The effect of Carbon on Si to SiC ratio in Si-SiC composite from natural sand

Chutima Kaemkit[a,b], Sutham Niyomwas[b,d],* and Tawat Chanadee[c,d]

[a]*Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90110, Thailand*

[b]*Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai, Songkhla 90110 ,Thailand*

[c]*Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90110 ,Thailand*

[d]*Ceramic and Composite Materials Engineering Research Group (CMERG), Center of Excellence in Metal and Material Materials Engineering (CEMME)), Prince of Songkla University, Hat Yai, Songkhla 90110, Thailand*

Silicon-Silicon Carbide (Si-SiC) composite particles were synthesized by self-propagating high temperature synthesis (SHS) from a powder mixture of natural sand with activated carbon and magnesium (SiO_2-C-Mg). The Si-SiC ratio in Si-SiC composites was manipulated via the carbon mole ratio in the precursor mixture were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that the carbon molar ratio in the precursor mixture significantly affects the Si to SiC ratio in Si-SiC composite. The intensity of SiC were increased with an increase carbon mole ratio; the intensity of Si were gradually decreased and disappeared with a sufficient carbon amount consuming all of it. The synthesized product powders were leached in three steps with HCl: CH_3COOH (1:1 v/v), 2M HCl and HF: H_2O (1:1 v/v) solutions, respectively. The morphology showed SiC whisker. SiC whiskers have been one of the more popular reinforcing materials for both metal matrix composites and ceramic matrix composites, which can make these Si-SiC composites suitable for use as reinforcing fillers.

Keywords: Self-propagating high temperature synthesis, Combustion synthesis, Silicon-silicon carbide composite, Natural sand.

Introduction

Silicon carbide is non-oxide ceramic materials. It has been used widely in industrial applications because it generally exhibits excellent properties, especially in hardness, strength, chemical and thermal stability, melting point, oxidation resistance and erosion resistance, etc. These properties make SiC a perfect candidate for high-power and elevated temperature electronic devices as well as for abrasion and cutting applications [1, 2]. Many methods could be used to produce SiC powders, such as carbothermal reduction [5], sol–gel [6, 7], thermal plasma [8], microwave [9] and self-propagating high temperature synthesis (SHS) [2-4, 10-14]. The self-propagating high temperature synthesis is also known as combustion synthesis, which produces in-situ composites from initial reactive substances through an exothermic chemical reaction [15]. SHS is based on systems that react exothermally when ignited to sustain a combustion wave [16]. The combustion reaction is initiated in a point, and propagates rapidly through the reaction mixture. SHS have a specific features such as energy conservation, short reaction times, simple equipment and high-purity product [17]. Compared with conventional ceramic processing, SHS is distinctive because of its very high temperatures that can volatilize low boiling point impurities and, therefore, result in higher product purity., The simple exothermic nature of the SHS reaction avoids the need for expensive processing facilities and equipments, while the short exothermic reaction times result in low operating and processing costs [18]. SHS is a feasible technique for manufacturing advanced ceramics, catalysts, and nano-materials [15,19]. SHS reactions may be characterized by an adiabatic combustion temperature (T_{ad}), as ideally the enthalpy of reaction is heating the products, and there is no energy lost to the surroundings [20].

In this study, Si-SiC composite particles were synthesized by SHS from powder mixture of SiO_2-C-Mg by using natural sand as a silica source. Natural sand is abundant, low cost, and contains more than 80 % of SiO_2. Therefore, natural sand is suitable for use as a source of SiO_2 in the synthesis of Si-SiC composites. Furthermore, natural sand contains more than 7% of aluminum oxide (Al_2O_3), which can react with Mg to form magnesium aluminate ($MgAl_2O_4$). $MgAl_2O_4$ is one of the most common compounds in the family of

*Corresponding author:
 Tel : +66-74-287-196
 Fax: +66-74-558-834
 E-mail: sutham.n@psu.ac.th

oxide spinels with a cubic structure. It is an important refractory material because of its excellent properties such as high melting point, low thermal expansion and good slag resistance. $MgAl_2O_4$ and SiC composites can achieve overall good properties [21]. Our previous work, Niyomwas (2008), reported the possibility to synthesize SiC and Si-SiC composites depending on carbon molar ratio in the precursor SiO_2-C-Mg system. As the molar ratio of carbon and SiO_2: Mg increased from 2:1:2 to 3:1:2, the SHS reaction product turned into SiC-MgO composite while no Si-SiC composite was formed [22]. Thus, the effects of carbon molar ratio on synthesized products, along with the ratio of Si to SiC in the products were investigated further in this current study.

