FABRICATION OF SILICON CARBIDE CERAMICS FROM RICE HUSKS

Chalermkwan Makornpan[1,2], Charusporn Mongkolkachit[3], and Thanakorn Wasanapiarnpong[1,2*]

Received: August 22, 2012; Revised: August 13, 2013; Accepted: August 28, 2013

Abstract

Silicon carbide ceramics were prepared by 2 paths; first, carbothermal reduction in powder form preparation before sintering and secondly, carbothermal reduction plus *in situ* reaction bonding. The carbothermal reductions of silicon carbide powders were prepared from rice husks which were carbonized in an incineration furnace. The carbonized rice husks were ground under various conditions. The ground powders were placed in alumina crucibles, closed with graphite lids, and pyrolized at different temperatures and soaking times in argon and nitrogen atmospheres. Pyrolized samples were characterized. The beta silicon carbide phase was present in all samples that were pyrolized in the argon atmosphere. Samples pyrolized in the nitrogen atmosphere consisted of beta-silicon carbide and silicon oxynitride. The main phase in the synthesized sample is beta-silicon carbide in particle form with a small amount number of whiskers. The beta-silicon carbide particles were increased when the soaking time was increased. On the other hand, the silicon carbide whiskers decreased when the soaking time was increased. The sample which was pyrolized in the argon atmosphere at 1600°C was selected to be pressed and sintered at different temperatures and compared with a commercial powder. With an increased sintering temperature, the density of the sintered sample was increased. The density of the sintered sample is closed to samples prepared from the commercial powder when the sintering temperature was increased upto 1850°C. For the carbothermal reduction plus *in situ* reaction bonding, carbonized rice husks were treated with HCl solution, mixed with Si metal powder and pyrolized in argon at various temperatures. The silicon carbide quantity and porosity increased when the pyrolysis temperature was increased due to the reaction and gas phase in the system.

Keywords : Silicon carbide, carbonization, rice husks, carbothermal reduction, pyrolysis, *in situ* reaction bonding

[1] *Research Unit of Advanced Ceramics, Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, 10330,Thailand. Tel.: 0-2218-5541; Fax.: 0-2218-5561; E-mail: thanakorn.w@chula.ac.th*

[2] *Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok, 10330, Thailand.*

[3] *National Metal and Materials Technology Center, KlongLuang, Phathumthani, 10120, Thailand.*

* *Corresponding author*

Introduction

Silicon carbide (SiC) is a ceramic compound of silicon (Si) and carbon (C). SiC has excellent properties such as a high melting point, high hardness, high strength, high creep resistance at high temperature, high oxidation resistance, and thermal and chemical stability; hence this material is used for cutting tools and as a refractory material. Porous SiC is another kind of SiC that is used. Applications of for porous SiC are catalyst supports, molten-metal filters, diesel particulate filters, etc.

Rice husks are the hard protective skin of rice grains. In Thailand, there is a lot of rice cultivation which results in a lot of rice husks which are an agricultural leftover. Rice husks are used in many applications such as bio-fuel, fertilizer, insulation materials, and ceramic fabrication (Prasada *et al*., 2001; Prasetyoko *et al*., 2006; Khemthong *et al*., 2007). The main compositions of rice husks are 15-20% of silica and 75-80% of carbon from its organic structure, lignin, and cellulose (Sun and Gong, 2001). For this reason, rice husks have been used as raw materials for fabricated SiC. Fabrication of SiC using rice husks is of interes many researches. SiC from rice husks was fired and mixed with carbon black and then fired at 1300-1600°C to obtain SiC whiskers (Krishnarao and Subrahmanyam, 1995). Chemicals were used to treat rice husks in order to remove alkali oxide and other oxides except silica. Rice husks were treated with hydrochloric acid (Krishnarao and Godkhindi, 1992), sodium hydroxide (Mizuki *et al*., 1993), and acetic, oxalic, and nitric acids (Chandrasekhar *et al*., 2005); after the chemical treatment process the rice husks were fired to obtain SiC.

