Journal of the Australian Ceramic Society (2022) 58:777–791
https://doi.org/10.1007/s41779-022-00714-5

RESEARCH

Production of B_4C-TiB_2 composite powder by self-propagating high-temperature synthesis

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Received: 29 July 2021 / Revised: 21 December 2021 / Accepted: 6 February 2022 / Published online: 25 March 2022

Abstract

Advanced ceramics find significant application areas due to their superior mechanical, electrical, magnetic chemical and thermal properties. By combining these materials, significant properties can be obtained as a result of production of the composites of hard metal compounds in nanoscale dimensions. Self-propagated high-temperature synthesis (SHS) is one of the prominent methods for the production of such nanoparticles. SHS is a combustion synthesis method. In this study, nanocomposite powders of B_4C-TiB_2 were synthesized by SHS method. FactSage software was used for thermochemical simulation and computational stoichiometric optimization. In the experimental step, 2 different SHS sets were prepared. In the first stage, B_4C and TiB_2 powders were synthesized. The B_4C-TiB_2 composite was produced in the final set of experiments. Then, production parameters of B_4C-TiB_2 composite powders, from B_2O_3, TiO_2, and carbon black, were investigated. Magnesium powder was used as reductant agent. Afterwards, HCl leaching process was performed, and acid concentration was optimized. The effect of carbonic acid and H_2O_2 addition on dissolution of undesired phases was also been investigated as a new method. Products were characterized by XRD, SEM and BET analysis. B_4C-TiB_2 composite powder with quite high surface area, fine particle size and high porosity could be synthesized with reasonable purity. According to the results, the optimum molar ratios were determined as TiO_2:B_2O_3:Mg:C = 1:3:12:1.6. Optimum acid concentration was found to be 10.5 M for leaching process, and carbonic acid addition on leaching step found to be effective on TiO_2 removal. The highest purity could be obtained with 50%-50% stoichiometry. It has also been determined that the synthesis of B_4C-TiB_2 composite powder has a positive effect on both the chemical content and the morphology that will increase the sintering ability.

Keywords Combustion synthesis · Self-propagating high-temperature synthesis · SHS · Boron carbide · Titanium diboride · Nanoparticle synthesis

Introduction

Hard metal compounds are widely used due to their superior mechanical, thermal, physical and chemical properties. With the synthesis of composite powders, it is possible to obtain materials that combine these superior properties.

Boron carbide has superior properties such as low density, high hardness and abrasion resistance, high strength, high-temperature resistance and high resistance to chemicals [1–3]. Under favour of its low density and very high hardness, it is used in armour applications that require high ballistic properties [4–6]. In addition, it has higher hardness than diamond above 1300 °C [7]. Due to the good wear resistance of boron carbide, the material is used in abrasive powders, hard coatings, nuclear applications and neutron absorption [5]. It is also a thermoelectric material that can be used in electronic applications as a semiconductor in high-temperature applications [8–10]. Boron carbide's low toughness and low thermal and electrical conductivity are its features that limit it in terms of use [11]. In addition, its sintering ability is quite low due to its strong covalent bonding, low plasticity and the B_2O_3 layer formed on its surface [12].

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Titanium diboride also has properties such as high melting temperature, high hardness and wear resistance. In addition, by virtue of its good thermal and electrical conductivity, it can be used as electrode materials, cathodes, cutting and abrasive tools [13]. Other important properties of titanium diboride are high toughness, thermal shock resistance and corrosion resistance [14–17].

In B_4C TiB_2 composites, by combining the superior properties of the two materials, it was revealed that fracture toughness and sintering ability were increased [12]. There are many production methods for both materials. These are carbothermic reduction [18–21], mechanical alloying [22, 23], synthesis from elements [24, 25], sol–gel [26–28], mechanochemical synthesis [29, 30] and solvothermal synthesis. Combustion synthesis stands out due to its suitability for mass production, low cost and high product quality. Self-propagating high-temperature synthesis (SHS) is a method that has been studied extensively in the production of these materials in recent years and provides very important advantages [31–35].

Studies have been carried out with different methods for the production of boron carbide-titanium diboride composite. Thermal and electric field activated combustion synthesis [36, 37], borothermic reduction [38], carbothermal reduction (using boric acid, carbon black and TiO_2) [39], in situ synthesis (using boric acid, sugar and $C_8H_{20}O_4Ti$ (titanium(IV) ethanolate)) [40], co-precipitation process [41] and sol–gel methods [42] (using B_4C, $TiCl_4$ and Y_2O_3 reactants) have been reported recently. Especially in recent years, an important study on B_4C-TiB_2 production was carried out by Mikeladze et al. [43]. $B_4C + 30$wt-%TiB_2 with a hardness of 45.6 GPa and a flexural strength of 834 MPa was produced by chemical synthesis from suspension solutions using boric acid/boron anhydride, titanium dioxide and glycerin followed by spark plasma sintering. In some studies, complex composites were obtained by incorporating metal or ceramic components into the B_4C-TiB_2 composite. L. Chkhartishvili et al. [44] successfully produced the B_4C-TiB_2-WC–Co complex composite with the chemical route of gel drying, pyrolysis, reduction, carburization and boronization and revealed that the grain size decreased significantly with the addition of Co and WC to the B_4C-TiB_2 composite. All these methods have significant disadvantages, and the SHS method stands out as a method that eliminates these drawbacks, such as high energy consumption due to high temperature and/or pressure requirements, extensive mechanical milling requirements, expensive alkoxide requirements and long gelation duration. Moreover, the SHS method makes it possible to produce ceramic materials that are difficult to produce with traditional methods. For example, Tolendiuly et al. [45] were able to produce superconducting MgB_2 doped with carbon nanotube by SHS method. B_4C-TiB_2 composite was produced via SHS by Nikzad et al. [46]. However, they carried out this process by using elemental B, C and Ti. In order to eliminate the disadvantageous of low adiabatic temperature of the B-C system, they provided the production by using Teflon as a chemical booster and also by performing mechanical activation. By chemical activation with using 30% Teflon or using 18% Teflon additionally mechanical activation with ball milling, B_4C-TiB_2 composite could be synthesized by SHS. However, the use of elemental raw materials presents a great disadvantage with making the method expensive. Another study for the production of B_4C-TiB_2 composite by SHS with the B-C-Ti system was carried out by Ziemnicka-Sylwester [47]. In the study using elemental raw materials, the effect of charge stoichiometry was investigated, and it was determined that the combustion reaction did not occur at 40% and below TiB_2 charge stoichiometry. In addition, it was determined that the boron carbide obtained was $B_{13}C_2$. Moreover, the SHS process was started under 10 Pa vacuum, and the process was continued with 100 MPa high pressure after combustion. The grain size of the carbon used is 10 µm and below. All these make the method expensive, and production cannot be achieved in all charge stoichiometry. However, it is an important study in terms of investigating the effect of charge stoichiometry.

