Synthesis of Titanium Carbide from Wood by Self-Propagating High Temperature Synthesis

Sutham Niyomwas
Ceramic and Composite Material Research Group (CMRG)
Department of Mechanical Engineering, Faculty of Engineering,
Prince of Songkla University, Hat Yai, Songkhla, Thailand 90112

Abstract: Titanium carbide (TiC) particles were obtained in situ by self-propagating high temperature synthesis (SHS) of wood dusts with TiO2 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 TiO2 and wood dusts were investigated. XRD and SEM analyses indicate complete reaction of precursors to yield TiC-MgO as product composite. The synthesized composites were leached with 0.1M HCl acid solution to obtain TiC particles as final products.

Key Words: self-propagating high temperature synthesis (SHS), wood dust, titanium carbide

1. INTRODUCTION

Titanium carbide 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 [1].

TiC can be synthesized by direct reaction between Ti and carbon under vacuum at high temperature of 1900°C-2900°C [2]. This method is expensive because of the high cost of elemental Ti and energy intensive process. From these reasons many synthesis routes to produce TiC were studied and proposed such as thermal plasma synthesis [3], carbothermal reduction process [4,5], chemical vapour deposition (CVD) [6], and self-propagating high temperature synthesis (SHS) [7,8]. The thermal plasma synthesis and CVD have very high operating cost; on the other hand carbothermal reduction of TiO2 with carbon require high temperature furnace to synthesis at 1500°C.

SHS process is considered as less expensive operating cost to produce TiC with low cost reactor and less require power source. One weak point of this method is requiring expensive starting materials in pure elemental materials of Ti and C [8]. This can be solve by using TiO2, C and Mg in SHS process to synthesis of TiC [7].

In this study, the productions of TiC powders were obtained by self-propagating high temperature synthesis (SHS) of mixture of wood dusts as a carbon source, TiO2 and Mg couple with leaching process. The effects of increasing Mg mole ratio to the precursor mixture of TiO2 and wood dusts were investigated.

2. THERMODYNAMIC ANALYSIS

Calculations for equilibrium concentration of stable species produced by SHS reaction were performed based on the Gibbs energy minimization method [9]. 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 ideal gas mixture, and condensed phases are pure. The total Gibbs energy of the system can be expressed by the following equation:

\[
G = \sum_{gas} n_i g_i^{\circ} + RT \ln P_i + \sum_{condensed} n_i g_i^{\circ} + \sum_{solution} n_i g_i^{\circ} + RT \ln x_i + RT \ln y_i
\]

where, \( G \) is the total Gibbs energy of the system; \( g_i^{\circ} \) is the standard molar Gibbs energy of species \( i \) at \( P \) and \( T \); \( n_i \) is the molar number of species \( i \); \( P \) is the partial pressure of species \( i \); \( x_i \) is the mole fraction of species \( i \); and \( y_i \) is the activity coefficient of species \( i \). The exercise is to calculate \( n_i \) such that \( G \) is a minimized subject to mass balance constraints.

The equilibrium composition of TiO2−Mg−C system at different temperatures was calculated using Gibbs energy minimization method and the result is shown in
Mean Particle Size = 46.34 µm

Figure 1. The overall chemical reactions can be expressed as:

\[
\text{TiO}_2(s) + C(s) + 2\text{Mg}(s) = \text{TiC}(s) + 2\text{MgO}(s) \quad (2)
\]

During the process of SHS, the mixture of TiO\textsubscript{2}, Mg and C may interact to form some possible compounds as following intermediate chemical reactions below:

\[
\begin{align*}
\text{TiO}_2(s) + 2\text{Mg}(s) &= \text{Ti}(l) + 2\text{MgO}(s) \quad (3) \\
\text{Ti}(l) + C(s) &= \text{TiC}(s) \quad (4) \\
\text{TiO}_2(s) + 2C(s) &= \text{Ti} + 2\text{CO}(g) \quad (5)
\end{align*}
\]