Experimental

Materials

The raw materials used in this study were commercial powders of activated carbon (Ajax–Finechem, 99%), magnesium (Riedel–deHaen, 99%) and natural sand (Haad Kaew, Singhanakorn, Songkhla, Thailand) as a source of SiO_2. The compositions of natural sand used in this work was analyzed by X-Ray fluorescence (XRF: Zetium,PANalytical, Netherlands) are given in Table 1 (84.5 wt% of SiO_2). These powders were taken in a stoichiometric molar ratio ($2SiO_2$-nC-4Mg) dictated by reaction equation (1) and then C was added in amounts corresponding to n = 1, 1.3, 1.5, and 1.7.

$$2SiO_2(s) + nC(s) + 4Mg(s) = Si(s) + SiC(s) + 4MgO(s) + (n-1)C \quad (1)$$
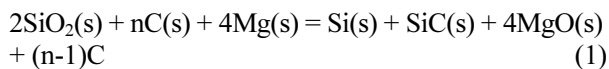
Experimental procedure

The weighed amounts of the reaction powders taken in stoichiometric ratios were dry-mixed in a ball mill at speed 250 rpm for 3 hours. Then the dry-mixed powder was compressed uniaxially to obtain cylindrical disks 35 mm in diameter and 15 mm thick with a relative density of 50–60%. The green sample was placed into the SHS reactor. The reaction chamber was evacuated and filled with argon at 0.5 MPa pressure. The SHS reaction was initiated by igniting with tungsten filament located above the green sample surface. As-prepared SHS products were leached to obtain final product of Si-SiC composite.

In the leaching step, As-prepared SHS products were leached to remove the unwanted phases such as MgO, Mg_2SiO_4 and SiO_2 by using HCl acid, CH_3COOH acid and HF acid solution. The first step was leaching with HCl–CH_3COOH solution (1:1 v/v) at 75 ºC for 30 min. and then the second step was leaching with 2 M HCl solution at 75 ºC for 30 min and the last step was leaching with HF–H_2O solution (1:1 v/v) at 95 ºC for 30 min. The process included moderate intensity stirring. The ratio of the as-synthesized SHS products

Table 1. Composition of natural sand from XRF analysis

Compound	wt%
SiO_2	84.522
Al_2O_3	7.538
TiO_2	0.218
Fe_2O_3	1.481
Cr_2O_3	0.154
Trace elements	Bal.

to the leaching agent was 1 g/60 ml throughout the experiment. The leached powders were collected by filtering, an washed with distilled water until the wash water pH was in the neutral range, and dried at 90 ºC [14].
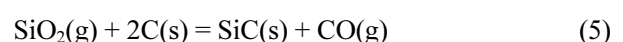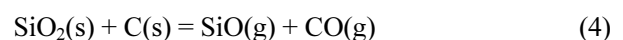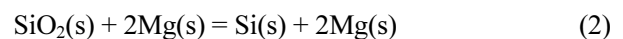
Characterization

The chemical composition of natural sand was identified by semi-quantitative analysis of X-ray fluorescence energy dispersive spectrometer (XRF, Zetium,PANalytical, Netherlands) as shown in Table 1. The phases and crystalline structures of synthesis products were identified by powder X-ray diffraction (XRD, Empyrean, PANalytical, Netherlands). Spectra were recorded at 30 mA and 40 kV, using Cu-Kα radiation (λ = 1.54 Å). The scan rate (2θ) was 3°/min with a step size (2θ) of 0.026º. Morphologies were observed by scanning electron microscope (SEM, Quanta 400, FEI, USA).
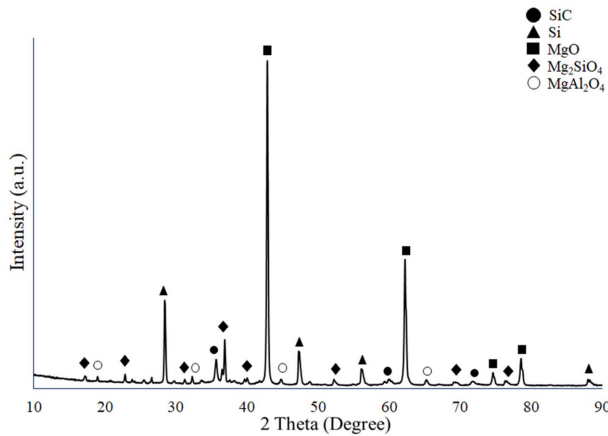
Results and Discussion