It has been demonstrated that the use of elemental raw materials provides higher purity [48]. However, it is an important disadvantage that it makes the method very expensive. The production of B_4C-TiB_2 by SHS from oxide raw materials offers great economic advantages. Here, as a result of the use of magnesium as a reductant, the concern of low adiabatic temperature of the B-C system is eliminated, and additional activation processes will not be necessary. High purity and economical synthesis of B_4C-TiB_2 composite powder is also possible by using oxide raw materials. In this sense, the only study was conducted by Bahaabad [49]. The effect of mechanical activation with ball milling was investigated in the volume combustion SHS process using B_2O_3, TiO_2, Mg and C. However ignition was provided by continuous argon gas flow at 900 °C which increases the cost of process extremely. The product obtained after HCl leaching is quite good in terms of purity and grain size, but it is also seen that the amount of boron carbide is quite low. Such studies should be developed by optimizing the mole ratios of the reactants, TiB_2 and B_4C charge stoichiometry and optimizing and improving the HCl leaching process.

In this study, B_2O_3, TiO_2, carbon black and Mg powder were used to produce B_4C and TiB_2 separately, as well as B_4C-TiB_2 composite powder with 25%-75%, 50%-50% and 75%-25% charge stoichiometry by SHS method. Optimization of Mg and C stoichiometry was performed by thermochemical simulation. In addition, acid concentration optimization was carried out for leaching processes after SHS. In addition, the effect of carbonic acid and H_2O_2 on

the improvement of leaching processes was also investigated. The novelty of the study is to synthesize B_4C-TiB_2 composite particles not by using elemental raw materials but by using oxide raw materials by combustion synthesis. Thus, production costs could significantly be reduced. Also, the purity of the product could be provided without using argon atmosphere, and ignition was provided not in volume combustion mode but by using Cr-Ni wire. These are other effects that reduce the production costs extremely. One another novelty of the study is to make investigation on the leaching step for dissolving the undesired phases, especially TiO_2.

Materials and methods

In this study, boron carbide (B_4C), titanium diboride (TiB_2) separately and B_4C-TiB_2 composite powders were produced via SHS process. Before SHS processes, thermochemical simulation studies were realized for SHS reactions in order to determine the optimum mole ratio of carbon and magnesium. FactSage software was also used to determine the adiabatic temperature of the reactions. Moreover, the probable phases of different SHS B_4C-TiB_2 combinations were investigated. After SHS processes, acid leaching was performed in order to dissolve the undesired oxide phases and optimum HCl concentrations were determined. Both SHS products and leached products were characterized by XRD analysis, and final product of B_4C-TiB_2 composite powder was characterized by SEM–EDS and BET analysis. The flowchart of experimental study is given in Fig. 1.

The maximum temperature that can be obtained with the heat energy released as a result of a reaction under adiabatic conditions is called the adiabatic temperature (T_{ad}), and the adiabatic temperature value formed as a result of the reaction is the most important criterion for obtaining a compound by combustion synthesis method. This criterion was first put forward in 1972 by Merzhanov et al. [50]. According to the criteria they put forward on the basis of the experiments they have carried out and the data they have obtained, the adiabatic temperature must be above 1800 K ($T_{ad} > 1800$ K) in order to obtain a compound by combustion synthesis. This criterion has been developed over the years by including the melting temperatures of the components and the kinetic criteria (Su et al. [51] in 2014 and Tan et al. [52] in 2021); the criterion set forth by Merzhanov et al. is the first

