics. It is a cost effective method as it uses lower working temperature than conventional process. Besides, it can be called as ecoceramic material or environmental friendly material. This is because the precursors especially woods are renewable resources. Variety of applications have been explored for the usage of biomorphic ceramics including heat exchanger, automotive component, filtration and separation [2]. Biomorphic ceramics/composites such as SiC, TiC, Si-SiC, Al_2O_3, and ZrO can be fabricated by various methods either transformation or substitution process [2].

Biomorphic silicon carbide (SiC) has been extensively studied using wood precursors due to easy set up process. Previous methods involved converting pyrolyzed biocarbon template into biomorphic SiC using infiltration of liquid Si, gas Si, sol-gel and carbothermal reduction reaction. However, sol gel and carbothermal reduction required longer working hours and higher temperature [3]. Infiltration of Silicon (Si) gas requires higher cost and longer reaction time compared to liquid Si. Therefore, reactive infiltration using liquid Si is more convenient because of the simple preparation processing. It requires two crucial steps which are pyrolysis and infiltration. Pyrolysis process is needed in order to produce porous carbon template. The biocarbon template subsequently infiltrates with melt Si powders to form SiC.

Past researches focused on the fabrication of biomorphic SiC from natural wood blocks [4]-[6]. However, little work has been done on the study of production of SiC from wood powder precursors. Zili Yan *et al*. compared the microstructures and properties of SiC from porous birch block and compacted birch powder precursors [6]. The results indicated that the usage of wood powders precursors led to denser, low porosity and uniform microstructure.

In the present work, the biocarbon was derived from compacted Asian wood powders which are Kapur and Dark Red Meranti. The effect of holding time during Si infiltration process on the SiC formation was also investigated.

Experimental Work

Materials preparation

Biocarbon and biomorphic silicon carbide were processed from two hardwood precursors; Kapur and Dark Red Meranti. Wood powders having average particle size of about 80µm were provided by Nusantara R&S Enterprise timber factory in Johor Bahru, Malaysia. The wood powders were compacted into a cylindrical shape with diameter 25mm without any adhesive. The compaction process took place at 160°C for 20 minutes in order to produce pre templates. The pre templates undergo pyrolysis process at 850°C in argon atmosphere to produce biocarbon template. Double stage carbonization process was used to prevent any crack on the samples. The first heating stage was conducted at heating rate of 1°C/min from 200°C to 500°C. The heating rate was slowly increased to 2°C/min after 1 hour until the pyrolysis process completed. The carbon templates were then packed in excess silicon powders and subsequently heated up at 1500°C in controlled atmosphere to form silicon carbides. The holding time of infiltration process varied from 2 to 4 hours. In order to ensure complete carbon reaction, excess silicon powders content was used at Si/C ratio of 3:2. It is expected to have SiC/Si with excess Si. Thus, unreacted silicon was removed by continuously stirring the mixture of hydrofluoric acid and nitric acid (HF/HNO_3) at weight ratio of 1:1. Figure 1 summarizes the flowchart of SiC ceramic manufacturing process from wood powders precursors.

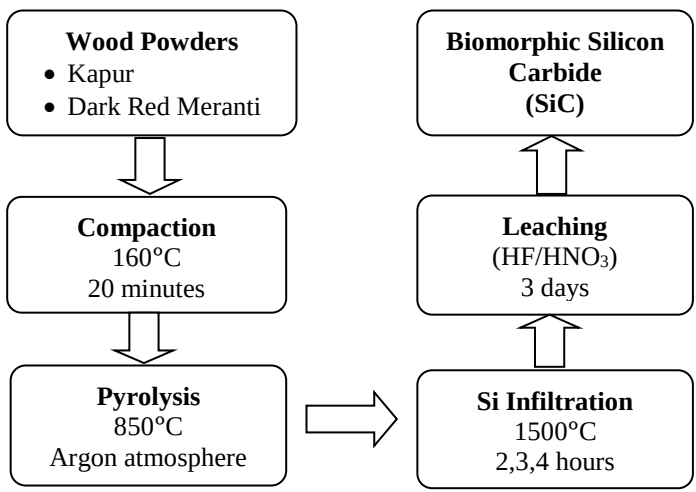

Figure 1: Biomorphic SiC manufacturing process from wood powders

Characterization methods

The X-ray diffraction patterns of biocarbon templates and resulting biomorphic SiC were recorded by X-ray diffractometer (Rigaku Ultimate IV, Japan) with CuKα radiation at 1.542 wavelengths. The microstructure morphology was examined by using scanning electron microscope (SEM, Hitachi S-2500), equipped with energy-dispersive X-ray spectroscopy (EDS) analysis. The pore size distribution and porosity of carbon templates were analyzed using mercury porosimeter (Micrometrics, Autopore IV), meanwhile the density was determined by using Archimedes principle. Wet chemical leaching process was done to remove excess Si particle of the samples. The chemical reactions during the leaching process are as follow:

$$3Si + 4HNO_3 \longrightarrow 3SiO_2 + 4NO + 2H_2O \quad (1)$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O \quad (2)$$

$$SiF_4 + 2HF \longrightarrow H_2SiF_6 \quad (3)$$

Results and Discussion

Phase determination

Figure 2 shows the XRD patterns of biocarbon template of both Kapur and Dark Red Meranti. There are two broad and weak peaks at the charcoals pattern. This is attributed to diffraction from (002) plane and (100) that suggests the bio carbon is graphitized amorphous. Similar results has also been reported by P. Gao *et al*. in various pyrolysis temperatures ranging from 800°C to 1700°C [7].

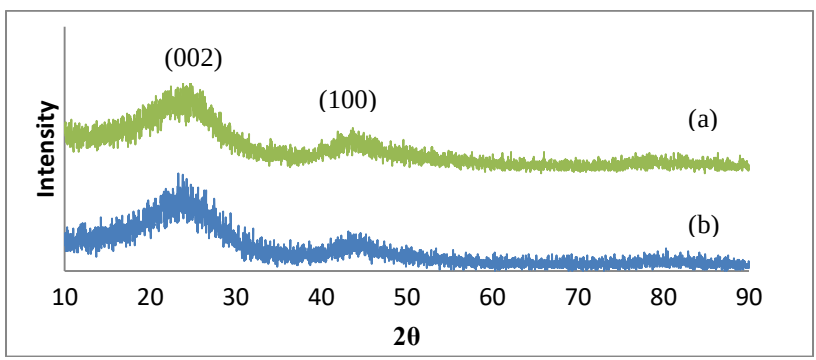

Figure 2: XRD pattern of biocarbon of (a) Kapur and (b) Dark Red Meranti

Figure 3 and Figure 4 represent the XRD patterns of bioSiC from Kapur and Dark Red Meranti fabricated at three holding times. The diffraction profiles show the presence of SiC, excess Si and unreacted C peaks (C). With increasing reaction time, the intensity of amorphous carbon decreases due to formation of graphitized carbon. For Kapur, the major peaks are found at 35.68°, 41.4°, 60° and 71.8° respectively showing β-SiC. Meanwhile, major peaks of Dark Red Meranti are found at 35.7°, 60° and 72°. Amount of SiC found increases as the holding time prolongs. The unreacted carbon peak on 2 hours holding time of Kapur decreases as the holding time prolongs and the excess Si peak completely disappears at 4 hours holding time. This result was supported by SEM images in Figure 6. Increasing the holding time has improved the SiC thickness. Dark Red Meranti does not show any unreacted C peak, which attributes to higher efficiency in Si infiltration as compared to Kapur.

