

## Synthesis of Nano-sized TiB<sub>2</sub> Powder by Self-Propagating High Temperature Synthesis

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### ABSTRACT

*The nano-sized titanium diboride (TiB<sub>2</sub>) was synthesized by self-propagating high temperature synthesis (SHS) from a reactant mixture of TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, Mg and NaCl. The NaCl was added to the reactant mixture with a difference amount from 0 to 2 moles as a diluent. The synthesized product was a composite of TiB<sub>2</sub>, MgO, Mg<sub>2</sub>TiO<sub>4</sub> and NaCl. The final product of TiB<sub>2</sub> was obtained from washing out NaCl from synthesized product by distilled water and leaching the rest with 37% HCl. The products were investigated by XRD, SEM and BET to identify phases, study morphology and size estimation. The results showed that increase amount of NaCl into the precursor, could reducing the size of TiB<sub>2</sub> particle to nanometer range of 201-167 nm.*

**Key words:** Titanium diboride (TiB<sub>2</sub>), Self-propagation High Temperature Synthesis (SHS), NaCl

### INTRODUCTION

TiB<sub>2</sub> is an intermetallic compounds between titanium and boron system which has the excellence properties such as high melting point (3225°C), high hardness (25 GPa), chemical inertness and resistance of acids. (Subramanian et al., 2007; Calka and Oleszak, 2007).

At presents, the TiB<sub>2</sub> powder was successfully synthesized with the different processes such as the carbothermal reduction of TiO<sub>2</sub>, B<sub>4</sub>C and C powder (Subramanian et al., 2007), an electric discharge assisted mechanical milling of Ti and B powder (Calka and Oleszak, 2007), cold spraying of Ti, B and Cu powder (Dudina et al., 2007) and self-propagating high temperature synthesis (SHS) of Mg, TiO<sub>2</sub> and H<sub>3</sub>BO<sub>3</sub> powder (Khanra et al., 2007).

The self-propagating high temperature synthesis (SHS) is a once process to synthesis  $TiB_2$  powder with the exploits self-sustaining solid-flame combustion which develops very high temperature inside materials over a short period. It therefore offers many advantages over traditional methods, such as a much lower energy lost, a lower environmental impact, more convenient many manufacturing process and unique properties of the product (Niyomwas, 2007; Chaichana et al., 2007; Suryanarayana, 2001; Millet et al., 1996).

Many studies have shown the particle size reduction by adding NaCl into the precursors of SHS process (Khanra et al., 2004; Nerisyan et al., 2003). In this work the combustion of the system  $TiO_2$ ,  $B_2O_3$  and Mg in the presence of NaCl were investigated with the intention of nano-sized  $TiB_2$  powder synthesis.

### MATERIALS AND METHODS

The raw materials used in this study were  $TiO_2$  (79.90% purity),  $B_2O_3$  (99.0% purity), Mg (99.0% purity) and NaCl (99.0% purity) powder.

The experimental set up in this work was 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 (Chaichana et al., 2007).

The precursor powders of  $TiO_2$ ,  $B_2O_3$ , Mg and NaCl were weighted as mole ratio of 1:1:5: n (n = 0, 0.5, 1.0, 1.5 and 2.0), respectively, and mixed in a planetary ball mill (Fritsch GMBH, Pulverisette 6) for 15 min. The obtained mixture was uniaxially pressed to form cylindrical pellets (25.4 mm diameter) represented in Figure 1(a). Green sample was 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 one sample end by using a heated tungsten filament. Then, under self-propagating conditions, the reaction front travels until reaches the opposite end of the sample. The synthesized product shown in Figure 1(b) was washed with distilled water to get rid of NaCl and the byproduct MgO was leached out by 37%HCl.



**Figure 1.** Photographs of (a) green pellet of precursors and (b) as-synthesized product.

## RESULTS AND DISCUSSION

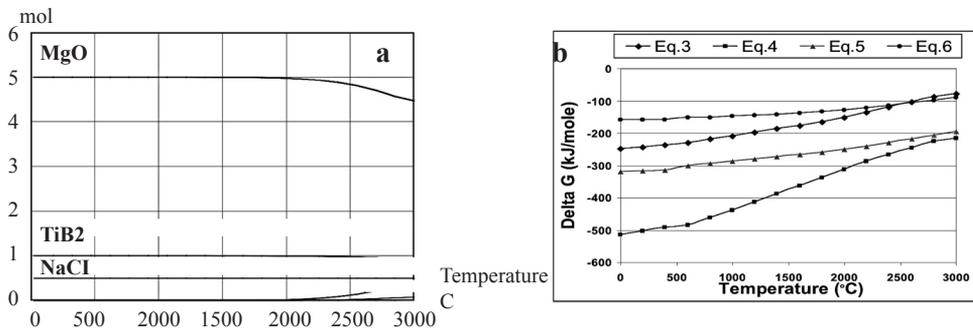
### Thermodynamics Analysis

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 ideal gas mixture, and condensed phases are pure. The total Gibbs energy of the system can be expressed by the following equation:

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

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  $\gamma_i$  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  $TiO_2$ - $B_2O_3$ - $Mg$ - $NaCl$  system at difference temperature was calculated using Gibbs energy minimization method and the results was shown in Figure 2(a). The overall chemical reaction of the  $TiO_2$ - $B_2O_3$ - $Mg$ - $NaCl$  system can be expressed as:

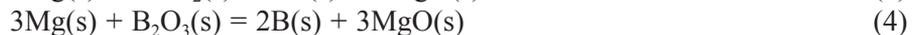


**Figure 2.** Thermodynamics analysis.

(a) Equilibrium composition of  $TiO_2$ - $B_2O_3$ - $Mg$ - $NaCl$  system in Ar gas atmosphere

(b) Relation of Gibbs energy of reactions and temperature

During the process of SHS the reactants of  $TiO_2$ ,  $B_2O_3$ ,  $Mg$  and  $NaCl$  may be interacted to form some possible compounds as following intermediate chemical reactions below:



It can be seen from Figure 2(a) that it is thermodynamically feasible to synthesis composites by heat up the system of reaction (1). As accepted that the reaction can be self-sustained combustion when adiabatic temperature of the reaction higher than 1800°C (Moore and Feng., 1995). From calculation, adiabatic temperature ( $T_{ad}$ ) of the reaction system is higher than 1800°C, thus the using of SHS is feasible for this systems. From Figure 2(b) the reaction (4) is the lowest Gibbs energy of reaction. Mg reacts first with  $B_2O_3$  then with  $TiO_2$  to yield elemental boron and titanium, which combine to give  $TiB_2$ . Gibbs energy of reaction (5) (yield  $TiB_2$ ) is lower than that of reaction (6) (yield  $TiB$ ) means  $TiB_2$  is more stable than  $TiB$  for all temperature range.

Adiabatic temperature of each sample with the difference amount of NaCl was calculated and shown in Table 1 (HSC Chemistry<sup>®</sup>).

**Table 1.** Adiabatic temperature of the chemical reaction of  $TiO_2$ - $B_2O_3$ -Mg-NaCl system.

NaCl (mole)	0	0.5	1.0	1.5	2.0
$T_{ad}$ (°C)	2831.8	2831.8	2635.2	2438.6	2266.8

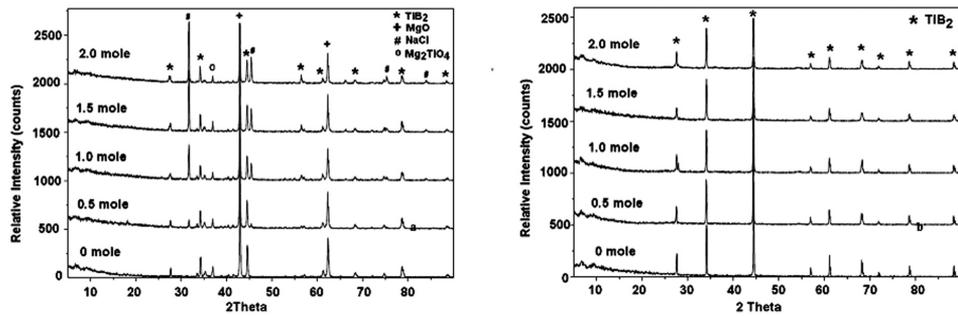
It can be seen that  $T_{ad}$  of all reactions were higher than 1800°C thus those reactions were feasible for SHS process. The reduction of  $T_{ad}$  with adding NaCl resulted from the melting of NaCl and absorbed by molten salt.