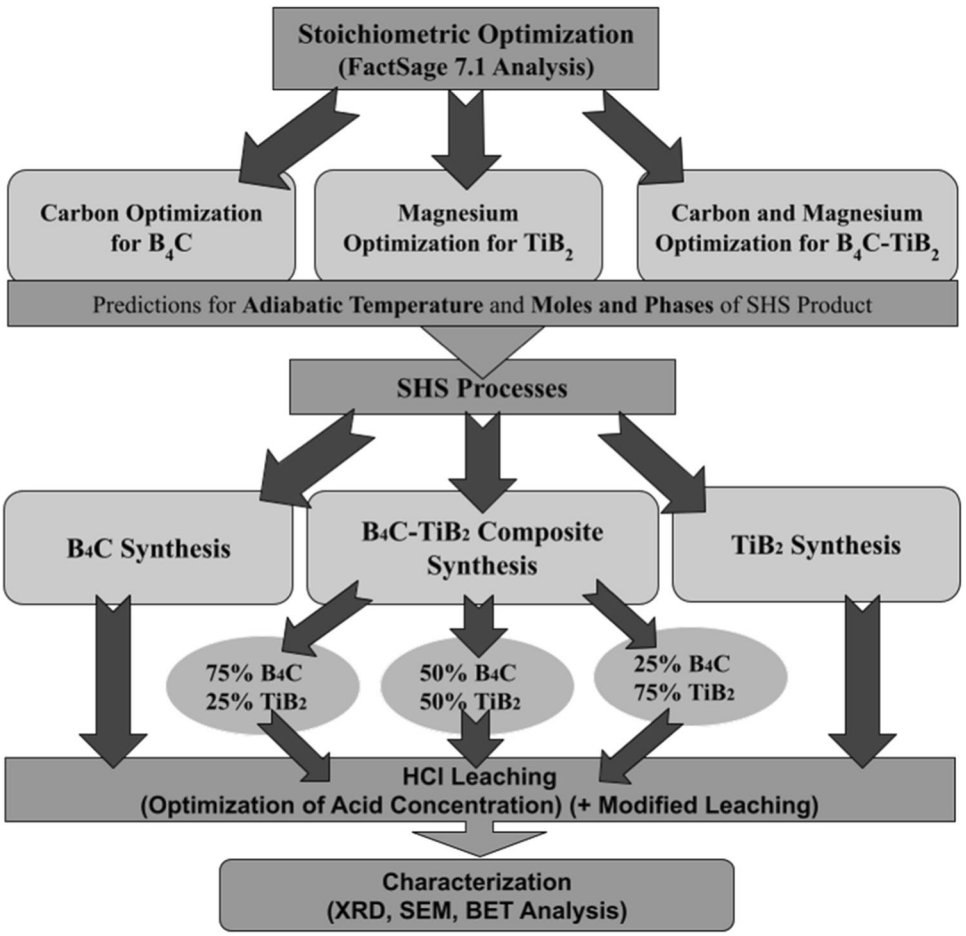

Fig. 1 Flowchart of experimental study

essential to be evaluated in the powder synthesis method by SHS. Accordingly, based on the reactions specified in Eqs. 1, 2 and 3, adiabatic temperatures were calculated by using FactSage 7.1 Thermochemical Simulation Software for obtaining B_4C, TiB_2 and B_4C-TiB_2 sequentially by SHS method.

$$2B_2O_3 + 6Mg + C \rightarrow B_4C + 6MgO \quad (1)$$

$$TiO_2 + B_2O_3 + 5Mg \rightarrow TiB_2 + 5MgO \quad (2)$$

$$TiO_2 + 3B_2O_3 + 11Mg + C \rightarrow TiB_2 + B_4C + 11MgO \quad (3)$$

After determination of stoichiometry, 5 different charges were prepared for obtaining 3 different materials which are B_4C, TiB_2 and B_4C-TiB_2. The stoichiometries of limiting reactants for each are given in Table 1.

The stoichiometry which was optimized by thermochemical calculation method for B_4C by us has been experimentally optimized by Alkan et al. [53], and they reported the optimum mole ratios for synthesis of B_4C by SHS as B_2O_3:Mg:C = 2:6:1.6. Optimum carbon mole ratio was reported to be same with ours. In this study, optimum mole ratio of Mg for B_4C synthesis was decided as 6 mol as Alkan et al. reported.

After performing stoichiometric optimization for TiB_2 and B_4C separately, and for B_4C-TiB_2 samples, composite powders in the components shown in Table 2 were produced by SHS method by charging the ladle in the amounts given in the same table in a total amount of 100 g, according to the best stoichiometry determined by FactSage.

Technical grade TiO_2, Mg and B_2O_3 (obtained by calcination of H_3BO_3, Eti Mine) powders were used in experimental studies. The purity and particle size of raw materials used in the experimental study is given in Table 3.

After SHS processes, the products were leached in HCl with different concentrations. For leaching step of TiB_2 production via SHS, A. Turan et al. [54] reported optimum acid concentration as 9.3 M and solid liquid ratio as 1/5 at room temperature. For leaching step of B_4C production via SHS, Alkan et al. [53] reported optimum acid concentration as 12.06 M and solid liquid ratio as 1/5 at 80 ^{0}C. The leaching conditions for each sample are given in Table 4.

In the experimental studies, after weighing the powders in the determined mixtures, they were mixed in turbula mixer for 10 min, then kept in ETUV at 105 °C for 2 h and dehumidified. After drying, they were charged into a copper crucible. Copper crucibles for SHS processes have been used in many studies [55–57]. Owing to its high thermal shock resistance and high toughness, it is not damaged by the combustion wave. However, due to its high thermal conductivity, it is not used especially in centrifugal SHS systems as it increases heat dissipation. Alkan et al. [55] used a copper crucible under normal gravity conditions and a C/SiC crucible in the centrifugal SHS system. The inner diameter of crucible was 10 cm and thickness was 2 cm. Cr-Ni wire and direct current power supply connected to it by copper wire were used to reach the ignition temperature in order

Table 1 The optimized stoichiometries of reactants for experimental studies

Sample	Mole ratios and stoichiometric percentage			
	TiO_2	B_2O_3	Mg	C
100% B_4C	-	1	3	0.8 (160%)
100% TiB_2	1	1	6 (120%)	-
50% B_4C-50% TiB_2	1	3	12 (110%)	1.6 (160%)
75% B_4C-25% TiB_2	1	3	12 (110%)	1.6 (160%)
25% B_4C-75% TiB_2	1	3	12 (110%)	1.6 (160%)

Table 3 The purity and particle size of raw materials used in the experimental study

Raw materials	Purity, wt %	Particle size, μm
Mg	99.7	< 150
B_2O_3	97	< 53
TiO_2	98.8	< 75
C	98	< 30

Table 2 Charge amounts of raw materials used in experimental studies

Sample	Stoichiometry	Charge Amounts											
		TiO_2		B_2O_3 (for B_4C)		C		Mg (for B_4C)		B_2O_3 (for TiB_2)		Mg (for TiB_2)	
		[g]	mol	[g]	mol	[g]	mol	[g]	mol	[g]	mol	[g]	mol
1	100% B_4C-0% TiB_2	0.00	0.00	45.67	0.66	6.30	0.52	47.92	1.97	0.00	0.00	0.00	0.00
2	50% B_4C-50% TiB_2	13.58	0.17	22.84	0.33	3.15	0.26	23.96	0.98	11.79	0.17	24.69	1.02
3	0% B_4C-100% TiB_2	27.15	0.34	0.00	0.00	0.00	0.00	0.00	0.00	23.58	0.34	49.37	2.03
4	75% B_4C-25% TiB_2	6.79	0.08	34.26	0.49	4.725	0.39	35.94	1.47	5.89	0.08	12.35	0.51
5	25% B_4C-75% TiB_2	20.37	0.25	11.42	0.16	1.57	0.13	11.98	0.49	17.68	0.25	37.03	1.53

Table 4 The conditions of leaching experiments for each sample

Stoichiometry	Acid concentration	Leaching temperature	Leaching duration	Stirring rate	Solid/liquid ratio
100% B_4C	8 M/10 M/12 M/14 M	90 °C	60 min	500 rpm	1/5
100% TiB_2	5 M/7 M/9 M/11 M	90 °C	60 min	500 rpm	1/5
50% B_4C-50% TiB_2	6.5 M/8.5 M/10.5 M/12.5 M	90 °C	60 min	500 rpm	1/5
75% B_4C-25% TiB_2	11 M	90 °C	60 min	500 rpm	1/5
25% B_4C-75% TiB_2	10 M	90 °C	60 min	500 rpm	1/5
50% B_4C-50% TiB_2	Modified leach (10.5 M HCl + carbonic acid and H_2O_2 addition)	90 °C	60 min	500 rpm	1/5

to start the combustion reaction. After the reaction started by applying 11–12 V for 3–4 s from the power supply, the power was cut off. Due to highly exothermic reactions, combustion wave propagated through mixture rapidly, and the process was completed for 100 g of charge within 10–20 s. Afterwards the crucible which contains SHS product was emerged into water for cooling. One another reason for usage of copper crucible is to provide rapid cooling. Sponge like SHS product was obtained, and after grinding the powder by using an agate mortar, leaching was carried out using a magnetic stirrer with heater.

