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# Formation of TiB<sub>2</sub> by volume combustion and mechanochemical process

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#### Abstract

Titanium diboride was produced both by volume combustion synthesis (VCS) and by mechanochemical synthesis (MCP) through the reaction of TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and Mg. VCS products, expected to be composed of TiB<sub>2</sub> and MgO, were found to contain also side products such as Mg<sub>2</sub>TiO<sub>4</sub>, Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, MgB<sub>2</sub> and TiN. HCl leaching was applied to the reaction products with the objective of removing MgO and the side products. Formation of TiN could be prevented by conducting the VCS under an argon atmosphere. Mg<sub>2</sub>TiO<sub>4</sub> did not form when 40% excess Mg was used. Wet ball milling of the products before leaching was found to be effective in removal of Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub> during leaching in 1 M HCl. When stoichiometric starting mixtures were used, all of the side products could be removed after wet ball milling in ethanol and leaching in 5 M HCl when pure TiB<sub>2</sub> was obtained with a molar yield of 30%. Pure TiB<sub>2</sub> could also be obtained at a molar yield of 45.6% by hot leaching of VCS products at 75 °C in 5 M HCl, omitting the wet ball milling step. By MCP, products containing only TiB<sub>2</sub> and MgO were obtained after 15 h of ball milling. Leaching in 0.5 M HCl for 3 min was found to be sufficient for elimination of MgO. Molar yield of TiB<sub>2</sub> was 89.6%, much higher than that of VCS. According to scanning electron microscope analyses, the TiB<sub>2</sub> produced had average grain size of 0.27 ± 0.08 µm. © 2007 Elsevier Ltd. All rights reserved.

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#### 1. Introduction

Titanium diboride  $(TiB_2)$  is a transition-metal boride which has important chemical, electrical, thermal and mechanical properties. It is the most stable among the several titanium–boron compounds [1]. It has high hardness, high electrical conductivity, thermal stability, high melting point [2] and high wear resistance [3,4]. It is chemically inert to molten metals [5]. Due to these attractive properties, it is utilized in variety of applications including cutting tools, wear resistant parts [6], armors [7], and as a cathode material in electrolytic production of aluminum [8]. It also finds application as a grain refining agent in aluminum castings and in production of vacuum metallization boats [9,10].

There are a number of methods for production of  $TiB_2$ . It can be produced through a solid state reaction between titanium and boron [11]. It is produced from oxides by carbothermic [12] or metallothermic [13,14,5] reduction processes. Fused salt electrolysis [15–17], vapor phase deposition [18] and mechanochemical synthesis [19,20] are other techniques for production of titanium diboride.

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In the metallothermic process,  $TiB_2$  is synthesized through reduction of  $TiO_2$  and  $B_2O_3$  by magnesium according to:

$$\mathrm{TiO}_2 + \mathrm{B}_2\mathrm{O}_3 + 5\mathrm{Mg} = \mathrm{TiB}_2 + 5\mathrm{MgO} \tag{1}$$

Due to high exothermic enthalpy of reaction (1) (-1120 kJ, as calculated from the data compiled by Turkdogan [21]), it can be started by partial ignition of the reactant mixture, which then becomes self-sustaining. Due to this property, self-propagating high-temperature synthesis (SHS) method can be used for production of TiB<sub>2</sub> [13,14]. Apart from SHS, if the reactants are heated at a sufficiently fast rate (>15 °C/min), at a certain ignition temperature the reaction takes place instantaneously with a sudden release of heat. Since all of the reactants are converted into products simultaneously throughout the sample volume, this technique is termed as the volume combustion synthesis (VCS) or thermal explosion [22].

MgO, formed in the products through these combustion synthesis techniques, can be removed from the products by leaching in dilute HCl solutions easily [13,14]. However, in both SHS and VCS, it was reported that during reaction (1), side reactions take place leading to formation of  $Mg_2TiO_4$  and  $Mg_3B_2O_6$  side products [13,14]. These phases are difficult to leach and they require high concentrations of acids during leaching. This causes loss of TiB<sub>2</sub> due to its dissolution in HCl solutions [14]. However, in these studies efficiency of the process in terms of TiB<sub>2</sub> yield was not stated. In the present study, prevention and elimination of these side products formed during volume combustion was investigated.

