

Synthesis and Characterization of Silicon-Silicon Carbide Composites from Rice Husk Ash via Self-Propagating High Temperature Synthesis

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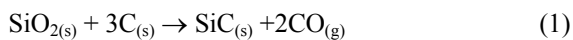
Abstract

Silicon-Silicon Carbide (Si-SiC) composites were synthesized by self-propagating high temperature synthesis (SHS) from a powder mixture of rice husk ash (RHA)-C-Mg. The reaction was carried out in a SHS reactor under static argon gas at a pressure of 0.5 MPa. The standard Gibbs energy minimization method was used to calculate the equilibrium composition of the reacting species. The comparison of silica from RHA and commercial sources in the precursor mixture on the Si-SiC conversion has investigated using X-ray diffraction and scanning electron microscope technique. The as-synthesized products of Si-SiC-MgO powders were leached with 0.1M HCl acid solution to obtain the Si-SiC composite powders.

Key words: Rice husk ash, Silicon-silicon carbide composite, Self-propagating high temperature synthesis

Introduction

Silicon carbide is one of the most important non-oxide ceramic materials which are produced on a large scale in the form of powders, molded shapes and thin film.^(1, 11) It has wide industrial application due to its excellent mechanical properties, high thermal and electrical conductivity, excellent chemical oxidation resistance, and it has potential application as a functional ceramic or a high temperature semiconductor. The main synthesis method of SiC is a carbothermal reduction known as the Acheson process. The general reaction Pierson (1996) is:



A conventional carbothermal reduction method for the synthesis of pure SiC powders involves many steps and is an energy-intensive process. Several alternate methods such as sol-gel Meng, *et al.* (2009), thermal plasma Tong and Reddy (2006), carbothermal reduction Gao, *et al.* (2001), microwave Satapathy, *et al.* (2005) and SHS Morançais, *et al.* (2003), Gadzira, *et al.* (1998), Feng, *et al.* (1994) and Niyomwas (2008) have been reported in the literature for the synthesis of SiC powders. Sol-gel process requires expensive precursor solutions and complicated process while the thermal plasma synthesis, laser synthesis and

microwave synthesis have very high operating costs with expensive equipments; on the other hand SHS is considered as less expensive to produce SiC powders.

SHS process can be used to prepare a fine powder of high temperature materials at 1800 to 4000°C, using their high exothermic heats of reaction. It is well known that the SHS process is a very energy-efficient method because a high-temperature furnace is not required and the process is relatively simple. Many researchers reported of using elemental silicon and carbon to synthesize SiC via SHS.^(9, 4, 2) However, this reaction is not strong enough and without constant maintenance of temperature at a certain level, SHS for SiC does not take place. Our previous work Niyomwas (2008) has reported the possibility to synthesize SiC and Si-SiC composite from varying carbon in the precursor mixture of SiO₂-C-Mg system with no required preheating system.

In this study, Si-SiC composite particles were synthesized by SHS from powder mixture of SiO₂-Mg-C by using rice husk ash as a silica source. A thermodynamics model for SHS reaction was developed. The experimental results of the synthesis of Si-SiC composite particles were compared with the model calculation. An excellent agreement between model results and experimental data from this study was obtained.

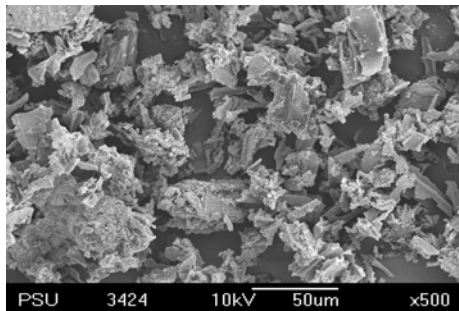
Materials and Experimental Procedures

Experimental

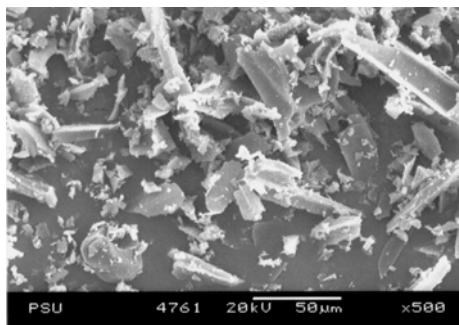
The raw materials used in this study were Mg (Riedel-deHaen, 99.0%), activated carbon (Ajax Finechem, 99.0%), and rice husk ash powder as a source of SiO₂, the composition of which is listed in Table 1 and shown in Figure 1.

