Songklanakarin J. Sci. Technol.
32 (2), 175-179, Mar. - Apr. 2010

Songklanakarin Journal
of Science and Technology
http://www.sjst.psu.ac.th

Original Article

Synthesis of titanium carbide from wood by self-propagating high temperature synthesis

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Received 28 September 2007; Accepted 27 October 2008

Abstract

Titanium carbide (TiC) particles were obtained in situ by a self-propagating high temperature synthesis (SHS) of wood dust with TiO_2 and Mg. The reaction was carried out in a SHS reactor under static argon gas at the 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 increasing Mg mole ratio to the precursor mixture of TiO_2 and wood dusts were investigated. XRD and SEM analyses indicate a complete reaction of the precursors to yield TiC-MgO as a product composite. The synthesized composites were leached with 0.1M HCl acid solution to obtain TiC particles as final products.

Keywords: self-propagating high temperature synthesis (SHS), wood dust, magnesium, titanium carbide

1. Introduction

Titanium carbide (TiC) attracted great interest for many structural applications due to its extremely high melting temperature, high hardness, high chemical resistance and good electrical conductivity. Therefore TiC can be used in cutting tools, grinding wheels, wear-resistant coatings, high-temperature heat exchangers, magnetic recording heads, turbine engine seals, and bullet-proof vests, etc. In addition, a promising field of application comprises plasma and flame spraying processes in air, where titanium carbide-based powders show higher-phase stability than tungsten carbide-based powders (Ling and Dutta, 2001).

TiC can be synthesized by a direct reaction between Ti and carbon under vacuum at high temperatures of 1,900°C to 2,900°C (LaSalvia *et al.*, 1995). This method is expensive because of the high cost of elemental Ti and the involved energy intensive process. Because of these reasons many synthesis routes to produce TiC were studied and proposed such as thermal plasma synthesis (Tong and Reddy, 2005), carbothermal reduction process (Swift and Koc, 1999; Gotoh *et al.*, 2001), chemical vapour deposition (CVD) (Yin *et al.*, 2005), and self-propagating high temperature synthesis (SHS) (Ashitani *et al.*, 2002; Nersisyan *et al.*, 2003; Licheri *et al.*, 2004). The thermal plasma synthesis and CVD have very high operating costs; and on the other hand carbothermal reduction of TiO_2 with carbon requires a high temperature furnace for synthesis at 1,500°C.

The SHS process is considered a less expensive method to produce TiC with a low cost reactor and a power source with fewer requirements. One weak point of this method however is the requirement for expensive starting materials with pure elemental materials of Ti to react with C (Licheri *et al.*, 2004) and with woody materials (Ashitani *et al.*, 2002). This can be solved by using TiO_2, C and Mg in SHS process to synthesis of TiC (Nersisyan *et al.*, 2003).

In this study, the productions of TiC powders were obtained by self-propagating high temperature synthesis (SHS) from a mixture of wood dust as the carbon source, TiO_2 and Mg coupled with leaching processes. The effects

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of increasing Mg mole ratio to the precursor mixture of TiO_2 and wood dust were investigated.

2. Thermodynamic Analysis

Calculations for equilibrium concentration of stable species produced by the 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°C to 3,000°C. Calculations assume that the evolved gases are ideal and form ideal gas mixture, and condensed phases are pure. The total Gibbs energy of the system can be expressed by the following equation:

$$G = \sum_{gas} n_i\left(g_i^o + RT\ln P_i\right) + \sum_{condensed} n_i g_i^o + \sum_{solution} n_i\left(g_i^o + RT\ln x_i + RT\ln \gamma_i\right) \quad (1)$$

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 g_i is the activity coefficient of species i. The exercise is to calculate n_i such that G is a minimized subject to the mass balance constraints.

