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Materials Research Bulletin 42 (2007) 312-318

Materials Research Bulletin

www.elsevier.com/locate/matresbu

# Effect of HCl concentration on TiB<sub>2</sub> separation from a self-propagating high-temperature synthesis (SHS) product

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#### Abstract

This paper presents a synthesis of TiB<sub>2</sub> powder via self-propagating high-temperature synthesis (SHS) method using a mixture of TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and Mg followed by acid leaching. In the acid leaching step, the MgO content in the SHS product was leached in different HCl concentrations. X-ray diffraction (XRD) analysis showed that when 9.3 M HCl was used, the leached SHS product was found similar to that of the commercial TiB<sub>2</sub> powder. However, scanning electron microscopy (SEM) and BET surface area analysis revealed that the leached product was agglomerated and exhibited very high surface area.  $\bigcirc$  2006 Elsevier Ltd. All rights reserved.

Keywords: A. Ceramics; B. Chemical synthesis; C. X-ray diffraction

## 1. Introduction

 $TiB_2$  (31.1 wt.% boron) is a transition metal boride, with high melting point (~3243 K), high hardness, low density, high electrical conductivity, excellent wear and corrosion resistance properties.  $TiB_2$  is widely used as ballistic armour, cathodes and thermocouple sheaths in Hall-Heroult cells for aluminum smelting, crucibles for molten metals, metal evaporation boats, coating on cutting tools and in MMCs and CMCs [1–4].  $TiB_2$  powder is synthesized by different methods such as carbothermic reduction of  $TiO_2$  and  $B_2O_3$  mixture, gas-phase Na/TiCl<sub>4</sub>/BCl<sub>3</sub> flame reaction, direct reaction of Ti, its oxide and its hydrides with elemental boron, reaction of NaBH<sub>4</sub> and TiCl<sub>4</sub>, and ball-milling or self-propagating high-temperature synthesis (SHS) followed by acid leaching technique [2–9].

A variety of advanced ceramics, intermetallics, organic and inorganic compounds, oxygen free single crystals, and polymers can be synthesized by using different SHS techniques [1–10]. In the SHS process, after initiation, reaction becomes self-sustaining and propagates in the reactant mixture. A high amount of heat, which is generated during the process accelerates the reaction rate and thus it makes the process highly productive and economically feasible for different production scales. However, in case of TiB<sub>2</sub> synthesis, after a high velocity process with SHS, a following "time consuming" leaching procedure has to be carried out to eliminate byproduct MgO. In the literature, leaching procedures for MgO eliminations were examined between 1 and 2 M HCl, 1/100 and 1/5 solid/liquid (S/L) ratios and 1 and 2 h for different temperatures [4–8] and it was also indicated that with a complete MgO elimination, a small amount of TiB<sub>2</sub> also dissolves and the smaller crystallite size of TiB<sub>2</sub> accelerates the dissolution rate [6–8].

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<sup>0025-5408/\$ –</sup> see front matter 0 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.materresbull.2006.05.032

In this paper, the synthesis of  $TiB_2$  through SHS followed by acid leaching was investigated. In the experiments,  $TiO_2$  and  $B_2O_3$  were reduced by magnesium under argon atmosphere. Then MgO content of the SHS products was leached in different HCl concentrations to achieve pure  $TiB_2$  powder within 30 min.

#### 2. Theoretical background

The specific heat generated in a metallothermic reaction dictates whether the reaction can self-propagate or not. The specific heat of a reaction is evaluated by dividing reaction's enthalpy by the sum of the products weight. If this value is between 2250 and 4500 J/g, the process results in a controlled and self-sustaining reaction [11–13]. The chemical reactions of TiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> mixtures reacted with suitable reducing agents are shown in Eqs. (1)–(3). Specific heat values of these reactions were calculated using Factsage 5.3 [14] thermochemistry software as 3950, 3539 and 3573 J/g, respectively. Although all these reactions are self-sustaining, for TiB<sub>2</sub> synthesis, Eq. (1) is the favored process in SHS technique having very high adiabatic temperature ( $T_{ad} = \sim 3105$  K), since MgO can be leached out easily from the SHS product by following acid leaching process [4–8].

$$TiO_2 + B_2O_3 + 5Mg = TiB_2 + 5MgO$$
 (1)

$$TiO_2 + B_2O_3 + 5Ca = TiB_2 + 5CaO$$
<sup>(2)</sup>

$$TiO_2 + B_2O_3 + (10/3)AI = TiB_2 + (5/3)AI_2O_3$$
(3)