Table 1. Composition of RHA from XRF analysis

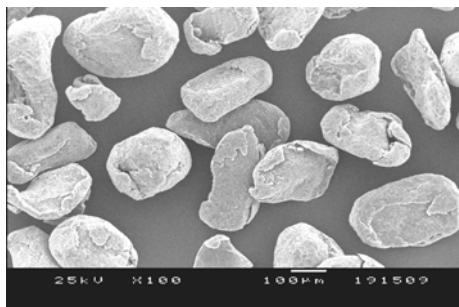
Compound	wt%
SiO ₂	89.96
K ₂ O	7.68
CaO	1.64
P ₂ O ₅	0.7



(a)



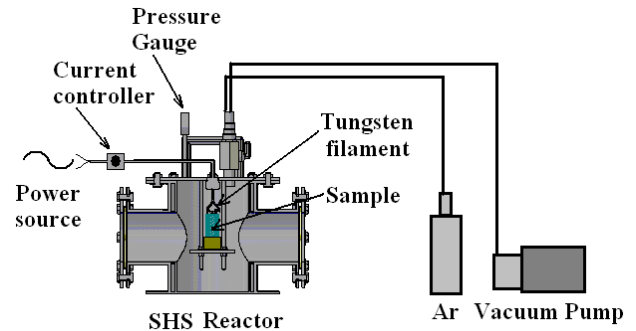
(b)



(c)

Figure 1. SEM image of (a) RHA, (b) activated carbon, (c) Mg

The experimental setup used in this work is schematically represented in Figure 2. It consisted of a SHS reactor with controlled atmospheric reaction chamber and tungsten filament connected to power source through current controller which provides the energy required for the ignition of the reaction.



(a)



(b)

Figure 2. (a) Schematic of the experimental setup, (b) SHS reactor

Reactant powders were weighted as stoichiometric ratio and milled in a planetary ball-mill with the speed of 250 rpm for 30 minutes. The obtained mixture was uniaxially pressed to form cylindrical pellets (25.4 mm diameter and about 25 mm high) with green density in the range of 50-60% of the theoretical value. The green sample was then loaded into reaction chamber of the SHS reactor. The reaction chamber was evacuated and filled with argon. This operation was repeated at least twice in order to ensure an inert environment during reaction revolution. The combustion front was generated at one sample end by using a heated tungsten filament. Under self-propagating conditions, the reaction front then travels until it reaches the opposite end of the sample.

The obtained products were characterized in terms of chemical composition and microstructure by XRD (PHILIPS with Cu K α radiation) and SEM (JEOL, JSM-5800 LV) analyses.

Thermodynamic Analysis

Calculations for equilibrium concentration of stable species produced by SHS reaction were performed based on the Gibbs energy minimization method.⁽⁶⁾ The evolution of species was calculated for a reducing atmosphere and as a function of temperature in the temperature range of 0-3000°C. Calculations assume that the evolved gases are ideal and form an ideal gas mixture, and condensed phases are pure. The total Gibbs energy of the system can be expressed by the following equation:

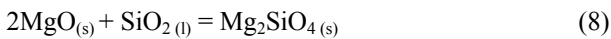
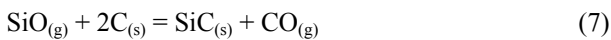
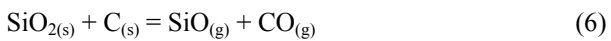
$$G = \sum_{gas} n_i (g_i^o + RT \ln P_i) + \sum_{condensed} n_i g_i^o + \sum_{solution} n_i (g_i^o + RT \ln x_i + RT \ln \gamma_i) \quad (2)$$

where G is the total Gibbs energy of the system; g_i^o is the standard molar Gibbs energy of species i at P and T ; n_i is the molar number of species i ; P_i is the partial pressure of species i ; x_i is the mole fraction of species i ; and γ_i is the activity coefficient of species i . The exercise is to calculate n_i in a way G is a minimized subject to mass balance constraints.

The equilibrium composition of the C-SiO₂-Mg system at different temperatures was calculated using Gibbs energy minimization method and the result is shown in Figure 3. The overall chemical reactions can be expressed as:



During the process of SHS, the mixture of SiO₂, Mg and C may have interacted to form some possible compounds as the following intermediate chemical reactions.



The adiabatic temperature of the SHS process can be calculated from the enthalpy of reaction.⁽⁸⁾ This is the maximum theoretical

temperature that the reactants reach, and determined from Equation (9). This equation applies to a phase change occurring between initial temperature and T_{ad} . The calculated result of overall reaction from Equation (3) is 2162.7 °C.

$$\Delta H = \int_{298}^{T_m} C_{p,solid} dT + \Delta H_f + \int_{T_m}^{T_{ad}} C_{p,liquid} dT \quad (9)$$

where, ΔH is the enthalpy of reaction, ΔH_f is the enthalpy of transformation, C_p is specific heat capacity, T_m is the melting temperature and T_{ad} is adiabatic temperature.

