Combustion synthesis of Si-SiC composite powders derived from different silica precursors

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Silicon-silicon carbide (Si-SiC) composite powders were produced by in-situ magnesiothermic self-combustion synthesis in a static argon atmosphere, using precursors of carbon, magnesium and either rice husk ash (RHA) or natural sand. The description of the reaction involves initial the combustion reaction, the phase conversion through the product, and the cooling rate. The adiabatic temperature (T_{ad}), the enthalpy of the reaction (ΔH) and the equilibrium composition of the reacting species were calculated. Pure Si-SiC powders were obtained by leaching with a solution of $HCl: CH_3COOH$ followed by $HF : H_2O$ solution. Both the experimental results and the thermodynamic analysis indicated that the exothermic effect on the conversion of Mg_2SiO_4 had a large influence on the resultant Si-SiC composite.

Key words: Combustion synthesis, Si-SiC composite, RHA, Natural sand, Silica, leaching.

Introduction

Silicon carbide (SiC) is a non-oxide ceramic which has various engineering applications. Its essential properties are extreme hardness, great strength, chemical stability, high melting point, resistance to oxidation, and durability [1, 2]. Due to these qualities, it can be used in high temperature devices as well as in abrasion and cutting applications.

The typical manufacturing processes for fully-dense-SiC are pressureless sintering, hot pressing and hot isostatic pressing, but the required temperature, pressure and materials preparation make these processes expensive [3]. Reaction bonded silicon carbide (RBSiC) or Si-SiC can be added to facilitate the sintering process by enabling a lower sintering temperature. The typical microstructure of RBSiC composites consists of about 65-85% silicon carbide, and residual free silicon [4]. During the sintering progression, the molten trace silicon element of the Si-SiC help to bond the SiC particles, achieving a good sinter with full densification [5, 6].

Traditionally, SiC has been produced through the solid-state reaction between commercial silica (SiO_2) and carbon (C) known as "carbothermal reduction". However, the disadvantage of this process includes a complicated synthesis, high energy consumption, long heat-treatment at high temperature and low production rate [7].

Combustion synthesis, which is also known as self-propagating high-temperature synthesis (SHS), is a method of producing inorganic materials from exothermic reactions. The advantages of this process are its uses of the heat energy released in the combustion reaction and consequent, energy savings, self-purification due to enhanced outgassing of impurities, and rapid synthesis. In addition, several kinds of materials can be synthesized by this method, including carbides, borides, silicides, nitrides, sulfides, hydrides, intermetallics and composites [8].

Rice husk ash (RHA) and natural sand can be used as silica precursors to synthesize SiC, because both substances are rich in SiO_2. In Thailand, rice husks are widely available in the form of waste from rice milling industries. RHA with a high amount of SiO_2 is produced by burning the rice husks in air at elevated temperatures. The natural sand which is commonly used as a raw material for glass manufacturing, especially in Haad Kaew, Singhanakorn, Songkhla also has a high SiO_2 content as well.

The aim of the present work is to synthesize Si-SiC composite powders by combustion reaction obtained from $SiO_2/C/Mg$ powders mixed in the mole ratio of 0.5/0.4/1.0 using RHA and natural sand as a silica source. The thermodynamic behavior, microstructure and chemical composition of the Si-SiC composites were also investigated.

Materials and Methods

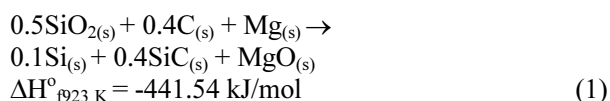Si-SiC composite powders were produced from RHA,

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natural sand, activated carbon (Ajax-Finechem, 99%) and Mg metal reduction powders (Riedel-deHaen, 99%). The morphologies of the reactant powders are shown in Fig. 1.

The general magnesiothermic reaction can be expressed as:

$$0.5SiO_{2(s)} + 0.4C_{(s)} + Mg_{(s)} \rightarrow$$
$$0.1Si_{(s)} + 0.4SiC_{(s)} + MgO_{(s)}$$
$$\Delta H^{o}_{f923\ K} = -441.54\ kJ/mol \qquad (1)$$

The compositions of RHA and natural sand used in this work analyzed by X-Ray fluorescence (XRF: Philips, PW2400, the Netherlands) are given in Table 1 and Table 2, respectively. In a typical procedure, the reactant powders were weighed according to the required reaction stoichiometry. The mixtures were dry mill-mixed for 2 hrs using a nylon jar and zirconia balls. Then, the mixture was compacted into cylindrical pellets with a diameter of 25.4 mm. The consolidated green density of the compacts was in a range of 50-60% of their theoretical density.