For characterization study, XRD, BET and SEM–EDS analysis were carried out. PANalytical Aeris X-Ray powder Diffractometer (40 kV – 15 mA), Micromeritics ASAP 2020 Surface Area and Porosity Analyzer and Zeiss GeminiSEM 500 Field Emission Scanning Electron Microscope were used for analysis.

Results and discussions

Stoichiometric optimization results

The effect of varying carbon ratio on adiabatic temperature and probable phases in B_4C production by SHS process according to the reaction given on Eq. 1 was investigated. Adiabatic temperature was found to be 1815 °C with the addition of 0.2 to 1.0 mol carbon. Since this value is above 1527 °C (the temperature specified in the criterion put forward by Merzhanov et al. [50], 1800 K), it does not pose any obstacle to the start of the reaction. When the probable phases are also evaluated for 100% B_4C sample, the carbon mole ratio to be used in experimental studies was determined as 0.8, that is, 160% stoichiometry, since no more increase in B_4C amount was observed over that value. The change of adiabatic temperature and probable phases over varying magnesium mole ratios for obtaining TiB_2 according to Eq. 2 was investigated. Accordingly, the maximum adiabatic temperature value of 1965 °C is achieved between approximately 3.2 and 7.2 mol. When the probable phases are also evaluated for 100% TiB_2 sample, Mg mole ratio to be used in experimental studies was determined as 6 mol value, which is 120% stoichiometry.

FactSage simulations of adiabatic temperatures determined for varying Mg and C ratios in the production of B_4C-TiB_2 composite by SHS method according to the reaction given on Eq. 3 are shown in Fig. 2. It is seen that in all carbon and magnesium mole ratios, the adiabatic temperatures are above the critical value of 1527 °C. When the variation of adiabatic temperatures according to magnesium ratios was examined, the maximum adiabatic temperature value of 1815 °C was obtained for 11 mol as can be seen in Fig. 2b.

The changes in the ratios of the possible phases and the decrease in the adiabatic temperature were evaluated. According to the thermochemical simulation of possible products for B_4C-TiB_2 composite production by SHS given in Fig. 3, the amount of B_4C showed a significant increase up to 1.0 mol value, and the increase in the following values continued. Above 1.0 mol C value, the amount of undesired $Mg_3B_2O_5$ decreases significantly. The changes in adiabatic temperature and possible phase amounts by increasing the carbon ratio from 1.0 to 1.6 moles are given in Table 5. Accordingly, increasing the carbon ratio from 1.0 to 1.6, a small decrease of 0.52% in the adiabatic temperature but a significant increase of 20.9% in the amount of B_4C and such a significant decrease of 44.4% in the amount of $Mg_3B_2O_5$ were detected. Although it is predicted that a further increase in the carbon ratio will increase the amount of B_4C, the potential for TiC formation in the structure will increase too much since titanium is a carbide-forming element. Considering the kinetic effect as well as the thermodynamic simulation, when SHS is performed with such carbide-forming elements, different carbides are expected to form in the reaction medium. In the study carried out by Bugdayci et al. for the production of B_4C-ZrB_2 by SHS, it was determined that ZrC is formed in the structure at 160% stoichiometry [58]. For these reasons, it was decided to use 160% stoichiometric ratio of carbon, which is also the optimized value in B_4C acquisition, as the optimum value for B_4C-TiB_2 synthesis.

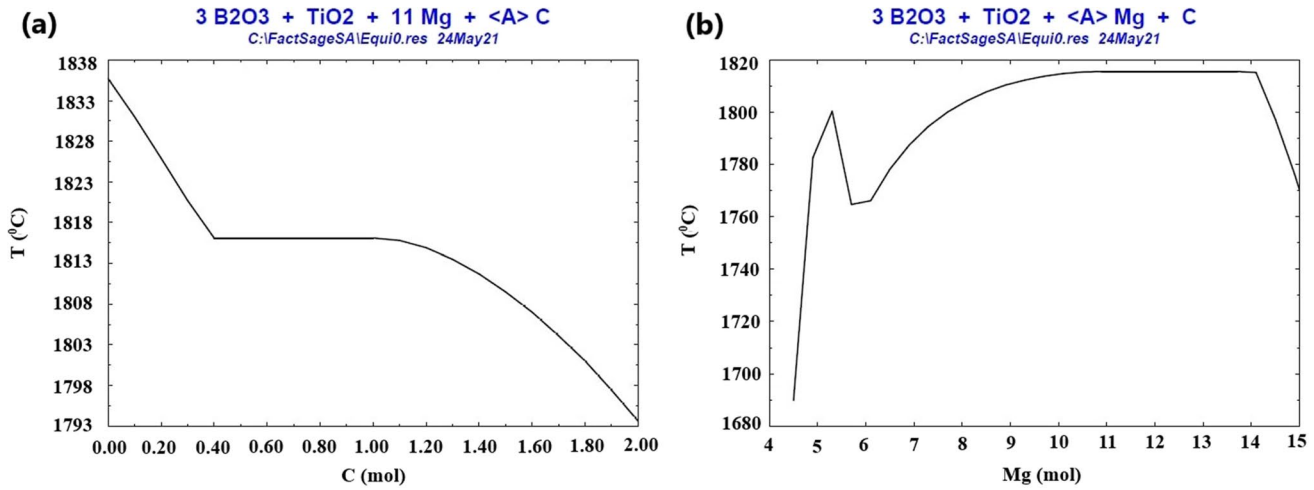

Fig. 2 Effect of (**a**) carbon and (**b**) magnesium mole on adiabatic temperature of SHS reaction of B_4C-TiB_2