It has been accepted that the reaction can be a self-sustained combustion when the adiabatic temperature of the reaction is higher than 1800°C.⁽⁸⁾ The calculated adiabatic temperature of the reaction is 2162.7 °C, thus using SHS is feasible for this system.

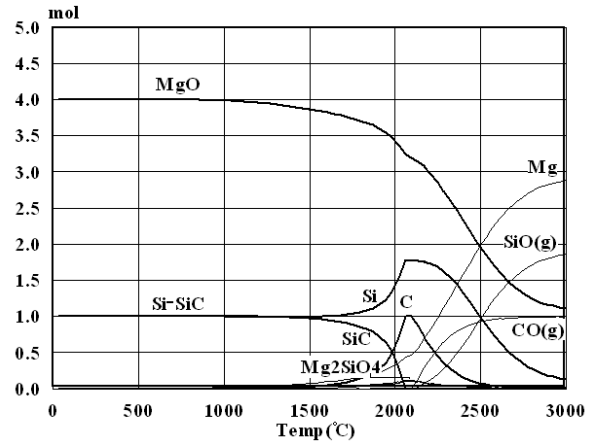


Figure 3. Equilibrium composition of SiO₂-Mg-C systems in Ar gas atmosphere

It can be seen from Figure 3 that it is thermodynamically feasible to synthesize Si-SiC-MgO by igniting the reactant of reaction (3). Due to a highly exothermic reaction at room temperature ($\Delta H = -655.15$ kJ) and thermodynamic instability at room temperature, the reactant phases of SiO₂, C and Mg were not shown in the calculated stable phases in Figure 3. After ignition the reaction (4) took place and has followed by reaction (5) to form Si-SiC-MgO phases. At temperatures higher than 1500°C, the system was unstable and formed an intermediate phase of Mg₂SiO₄ and gas phases. When the reaction front moved further away the products cooled down and rearranged phases in such a way that was shown in Figure 3.

Results and Discussion

Figure 4 shows XRD patterns of as synthesized product from SHS reaction and the leached product. It shows the presence of Si, SiC, MgO and Mg₂SiO₄, and no Mg peak appeared for the as-synthesized product. After leaching with dilute HCl, only Si-SiC phases were found. The resulting SiC were in both α -SiC phase and β -SiC phase. The peak at $2\theta = 33.82^\circ$ in XRD patterns of leached product was detected near the peak of cubic structure (β -SiC phase) of silicon carbide at $2\theta = 35.64^\circ$ which is characteristic of hexagonal polytypes (α -SiC phase).⁽³⁾

Figure 5 (a) and (b) shows SEM image of as-synthesized product from SHS reaction and the product after leaching process, respectively. The morphology of products reveals an agglomerated particle of Si-SiC as identified by XRD patterns in Figure 4. It is believed that the agglomeration of fine SiC particles occurred because the Si-SiC-MgO composite powder was synthesized by melting of the reactants followed by recrystallization. The reactants are in the solid state at the early stage of the reaction. As the reaction temperature increases to 650°C, the Mg particles start to melt. At temperatures higher than 650°C, the carbon and SiO₂ particles are surrounded by the Mg melt, and the SiO₂ particles are reduced by the Mg melt. It is assumed that when the theoretical adiabatic temperature of 2162.7°C is reached, the Si is completely melted; hence, the diffusion of the carbon, Si, and oxygen is rapid, and it is believed that the SiC and MgO particles are synthesized simultaneously from the thermodynamic calculation resulted (Figure 3). The existence of Mg₂SiO₄ in the product may be due to incomplete reaction from the rapid nature of SHS reaction.