Mechanochemical processing (MCP) or synthesis is another method for production of TiB<sub>2</sub>. Mechanochemical processing is the term applied to the powder process in which chemical reactions and phase transformations take place due to application of mechanical energy [23]. It is a very efficient way to prepare many metal alloys and ceramic compositions [24]. In order to produce TiB<sub>2</sub>, this technique has been used by reaction between TiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and Mg during milling for between 10 and 15 h [20]. The resulting products are TiB<sub>2</sub> and MgO. Undesired MgO phase was removed by leaching in dilute HCl solution and pure TiB<sub>2</sub> was obtained with molar yield of 81% [19].

In this study, titanium diboride was produced by both volume combustion and mechanochemical synthesis processes. Products obtained by these two processes were compared in terms of presence of side products, molar yields and ease of obtaining pure  $TiB_2$ .

#### 2. Experimental

The starting materials were TiO<sub>2</sub> (Merck Chemicals, purity >99%, particle size <0.5  $\mu$ m, as observed from SEM micrographs), Mg (Aldrich, purity >99%, particle size <300  $\mu$ m). B<sub>2</sub>O<sub>3</sub> used in the experiments was obtained by calcination of H<sub>3</sub>BO<sub>3</sub> (Merck Chemicals, purity >99.8%).

In volume combustion experiments  $TiO_2$ ,  $B_2O_3$  and Mg reactant mixtures, prepared stoichiometrically according to reaction (1) or with 10–40 mol% excess amount of Mg were thoroughly mixed and put into a graphite crucible. Then, the crucible, which was closed with a graphite lid, was placed into a pot furnace preheated to 800 °C. Temperature of the reactants during heating and ignition in the crucible was measured by a K-type thermocouple inserted into the crucible. The thermocouple had an inconel protection tube, which is known to be inert to the used materials. Temperature was recorded by a computer software at a rate of one data per second. Due to the exothermic nature of reaction (1), a sudden increase in temperature occurred, indicating the ignition of the reactants. After reaction took place, the crucible was taken out of the furnace and left for cooling in air. Experiments were conducted in air or in argon atmosphere. Argon atmosphere in the graphite crucible was provided by a continuous flush of high purity argon gas (99.998%) into the crucible through an alumina pipe.

Volume combustion products were subjected to leaching at room temperature and at 75  $^{\circ}$ C in 1–5 M HCl solutions for 15 h for removal of the undesired phases. The powder to leachant ratio was 1 g/100 cm<sup>3</sup>. In some experiments, products were ball milled before leaching for particle size reduction to increase the leaching efficiency. Ball milling was performed in ethanol medium in a stainless steel bowl with 50 pieces of 10 mm diameter stainless steel balls for 7 h. Ball to powder weight ratio was approximately 60:1. A Retsch PM 100 planetary ball mill unit operated at 150 rpm (revolutions per minutes) was used for this process.

Mechanochemical synthesis experiments were performed in a Retsch PM 100 planetary ball mill unit. A 250 ml stainless steel bowl was filled with 30 g of  $TiO_2 + B_2O_3 + Mg$  mixture, which was prepared stoichiometrically according to reaction (1). Twelve stainless steel balls having 20 mm diameter were used, providing a ball to powder ratio of 10:1. After closing the bowl, it was evacuated by a vacuum pump and then back filled with argon gas. Milling

was conducted at 300 rpm for 5 and 15 h. The product obtained after 5 h was subjected to volume combustion. The resulting powder produced after 15 h of milling was leached in 0.25–1 M HCl solution for 2 h, 15 and 3 min.

Products obtained after volume combustion and mechanochemical synthesis were subjected to powder X-ray diffraction (XRD) analyses by a Rigaku Multiflex unit with Cu K $\alpha$  radiation in the 2 $\theta$  range of 20–80° with 0.02° steps at a rate of 2°/min. Smoothing, background subtraction, K $\alpha$ 2 elimination and phase identification operations were performed on the XRD patterns by the Qualitative Analysis Software. Scherrer formula [25] was utilized for calculation of the average crystal size of the formed MgO and TiB<sub>2</sub>. In order to examine grain size and morphology of the products a Jeol JSM 6400 scanning electron microscope (SEM) was used.