In this work, SiC was synthesized by the carbonization of rice husks. Carbonized rice husks (CRH) were divided into 2 portions for 2 difference paths. Firstly, CRH were ball milled in water and dried, and the powder was then pyrolized at different temperatures with different inert gas atmospheres, namely argon and nitrogen. The second CRH portion was ground and treated with hydrochloric acid then filtered, dried, pressed, and pyrolized in an argon atmosphere at various temperatures. The pyrolized samples were characterized for observed properties to compare the effects of milling, washing, and the pyrolization condition on the properties of the synthesized SiC samples.

Materials and Methods

Fabrication of Silicon Carbide Powder and Sintering of Samples

Rice husks were dried at 105°C to remove humidity and carbonized at 300°C to become (CRH). The CRH was 4 samples: the first sample was identified as as-carbonized; the second, identified as dry milled (DM), was milled with a vibration mill; the third, identified as wet milled (WM), was mixed with distilled water, ball milled for 6 h, filtered to leach some soluble alkali oxide compositions in the rice husks, and was then dried in an oven; the fourth, identified as sweet wet milled (SWM), was WM-CRH that was seeded with 5 wt% β-SiC powder (DU B-1, Showa Denko K.K., Tokyo, Japan), washed, and dried. The 4 samples were put in alumina crucibles, which were closed with graphite lids, and were then pyrolyzed in a nitrogen or argon atmosphere by using a controlled atmosphere graphite furnace (Hi-Multi 5000, Fuji Dempa Kogyo Co., Ltd., Osaka, Japan) at 1400, 1500, and 1600°C for 1 h.

The SWM sample pyrolyzed at 1600°C in an argon atmosphere was selected to study the effect of the soaking time by soaking for 1, 2, and 3 h. After the pyrolysis, the SWM sample which was pyrolized at 1600°C for 3 h had the residual carbon burnt out in a box furnace at 700°C for 3 h. The powder was then ball milled in ethanol (99.5%, Mallinckrodt Pharmaceuticals, Dublin, Ireland) as amedium with alumina (Al_2O_3) (AKP-30, Sumitomo Corp., Tokyo, Japan) and magnesia (MgO) (MJ-30, Iwatani Corp., Tokyo, Japan) as sintering aids and polyvinyl butyral (PVB) as

a binder for 5%, 3%, and 1%, respectively. The mixed powder was dried, sieved, pressed, and sintered at 1650, 1750, and 1850°C for 2 h in an argon atmosphere.

Fabrication of Silicon Carbide by *in-situ* Technique

Rice husks were dried at 105°C to remove humidity and then carbonized in an incineration furnace at lower than 700°C. The CRH were divided into 2 samples. The first, identified as CS had do nothing done with the CRH. For the second, identified as ACS, the CRH were ball milled with 0.1 M hydrochloric acid for 24 h then filtered, washed, and dried. Both samples were mixed with silicon metal (Kojundo Chemical Laboratory Co., Ltd., Sekado-shi, Japan) with ethanol as a medium for 24 h. The mixed powders were pressed and pyrolized at 1400, 1500 and 1600°C for 1 h in an argon atmosphere.

After pyrolysis and sintering, the samples were characterized for the weight loss, the phases by X-ray diffractometer (XRD), the microstructure by scanning electron microscope (SEM), and the apparent porosity of the pyrolized samples.

Results and Discussion

Silicon Carbide Powder and Sintering Sample

The composition of CRH is showed in Table 1. After being ball milled with distilled water, potassium oxide (K_2O) and phosphorus oxide (P_2O_5) in the WM sample decreased that which means that the WM powder is purer than the CRH. Therefore, leaching out some metal oxide with distilled water can be used for the prepared raw materials in SiC fabrication.

The major mechanisms (Han and Liu, 1999; Sujirote and Leangsuwan, 2003) in the conversion of SiC from rice husks can be represented by the following Equations:

$$SiO_{2(s)} + C_{(s)} = SiO_{(g)} + CO_{(g)} \quad (1)$$

$$SiO_{(g)} + 2C_{(s)} = SiC_{(g)} + CO_{(g)} \quad (2)$$

Thus, the carbothermal reaction of SiC from rice husks is:

Table 1. Composition of dry milled (DM) and wet milled (WM) carbonized rice husks