The compacts were placed on a refractory plate and then transferred into a combustion reactor under a static argon atmosphere. The combustion reaction was initiated by igniting the top of the compacts with a tungsten-filament. The details of the experimental setup were reported in a previous work [9]. Once the combustion reaction began, most of the heat generated by the chemical reactions served to increase the temperature of the compacts. Under the self-propagating condition, the combustion front moved rapidly as expected until it reached the opposite end of the compact and the combustion products were recovered after cooling to room temperature. They were leached to remove the unwanted phases by using solutions of HCl: CH_3COOH at 70 °C for 30 min and HF: H_2O at 95 °C for 30 min, all under moderate stirring. After each leaching step,

Table 1. Composition of RHA from XRF analysis.

Compound	wt%
SiO_2	90.00
K_2O	7.68
CaO	1.64
Trace elements	balance

Table 2. Composition of natural sand from XRF analysis.

Compound	wt%
SiO_2	97.55
Fe_2O_3	0.94
TiO_2	0.38
Al_2O_3	0.32
Trace elements	balance

the leached product was filtered and washed with distilled water several times and finally dried at 100 °C [10].

To study the effect of different silica sources on the combustion reaction mechanisms, the mixed reactant powders of $SiO_2/C/Mg$ were prepared and tested using a differential thermal analyzer (DTA: Perkin Elmer, DTA7, USA). All samples were heated from 50 to 1,300 °C at a rate of 10 °C/ min under a flowing N_2 atmosphere. The morphologies and the phase compositions of combustion products were characterized by a scanning electron microscope (SEM: Quanta 400, FEI, the Netherlands) coupled with an energy dispersive X-Ray spectrometer (EDS: X-Max, Oxford, UK) and the phase identification was carried out by X-Ray diffraction analysis using an X-Ray diffractometer (XRD: Philips, X' Pert MPD with CuK_a radiation of 1.5406 Å, the Netherlands).

Results and Discussion

Thermodynamics investigation

The maximum theoretical temperature that the reactants can reach under adiabatic conditions, or the adiabatic temperature (T_{ad}) [9], was calculated from the enthalpy of the reaction. The calculated adiabatic temperature of reaction (1) is 2,826.9 °C. Since it is accepted that a reaction can only be exothermically self-sustaining if the adiabatic temperature exceeds 1,800 °C [11], this being so the use of SHS is reasonable for this system.

The equilibrium composition of the $SiO_2/C/Mg$ system at different temperatures was calculated using the thermodynamic calculation software "HSC®" based on Gibbs energy minimization method [9]. The results of these calculations, shown in Fig. 2 indicated that it is thermodynamically feasible to synthesize Si-SiC by heating these reactants. The formation of Si and SiC was initiated at a temperature of about 1,900-2,000 °C, resulting in a decrease of the reactants and increase of the products.

Due to a high exothermicity, the ideal combustion reaction occurs at room temperature ($\Delta H_{f298\ K} = -418.04$ kJ/ mol). Each chemical reactant may react with another to form several possible compounds during the *in-situ* combustion reaction of the reactant mixture ($SiO_2/C/ Mg$). The detail of reaction's development was reported in previous works [9, 12]. The complete gaseous phases (Mg, SiO and CO) were generated at the adiabatic temperature, which is higher than the melting point of Mg (650 °C), Si (1,414 °C) and SiO_2 (1,600°C). At that point, the SiC was produced from the reaction of the gaseous phases. However, not only SiC was formed but also an intermediate phase Mg_2SiO_4 was generated under the conditions used. Upon further propagation of the combustion wave, the products cooled and rearranged their phases [9, 12].

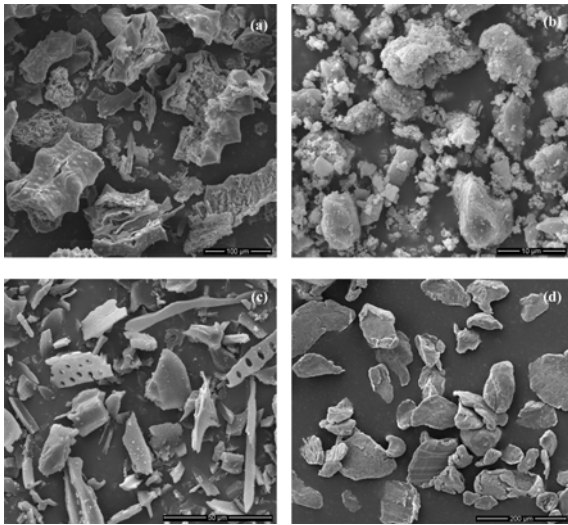The DTA plot of the reactant mixture ($SiO_2/C/Mg$)

Fig. 1. Morphologies of the reactant powders (a) RHA (b) natural sand (c) activated carbon and (d) Mg reducing metal powder.