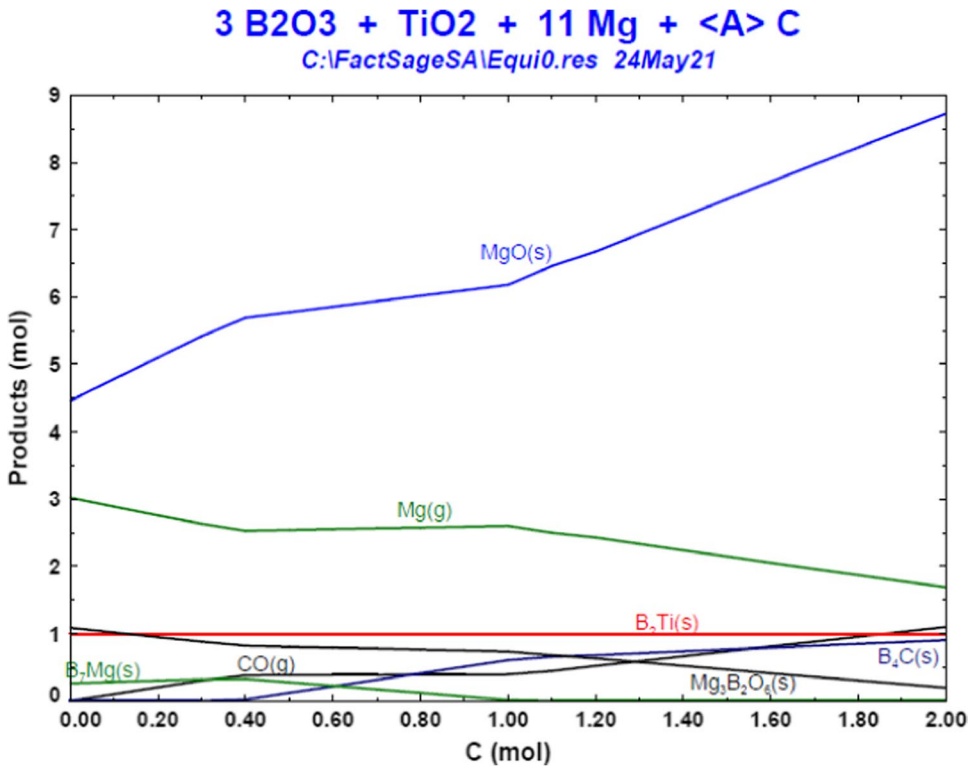

Fig. 3 Thermochemical predictions of products for varying C moles for SHS reactions of B_4C-TiB_2

Table 5 Effect of increase of carbon mole on the amounts of B_4C and $Mg_3B_2O_6$ and on adiabatic temperature

	1.0 mol C (100%)	1.6 mol C (160%)	Percentage change
B_4C amount (mole)	0.620	0.750	20.9% increase
$Mg_3B_2O_6$ amount (mole)	0.750	0.417	44.4% decrease
Adiabatic temperature (°C)	1816	1806.5	0.52% decrease

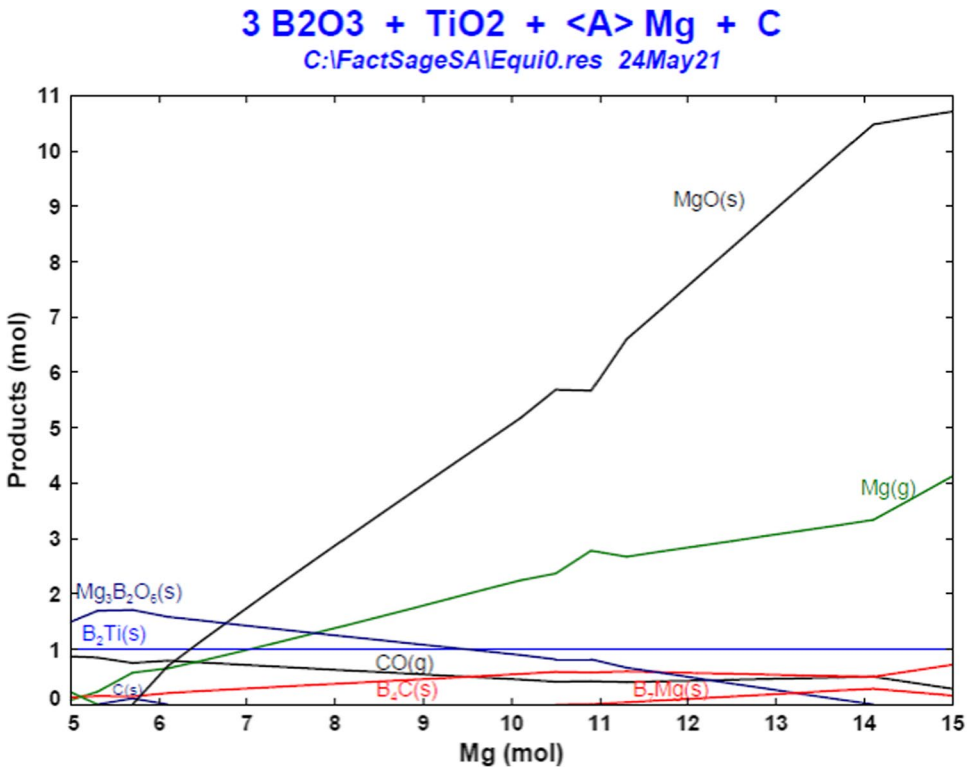

Fig. 4 Thermochemical predictions of products for varying Mg moles for SHS reactions of B_4C-TiB_2

FactSage analysis result for the possible phases and quantities foreseen in the SHS product depending on the varying magnesium ratios for B_4C-TiB_2 production is given in Fig. 4. MgO, Mg, TiB_2, B_4C and $Mg_3B_2O_5$ phases are predicted to form in 11 moles of SHS product with 100% stoichiometry. The products to be obtained according to the 12 moles magnesium mole ratio are examined. Since there is a significant decrease in the amount of $Mg_3B_2O_5$ compared to 11 moles and, in addition, there is no change in the amount of B_4C in the values above, 12 moles magnesium mole ratio (110% stoichiometry) was determined as optimum.