Composition	Dry milled (DM) (wt %)	Wet milled (WM) (wt%)
SiO_2	20.17	19.73
Al_2O_3	0.04	0.24
Fe_2O_3	0.12	0.11
CaO	0.22	0.22
MgO	0.07	0.06
Na_2O	0.02	0.02
K_2O	0.61	0.30
TiO_2	0.01	0.01
P_2O_5	0.13	0.03
CuO	0.01	0.01
ZnO	0.01	0.01
MnO	0.05	0.05
LOI	78.54	79.19

$$SiO_{2(s)} + 3C_{(s)} = SiC_{(s)} + 2CO_{(g)} \quad (3)$$

Figure 1 shows the XRD patterns of the pyrolized samples at 1600°C. In a comparison between the samples that were pyrolized in nitrogen and argon atmospheres, the pyrolized samples in nitrogen included some amount of Si_2N_2O. This does agree with the reaction between C and SiO_2 which produced SiO gas (Krishnarao and Subrahmanyam, 1995). SiO reacted with nitrogen gas which filled into process. In the SWM sample, beta-SiC (3C) is the main SiC (6H) phase mixed in the products. On the other hand, there is no Si_2N_2O found in the samples pyrolized in an argon atmosphere. The beta-SiC seeding assists the formation of beta-SiC after pyrolization.

Figure 2 shows the SEM micrographs of pyrolized SWM which were pyrolized in an argon atmosphere at 1400, 1500, and 1600°C for 1 h after the burning out of unreacted carbon. SiC whiskers as the main phase were found with a small amount of SiC particles, whereas the number of SiC particles increased as the main phase at a higher temperature of 1600°C.

SEM micrographs of the pyrolized SWM in an argon atmosphere at 1600°C for 1, 2, and 3 h after the burning out of unreacted carbon are shown in Figure 3. They can show that the SiC whiskers/particles ratio decreased with an increasedthe soaking time

Table 2 shows the density and weight loss of samples after sintering. The density of the sintered samples increased when the sintering temperature increased. Moreover, the weight loss of the sintered samples increased due to the volatilization of the PVB binder.

Silicon Carbide by *in-situ* Technique

As shown in Table 3, the composition of the ACS powder is purer than the CS powder. Some compositions, for example

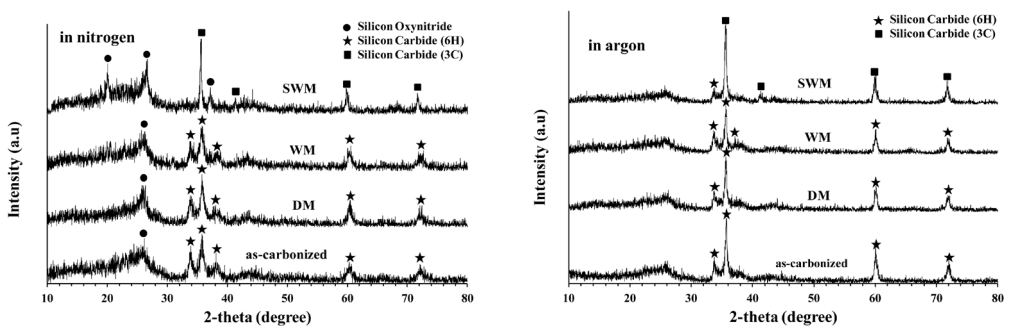

Figure 1. XRD pattern of samples pyrolized at 1600°C for 1 h in nitrogen and argon atmospheres

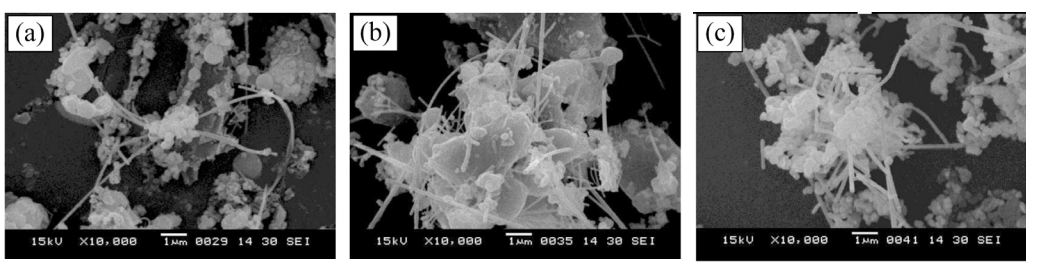

Figure 2. SEM micrographs of pyrolized SWM (a) 1400°C, (b) 1500°C, (c) 1600°C in an argon atmosphere

CaO, K_2O, P_2O_5, and MnO were leached out by more than 70%. Therefore, acid treatment can be used as the purification process to prepared powder for porous SiC sample fabrication.