The study of the synthesis of Si-SiC by SHS method-using SiO_2-C-Mg in 2: n: 4 (n = 1) molar ratios, as in equation 1 by XRD analysis has been shown in Fig. 1. The XRD pattern shows that it consisted of Si, SiC, MgO, Mg_2SiO_4 and $MgAl_2O_4$ as reference in JCPDS No.01-079-0613, No.01-075-0254, No.01-087-0653, No.01-077-9267 and No.01-071-3851 respectively.
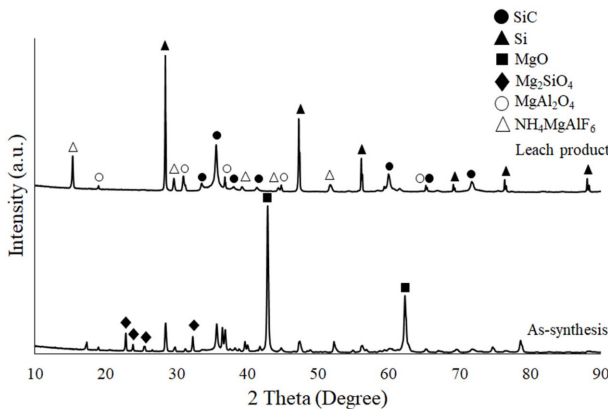
Fig. 2 shows XRD patterns of the as synthesized product from SHS reaction and the leached product. It shows the presence of Si, SiC, MgO, Mg_2SiO_4 and $MgAl_2O_4$. After leaching with HCl, CH_3COOH and HF, only Si, SiC and $MgAl_2O_4$ remain. The $MgAl_2O_4$ is a stable phase that can-not be leached off with an acid. While, MgO and Mg_2SiO_4 as unwanted products were leach completely by acid.

During the process of SHS, the SiO_2-C-Mg mixture may have formed various compounds via the following candidate intermediate chemical reactions can be shown as equation (2-6)
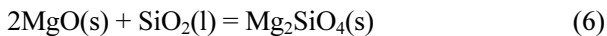
$$SiO_2(s) + 2Mg(s) = Si(s) + 2Mg(s) \quad (2)$$

$$Si(l) + C(s) = SiC(s) \quad (3)$$

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \quad (4)$$

$$SiO_2(g) + 2C(s) = SiC(s) + CO(g) \quad (5)$$

Fig. 1. XRD patterns of as-synthesized product powder from natural sand (2SiO$_2$-C-4Mg).

Fig. 2. XRD patterns of as-synthesized product and leached product (2SiO$_2$-C-4Mg).

$$2MgO(s) + SiO_2(l) = Mg_2SiO_4(s) \qquad (6)$$

From equation (4) and (5) would generate carbon monoxide (CO(g)). Then loss of CO(g) could deplete carbon from the reaction mixture and less SiC would then be formed. Therefore, the produced gas was analyzed to investigate the forming of CO(g) by Gas Chromatography-Mass Spectrometry (GC-MS) with results shown in Table 2. The results show that CO$_2$(g) and CO(g) were formed. In order to find the optimum carbon molar ratio in synthesis of SiC, varying the carbon molar ratio to SiO$_2$ and Mg were investigated experimentally.

The adiabatic temperature (T$_{ad}$) of the SHS process can be calculated from the enthalpy of the reaction. Total enthalpy of reaction can be used to calculate T$_{ad}$ from equation (7).

Table 3. Adiabatic temperature of reactions

Reaction System	Adiabatic Temperature (ºC)
1) 2SiO$_2$ + C + 4Mg	2179.9
2) 2SiO$_2$ + 1.1C + 4Mg	2155.7
3) 2SiO$_2$ + 1.3C + 4Mg	2126.0
4) 2SiO$_2$ + 1.5C + 4Mg	2100.8
5) 2SiO$_2$ + 1.7C + 4Mg	2069.0

$$\Delta H = \int_{298}^{T_M} C_{p,solid} \, dT + \Delta H_f + \int_{T_M}^{T_{ad}} C_{p,liquid} dT \qquad (7)$$

where, ΔH is the enthalpy of the reaction, ΔH_f is the enthalpy of transformation, C_p is the specific heat capacity, T_m is the melting temperature, and T_{ad} is the adiabatic temperature. Self-sustained combustion requires that the T_{ad} of reaction is higher than 1800 ºC. Table 3 shows T_{ad} in our experimental cases exceeds 1800 ºC.