The equilibrium composition of the TiO_2-Mg-C system at different temperatures was calculated using Gibbs energy minimization method and the result is shown in Figure 1(a). The overall chemical reactions can be expressed as:

$$TiO_{2(s)} + C_{(s)} + 2Mg_{(s)} = TiC_{(s)} + 2MgO_{(s)} \quad (2)$$

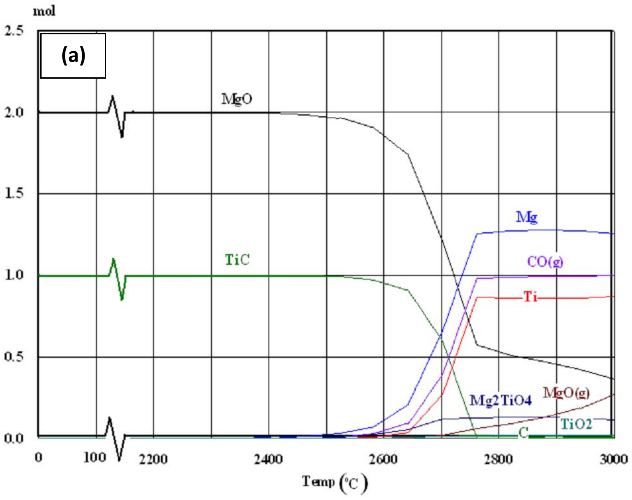
During the process of SHS, the mixture of TiO_2, Mg, and C may interacted to form some possible compounds as following intermediate chemical reactions below:

$$TiO_{2(s)} + 2Mg_{(s)} = Ti_{(s)} + 2MgO_{(s)} \quad (3)$$

$$Ti_{(l)} + C_{(s)} = TiC_{(s)} \quad (4)$$

$$TiO_{2(s)} + 3C_{(s)} = TiC_{(s)} + 2CO_{(g)} \quad (5)$$

Figure 1 (b) shows the calculated results of Gibbs energy of reaction of product and temperature from equation (3) to (5).



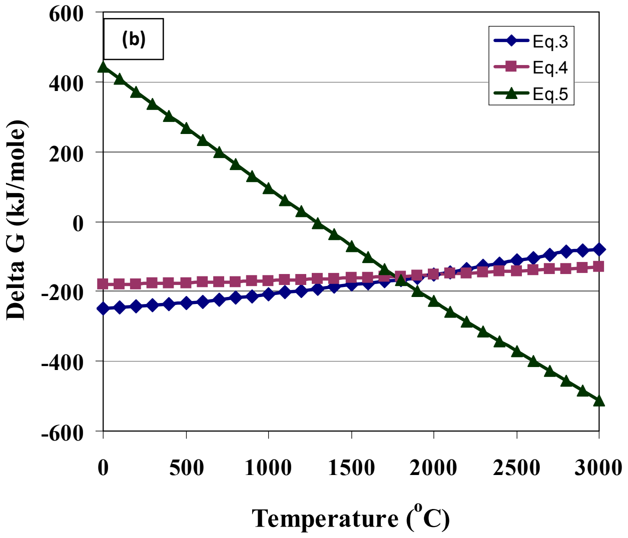


Figure 1. (a) Equilibrium composition of TiO_2-Mg-C systems in Ar gas atmosphere (b) Relation of Gibbs energy of reaction of product and temperature.

3. Experimental

The raw materials used in this paper were Mg, Wood dusts (WD: carbon source), and TiO_2 powders whose properties are listed in Table 1. The particle size of wood dust was analyzed by LPSA (laser particle size analyzer: COULTER LS230) as shown in Figure 2, which had a mean

Table 1. Properties of the reactant powders

Reactant	Vendor	Size	Purity (%)
Mg	Riedel-deHaen	-	99
TiO_2	Unilab	-325 mesh	99.5
Wood Dust (WD)	Para-rubber wood	46.34 µm	-

