Songklanakarin J. Sci. Technol.
30 (2), 227-231, Mar. - Apr. 2008

Songklanakarin Journal
of Science and Technology

http://www.sjst.psu.ac.th

Original Article

The effect of carbon mole ratio on the fabrication of silicon carbide from SiO_2-C-Mg system via self-propagating high temperature synthesis

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Received 28 September 2007; Accepted 8 May 2008

Abstract

Silicon Carbide (SiC) particles were synthesized by self-propagating high temperature synthesis (SHS) from a powder mixture of SiO2-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 effects of carbon mole ratio on the precursor mixture (C/SiO2/Mg: 1/1/2 to 3/1/2) and on the SiC conversion were investigated using X-ray diffraction and scanning electron microscope technique. The as-synthesized products of SiC-MgO powders were leached with 0.1M HCl acid solution to obtain the SiC particles.

Keywords: silicon carbide, self-propagating high temperature synthesis, standard Gibbs energy minimization method

1. Introduction

Silicon carbide (SiC) is one of the most important non-oxide ceramic materials, produced on a large scale in form of powders, molded shapes, and thin film (Boulos *et al.*, 1994; Pierson, 1996). It has wide industrial applications due to its excellent mechanical properties, high thermal and electrical conductivity, and excellent chemical oxidation resistance and it has a 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:

$$SiO_{2(s)} + 3C_{(s)} \rightarrow SiC_{(s)} + 2CO_{(g)} \qquad (1)$$

A conventional carbothermal reduction method for the synthesis of pure SiC powders involves numerous steps and it is an energy intensive process. Several alternative methods have been reported in the literature for the synthesis of SiC powders, such as sol-gel (Meng *et al.*, 2000), thermal plasma (Tong and Reddy, in press), carbothermal reduction (Gao *et al.*, 2001), microwave (Satapathy *et al.*, 2005), and self-propagating high temperature synthesis, or SHS (Feng and Munir, 1994; Gadzira *et al.*, 1998; Morancais *et al.*, 2003). The sol-gel process requires expensive precursor's solutions and is overall a complicated process, while the thermal plasma synthesis, laser synthesis, and microwave synthesis have very high operating cost with expensive equipments. On the other side, SHS is considered a less expensive method to produce SiC powders.

The SHS process can be used to prepare a fine powder of high temperature materials at 1800 to 4000°C, using the high exothermic heats from the reaction. It is well known, that the SHS process is a very energy-efficient method, because it does not require a high-temperature furnace and the process itself is relatively simple. Many researchers reported the synthesis of SiC by SHS using silicon and carbon (Feng and Munir, 1994; Gadzira *et al.*, 1998; Morancais *et al.*, 2003). However, this reaction itself is not strong enough so that without a constant maintenance of the temperature at a certain level the self-propagating high temperature synthesis of SiC does not take place.

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In this study, SiC particles were synthesized by SHS from a powder mixture of SiO_2-Mg-C without preheating the precursors. Further, a thermodynamics model for the SHS reaction was developed. The experimental results of the synthesis of SiC particles were compared with the model calculation. The effects of carbon mole ratio to the precursor mixture ($C/SiO_2/Mg$: 1/1/2 to 3/1/2) to the synthesized products were investigated. An excellent agreement was obtained between the model results and experimental data from this study.

2. Experimental

The raw materials used in this study were Mg, activated carbon (C), and SiO_2 powders, whose properties are listed in Table 1 and shown in Figure 1.

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

Table 1. Properties of the reactant powders

Reactant	Vendor	Size	Purity (%)
Mg	Riedel-deHaen	-	99
SiO_2	Aldrich	-325 mesh	99.6
C	Ajax Finechem	-	99

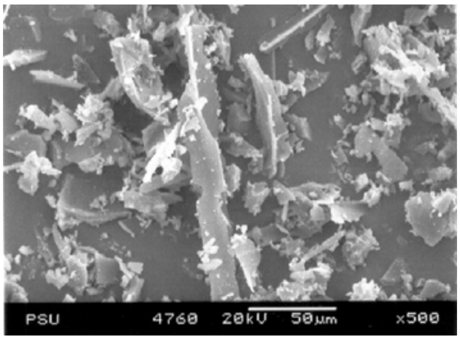

Figure 1. SEM image of as-the received activated carbon.