#### Effect of NaCl for the synthesized product

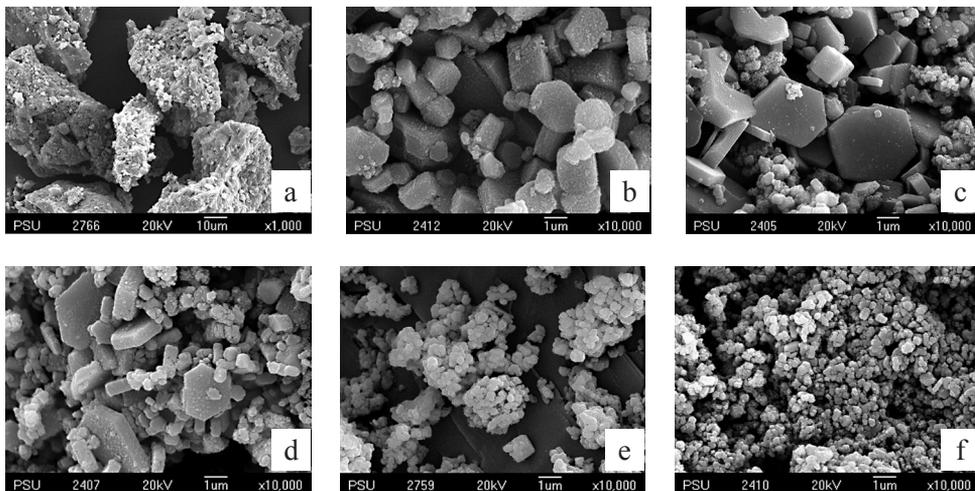
The final product  $TiB_2$  were obtained from washing out NaCl from synthesized product by distilled water and leaching the rest with 37% HCl for 12 hours and identifying with XRD were shown in Figure 3(a) and (b).

It can be seen in Figure 3(a) the intensity peak of NaCl was increased with the increasing of the NaCl in the precursor. The intermediate phase of  $Mg_2TiO_4$  was found in every condition which may be the incomplete reaction of reaction (3) and Figure 3(b) the final products clearly confirm the formation of  $TiB_2$  for all conditions. The SEM image in Figure 4(a) shows an agglomerated of oxide compounds ( $MgO$  and  $Mg_2TiO_4$ ),  $TiB_2$  and NaCl.

Figure 4(b), (c), (d), (e) and (f) showed the surface morphology after leaching of  $TiB_2$  with NaCl of 0, 0.5, 1.0, 1.5 and 2.0 moles respectively. The microstructure observations of  $TiB_2$  particles revealed the generation of fine powders. By the addition of NaCl, the particles were observed be very fine and narrow particle size distribution. Since the studied SHS reactions were very high temperature (> 2266.8°C) and achieved in less than a minute, the evaporation of NaCl (boiling point of NaCl is 1465°C) was expected. The presence of NaCl in the XRD analysis (Figure 3(a)) indicates that all the NaCl did not evaporate out of the system after the synthesis. The melted NaCl that remain in the system during the SHS reaction may play an important role of coating on the nucleated  $TiB_2$  powder that could reduce the grain growth of the particle and finally decrease the particle sizes.



**Figure 3.** XRD patterns of synthesized products (a) before leaching (b) after leaching.

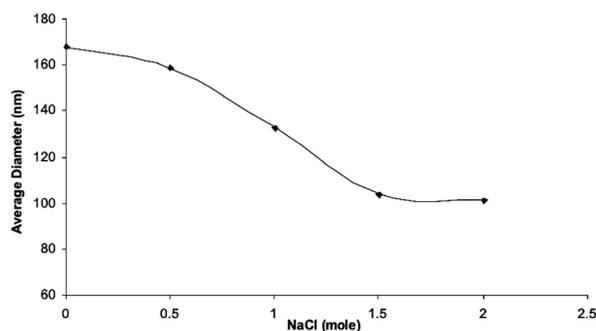


**Figure 4.** SEM images of (a) typical synthesized product before leaching (the synthesized product with NaCl 0.5 mole) and synthesized product after leaching (b) NaCl 0 mole (c) NaCl 0.5 mole (d) NaCl 1.0 mole (e) NaCl 1.5 mole (f) NaCl 2.0 mole.

The average surface area of the synthesized product was used to measure the particle sized using the COUNTER SA 3000 analyzer (BET). Assuming the sample powder particles to be spherical, once the total surface area of sample powders has been measured, the average particle size of product can be obtained from the following equation:

$$D = \frac{6}{A_p} \tag{7}$$

where D is the average diameter of TiB<sub>2</sub> powders, A is the surface area of sample powders per gram and is TiB<sub>2</sub> density (Tong and Reddy, 2005; Ringuede et al., 2001).



**Figure 5.** Particle size of  $TiB_2$  with NaCl 0-2.0 mole.

Figure 5 the trends of the particle sized of synthesized product  $TiB_2$  was reduced with the increasing among of NaCl from 0-2.0 mole and the particle sized was found in the range of 201-167 nm.

### CONCLUSION

The nano-sized  $TiB_2$  powder was successfully synthesized via self-propagating high temperature synthesis (SHS) from the reactants of  $TiO_2$ ,  $B_2O_3$ , and Mg with the mole ratio 1:1:5 and  $nNaCl$  ( $n = 0.5-2.0$  mole). As increasing the amount of NaCl in precursor mixture the resulted product showed decreasing of particle size of  $TiB_2$  powder.

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