Silicon metal was added to react with carbon in the powder to form SiC because the pyrolized powder used in a previous method had residual carbon. The reaction bonded between silicon and carbon is (Larpkiattaworn *et al*., 2006):

$$Si_{(s)} + C_{(s)} = SiC_{(s)} \quad (4)$$

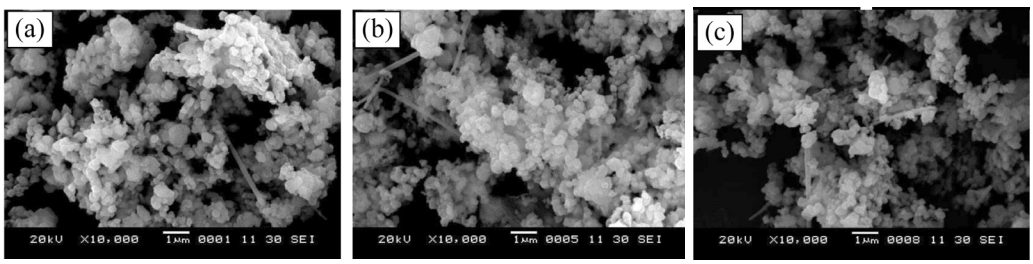

Figure 3. SEM micrographs of pyrolized SWM at 1600°C for (a) 1 h, (b) 2 h, (c) 3 h

Table 2. Density and weight loss of sintered samples

Sintering temperature (°C)	SiC-Commercial Sample		SiC-RH Sample	
	density (g/cm^3)	weight loss (%)	density (g/cm^3)	weight loss(%)
1650	1.80	4.6	1.48	23.8
1750	1.94	7.6	1.81	29.8
1850	2.21	10.0	2.21	36.1

Table 3. Composition of carbonized rice husks and acid treated carbonized rice husks

Composition	Carbonized rice husks (wt %)	Acid treated carbonized rice husks (wt%)
SiO_2	49.65	49.59
Al_2O_3	0.14	0.04
Fe_2O_3	0.13	0.06
CaO	0.63	0.10
MgO	0.12	0.12
K_2O	1.30	0.26
P_2O5	0.62	0.18
ZnO	0.01	0.01
MnO	0.19	0.03
ZrO_2	0.01	0.06
SO_3	0.22	0.12
Cl	0.05	0.01
LOI	46.94	49.43

Therefore, from Equations (3) and (4);

$$SiO_{2(s)} + (3+x)C_{(s)} + (x)Si = (1+x)SiC_{(s)} + 2CO \quad (5)$$

The apparent porosity of the pyrolized samples was showed shown in Figure 4. The porosity of both the CS and ACS samples was increased when the pyrolysis temperature was increased. Gas phases, SiO and CO, were made from the reaction between silica and carbon which is shown in Equation (1). Increasing the temperature is increases the gas phase. Hence, the apparent porosity of the samples as shown in Figure 4. The XRD patterns of the CS and ACS samples are shown in Figure 5. After being pyrolized at various temperatures, a beta-SiC phase was found in every sample. In addition, a cristobalite phase was found in samples which were pyrolized at 1400°C, and 1500°C. The ACS sample contains more cristobalite more than the CS sample, as show in Figure 6, due to the HCl solution leaching out alkali oxide in the CRH. The role of these oxides is as a catalyst for producing cristiobalite in the system. The aspect ratio of SiC whiskers at the sample surface was increased in the CS samples, the same as SiC particles in the ACS samples when the temperature was increased. Figure 7 shows SEM micrographs of the cross section of the samples. The SiC whiskers were decreased in contrast with the SiC particles which increased when the temperature was increased. When comparing the CS sample with the ACS sample, there is more cristobalite in the ACS sample than in the CS sample, which corresponded with the XRD pattern in Figure 5.