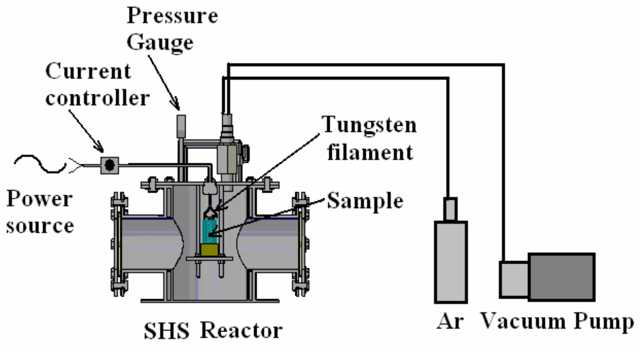

Figure 2. Schematic of the experimental setup.

Reactant powders were weighted according to the mole ratio of $C:SiO_2:Mg$ = 1:1:2 to 3:1:2 and milled in a planetary ball-milled using tungsten carbide balls at a 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 (gree density is the weight per unit volume of an unsintered compact). The green sample was then loaded into the reaction chamber of the SHS reactor. The reaction chamber was evacuated and filled with argon gas at a pressure of 0.5 MPa. This operation was repeated at least twice to ensure an inert environment during the reaction revolution. A combustion front was generated at one end of the sample by using a heated tungsten filament. Then, under self-propagating conditions, the reaction front travels through the sample until it reaches the opposite end. The obtain products were characterized in term of chemical composition and microstructure by X-ray diffraction (XRD: PHILIPS with Cu Kα radiation) and Scanning Electron Microscope (SEM: JEOL, JSM-5800 LV) analysis.

3. Results and Discussion

3.1 Thermodynamic Analysis

Calculations for the equilibrium concentration of the stable species produced by SHS reaction were performed based on the Gibbs energy minimization method (Gokcen and Reddy, 1996). The evolution of species was calculated for a reducing atmosphere and as a function of temperature, in the temperature range from 0 to 3000°C. During the calculations, it was assumed that the evolved gases are ideal that they form an ideal gas mixture, and that the condensed phases are pure. The total Gibbs energy of the system can be expressed by the following equation:

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

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 the way that G is a minimized subject to the mass balance constraints.

The equilibrium composition of the C-SiO_2-Mg system at different temperatures was calculated using Gibbs energy minimization method with the results is shown in Figure 3. The overall chemical reactions can be expressed as:

$$SiO_{2(s)} + C_{(s)} + 2Mg_{(s)} = SiC_{(s)} + 2MgO_{(s)} \quad (3)$$

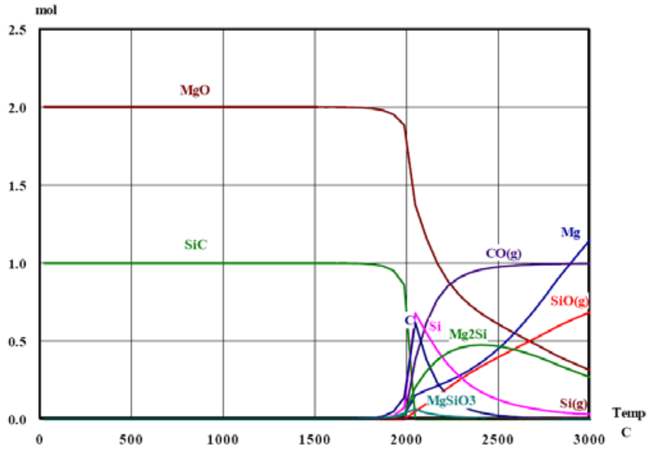

Figure 3. Equilibrium composition of the SiO_2-Mg-C systems in an Ar gas atmosphere.

