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In Situ Synthesis of Silicon-Silicon Carbide Composites from SiO₂-C-Mg System via Self-Propagating High-Temperature Synthesis

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1. 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 (Boulos et al., 1994). 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 (Morancais et al., 2003; Gadzira et al., 1998; Feng et al., 1994; Niyomwas 2008; and Niyomwas 2009) have been reported in the literature for the synthesis of SiC powders. Sol-gel process requires expensive precursor's solutions and complicated process while the thermal plasma synthesis, laser synthesis and microwave synthesis have very high operating cost 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 synthesis SiC via SHS. However, this reaction is not strong enough and without constant maintenance of temperature at a certain level, SHS for SiC does not take place.

Due to the high reaction temperature and long reaction time, the powders produced have a large particle size. It is well known that materials with fine microstructures exhibit markedly improved properties without change in their physical appearance. These characteristics include improved strength, stiffness, wear resistance, fatigue resistance and lower ductility and toughness. Nanoscale SiC particles have important potential application in nanoelectronics, field emission devices and nanocomposite therefore, efforts have been made by many research groups to fabricate SiC nanoparticles by method like dual-beam implantation of C⁺ and Si⁺ ions (Kogler et. al., 2003), solid state reaction of Si-C (Meng et. al., 2000; Larпкиattaworn et. al., 2006) and thermal plasma synthesis (Tong and Reddy, 2006). These methods involve multi-steps and energy intensive process that have difficulty in establishing commercial viability.

In this report, Si-SiC composite and nanocomposites particles were synthesized by SHS from powder mixtures of SiO₂-Mg-C and SiO₂-Mg-C-NaCl without preheating the precursors. Thermodynamics model for SHS reaction was developed. The experimental results of the synthesis of Si-SiC composite particles were compared with the model calculation. The effects of silica sources, carbon mole ratio in precursor mixture and the amount of added NaCl in precursor on the Si-SiC conversion were investigated. An excellent agreement between model results and experimental data from this study was obtained

2. Experimental

The raw materials used in this report were Mg, C, NaCl and different sources of SiO₂ powders; i.e. precipitated SiO₂, fumed silica, rice husk ash (RHA), and natural sand whose properties are listed in Table 1 and 2 and shown in Figure 1 and 2.

Reactant	Vendor	Size	Purity (%)
Mg	Riedel-deHaen	-	99
C	Ajax Finechem	-	99
SiO ₂ (pp)	Aldrich	-325 mesh	99.6
SiO ₂ (Fumed)	Aldrich	-	99.8
SiO ₂ (RHA)	-	-325 mesh	90.0
SiO ₂ (Sand)	-	-325 mesh	98.5
NaCl	Lab-Scan Analytical Science	-	99.0

Table 1. Properties of the reactant powders

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

Table 2. Composition of RHA from XRF analysis

Fig. 1. SEM image of (a) RHA, (b) fumed silica (c) precipitated SiO₂ and (d) natural sand

Fig. 2. SEM image of (a) Mg and (b) activated carbon

The experimental setup used in this work is schematically represented in Figure 3. 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.

Fig. 3. (a) Schematic of the experimental setup and (b) SHS reactor

Reactant powders were weighted as stoichiometric ratio and milled in planetary ball-milled with the speed of 250 rpm for 30 minute. 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. Green sample was then loaded into reaction chamber of 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 the top end of a sample by using a heated tungsten filament. Then, under self-propagating conditions, the reaction front 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), TEM (JEM-2010, EOL), and SEM (JEOL, JSM-5800 LV) analyses.

3. Thermodynamic Analysis

Calculations for equilibrium concentration of 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 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 SiO₂-Mg-C system at different temperatures was calculated using Gibbs energy minimization method and the results were shown in Figure 4. 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 (Moore and Feng, 1995). This is the maximum theoretical temperature that the reactants can be reached, 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.

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

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.

In order to synthesize nanocomposites particles, NaCl was added to the precursor as a diluents and the reaction can be expressed as:

Adiabatic temperature of each sample with the difference amount of NaCl was calculated from Equation (3) and shown in Table 3 .