# 3. Results and discussions

Volume combustion experiments were performed by placing the graphite crucible containing  $TiO_2 + B_2O_3 + Mg$  mixtures into the preheated pot furnace at 800 °C. Initial experiments were conducted in air atmosphere. Products had a fragile sponge-like structure and they could easily be ground in an agate mortar and pestle. In powder form, they were subjected to XRD analyses.

Although according to reaction (1), only TiB<sub>2</sub> and MgO were expected as products, from the XRD analyses it was seen that in addition to these major phases, three minor phases  $Mg_2TiO_4$ ,  $Mg_3B_2O_6$  and TiN were also present as shown in Fig. 1(a). Formation of  $Mg_2TiO_4$  minor phase may be caused by the reaction between unreacted TiO<sub>2</sub> and formed MgO according to the following reaction:

$$\mathrm{TiO}_2 + 2\mathrm{MgO} = \mathrm{Mg}_2\mathrm{TiO}_4 \tag{2}$$



Fig. 1. XRD patterns of (a) stoichiometric sample after VCS in air; (b) product in (a) after leaching in 1 M HCl (RT); (c) sample containing 40% excess Mg after VCS in air; (d) stoichiometric sample ignited in air, ball milled in ethanol and leached 1 M HCl for 15 h at room temperature; (e) product in (a) after ball milling in ethanol and leaching in 5 M HCl (RT); (f) stoichiometric sample after VCS in argon, ball milling in ethanol and leaching in 5 M HCl (RT); (h) stoichiometric sample after VCS in argon and leaching in 5 M HCl at 75 °C. (1) TiB<sub>2</sub>, (2) TiN, (3) C, (4) MgB<sub>2</sub>, (5) MgO, (6) Mg<sub>2</sub>TiO<sub>4</sub>, (7) Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>.

Similarly, formation of  $Mg_3B_2O_6$  minor phase may have resulted by the reaction between MgO and unreacted  $B_2O_3$ :

$$B_2O_3 + 3MgO = Mg_3B_2O_6$$
(3)

TiN formation may have taken place through reduction and nitridation of  $TiO_2$  according to reaction (4). The source of N<sub>2</sub> is the air inside the graphite crucible:

$$2\text{TiO}_2 + 2\text{Mg} + \text{N}_2 = 2\text{TiN} + 2\text{MgO}$$
 (4)

Fig. 1(b) shows the XRD pattern of the leached product of the sample obtained by igniting in air. It can be seen that peaks of MgO were almost completely removed in the leaching process. In addition, peaks of MgB<sub>2</sub> and TiN were observed in the XRD patterns of the leached sample. Since after leaching MgO peaks were eliminated, MgB<sub>2</sub> and TiN peaks which were placed at the same position with the MgO, became distinguishable. Minor phases were still observed in the XRD patterns given in the Fig. 1(b), which indicates the insolubility of these phases in 1 M HCl.

Due to the difficulty in removing the impurity phases, possible ways for preventing the formation of these side products were searched for. The existence of  $Mg_2TiO_4$  and  $Mg_3B_2O_6$  in the reaction products indicates that the reduction of TiO<sub>2</sub> and  $B_2O_3$  are not complete and some TiO<sub>2</sub> and  $B_2O_3$  remain in the products which then react with the formed MgO (reactions (2) and (3)). Therefore, the effect of adding an excess of Mg on the completion of reduction reactions of TiO<sub>2</sub> and  $B_2O_3$  was investigated by adding 10–40 wt.% excess Mg into the reactant mixture. It was observed from the XRD analyses that relative peak intensities of  $Mg_2TiO_4$  decreased while those of  $Mg_3B_2O_6$  did not change with increasing excess Mg amount and that when 40 wt.% excess Mg was used, formation of  $Mg_2TiO_4$  could be prevented (Fig. 1(c)). These results may be taken as indications that when excess Mg is used, no unreacted TiO<sub>2</sub> remains in the system and; therefore, formation of  $Mg_2TiO_4$  could be prevented. However, formation of TiN was observed to increase after leaching the product obtained when 40 wt.% excess Mg was used.

It was seen from the SEM analyses that ground powders obtained by volume combustion were composed of irregular shaped agglomerates having  $\sim 50 \ \mu m$  dimensions. In the SEM micrograph given in Fig. 2, the structure of one of the agglomerates is presented. According to the XRD analyses, these aggregates are composed of mainly MgO and TiB<sub>2</sub> and some Mg<sub>2</sub>TiO<sub>4</sub>, Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub> and TiN are also present.