During the process of SHS, the mixture of SiO_2, Mg, and C may have been interacted to form some possible compounds as shown in the following intermediate chemical reactions below:

$$SiO_{2(s)} + 2Mg_{(s)} = Si_{(s)} + 2MgO_{(s)} \quad (4)$$

$$Si_{(l)} + C_{(s)} = SiC_{(s)} \quad (5)$$

$$SiO_{2(s)} + C_{(s)} = SiO_{(g)} + CO_{(g)} \quad (6)$$

$$SiO_{(g)} + 2C_{(s)} = SiC_{(s)} + CO_{(g)} \quad (7)$$

3.2 The effects of carbon mole ratio to the precursor mixture

The adiabatic temperature (Tad) of the SHS process can be calculated from the enthalpy of the reaction (Moore and Feng, 1995). This is the maximum theoretical temperature that the reactants can reach, and it is determined from Equation (8). This equation applies to a phase change occurring between the initial temperature and Tad. The calculated results are shown in Table 2.

$$\Delta H = \int_{298}^{T_m} C_{p,solid}\, dT + \Delta H_f + \int_{T_m}^{T_{ad}} C_{p,liquid}\, dT \quad (8)$$

Table 2. Adiabatic temperature of reactions

Reaction System	Adiabatic Temperature (°C)
1) $SiO_2 + C + 2Mg$	2393.2
2) $SiO_2 + 2C + 2Mg$	2125.3
3) $SiO_2 + 3C + 2Mg$	1916.2
4) $SiO_2 + 4C + 2Mg$	1748.5

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.

Figure 3 shows that it is thermodynamically feasible to synthesize SiC-MgO by heating up the system following reaction (3). Accepting that, the reaction can be a self-sustained combustion when the adiabatic temperature of the reaction is higher than 1800°C (Moore and Feng, 1995). From Table 2, the adiabatic temperature of the reaction systems 1 to 3, which have a precursor mole ratio of C:SiO_2:Mg = 1:1:2 to 3:1:2, are higher than 1800°C, thus the use of SHS is feasible for these systems. Figure 4 shows that reaction (4) has the lowest Gibbs energy of all reactions (at a temperature lower than 2200°C). It means that Mg reacts first with SiO_2 to yield elemental Si and then forms MgO together with the generated heat. The heat of reaction causes Si to melt and the melted Si coats the C powder by capillarity action. The silicification reaction takes place by a liquid-solid reaction as shown in Equation (5). Although the Gibbs energy of the gas-solid reaction of Equation (7) is lower than that of Equation (5), at a temperature higher that 935°C, the resident time of the contact between the vaporized SiO and C is relatively short. Thus, the contribution of this gas-solid reaction would be less significant. The morphology of the product particle shown in Figure 5 confirmed this suggest as the SiC particles were in particulate form. The shape of the SiC powders are retained from those of the carbon sources suggests that the silicification reaction is a diffusion-controlled reaction in the reaction region.

Figure 5 shows typical SEM micrograph of the products from the SHS reaction before and after the leaching process. The morphology of the products before the leaching process shows a composite of MgO and SiC, but the leaching reveals an agglomerated particle of SiC as identified by XRD patterns in Figure 6. It is believed that the agglomeration of the SiC particle occurred because the SiC-MgO composite powder was synthesized by melting of the reactants

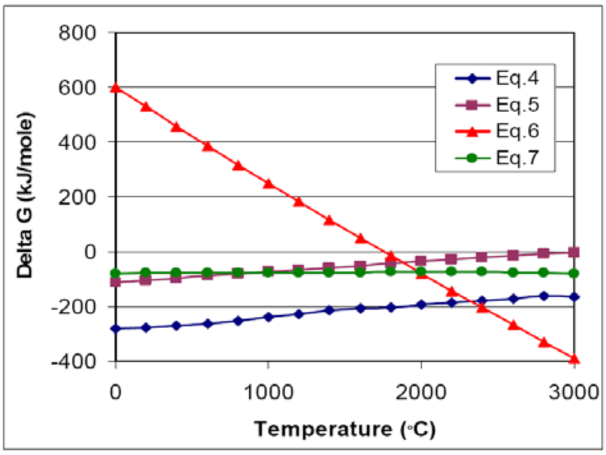

Figure 4. Gibbs Free Energy (delta G, in kJ/mole) of four different reactions (Equation 4, 5, 6, and 7, see text) at a temperature range from 0 to 3000°C.