NaCl (mole)	0	0.25	0.5	0.75	1.0
T _{ad} (°C)	2162.7	2036.9	1924.2	1816.6	1725.4

Table 3. Adiabatic temperature of the chemical reaction of TiO₂-C-Mg-NaCl system

It can be seen that T_{ad} of all reactions which added 0 - 0.75 mole of NaCl were higher than 1800 °C thus those reactions were feasible for SHS process. The reduction of T_{ad} with adding NaCl resulted from the melting of NaCl and absorbed by molten salt.

It has been accepted that the reaction can be self-sustained combustion when adiabatic temperature of the reaction higher than 1800°C (Moore and Feng, 1995). From calculated adiabatic temperature of the reactions, they are higher than 1800°C, thus the using of SHS is feasible for these systems.

It can be seen from Figure 4 that it is thermodynamically feasible to synthesize Si-SiC-MgO by igniting the reactant of reaction (3) and (10). Due to a highly exothermic reaction at room temperature ($\Delta H = -655.15$ kJ) and thermodynamic instability at room temperature, the reactant phases of SiO_2 , C and Mg were not shown in the calculated stable phases in Figure 4. 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 Mg_2SiO_4 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 4.

Fig. 4. Equilibrium composition of SiO_2 -C-Mg systems in Ar gas atmosphere

4. Synthesis of Si-SiC Composites

4.1 The effects of carbon molar ratio in the precursor mixture

Figure 5 shows XRD patterns of reaction products with different relative amounts of carbon at a constant molar ratio of SiO_2 :Mg = 2:4. All three conditions can produce resulting

products as in Equation (3) and intermediate phase of Mg₂SiO₄. As the relative amount of carbon to SiO₂:Mg increased, the Si content in the final products changed accordingly. The Si content was highest when using 1 mole of carbon in the precursor mixture which is the stoichiometric ratio of precursors of Equation (3). When mixing 2 mole of carbon into the reaction, it is more favorable to form SiC (Niyomwas 2008), as shown in Equation (11), that results in less Si in the product. The other evidence of higher reaction temperature is the relative higher intensity of α-SiC phase which forms at higher temperature than β-SiC phase appeared at the condition of 2 mole carbon reaction. For adding 3 mole of carbon into the precursor mixture, Si content in the product increases while SiC decreases and some free carbon is left in the system. This may be due to the excess carbon absorbed heat released from exothermic reaction that causes the decrease of overall heat of reaction and less favor for forming SiC.

Fig. 5. XRD patterns of as-synthesized products and leached products of different carbon mole ration in the precursor mixture

Figure 6 (a) to (f) shows low and high magnification SEM micrographs of the products from SHS reaction after leaching process from the precursor mixture of 1, 2, and 3 mole of carbon, respectively. The morphology of products reveals an agglomerated particle of Si-SiC as identified by XRD patterns in Figure 5. Figure 6 (a), (c) and (e) shows the free carbon left in the products which is more apparent when 3 mole of carbon was added into the precursor mixture.

Fig. 6. SEM image of leached products from different carbon mole ratio on mixture of SiO₂ (pp) as silica sources: (a) and (b) for 1 mole C, (c) and (d) for 2 mole C, and (e) and (f) for 3 mole C

It is believed that the agglomeration of fine SiC particle 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 increase to 650°C, the Mg particles start to melt. At the higher temperature 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 the theoretical adiabatic temperature, 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 based on the thermodynamic calculation resulted (Figure 4).

4.2 The effects of silica sources in the precursor mixture

Figure 7 shows XRD patterns of reaction products with different silica sources at a constant molar ratio of C:SiO₂:Mg = 2:2:4. 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. Not much difference was found in the as-synthesized products from different silica sources, only the products from fumed silica that showed relatively higher intensity of Si. 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). Peaks due to Si-SiC phases are observed together with the broad peak of amorphous carbon, indicating that the formation of SiC has taken place and that residual free carbon still exists. To get rid of free carbon in the final products, the more studies on lower molar ratio of carbon in the precursor mixtures are planned in the future.

Figure 8 shows SEM micrograph of the products from SHS reaction after leaching process from the precursor mixture of different silica sources, i.e. (a) RHA, (b) fumed silica, (c) sand and (d) precipitated silica. The morphology of products reveals an agglomerated particle of Si-SiC as identified by XRD patterns in Figure 7. The existence of Mg₂SiO₄ in the product may be due to incomplete reaction from the rapid nature of SHS reaction. Free carbon left in the products is also evidently found in every condition.