In Fig. 3 a SEM micrograph of the leached sample obtained by volume combustion of reactant mixture containing stoichiometric amounts of  $TiO_2$ ,  $B_2O_3$  and Mg according to reaction (1) is presented. It is seen that after leaching, a sponge-like structure was obtained. Therefore, it may be inferred that  $Mg_2TiO_4$ ,  $Mg_3B_2O_6$  and mainly MgO was leached out from the structure given in Fig. 2 and a porous structure was obtained as seen in Fig. 4.

It was concluded from the XRD analyses that elimination of all of the side products by altering the stoichiometry of the reactant mixture was not possible. Therefore, methods for the removal of these side products were investigated. One possible way for increasing the efficiency of the leaching process can be reduction of the grain size of the products thereby liberating the impurity phases for easier leaching. For this purpose, products were subjected to ball milling in



Fig. 2. SEM micrograph of volume combustion product of sample containing stoichiometric amount of Mg.



Fig. 3. SEM micrograph of leached (in 1 M HCl solution for 15 h) product obtained from volume combustion of sample containing stoichiometric amount of Mg.

dry and wet (in ethanol (Et-OH)) conditions. It was seen from XRD analyses that ball milling of the products before leaching for 7 h in dry condition did not affect the leaching behavior (not shown). This can be attributed to the agglomeration in dry condition of powders leading to a decrease in the efficiency of grinding. Therefore, in order to obtain finer particles and to increase the solubility of the undesired phases, ball milling was performed in ethyl alcohol medium for 7 h. As it can be differentiated in Fig. 1(b) and (d),  $Mg_3B_2O_6$  could be eliminated after leaching in 1 M HCl when ball milling operation in ethanol medium was performed before leaching. It was deduced from the SEM observations performed on the as produced samples and also on the wet ball milled products that ball milling in the



Fig. 4. XRD patterns of (a) sample after MCP for 5 h; (b) sample after MCP for 5 h, VCS in air and leaching in 1 M HCl (RT); (c) sample after MCP for 15 h; (d) sample after MCP for 15 h and leaching for 3 min in 0.5 M HCl. (1) TiB<sub>2</sub>, (2) MgO, (3) Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>, (4) Mg<sub>2</sub>TiO<sub>4</sub>, (5) C, (6) MgB<sub>2</sub>, (7) TiN, (8) Mg, (9) TiO<sub>2</sub>.

ethanol medium helped in breaking up the agglomerates, which were present in the unmilled product. These results indicate that ball milling in the ethanol medium reduces the particle size and liberates the particles, providing easier leaching of  $Mg_3B_2O_6$  particles. This effect was less pronounced on removal of  $Mg_2TiO_4$ .

Another possible way of removing impurities can be increasing the concentration of the HCl/water solution. However, this method may also have the potential to increase the loss of  $TiB_2$  due to dissolution. After ball milling in ethanol, products were subjected to leaching in 1, 3 and 5 M HCl solutions. It was seen that increasing the acid concentration to 3 M was successful in removing the Mg<sub>2</sub>TiO<sub>4</sub>. However, TiN could not be eliminated by leaching even in 5 M HCl solution as shown in Fig. 1(e), most probably due to its chemical resistance to acids.

Since formation of TiN is due to the presence of nitrogen in air, in order to prevent the formation of TiN, volume combustion experiments were performed under an argon atmosphere. To achieve this, a continuous flow of argon gas was applied into the graphite crucible before placing the crucible with its contents into the furnace, and also during and after the ignition in the furnace. It can be seen from the XRD pattern given in Fig. 1(f) that when ignition was conducted under an argon atmosphere formation of the TiN phase could be prevented. Other side products were removed by leaching in 5 M HCl solution and a pure TiB<sub>2</sub> phase could be obtained. The molar yield of the TiB<sub>2</sub> produced was calculated as 30%. Molar yield was calculated as the ratio of the obtained amount of TiB<sub>2</sub> after leaching to the stoichiometrically expected amount of TiB<sub>2</sub> according to reaction (1).