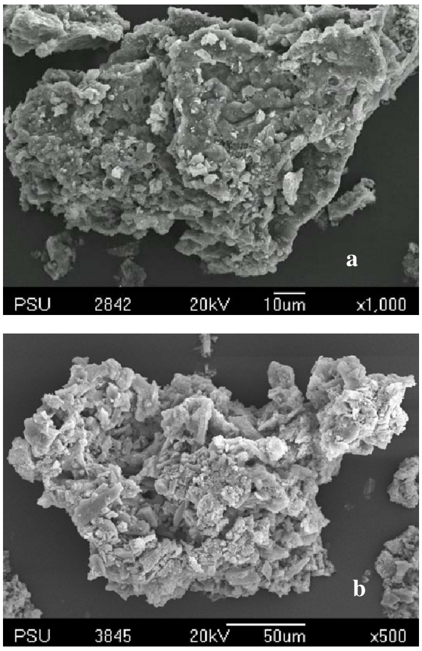

Figure 5. SEM image of the products from (a) SiC-MgO (before leaching) and (b) SiC (after leaching)

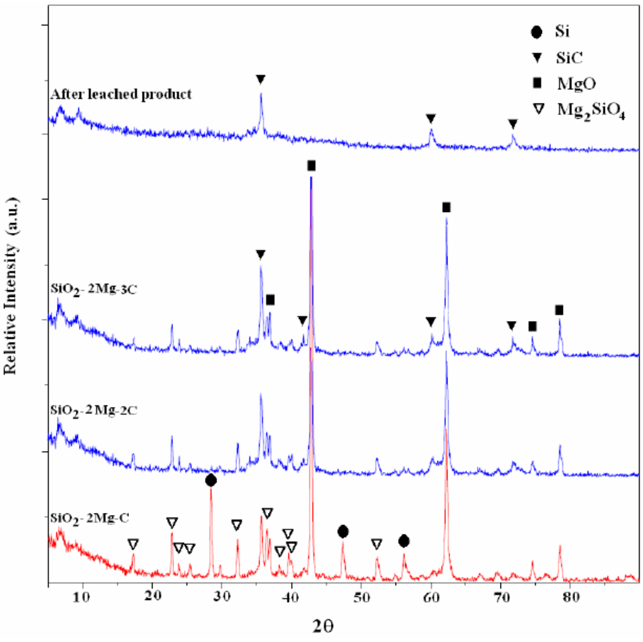

Figure 6. XRD patterns of three different reaction products varying in the relative amount of carbon:SiO2:Mg and of the leached product.

followed by a silicification reaction. The reactants are in the solid state at the early stage of the reaction. As the temp erature of the sample surface increase to 650°C by the hot tungsten wire, the Mg particles start to melt. At a temperature higher than 650°C, the carbon and SiO_2 particles are surrounded by the Mg melt, and the SiO_2 particles are first reduced by the Mg melt and by this releasing high heat of the reaction and starting so the self-propagating reaction process. Assuming that the theoretical adiabatic temperature of the SHS process, 1916-2393°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 and 4).

Figure 6 shows the XRD patterns of the reaction products with different relative amounts of carbon at a constant molar ratio of SiO_2:Mg = 1:2. Si content in the product was observed when there was stoichiometric amount of carbon. This can be explained by the lost content of carbon to form CO gas. As the relative amount of carbon to SiO_2:Mg increased, the unreacted Si disappeared and the SHS reaction was completed and formed the SiC-MgO composites. The free carbon left in the system could be eliminated by roasting the final reaction product at 650°C in air. The as-synthesized powders were leached with the 0.1M HCl solution for 24 hours and the XRD phase identification shows only the SiC phase left in the system.

4. Conclusions

The SiC powders were produced from leaching out MgO from SiC-MgO that were *in-situ* synthesized by a self-propagating high temperature synthesis reaction from precursors of SiO_2-Mg-C. An incompleted SHS reaction was observed when using the stoichiometric molar ratio of carbon in the precursor mixture. As the relative molar ratio of carbon to SiO_2:Mg increased (2:1:2 and 3:1:2), the SHS reaction was completed and formed SiC-MgO composites. After the leaching process the final product shows only SiC phase left in the system.

Acknowledgements

The author is pleased to acknowledge the financial support for this research by the Ceramic and Composite Material Research Group (CMRG) of the Faculty of Engineering, Prince of Songkla University, Thailand.

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