Fig. 7. XRD patterns of (a) as-synthesized products and (b) leached products of different silica sources

Fig. 8. SEM image of leached products from difference silica (a) RHA, (b) fumed silica, (c) sand and (d) precipitated silica

4.3 The effects of adding NaCl in the precursor mixture

The final product Si-SiC nanoparticle composites were obtained from washing out NaCl from synthesized product by distilled water and leaching the rest with 0.1M HCl for 12 hours and identifying with SEM, XRD and TEM images, shown in Figure 9, 10 and 11, respectively.

The XRD patterns of the samples after reaction showed the presence of MgO, Mg₂SiO₄ in the as-synthesized powder and no Mg peak appeared. After leaching with dilute HCl, only Si-SiC phase were found. When NaCl was added with the reaction mixture, diffraction peak due to NaCl were also detected. As the NaCl content was increased, the intensity of the Si peaks were increased, at the same time α -SiC peaks were decreased. This is due to the lower reaction temperature caused by NaCl diluents to the reactions. As the reaction temperature goes down, the reaction in Equation 3 was incomplected and left more Mg₂SiO₄ phase and also have less energy to form SiC from element Si and carbon causing higher peak of Si.

The morphology of leached and washed Si-SiC powders were shown in Figure 9. They appeared as lumpys of agglomerated powders with finer powders for higher NaCl content. The microstructure observations of the leached samples revealed the generation of fine powders. Transmission electron micrographs of 0, 0.25 and 0.75 mole of NaCl samples are

given in Figure 11 (a), (b) and (c), respectively. The micrographs revealed that the powders remained agglomerated even after leaching and drying. With the addition of NaCl, the particles were observed to be very fine and less agglomerated. During exothermic reactions, very high temperature ($>1800\text{ }^{\circ}\text{C}$) were achieved within a fraction of minutes. Since the combustion temperature was much higher than the boiling point of NaCl ($1465\text{ }^{\circ}\text{C}$) evaporation of NaCl was expected. The presence of NaCl in the XRD pattern indicated that all of the NaCl did not escape out from the mixture after the synthesis. This NaCl may have partially melted and vaporized which give a coating on the SiC particle. This coating could reduce the grain growth of particles and finally decrease the particle sizes. The decrease of adiabatic temperatures with the addition of NaCl may also have helped in reducing the grain growth.

Fig. 9. SEM micrographs of synthesized products after leaching when added (a) 0.25 and (b) 0.75 mole of NaCl

Fig. 10. XRD patterns of (a) as-synthesized and unleached products and (b) leached and washed products

Fig. 11. TEM micrographs of synthesized products after leaching when added (a) 0, (b) 0.25 and (c) 0.75 mole of NaCl

5. Conclusion

The Si-SiC composite powders were produced from leaching out MgO and Mg_2SiO_4 from reaction products that were *in-situ* synthesized via self-propagating high temperature synthesis reaction from precursors of SiO_2 -Mg-C. The highest Si to SiC was found when use mixture molar ratio of $\text{C}:\text{SiO}_2:\text{Mg} = 1:2:4$, while the lowest one was found on the result of mixture molar ratio of $\text{C}:\text{SiO}_2:\text{Mg} = 2:2:4$. As the relative molar ratio of carbon to $\text{SiO}_2:\text{Mg}$ increase ($\text{C}:\text{SiO}_2:\text{Mg} = 3:2:4$), the free carbon left in the final product was relatively high. The resulting products from different silica sources of RHA, fumed silica, sand and precipitated silica, show no significant different in Si-SiC composite. In all conditions, the resulting SiC were in both α -SiC phase and β -SiC phase.

The nano-sized Si-SiC nanoparticle composites were successfully synthesized via self-propagating high temperature synthesis (SHS) from the reactants of SiO_2 , C, and Mg with the mole ratio 2:1:4 and $n\text{NaCl}$ ($n = 0.1\text{-}0.75$ mole). As the amount of NaCl in precursor mixture was increased, the resultant product showed decreasing particle size to nanometer range.

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In this book, we explore an eclectic mix of articles that highlight some new potential applications of SiC and different ways to achieve specific properties. Some articles describe well-established processing methods, while others highlight phase equilibria or machining methods. A resurgence of interest in the structural arena is evident, while new ways to utilize the interesting electromagnetic properties of SiC continue to increase.

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