The effects of carbon mole ratio in the fabrication of silicon carbide from SiO$_2$-C-Mg system by SHS were investigated. The results showed that carbon mole ratio in the precursor mixture of the reactant powders significantly affects on the Si to SiC ratio in Si-SiC composite. The intensity of SiC were increased with an increase carbon molar ratio. On the other hand, intensity of Si were gradually decreased and disappeared at 1.7 moles of carbon. Si content in the product was observed when there was amount of carbon less than 1.7 moles. The lost of carbon as CO and CO$_2$ gases was confirmed by the GC-MS results. As the ratio of carbon to SiO$_2$: Mg increased, remaining unreacted Si decreased and more SiC was formed. This can be explained by the lost content of carbon to form CO and CO$_2$ gases. As the molar ratio of carbon to SiO$_2$: Mg increased, the unreacted Si disappeared and the SHS reaction was completed and formed the SiC-MgO composites. (see Fig. 3)

Fig. 4 shows typical SEM micrographs of the products from the SHS reaction before and after leaching, which have a precursor molar ratio of SiO$_2$:C:Mg = 2:1:4 and 2:1.3:4. The morphology of the products before leaching shows SiC whiskers. SiC whiskers have been one of the more popular as reinforcing materials in both metal matrix composites (MMC) and ceramic matrix composites (CMC). There are many reports on the synthesis of silicon carbide whiskers. The methods fall into the following three standard categories: (1) thermal decomposition (2) reaction between some halides in the presence of hydrogen and (3) carbothermal reduction [23]. In this research, SiC whiskers were synthesized by SHS process, which has in-situ process for producing

Table 2. Composition of gases from synthesis process

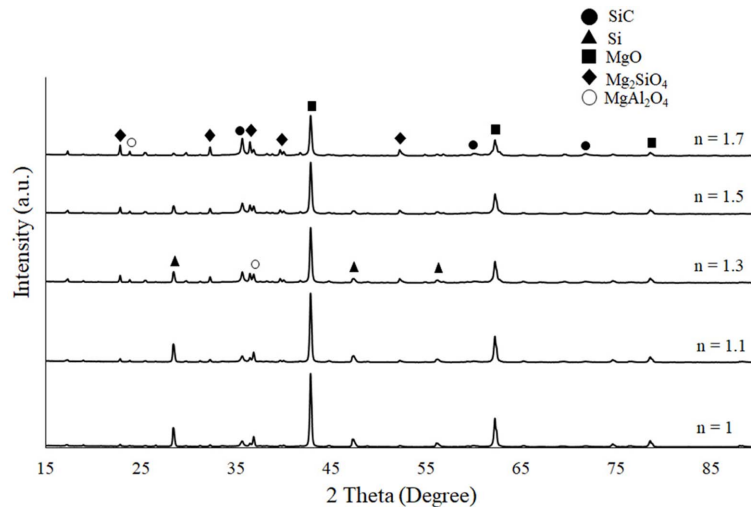| Properties	Test Method	Unit	Result
Carbon Monoxide	ASTM D 2504	ppm vol.	17
Carbon Dioxide	ASTM D 2505	ppm vol.	53

Fig. 3. XRD patterns of As-synthesized product powder from natural sand with different carbon molar ratio ($2SiO_2$-nC-4Mg).

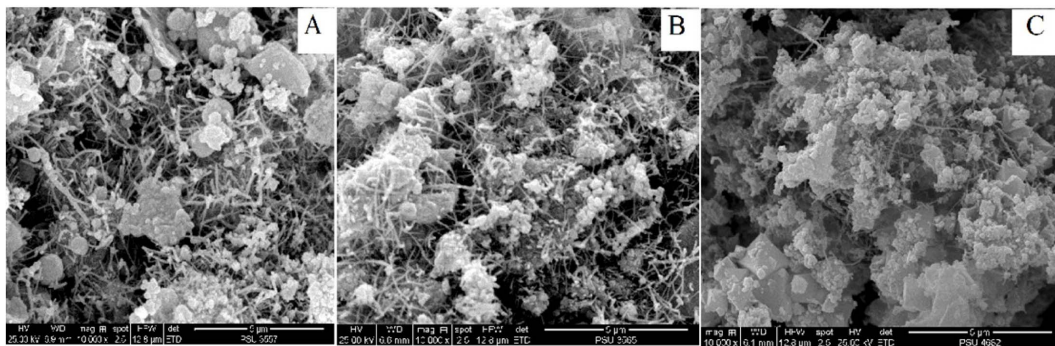**Fig. 4.** SEM image of the products from (A) $2SiO_2$-C-4Mg (B) $2SiO_2$-1.3C-4Mg (before leaching) and (C) $2SiO_2$-C-4Mg (after leaching).

Si-SiC composites.

Conclusion

Si-SiC composites were produced by leaching out MgO and Mg_2SiO_4 from SHS products that were synthesized from natural sand with activated carbon and magnesium. The carbon mole ratio of the precursor mixture of reactant powders significantly affected the intensity of Si and SiC in the product. The morphology showed SiC whiskers, which can make these Si-SiC composites suitable for use as reinforcing fillers. The presence of Al_2O_3 in natural sand, however, $MgAl_2O_4$ formation to the SHS product. The $MgAl_2O_4$ can to contribute $MgAl_2O_4$/SiC composites, which may have improved the mechanical properties and can be the subject of further studies.

Acknowledgements

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