The leaching process, which follows the SHS step is generally realized using diluted HCl solutions to obtain  $TiB_2$  as a filter cake. MgO dissolution reaction in HCl acid solution is shown in Eq. (4). It was indicated that  $TiB_2$  also dissolves in hot and concentrated HCl (1:1) solutions up to 40% [9].

$$MgO + 2HCl = Mg^{2+} + 2Cl^{-} + H_2O$$
(4)

#### 3. Experimental

TiO<sub>2</sub> (98.84% pure, mean particle size of 33  $\mu$ m), B<sub>2</sub>O<sub>3</sub> (99% pure and particle size < 53  $\mu$ m) and magnesium (99.95% pure and particle size <150  $\mu$ m) were used as SHS reaction mixture. B<sub>2</sub>O<sub>3</sub> was obtained by the calcination of 99.5% pure boric acid (Eti Holding Inc.) at 1073 K for 2 h in a nickel container followed by grinding and sieving. The SHS process was carried out in a MgO lined crucible with the inner height of 300 mm and inner diameter of 100 mm. Approximately 600 g of the dried mixture, which were prepared calculating the stoichiometric ratios of the TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and Mg from Eq. (1) were mixed thoroughly for 1 h in a Turbula mixer and it was poured into the SHS crucible. Cr–Ni resistance wire was placed at the top of the compacted mixture powder and the crucible was closed by using a steel cover. Under flow of argon gas, the crucible atmosphere was purged and then the experiment was initiated by passing electricity through the resistance wire. After the SHS process completed, the crucible was left to soak keeping flow of argon gas for 30 min. The SHS product was discharged, crushed and ground. The phase compositions of the SHS product were examined by X-ray diffractometer (Rigaku RINT, Co K $\alpha$  radiation at 2°/min scanning rate).

In the leaching step, the SHS product was leached by water and HCl solution. The effect of the acid concentration on the selective leaching was studied using the concentration range of 0–9.25 M HCl (Merck). All leaching experiments were investigated at 1/5 S/L ratio, 293 K and 400 rpm stirring rate for 30 min using 10 g of specimens. The temperature variations during the experiments were monitored using a contact thermometer. Water was added gradually when loss of water was observed through evaporation after obtaining highest solution temperature values. At the end of the experiments, filter cakes were obtained by S/L separation method. The solubilities of boron, magnesium and titanium in the spent solutions were analyzed using atomic absorption spectrometer (Perkin-Elmer 1100B). The phase compositions of the filter cakes were examined by X-ray diffractometer. The morphologies of the filter cakes were analyzed by scanning electron microscope (Jeol JSM-840). The specific surface areas and mean particle size of the filter cakes were measured by using BET absorption method (Quantachrome Nova 2200e) and sedigraph (Malvern, Mastersizer 2000), respectively.

Table 1The sieve analysis of the SHS product

Sieve size (µm)	wt.%
+500	0.4
-500, +425	0.4
-425, +300	1.5
-300, +250	1.6
-250, +212	2.0
-212, +150	6.3
-150, +100	9.5
-100, +53	21.8
-53	56.5
Total	100.0



Fig. 1. XRD analysis of the SHS product.

## 4. Results and discussion

The SHS product was obtained in the form of black, spongy solid. The sieve analysis and XRD analysis of the ground SHS product are given in Table 1 and Fig. 1, respectively. XRD patterns showed mainly MgO and TiB<sub>2</sub> phases and also minor phases as magnesium borate (Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>) and magnesium titanate (Mg<sub>2</sub>TiO<sub>4</sub>) which were formed by following reaction equations:

$$\mathbf{B}_2\mathbf{O}_3 + 3\mathbf{M}\mathbf{g}\mathbf{O} = 3\mathbf{M}\mathbf{g}\mathbf{O} \cdot \mathbf{B}_2\mathbf{O}_3 \tag{5}$$

$$\mathrm{TiO}_2 + 2\mathrm{MgO} = 2\mathrm{MgO} \cdot \mathrm{TiO}_2 \tag{6}$$

In the leaching procedure, the temperature change in the solutions is given in Fig. 2. A rise in solution temperature with increasing acid concentration showed that leaching of MgO with HCl was fairly exothermic. No temperature change was observed in the solution with water leaching. Highest temperature values were monitored as 308, 323, 326 and 332 K, as HCl concentrations increased to 2.6, 3.7, 5.6 and 7.4 M. However, when 9.3 M HCl was used, the temperature reached more than 373 K within 4 min and resulted in a rapid loss of 20% of the water. The effect of the HCl concentration on magnesium, boron and titanium dissolutions are given in Fig. 3. As can be seen, magnesium and boron dissolutions increased with increasing HCl concentration. However, the evident dissolution of titanium began only after 5.6 M HCl and exhibited a sharp increase after 6.7 M HCl giving a light violet color to the solution. After 7.4 M HCl, because of decreasing MgO content, while rate of Mg dissolution slowed down,



Fig. 2. Effect of HCl concentrations on solution temperature.