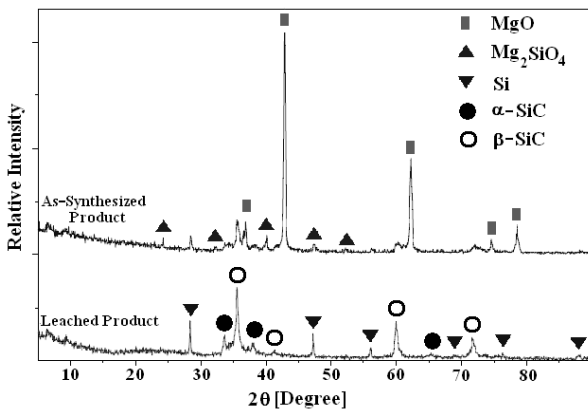


Figure 4. XRD patterns of as-synthesized product and leached product

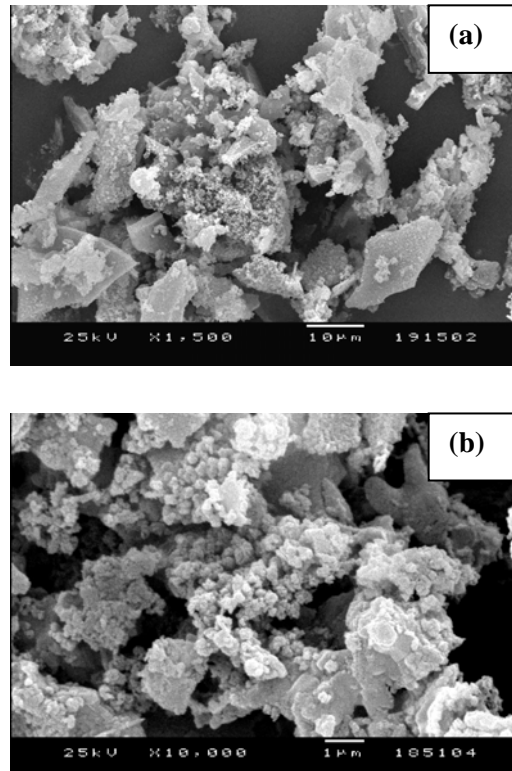


Figure 5. SEM image of (a) as-synthesized product and (b) leached product

Conclusions

The Si-SiC composite powders were produced from leaching out MgO and Mg₂SiO₄ from reaction products that were synthesized *in-situ* via self-propagating high temperature synthesis reaction from precursors of RHA-Mg-C. The resulting SiC were in both α -SiC phase and β -SiC phase. The final product after leaching process shows only Si-SiC phase left in the system.

Acknowledgements

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References

1. Boulos, M.I., Fauchais, P. and Pfender, E. 1994. *Thermal plasmas fundamentals and applications* Vol. 1. New York : Plenum Press: 37.

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2. Feng, A. and Munir, Z.A. 1994. Field-assisted self-propagating synthesis of β -SiC. *J. Appl. Phys.* **76**: 1927-1928.
3. Frevel, L.K., Peterson, D.R. and Saha, C.K. 1992. Polytype distribution in silicon carbide. *J. Mater. Sci.* **27(7)**: 1913-1925.
4. Gadzira, M., Gnesin, G., Mykhaylyk, O. and Andreyev, O. 1998. Synthesis and structural peculiarities of nonstoichiometric β -SiC. *Diamond Relat. Mater.* **7**: 1466-1470.
5. Gao, Y.H., Bando, Y., Kurashima, K. and Sato, T. 2001. The microstructural analysis of SiC nanorods synthesized through carbothermal reduction. *Scripta Mater.* **44**: 1941-1944.
6. Gokcen, N.A. and Reddy, R.G. 1996. *Thermodynamics*. New York : Plenum Press: 291.
7. Meng, G.W., Cui, Z., Zhang, L.D. and Phillipp, F. 2000. Growth and characterization of nanostructured β -SiC via carbothermal reduction of SiO₂ xerogels containing carbon nanoparticles. *J. Cryst. Growth* **209(4)** : 801-806.
8. Moore, J. and Feng, H. 1995. Combustion synthesis of advanced materials: Part I reaction parameters. *Prog. Mater. Sci.* **39**: 243-273.
9. Morançais, A., Louvet, F., Smith, D.S. and Bonnet, J.P. 2003. High porosity SiC ceramics prepared via a process involving an SHS stage. *J. Eur. Ceram. Soc.* **23**: 1949-1956.
10. Niyomwas, S. 2008. The effect of carbon mole ratio on the fabrication of silicon carbide from SiO₂-C-Mg system via self-propagating high temperature synthesis. *Songklanakarin J. Sci. Technol.* **30(2)**: 227-231.
11. Pierson, H.O. 1996. Handbook of refractory carbides and nitrides. Noyes : William Andrew: 137.
12. Satapathy, L.N., Ramesh, P.D., Agrawal, D. and Roy, R. 2005. Microwave synthesis of phase-pure, fine silicon carbide powder. *Mater. Res. Bull.* **40**: 871-1882.
13. Tong, L. and Reddy, R.G. 2006. Thermal plasma synthesis of SiC nano-powders/nano-fibers. *Mater. Res. Bull.* **41(12)**: 2303-2310.