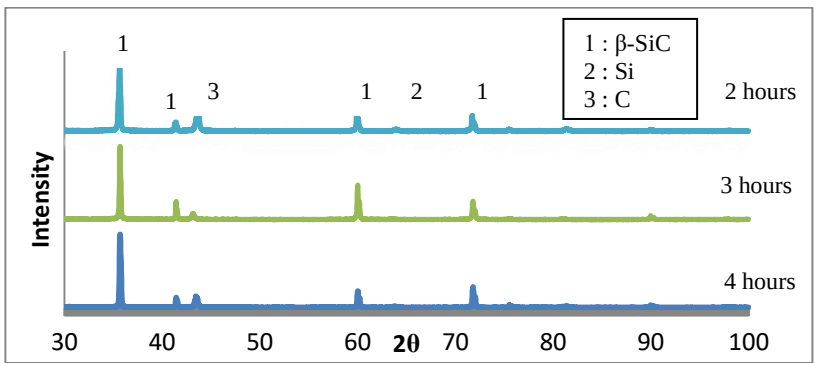

Figure 3: XRD pattern of biomorphic SiC from Kapur at various holding times

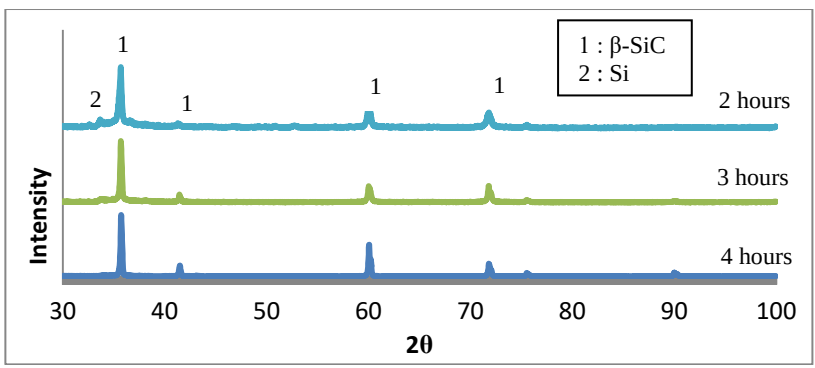

Figure 4: XRD pattern of biomorphic SiC from Dark Red Meranti at various holding times

Density

Carbon template was formed after the process of pyrolysis at 850°C in a controlled atmosphere. During the carbonization process, the woods experienced dehydration and decomposition of hemicellulose, cellulose and lignin. Despite weight loss and shrinkage due to pyrolysis process, the biocarbon template retained their original cylindrical shape. The characteristics of biocarbon and biomorphic SiC were summarized in Table 1. After Si infiltrated into biocarbon, the density of all samples increased. This is because the silicon powders melted and diffused into the biocarbon template which formed SiC. The density increased as the holding time prolonged. However, SiC ceramics were not fully formed as the densities of the samples were much lower than the theoretical value of SiC density, which was 3.2g/cm^3. The similar result was supported by K. Hyie *et al.* who compared the physical properties between SiC from Kapur and Dark Red Meranti wood block [8].

Table 1: Density of biocarbon and biomorphic SiC

	Kapur				**Dark Red Meranti**			
	Bio Carbon	**2hr SiC**	**3hr SiC**	**4hr SiC**	**Bio Carbon**	**2hr SiC**	**3hr SiC**	**4hr SiC**
Density g/cm3	1.06	1.46	1.48	1.58	1.19	2.25	2.30	2.47
Pore Size µm	0.52	-	-	-	1.02	-	-	-

Scanning electron micrograph (SEM)

The morphologies of biocarbon and biomorphic SiC are shown in Figure 5 and 6, respectively. It can be seen that biocarbon template retained original structure and has homogenous microstructure. However, due to compaction process, there were almost no visible pores as the pores were found less than 2 µm. Based on mercury porosimetry, Dark Red Meranti has a slightly bigger pore size which was 1.02 µm as compared to those of Kapur which was only 0.52 µm. Composition of biocarbon template after pyrolysis process was tabulated in Table 2. Dark Red Meranti showed a higher carbon content than Kapur but the differences between them are not too significant.

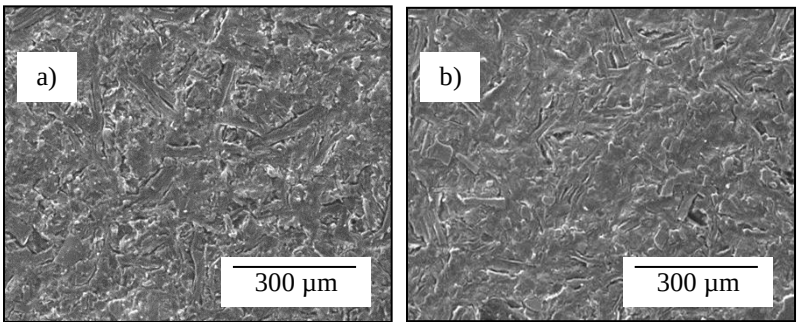

Figure 5: SEM images of surface of biocarbon template of a) Kapur and b) Dark Red Meranti

Table 2: Composition of biocarbon

	Carbon		**Oxygen**	
	Weight %	**Atomic %**	**Weight %**	**Atomic %**
Kapur	91.5	93.7	8.5	6.3
Dark Red Meranti	91.9	93.8	8.1	6.2

After infiltration of melt Si, the biocarbon was converted into SiC. The morphology of the ceramics has similar characteristics to those of biocarbon. Infiltration of silicon leads to a homogenous microstructure with excess Si content especially on the surface of samples. The excess Si was removed by leaching process using a mixture of hydrofluoric acid and nitric acid. The SEM images identified and differentiated the composition element found on the samples. The gray area was SiC, white area was residual Si and black area was unreacted carbon (C). Conversion into SiC occurred when the Si particle melted and infiltrated the pores of the biocarbon. Once the Si particles are in contact with the biocarbon template, spontaneous wetting and reaction process takes place to convert it into SiC [9].