XRD results

First of all, the first 3 samples (100% B_4C, 50% B_4C-50% TiB_2, 100% TiB_2) given in Table 1 were subjected to SHS process at the specified stoichiometry. As can be seen in Fig. 5a, the main component for 100% B_4C sample is MgO. Mg-Borate ($Mg_3(BO_3)_2$ and $Mg_2B_2O_5$) phases were also formed. As a result of the evaporation of some amount of magnesium, some of the B_2O_3 remained unreduced and combined with MgO to form Mg borate phases [49]. Significant amounts of B_4C could be synthesized. As can be seen in Fig. 5b, although the main component is MgO for the 100% TiB_2 sample, a significant amount of TiB_2 could be synthesized. A significant amount of unreacted Mg was also detected. Magnesium borate phases appear to occur much less frequently owing to lower charge amount of B_2O_3. Figure 5c shows the XRD result of 50% B_4C-50% TiB_2 sample. The main component of the SHS product is magnesium oxide. The significant amount of Mg and the very low amount of Carbon in the SHS product indicate that carbon has been removed from the system as CO and CO_2 by helping magnesiothermic reduction and contributed to the formation of titanium diboride by carbothermic reduction. Although there is a significant amount of titanium diboride in the SHS product, the low amount of boron carbide can be explained in this way. It can be said that the use of argon could have increased the amount of boron carbide, as Bugdayci et al. [58] presented in their study for the production of ZrB_2-B_4C by SHS. The presence of some unreduced amount of titanium oxide and small amounts of magnesium borate phases were also detected in the structure. However, the amount of undesired phases was detected as the lowest on 50% B_4C-50% TiB_2 sample when compared to the others which reveals that combining charging increased the efficiency of SHS process.

Afterwards the leaching processes of 100% B_4C and 100% TiB_2 samples were optimized. Accordingly, maximum B_4C and minimum Mg borate phases were determined at 12 M acid concentration for leaching process of 100% B_4C. The optimum acid concentration for leaching of 100% TiB_2 sample was determined as 9 M.

XRD results of the products for 50% B_4C-50% TiB_2 sample obtained by leaching with different acid concentrations

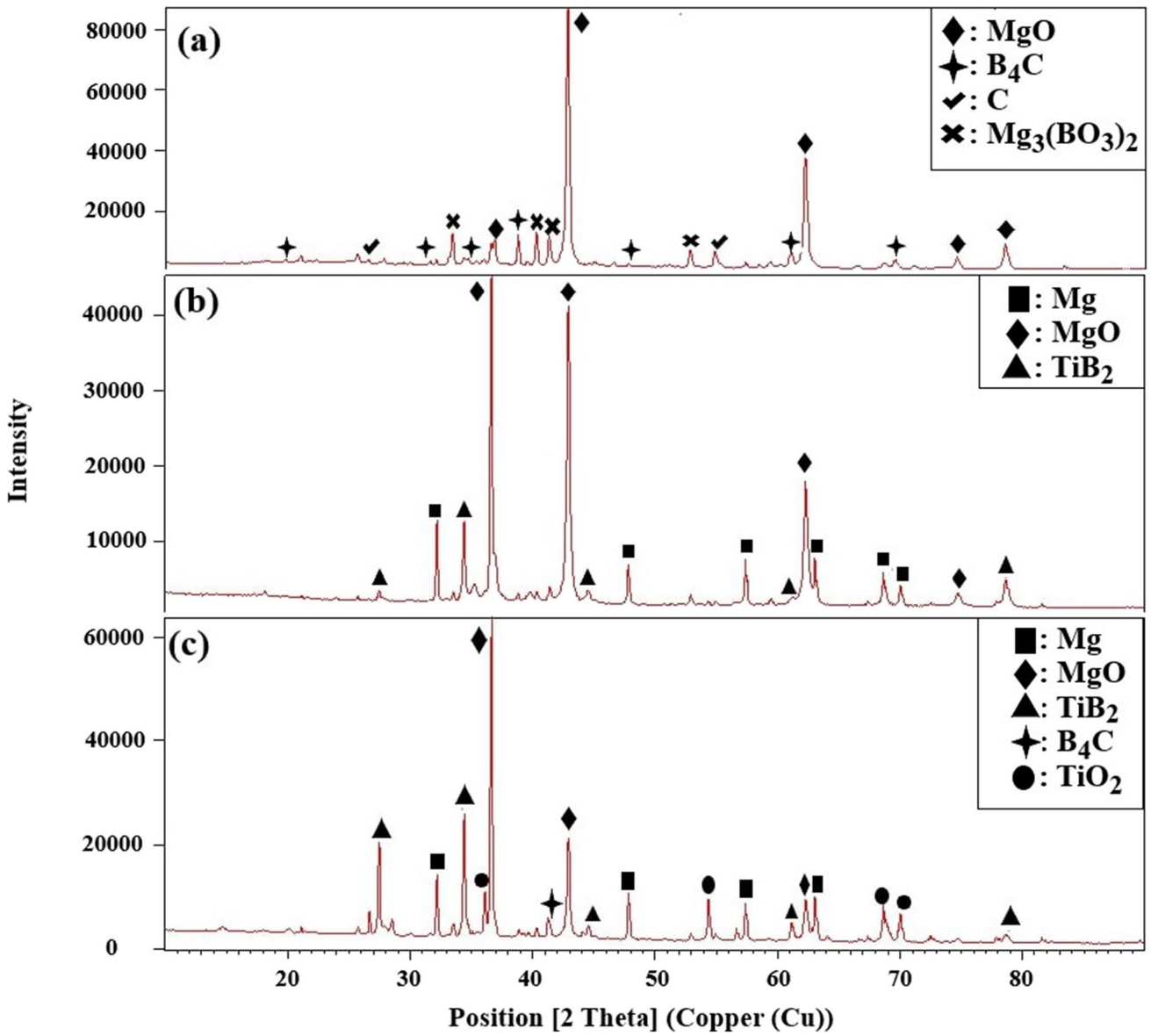

Fig. 5 XRD analysis result of SHS products of (**a**) 100% B_4C, (**b**) 100% TiB_2 and (**c**) 50% B_4C-50% TiB_2

are comparatively shown in Fig. 6. Accordingly, the main component of the product obtained after the leaching process performed in all acid concentrations is titanium diboride. Besides, it was also provided to obtain boron carbide. However, the phase with the highest amount after titanium diboride is titanium oxide (TiO_2). In addition, it was observed that some amount of magnesium, which did not participate in the SHS reaction and was detected in the SHS product, remained in the structure after leaching. It can be reported that the rate of Mg dissolution increases with the increasing acid concentration. However, it should be noted here that the MgO formed after SHS could be completely taken into solution for all concentrations, including the lowest acid concentration of 6.5 M, while Mg passed into the solution much less. This situation can be explained by the fact that the standard reduction electrode potential of H_2O electrochemically is higher than the standard reduction electrode potential of H_2. In other words, the solubility of MgO is higher than the solubility of Mg in HCl, since the formation of water vapour instead of hydrogen is easier both thermodynamically and kinetically. For this reason, it has been thought that adding H_2O_2 or external O_2 in leaching process will have a positive effect on Mg removal. Thus, the TiO_2 removal efficiency will also increase. It was detected that magnesium could be removed significantly by increasing the acid concentration up to 10.5 M, and the intensity of