Fig. 3. Effect of HCl concentrations on Mg, B and Ti dissolutions.



Fig. 4. XRD analysis of the unleached, leached SHS products and commercial  $TiB_2$  (slope = -15).



Fig. 5. SEM micrographs of: (a) commercial TiB<sub>2</sub> (2000×) and (b) leached (9.3 M HCl) SHS product particles (1000×).

Ti and B concentrations kept on increasing due to  $TiB_2$  dissolution. It is clear that in order to suppress the undesirable MgO in the filter cake, it is necessary to increase HCl concentration sacrificing small amount of  $TiB_2$ . When 9.3 M HCl was used, filter cake turned from black to gray, which is the original color of  $TiB_2$ . It was also observed that after 5.6 M HCl, the low pH values of the final solutions were evident that HCl were not consumed totally.

XRD analysis of the unleached and leached SHS products and commercial  $TiB_2$  are shown in Fig. 4. No difference was obtained between unleached and water leached SHS product. A increase in HCl concentration showed that intensities of MgO peaks decreased whereas the intensities of  $TiB_2$  peaks increased. The XRD pattern of the SHS product leached with 9.3 M HCl showed no evidence of MgO or minor  $Ti_2B_2O_4$  and  $MgB_2O_3$  phases and was found similar to that of the commercial  $TiB_2$  powder.

The SEM micrographs of commercial TiB<sub>2</sub> (HcStarck D grade) and the SHS product leached with 9.3 M HCl are given in Fig. 5(a) and (b). The commercial powder was composed of spherical particles of less than 10  $\mu$ m in size, but the leached SHS product had agglomerated particles in different size ranges (<1 to ~30  $\mu$ m), which are due to the high adiabatic temperatures and cooling rate of the SHS reaction [4–6]. However, the literature indicates that it is possible to achieve sub-micrometer sized (<100 nm) TiB<sub>2</sub> with the addition of NaCl as SHS diluents [4,5].

Table 2 The mean particle size and surface area of commercial  $\rm TiB_2$  and the leached SHS product

	Mean particle size (µm)	Surface area (m <sup>2</sup> /g)
Commercial TiB <sub>2</sub>	4.978	1.74
Leached SHS (9.3 M HCl)	9.605	23.22

The mean particle sizes and surface areas of the commercial TiB<sub>2</sub> and SHS product leached with 9.3 M HCl are given in Table 2. The mean particle size of the leached SHS product was approximately twice as large as that of commercial TiB<sub>2</sub>. The specific surface area of the leached SHS product, which was very high compared to that of commercial TiB<sub>2</sub> can be ascribed to the highly porous structures formed during HCl leaching [6]. Closer SEM micrographs of unleached and leached SHS particles given in Fig. 6(a) and (b) confirm that after the leaching treatment, the MgO phase of the unleached particle left the TiB<sub>2</sub> structure alone resulting smaller network grains having very high surface areas. Fig. 7 shows that these small grains are present as hexagonal prism ranging from 0.3 to 1.3  $\mu$ m in length and about 0.5  $\mu$ m in thickness due to the close-packed hexagonal crystal morphology of TiB<sub>2</sub> [15–18].



Fig. 6. SEM micrographs of: (a) an unleached (5000×) and (b) leached (9.3 M) SHS product particles (5000×).



Fig. 7. SEM micrograph of TiB<sub>2</sub> grains of a leached (9.3 M) SHS product particle (15,000×).

### 5. Conclusion

After the SHS process with magnesiothermic reduction of  $TiO_2$  and  $B_2O_3$  under argon gas,  $TiB_2$  powder was separated from byproduct MgO by HCl acid leaching. The XRD analysis showed that SHS product was mainly composed of MgO and  $TiB_2$  phases along with minor  $Mg_3B_2O_6$  and  $Mg_2TiO_4$  phases. Comparable experimental product to the commercial  $TiB_2$  was synthesized by leaching of the SHS product using 9.3 M HCl solution at 1/5 S/L ratio for 30 min. BET and SEM analysis revealed that this product consisted of porous agglomerated particles sized between less than 1 to around 30  $\mu$ m, which exhibited very high surface area (23.22 m<sup>2</sup>/g).

## Acknowledgements

The authors are pleased to acknowledge the financial support for this research from BOREN (National Boron Research Institute of Turkey) and TUBITAK (The Scientific and Technological Research Council of Turkey, project no: 105M339).

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