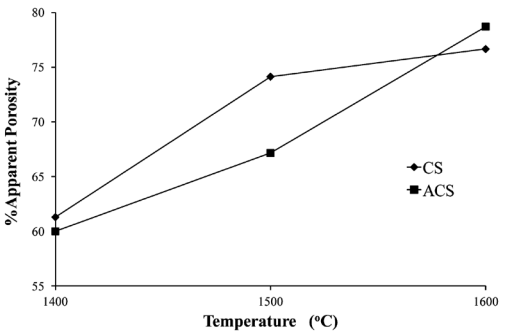

Figure 4. Apparent porosity of CS and ACS sample, after being pyrolized for 1 h by at various temperatures in an argon atmosphere

Conclusions

SiC powders which were prepared from rice husks which were carbonized in air were then pyrolized under various conditions. In the first method, every sample which was pyrolized in an argon atmosphere consisted of SiC; mean while samples which were pyrolized in

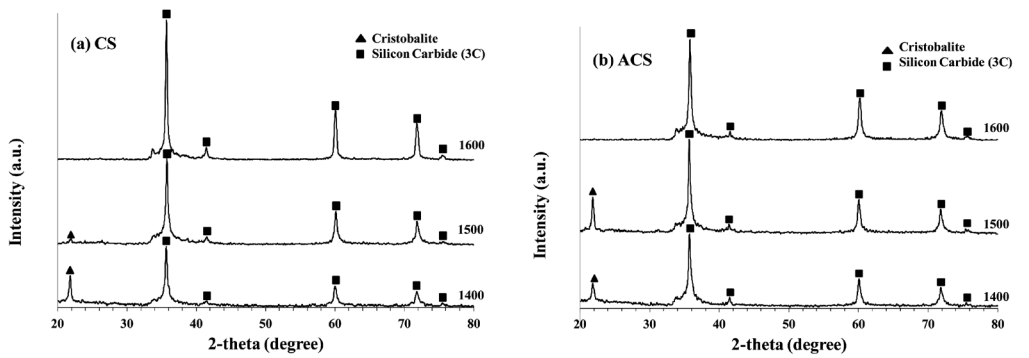

Figure 5. XRD patterns of (a) CS and (b) ACS samples pyrolized in an argon atmosphere at 1400°C, 1500°C, and 1600°C for 1 h

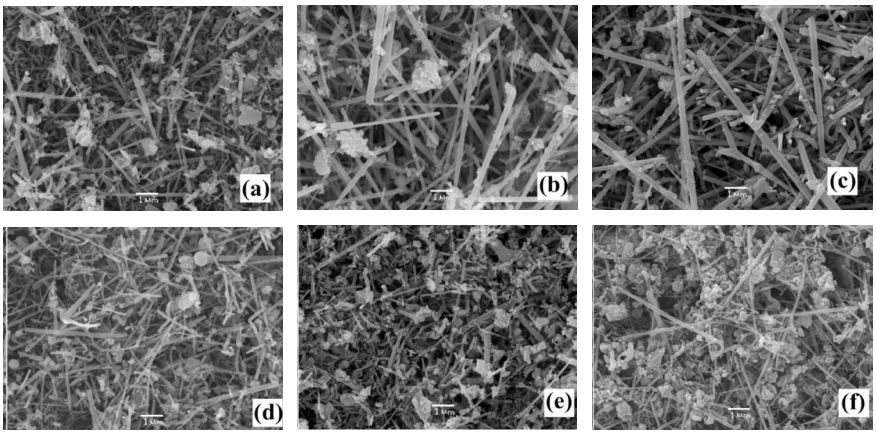

Figure 6. SEM micrographs of the sample surface of CS samples, (a), (b), (c) and ACS samples, (d), (e), (f) after pyrolysis at 1400, 1500, and 1600°C, respectively