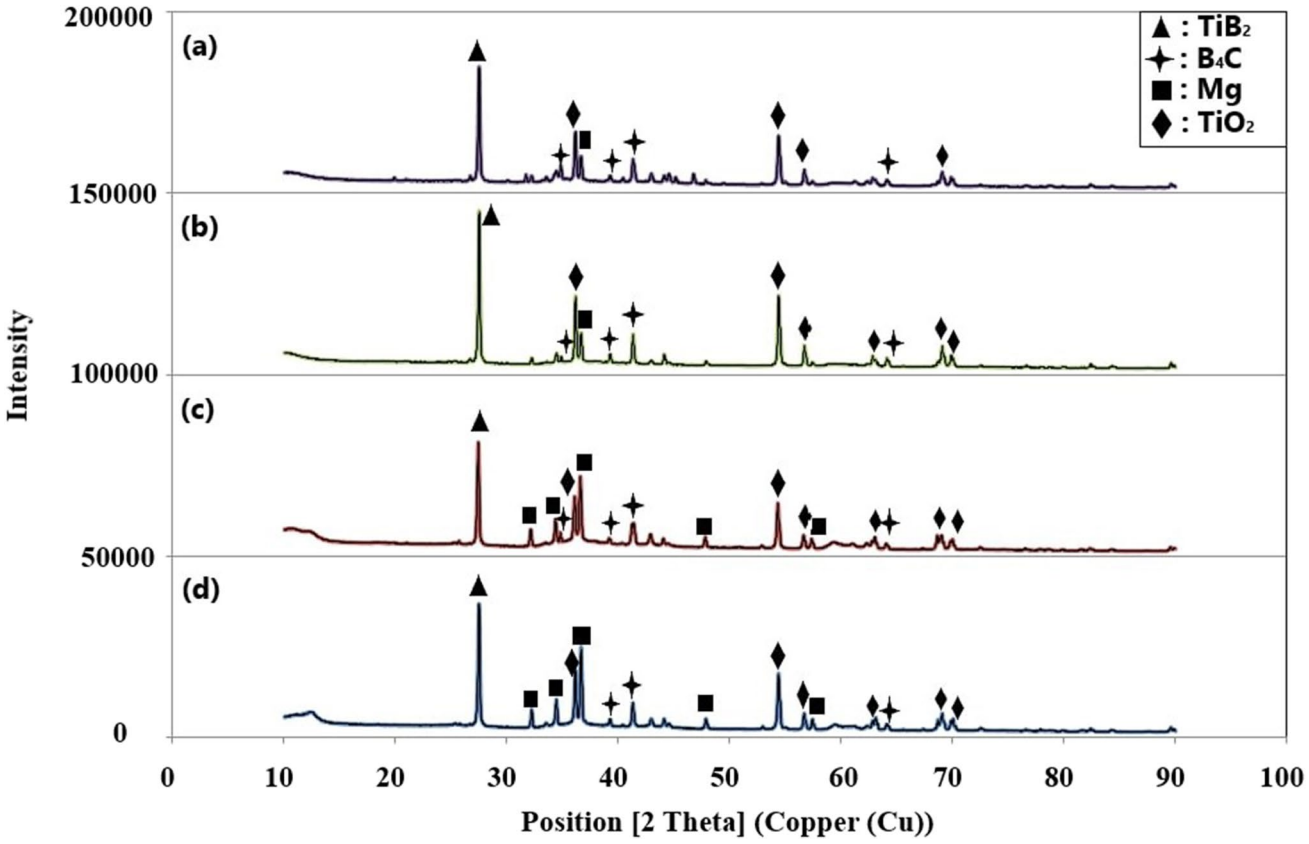

Fig. 6 XRD analysis results of products obtained as a result of HCl leaching in different concentrations after SHS of 50% B_4C-50% TiB_2 sample (**a**) 12.5 M, (**b**) 10.5 M, (**c**) 8.5 M and (**d**) 6.5 M

the TiO_2 peaks decreased with the increase to 12.5 M. It can be predicted that by increasing the acid concentration more, the amount of TiO_2 will decrease and Mg can be completely removed. However, in order to reduce the amount of TiO_2 and to prevent excessive acid consumption, addition of H_2O_2 and carbonic acid to the leaching process has been tried as a new method for leaching process of SHS synthesis inspired by the study patented by Yasushi et al. [59].

The pH value change of solution during leaching process was also investigated, and the results are given in Fig. 7. With the increase in acid concentration, the maximum pH value reached increases and the time required to reach this value decreases. This result supports the XRD results, given in Fig. 6, in terms of determining the optimum acid concentration.