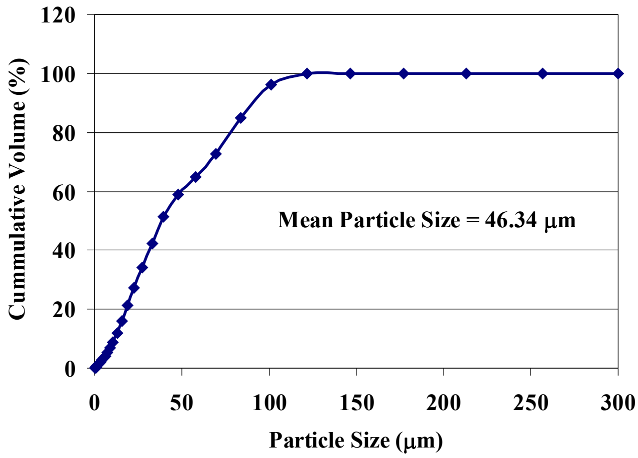


Figure 2. Particle size distribution of the wood dust.

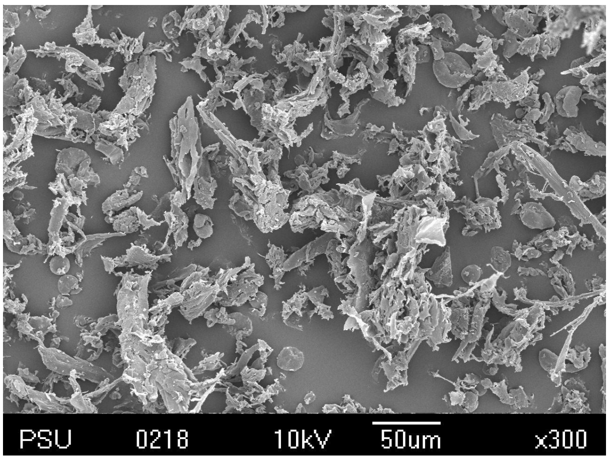


Figure 3. SEM micrograph of wood dust.

particle size of 46.34 mm. SEM micrographs of wood dust precursor are presented in the Figure 3. The elemental analysis of wood dust was performed by the dynamic flash combustion technique (CE Instruments Flash 1112 Series EA CHNS-O Analyzer) which had the results in mass-%, here 44.99 C, 6.04 H, and 29.66 O.

The experimental setup used in this work is schematically represented in Figure 4. It consisted of a SHS reactor with a controlled atmospheric reaction chamber and tungsten filament connected to power source through a current controller, which provides the energy required for the ignition of the reaction.

The dried woody materials were mixed with the TiO_2 and magnesium powders by mortar and pestle. The C/TiO_2 molar ratio was fixed at 1.0 and Mg/TiO_2 molar ratios were changed from 2 to 3.5 with weight ratio expressed in Table 2. The mixture precursor was then loaded into alumina crucible located in the 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 of a heated tungsten filament. Then, under self-propagating conditions, the reaction front travels until reaches the opposite end of the sample. The obtained products were leached with 0.1 M HCl solution for 24 hours and characterized in term of chemical composition and microstructure by XRD (PHILIPS with Cu Ka radiation) and SEM (JEOL, JSM-5800 LV) analyses.

4. Results and Discussion

By varying the amount of Mg in the mixture of precursors, the resulted products from the SHS reactions can be identified by XRD technique (shown in Figure 5) and listed in the Table 3. This can be explained by the propose reactions shown in Equation 3 to 5. At first, the thermite reaction between TiO_2 and Mg took place and yielded Ti and MgO as products and released high heat of the reaction to the adjacent vicinity. The heat energy calcined the natural cellulose of WD into carbon and melted Ti to liquid phase (T_{melt} = 1668°C). The melted Ti coats the WD carbon powder by capillarity action and the liquid-solid reaction of Equation 4 took place. Although the Gibbs energy of the solid-solid reaction of Equation 5 is lower than that of Equation 3 and 4, at a temperature higher than 1750°C, the resident time of the contact between the solid TiO_2 and C is relatively short.