Ball milling process in ethanol medium was seen to be effective in removal of borate and titanate side products in the subsequent leaching step. However, it is a time consuming and tedious process. In order to omit this step, products were subjected to hot leaching in 5 M HCl solution at 75 °C for 15 h. This process was conducted on a magnetic stirrer/ heater connected to a contact thermometer which was kept inside the acid solution during leaching. It can be seen in Fig. 1(h) that when the sample produced under argon atmosphere was directly leached at 75 °C, without ball milling in ethanol, the secondary phases could be removed and pure TiB<sub>2</sub> could be obtained. When leaching was done in cold 5 M HCl solution, the impurities could not be removed as shown in Fig. 1(g). Molar yield of TiB<sub>2</sub> was 48.6% when hot leaching was applied. The increase in molar yield may be attributed to omitting the ball milling process in ethanol, leading to a decrease in the loss of TiB<sub>2</sub> by dissolution in HCl.

#### 3.1. Mechanochemical processing (MCP)

Ball milling for mechanochemical synthesis was performed for 5 and 15 h at 300 rpm. It was seen from the XRD pattern given in Fig. 4(a) that at the end of 5 h of ball milling, peaks of  $TiO_2$  and Mg were present. Due to the amorphous structure of  $B_2O_3$ , it did not present peaks in the XRD pattern. The presence of reactants and absence of expected products in the XRD analyses indicate that no reaction took place in 5 h of ball milling.

It was inferred from the SEM micrograph given in Fig. 5 that ball milling before ignition causes a decrease in particle size of reactant and agglomerates. According to SEM observations, the grain size of the initial Mg powder was between 25 and 100  $\mu$ m, and that of TiO<sub>2</sub> was about 300 nm and B<sub>2</sub>O<sub>3</sub> was ground to <1 mm before mixing. After milling for 5 h, the reactants were much finer than the unmilled mixture. In addition, the reactant agglomerates given in Fig. 5 are seen to be composed of intimately mixed reactant particles.

The 5 h ball milled powder mixture was subjected to volume combustion by igniting in a preheated furnace, similar to the VCS samples. The temperature of the samples were measured and recorded continuously via a thermocouple inserted into the graphite crucible inside the furnace. It was found that ball milling before ignition caused a decrease in ignition temperature of the reactant mixture. While without ball milling, ignition took place at approximately 690 °C; with introduction of ball milling before ignition, the mixtures ignited at about 220 °C. In addition, a more vigorous combustion behavior was observed during ignition of the milled reactants. The reasons for the vigorous combustion behavior and the decrease in the ignition temperature may be the reduction in the particle size, mechanical activation and intimate mixing which enhance particle contact and increase the specific surface area for reaction. Porous structure of the product shown in the SEM micrograph in Fig. 6 also indicates a more aggressive ignition when compared to Fig. 2. This structure may have formed as a result of gas evolution due to evaporation of Mg.

XRD pattern of the product after leaching in 1 M HCl solution for 15 h is given in Fig. 4(b). It can be seen that relative peak heights of  $Mg_3B_2O_6$  phase were lower than the leached sample which was not ball milled before ignition (Fig. 1(b)). This decrease may also be attributed to the intimate mixing of reactant mixture and reduction in particle size during ball milling. Thus, uneven mixing or presence of relatively coarse grains in the unmilled mixture may be the reason of high amount of impurity phases (Fig. 1(b)).



Fig. 5. Structure of an agglomerate in the Mg +  $TiO_2$  +  $B_2O_3$  reactant mixture after ball milling for 5 h with 300 rpm.

XRD pattern of the product obtained after 15 h of ball milling of  $Mg + TiO_2 + B_2O_3$  mixtures presented peaks of only TiB<sub>2</sub> and MgO (Fig. 4(c)), indicating that the reaction was complete. No unreacted species were detected in the XRD pattern of the products. All of the reactants may have been consumed or it is possible that some of the reactants were ground so fine that they had an amorphous structure. While XRD pattern of the product obtained from VCS contained Mg<sub>2</sub>TiO<sub>4</sub> and Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub> impurity phases (Fig. 1(a)), XRD pattern of the sample formed by ball milling for 15 h did not contain these minor phases (Fig. 4(c)).