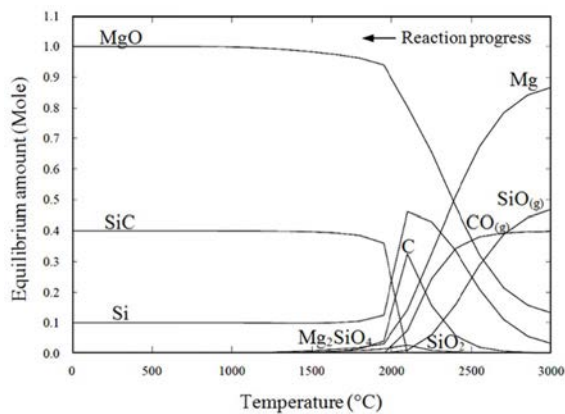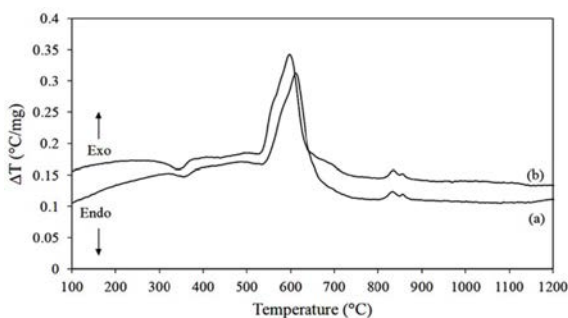**Fig. 2.** Equilibrium composition of SiO_2/C/Mg system in Ar atmosphere.

Fig. 3. DTA curves of the reactant mixture (SiO_2/C/Mg) (a) RHA and (b) natural sand.

using the different silica sources is presented in Fig. 3. Figs. 3(a) and 3(b) show endothermic peaks between 300-380 °C. These peaks are related to the decomposition of the trace elements which are the natural constituents of RHA and natural sand (as shown in Table 1 and 2). An exothermic peak between 600-650 °C represents the reduction reaction of silica by melt-Mg to form MgO and Si, whereupon the generated Si reacted with C to

simultaneously form SiC [12]. In fact, an endothermic peak which corresponds to the melting point of Mg should also be present in this temperature range, but it does not appear in the thermogram (Fig. 3). This may be due to the greater exothermic reaction between Mg and SiO_2 to form MgO and Si. The endothermic peak between 835-850 °C corresponds to the formation of unstable Mg_2SiO_4.

Identification of phases

The XRD patterns of the as-combusted products are presented in Figs. 4(a) and 4(b). The results show that the products consisted of Si, SiC, MgO, Mg_2SiO_4 and SiO_2 (cristobalite and quartz structures). The presence of unstable Mg_2SiO_4 and unreacted SiO_2 in the XRD pattern of these products may be due to an incomplete conversion caused by the fast cooling rate of the combustion reaction [8, 12]. In Fig. 4(a), peaks of SiO_2 (quartz, $2\theta = 26$-28 °) can be observed where natural sand was the silica source but not where RHA was used. This is because the SiO_2 commonly found in natural sand has a quartz structure. In addition, it was evident that an XRD result in Fig. 4(b) confirms the presence of more unstable Mg_2SiO_4 phase when natural sand was used as the silica source, which is in good agreement with the DTA result in Fig. 3(b). We believe that the high silica content of natural sand significantly affected the reaction path of melt-SiO_2 and MgO promoting the formation of unstable Mg_2SiO_4.

The phase composition of the combustion and leached-combustion products were analyzed by a semi-quantitative method and the results are shown in Table 3.

When natural sand was used as a silica source, less Si and b-SiC phases appeared in the product because of the lesser exothermic effect and faster cooling rate from the high-temperature. Consequently, the unstable Mg_2SiO_4 phases did not have enough time to completely form free Si and MgO. Eventually, the few free Si elements which arose from Mg_2SiO_4 transformation were not enough to form SiC, hence the small amount of Si and SiC obtained. This phenomenon was confirmed by the DTA data in Fig. 3(b).
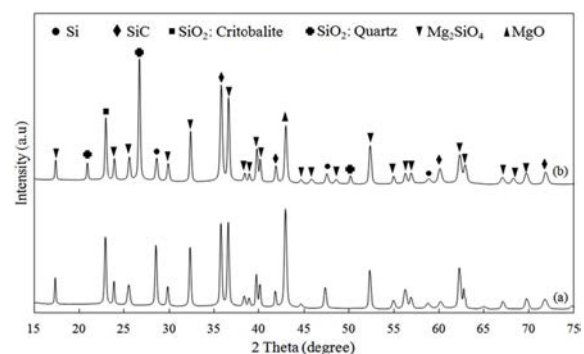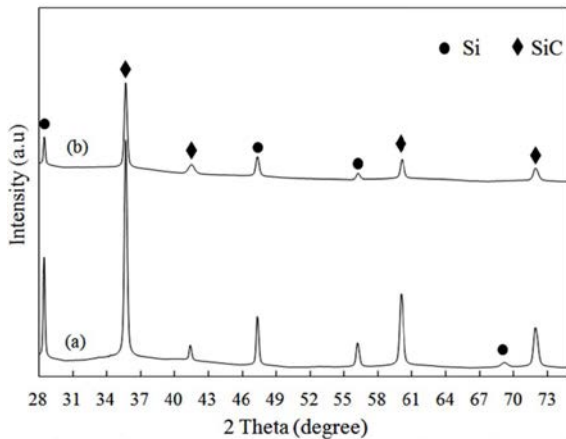