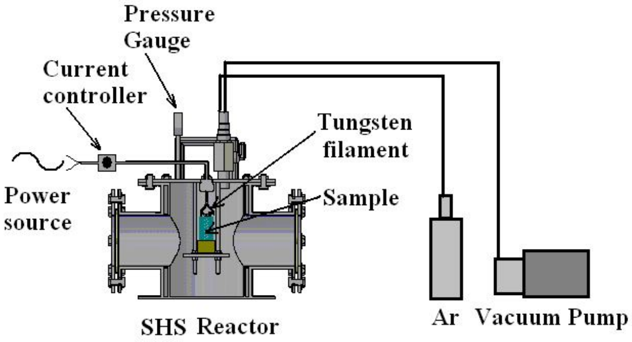


Figure 4. Schematic diagram of the experimental setup.

Table 2. Molar and weight ratio of precursors

	Wood Dust	TiO_2	Mg
Mol Ratio	1	1	2
Wt. Ratio (g)	1	2.9935	1.8212
Mol Ratio	1	1	2.5
Wt. Ratio (g)	1	2.9935	2.2765
Mol Ratio	1	1	3
Wt. Ratio (g)	1	2.9935	2.7318
Mol Ratio	1	1	3.5
Wt. Ratio (g)	1	2.9935	3.1871

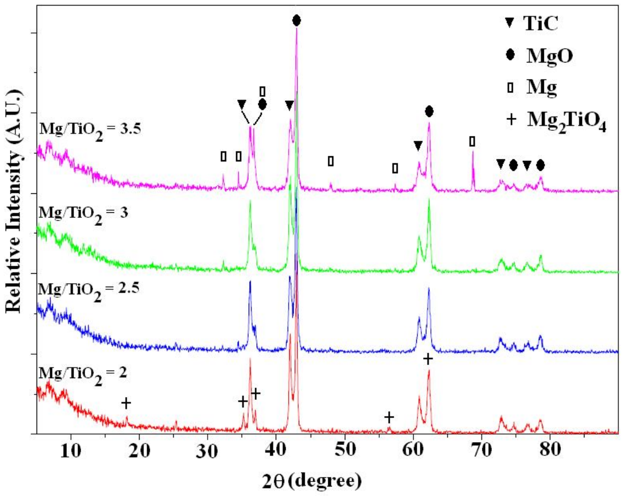


Figure 5. XRD patterns of reaction products varying with different relative mole ratio of Mg to TiO_2 (before leached).

Table 3. Resulted products from different precursors

Precursors	Product Phases
TiO_2 + WD + 2Mg	TiC, MgO, Mg_2TiO_4
TiO_2 + WD + 2.5Mg	TiC, MgO
TiO_2 + WD + 3Mg	TiC, MgO
TiO_2 + WD + 3.5Mg	TiC, MgO, Mg

Thus, the contribution of this solid-solid reaction would be less significant. For the first system of precursors from Table 3, the product phases consist of not only TiC and MgO but the complex oxide of Mg_2TiO_4. This result suggest that the reaction involve may have more intermediate reactions. The possible additional reactions may be written as:

$$2TiO_{2(s)} + 2Mg_{(s)} = Mg_2TiO_{4(s)} + Ti_{(s)} \tag{6}$$

$$Mg_2TiO_{4(s)} + 2Mg_{(s)} = 4MgO_{(s)} + Ti_{(s)} \tag{7}$$

The amount of Mg in the precursor played an important role in the overall reactions. The calculated adiabatic temperature of reaction from Equation 2 by HSC® program when using 2, 2.5, 3, and 3.5 mole of Mg were 2,739.3, 2,505.9, 2,301.2, and 2,125.0°C, respectively. When less amount of Mg to TiO_2 mole ratio was used as precursors (System 1), the higher adiabatic temperature cause the formation of Mg_2TiO_4 which was more stable at higher temperature left in the products (Equation 6). Increasing the amount of Mg to TiO_2 mole ratio (System 2 and 3), the adiabatic temperature of reaction decrease from higher energy used in melting more Mg and the Mg_2TiO_4 disappeared (Equation 7) from the products. These were agreeing well with the calculation showed in Figure 1(a) in which Mg_2TiO_4 formed at higher temperature than 2,600°C. On the other hand, using excess Mg in the precursors (System 4) would result in Mg left in the products.