SEM micrographs show the effect of holding time at 1500°C on the microstructure of samples. The samples infiltrated at 2 hours holding time consist of very little amount of SiC content. The formation of SiC occurred only on the surface of the samples; meanwhile non-reacted carbon was found at deeper layers. This is because of the infiltration rate of silicon dwarf due to formation of SiC on the outer layer. The reaction rate between the Si and C occurred much faster than the infiltration rate which led to “chocking-off” phenomenon [10]. Due to formation of primary formed solid SiC layer, liquid Si has to penetrate through it in order for latter reaction to occur.

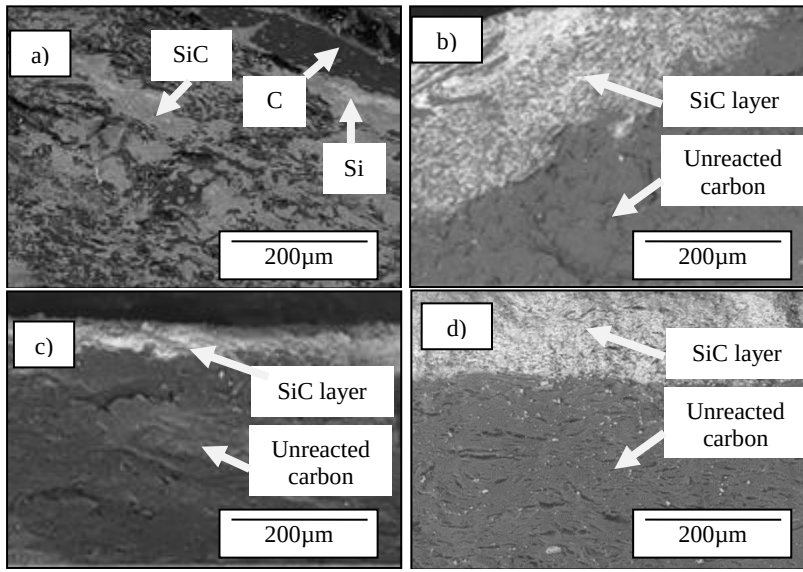

Figure 6: SEM images (cross section) of biomorphic SiC of Kapur after: a) 2 hour (surface), b) 4 hour and Dark Red Meranti after: c) 2 hour, d) 4 hour holding times

The samples prepared for 4 hours holding time in figure 4 (b),(d) show better formation of SiC layer as compared to those of 2 hours holding time. Due to early formation of primary layer of SiC, it is required for the liquid Si to permeate the layer and be in contact with the carbon in the inner part for reaction. However, this conversion cannot occur in a short period of time. As quoted by G. Hou [11], increasing reaction time may develop better conversion of carbon template to SiC. Thus, increasing the holding time of infiltration process encourages the Si particle to infuse and enhance SiC formation.

Furthermore, SiC formation of Dark Red Meranti wood showed better SiC formation than Kapur. This is because the average pore size of biocarbon of Dark Red Meranti is larger as compared to Kapur. The infiltration process is affected by the pore size of the biocarbon. This is because the reaction between the Si melt and carbon solid resulted in reduced pore size. For every formation of a mole SiC, there is approximately 58% volume increament. Therefore, Kapur has more difficulties in the formation of SiC as the pore closes and may chock, which limits further diffusion.

Conclusion

Biomorphic SiC ceramics were prepared by infiltrating liquid Si into biocarbon templates from Kapur and Dark Red Meranti. Biocarbon template and SiC ceramic have homogenous and uniform microstructure due to compaction process. SEM micrograph shows no visible pores and the pore sizes were found less than 2μm by mercury porosimetry analysis. Infiltration of liquid Si into biocarbon template results in early termination of SiC formation due to "chocking" phenomenon. However, varying the holding time improved the performance of the infiltration. By prolonging the holding time, the density of SiC samples increased; hence, it indicated better formation of SiC. It is also found that the thickness of SiC formation was also enhanced. Dark Red Meranti was found to be denser and exhibited better formation of SiC as compared to Kapur.

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