TiB<sub>2</sub>–MgO product, obtained at the end of 15 h of ball milling, was leached in HCl solution in order to remove MgO. It is known that TiB<sub>2</sub> is slightly soluble in HCl solutions and some TiB<sub>2</sub> may be lost during leaching. Therefore, before leaching, in order to determine the minimum possible leaching duration and acid concentration, leaching behavior of pure MgO in dilute HCl has been investigated. It was seen that MgO did not dissolve completely in 0.25 M HCl solution at a solid to leachant ratio of 1 g/100 cm<sup>3</sup>. However, pure MgO was found to dissolve completely in 0.5 M HCl solution in 3 min. Consequently, TiB<sub>2</sub>–MgO product was leached in 0.5 M HCl solution for 3 min. It can be seen in Fig. 4(d) that MgO was completely removed and pure TiB<sub>2</sub> phase was obtained. Molar yield of TiB<sub>2</sub> obtained by ball milling for 15 h and leaching for 3 min in 0.5 M HCl solution was calculated as 89.6%. This value was 86.1% after 15 min of leaching and it was 76.6% after 2 h of leaching in 1 M HCl solution. These results indicate that there is some loss of TiB<sub>2</sub> due to its dissolution in HCl solution.

As shown in Table 1, molar yield of  $TiB_2$  produced by mechanochemical synthesis was much higher than that of the yield obtained from volume combustion experiments (30%). After mechanochemical synthesis of  $TiB_2$ , in order to remove MgO from the products, lower concentration of HCl and shorter leaching duration was sufficient. As a result,



Fig. 6. SEM micrographs of ignited sample after ball milling for 5 h with 300 rpm.

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Table 1					
Molar yields of	of TiB <sub>2</sub>	obtained	by	different	processes

Process	Molarity of HCl	Leaching duration	Molar yield (%)
MCP + leaching	1	2 h	76.6
-	1	15 min	86.1
	0.5	3 min	89.6
VCS (air) + ethanol ball mill + leaching	1	15 h	57.0
	3	15 h	44.6
	5	15 h	33.0
VCS (argon) + ethanol ball mill + leaching	5	15 h	30.0
VCS + leaching at 75 °C	5	15 h	48.6



Fig. 7. SEM micrograph of a MCP sample leached for 3 min.

molar yield of TiB<sub>2</sub> produced by mechanochemical synthesis was higher. The possibility of shorter duration of leaching of the mechanochemically obtained products may be attributed to the smaller grain size of the formed MgO and also the absence of side products such as  $Mg_2TiO_4$  or TiN. The average crystal size of formed MgO in the mechanochemical synthesis after 15 h ball milling was 17.22 nm, as calculated by the Scherrer formula [24]. On the other hand, average crystal size of MgO formed after volume combustion synthesis was calculated as 47.18 nm. These results indicate that MgO obtained after mechanochemical synthesis had much smaller crystallites, which provides an easier leaching.

SEM micrograph of TiB<sub>2</sub> produced by mechanochemical processing is presented in Fig. 7. According to the measurements preformed on SEM micrographs, produced TiB<sub>2</sub> had an average grain size of  $0.27 \pm 0.08 \,\mu$ m. This value was obtained by measuring the size of at least 50 grains, and calculating their average and standard deviation. TiB<sub>2</sub> powder obtained by VCS did not present a noticable difference in grain size, as observed from SEM micrograph.

Average crystal size of  $TiB_2$  formed in VCS and MCP was not much different. It was 32 nm when produced mechanochemically and it was 41 nm after volume combustion. Higher crystal size was an expected result in VCS due to higher temperature attained.

### 4. Conclusion

Titanium diboride was produced both by volume combustion synthesis and by mechanochemical processing. In MCP, products containing only TiB<sub>2</sub> and MgO were obtained, however after volume combustion; secondary phases such as  $Mg_3B_2O_6$  and  $Mg_2TiO_4$  were also present in the products. Pure TiB<sub>2</sub> was obtained from the products of VCS after wet ball milling in ethanol and leaching in 5 M HCl with a molar yield of 30%. Pure TiB<sub>2</sub> could also be obtained at a molar yield of 45.6% by hot leaching of VCS products at 75 °C in 5 M HCl, omitting the wet ball milling step.

Leaching in 0.5 M HCl for 3 min was found to be sufficient for eliminating the MgO from the products of MCP. Molar yield of TiB<sub>2</sub> obtained by the MCP was calculated as 89.6%, which is significantly higher than that obtained by VCS.

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