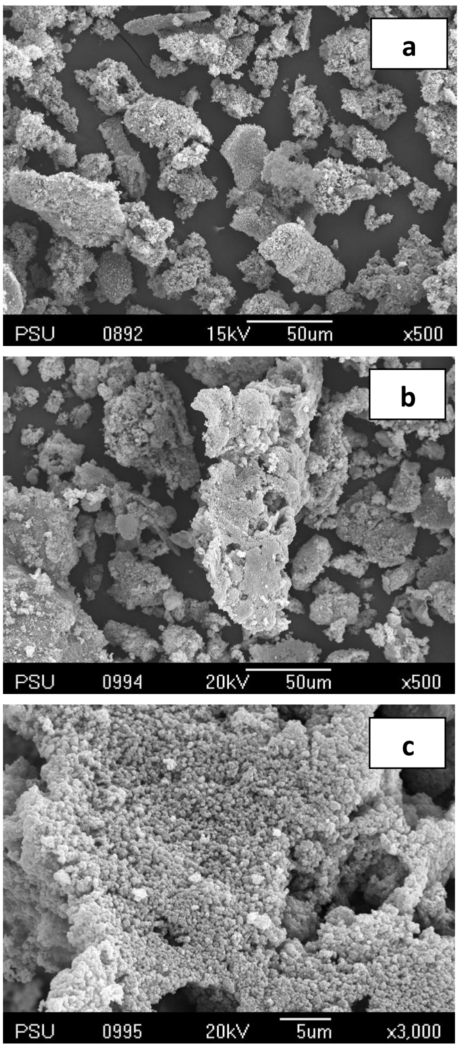


Figure 6. SEM micrographs of typical products before leached (a) and after leached (b) and (c).

Figure 6 shows typical SEM micrographs of the products from SHS reaction before and after the leaching process. The morphology of products before leaching process shows a composite of MgO and TiC (Figure 6a), but after leaching reveals and agglomerated particles of fine particle with smooth surface of TiC (Figure 6b and 6c) as identified by XRD pattern in Figure 7.

5. Conclusions

The TiC powders were produced from leaching out MgO from TiC-MgO composite that was in-situ synthesized via a self-propagating high temperature synthesis reaction from precursors of TiO_2, wood dust, and Mg. The incomplete reaction was observed when using molar ration of Mg to TiO_2 of 2. As the relative molar ratio of Mg to TiO_2 increased

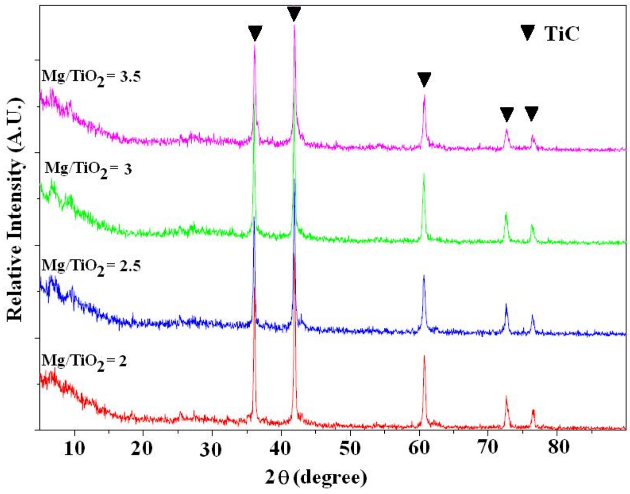


Figure 7. XRD patterns of reaction products varying with different relative mole ratio of Mg to TiO_2 (after leached).

(2.5 and 3), the SHS reactions were completed and formed TiC-MgO composites. When excess Mg was used (molar ratio of Mg to TiO_2 was 3.5), it was found that Mg left in the products without taken part in any reaction. The final products after the leaching process shows only TiC phase left in the system for all the different system of precursors.

Acknowledgements

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

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