Fig. 4. XRD patterns of the as-combusted products synthesized from the different silica sources (a) RHA and (b) natural sand.

Table 3. Comparison of the phase composition of combustion and leached-combustion products.

Silica sources	Composition (wt%)					
	As-combusted products					
	Si	SiC	MgO	Mg_2SiO_4	SiO_2: Cristobalite	SiO_2: Quartz
RHA	16.36	16.68	25.21	30.97	10.78	-
Natural sand	4.48	14.26	12.71	50.35	5.21	12.99
	Leached-combustion products					
RHA	35.98	64.02	–	–	–	–
natural sand	32.93	67.07	–	–	–	–

Fig. 5. XRD patterns of the as-combusted products synthesized from (a) RHA and (b) natural sand after two leaching steps.
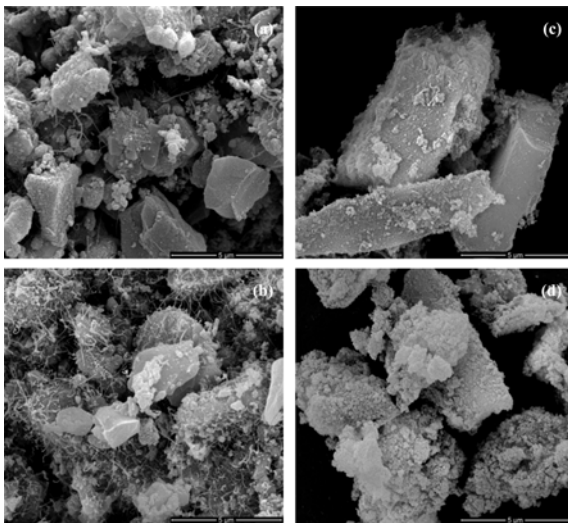
Fig. 6. SEM micrographs of product powders synthesized from RHA/Mg/C system (a) before and (c) after leaching, and synthesized from natural sand/Mg/C system (b) before and (d) after leaching.

Figs. 5(a) and 5(b) show the XRD pattern of the products synthesized from the two silica sources after leaching with a solution of HCl: CH_3COOH, followed by a solution of HF: H_2O. The SiO_2, MgO and Mg_2SiO_4 phases contained in the combustion products disappeared when the two leaching steps were completed.
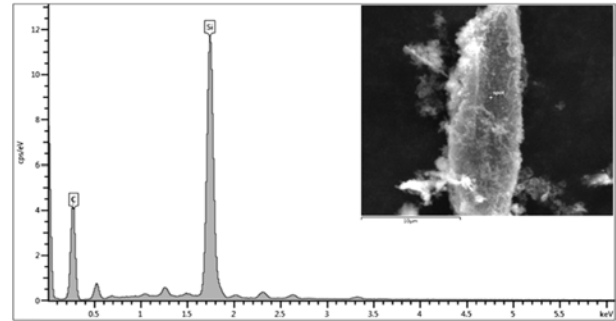
Fig. 7. SEM-EDS spectra of the typical product after leaching process (oxygen and minor contamination were not quantified).

Microstructures

Fig. 6 shows the morphology of the products obtained from the combustion reaction before, (a) and (c) and after, (b) and (d), the leaching processes. Prior to leaching, the as-combusted products displayed agglomerated particles which consisted of several phases.

Additional confirmation of the phase composition of Si-SiC particles after leaching is presented in Fig. 7, which shows the EDS analysis alongside an SEM micrograph.

Conclusions

Si-SiC composite powders were successfully synthesized by *in-situ* combustion synthesis using reactants of carbon, magnesium and either RHA or natural sand. In this study, the use of RHA as the silica source gave a higher content of Si-SiC composite, after leaching, than the use of natural sand. The exothermic character of the combustion reactions played an important role in the phase conversion process, especially with regard to the production of Mg_2SiO_4.

Acknowledgments

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