3. EXPERIMENTAL

3.1 Materials and Experimental Set-up
The raw materials used in this paper were Mg, Wood dust (WD: carbon source), and TiO\textsubscript{2} powders whose properties are listed in Table I.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Vendor</th>
<th>Size</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>Riedel-deHaen</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>Unilab</td>
<td>-325 mesh</td>
<td>99.5</td>
</tr>
<tr>
<td>Wood Dust</td>
<td>Para-rubber wood</td>
<td>46.34 µm</td>
<td>-</td>
</tr>
</tbody>
</table>

The particles size of wood dust was analyzed by LPSA (laser particle size analyzer: COULTER LS230) as shown in Figure 2 which had mean particle size of 46.34 µm. SEM micrographs of wood dust precursor is presented in the Figure 3. The elemental analysis of wood dust was performed by dynamic flash combustion technique (CE Instruments Flash 1112 Series EA CHNS-O Analyzer) which had the result of mass % of 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 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.

The dried woody materials were mixed with the TiO\textsubscript{2} and magnesium powders by mortar and pestle. The C/TiO\textsubscript{2} molar ratio was fixed at 1.0 and Mg/TiO\textsubscript{2} molar ratios were changed from 2 to 3.5. The mixture precursor was then loaded into alumina crucible located in 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 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 Kα 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 SHS reactions can be identified by XRD technique (shown in Figure 5) and listed in the Table 2.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Product Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)TiO₂ + WD + 2Mg</td>
<td>TiC, MgO, Mg₂TiO₄</td>
</tr>
<tr>
<td>2)TiO₂ + WD + 2.5Mg</td>
<td>TiC, MgO</td>
</tr>
<tr>
<td>3)TiO₂ + WD + 3Mg</td>
<td>TiC, MgO</td>
</tr>
<tr>
<td>4)TiO₂ + WD + 3.5Mg</td>
<td>TiC, MgO, Mg</td>
</tr>
</tbody>
</table>

This can be explained by the propose reactions shown in Eq.(3) to (5). At first, the thermit reaction between TiO₂ and Mg took place and yielded Ti and MgO as products. The thermit reaction also released huge heat of reaction in which transformed the natural cellulose of WD into carbon and also melted Ti element. The melted Ti coats the C powder and the liquid-solid reaction of Eq. (4) took place. For the first system of precursors from Table 2, the product phases consist of not only TiC and MgO but the complex oxide of Mg₂TiO₄. This result suggest that the reaction involve may have more intermediate reactions. The possible additional reactions may be written as:

\[
2\text{TiO}_2 + 2\text{Mg} \rightarrow \text{Mg}_2\text{TiO}_4 + \text{Ti} \quad (6)
\]

\[
\text{Mg}_2\text{TiO}_4 + 2\text{Mg} \rightarrow 4\text{MgO} + \text{Ti} \quad (7)
\]

The amount of Mg in the precursor played an important role of overall reactions. When less amount of Mg to TiO₂ mole ratio was used as precursors (system 1), the uncompleted reaction happened and Mg₂TiO₄ left in the products (Eq. (6)). When in crease the amount of Mg to TiO₂ mole ratio (system 2 and 3) the Mg₂TiO₄ disappear (Eq. (7)). In 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 5:** XRD patterns of reaction products varying with different relative mole ratio of Mg to TiO₂ (before leached)
5. CONCLUSIONS

The TiC powders were produced from leaching out MgO from TiC-MgO composite that in-situ synthesized via self-propagating high temperature synthesis reaction from precursors of TiO2-Wood Dust-Mg. The incompleted reaction was observed when using molar ration of Mg to TiO2 of 2. As the relative molar ratio of Mg to TiO2 increased (2.5 and 3), the SHS reactions were completed and formed TiC-MgO composites. When excess Mg was used (molar ratio of Mg to TiO2 was 3.5), it was found that Mg left unreact in the products. The final products after leaching process shows only TiC phase left in the system for all the different precursors.

6. ACKNOWLEDGEMENTS

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

7. REFERENCES