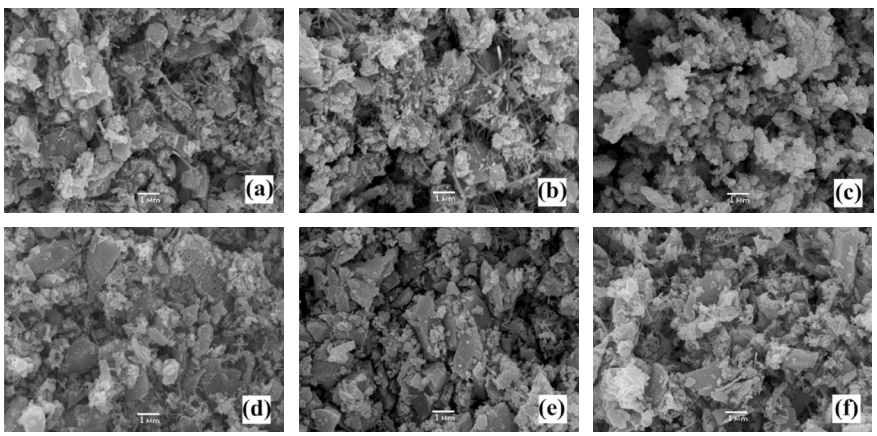

Figure 7. SEM micrographs of cross section of CS samples, (a), (b), (c) and ACS samples, (d), (e), (f) after pyrolysis at 1400, 1500, and 1600°C, respectively

a nitrogen atmosphere were found with silicon oxynitride (Si_2N_2O) together with SiC. The main phase is the SiC particles. When there was an increased soaking time, the amount of SiC particles was increased; mean while the SiC whiskers were decreased. The density of the sintered synthesized powder samples increased to almost the same as the samples prepared from a commercial powder when the temperature was increased up to 1850°C. In the second method, the apparent porosity of the somples samples increased when the temperature was increased. The aspect ratio of the SiC whiskers on the sample's surface increased the same as the SiC particles both in on the sample's surface and body when the pyrolysis temperature was increased.

Acknowledgments

The authors would like to acknowledge Thailand Graduate Institute of Science and Technology, the Research Unit of Advanced Ceramics, Faculty of Science, Chulalongkorn University and the Center of Excellence on Petrochemical and Materials Technology for facilities and financial support.

References

Chandrasekhar, S., Pramada, P.N. and, Praveen, L. (2005). Effect of organic acid treatment on the properties of rice husk silica. J. Mater. Sci., 40:6535-6544.

Han, H.W. and Liu, H.S. (1999). Characterization of vapour deposited products in furnace tube during SiC synthesis from carbonized rice hulls. Ceram. Int., 25:631-637.

Khemthong, P., Prayoonpokarach, S., and Wittayakun, J. (2007). Synthesis and characterization of zeolite LSX from rice husk silica. Suranaree J. Sci. Technol., 12(4):367-379.

Krishnarao, R.V. and Godkhindi, M.M. (1992). Effect of Si_3N_4 additions on the formation of SiC whiskers from rrice husk. Ceram. Int., 18:185-191.

Krishnarao, R.V. and Subrahmanyam, J. (1995). Formation of SiC from rice husk silica-carbon black mixture: Effect of rapid heating. Ceram. Int., 22:489-492.

Larpkiattaworn, S., Ngernchuklin, P., Khongwong, W., Pankurddee, N., and Wada, S. (2006). The influence of reaction parameters on the free Si and C contents in the synthesis of nano-sized SiC. Ceram. Int., 32:899-904.

Mizuki, E., Okumura, S., Saito, H., and Murao, S. (1993). Formation of silicon carbide from rice husks using enzymatic method for carbon control. Bioresource. Technol., 44:47-51.

Prasada, C.S., Maitib, K.N., and Venugopalc, R. (2001). Effect of rice husk ash in whiteware compositions. Ceram. Int., 27:629-635.

Prasetyoko, D., Ramli, Z., Endud, S., Hamdan, H., and Sulikowski, B. (2006). Conversion of rice husk ash to zeolite beta. Waste Manage., 26:1173-1179.

Sujirote, K. and Leangsuwan, P. (2003). Silicon carbide formation from pretreated rice husks. J. Mater. Sci., 38:4739-4744.

Sun, L. and Gong, K. (2001). Silicon-based materials from rice husks and their applications. Ind. Eng. Chem. Res., 40:5861-5877.