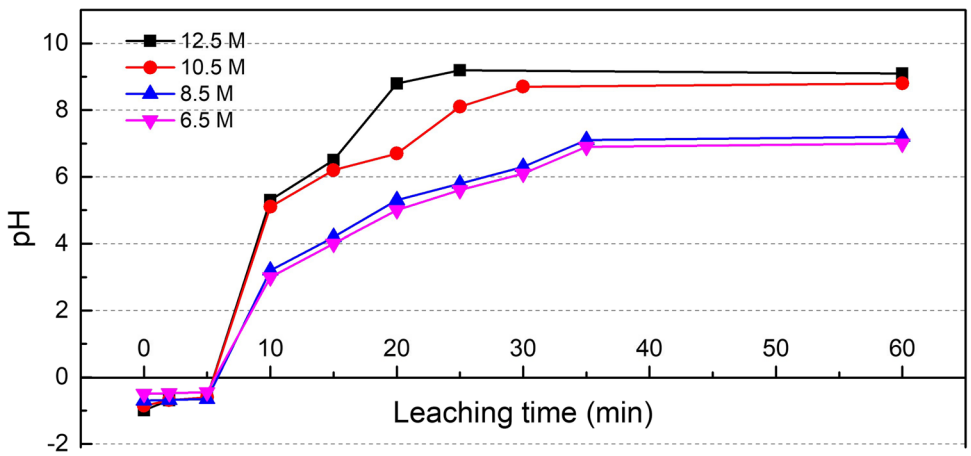

Fig. 7 pH value change of solution over time for leaching of B_4C-TiB_2 SHS product

According to the patented study conducted by Yasushi et al. [59], TiO_2 can be dissolved by leaching with carbonic acid and H_2O_2. In this study, 50 ml carbonic acid (pH = 4.4) and 50 ml H_2O_2 were added during HCl leaching process. Additions were made during the process when the pH value remained stable. As can be seen in Fig. 8, addition of carbonic acid to the leaching process significantly decreased the amount of TiO_2 and increased the amount of B_4C. However, the amount of magnesium borate phases (unsymbolized peaks) was observed to be increased owing to the increase in pH value during leaching process. After dissolution of TiO_2, extra HCl addition could have provided dissolution of magnesium borate phases and also residual MgO.

The effect of stoichiometric amount of charge composition was also investigated. It was observed that the most purified product could be obtained with 50% B_4C-50% TiB_2 sample, as can be seen in Fig. 9. It was determined to be the lowest magnesium borate containing sample. Only small amounts of MgO and TiO_2 were observed on 25% B_4C-75% TiB_2 sample. In order to produce composite powder which contains higher amount of B_4C, 75% B_4C-25% TiB_2 charge stoichiometry could also be used. As can be seen in XRD result given in Fig. 9a, 75% B_4C-25% TiB_2 sample contained higher amounts of undesired phases like magnesium borates and MgO. For the synthesis of higher B_4C containing composite powder, second leach process should be applied for obtaining higher purification.

SEM and BET analysis results

SEM micrographs of leached products for 100% B_4C, 50% B_4C-50% TiB_2 and 100% TiB_2 samples are given in Fig. 10a–c. 100% B_4C sample is composed of circular fine particles (Fig. 10a) of B_4C and magnesium borate phases. 100% TiB_2 sample composed of agglomerates with angular and sharp edges and agglomerates of fine particles (Fig. 10c). The particle size of 50% B_4C-50% TiB_2 was observed to be lower than the other samples as can be seen in Fig. 10b and also in Fig. 11b which is the image of same area with higher magnification. It was also seen that synthesizing B_4C-TiB_2 composite instead of synthesizing separately provided binding effect. This leads to increase in sintering ability of both B_4C and TiB_2 powders, as Heydari et al. [12] also reported.

SEM micrographs of SHS product and leached product of 50% B_4C-50% TiB_2 sample are given in Fig. 11a and b. It was observed that leaching process significantly reduced the particle size and increased the surface area. This was also can be seen on BET analysis results given in Table 6. In addition, leaching process significantly increased porosity. It was also observed that modified leaching process decreased the surface area of the product despite providing higher dissolution of TiO_2. Beside, modified leaching decreased the removal of magnesium borates (Fig. 8). This can be the reason of decrease in the surface area. When the SEM micrographs of leached product and modified leached

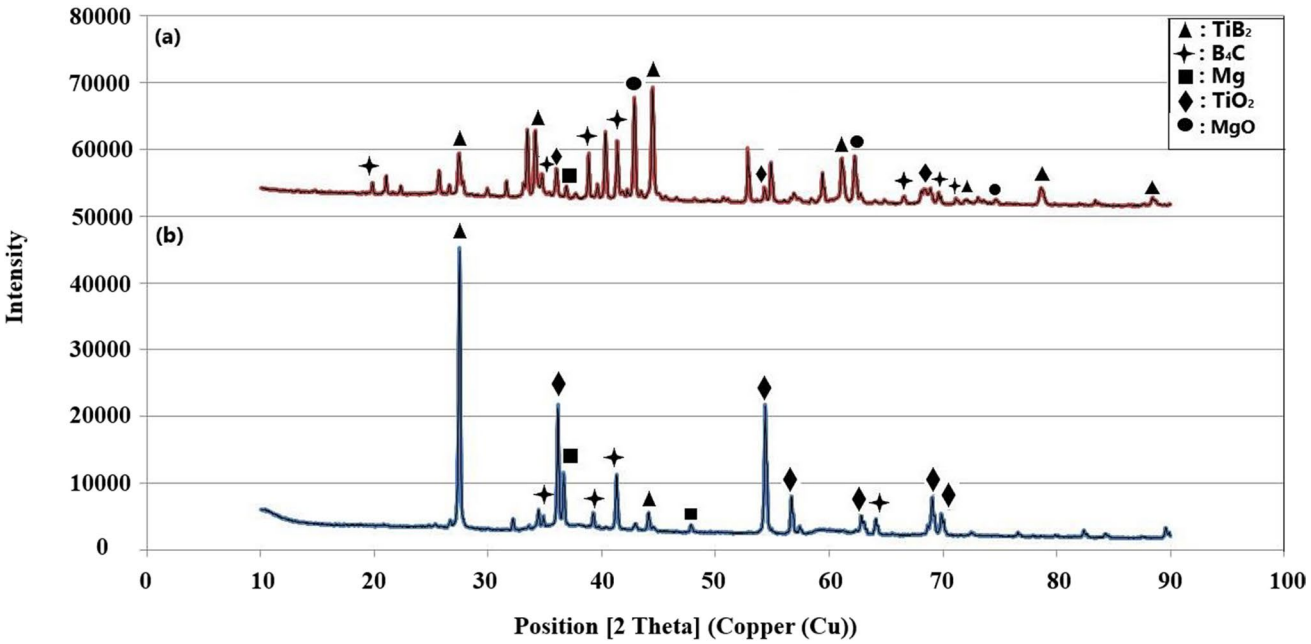

Fig. 8 XRD analysis results of products obtained as a result of (**a**) modified leaching and (**b**) optimized 10.5 M HCl leaching after SHS of 50% B_4C-50% TiB_2 sample

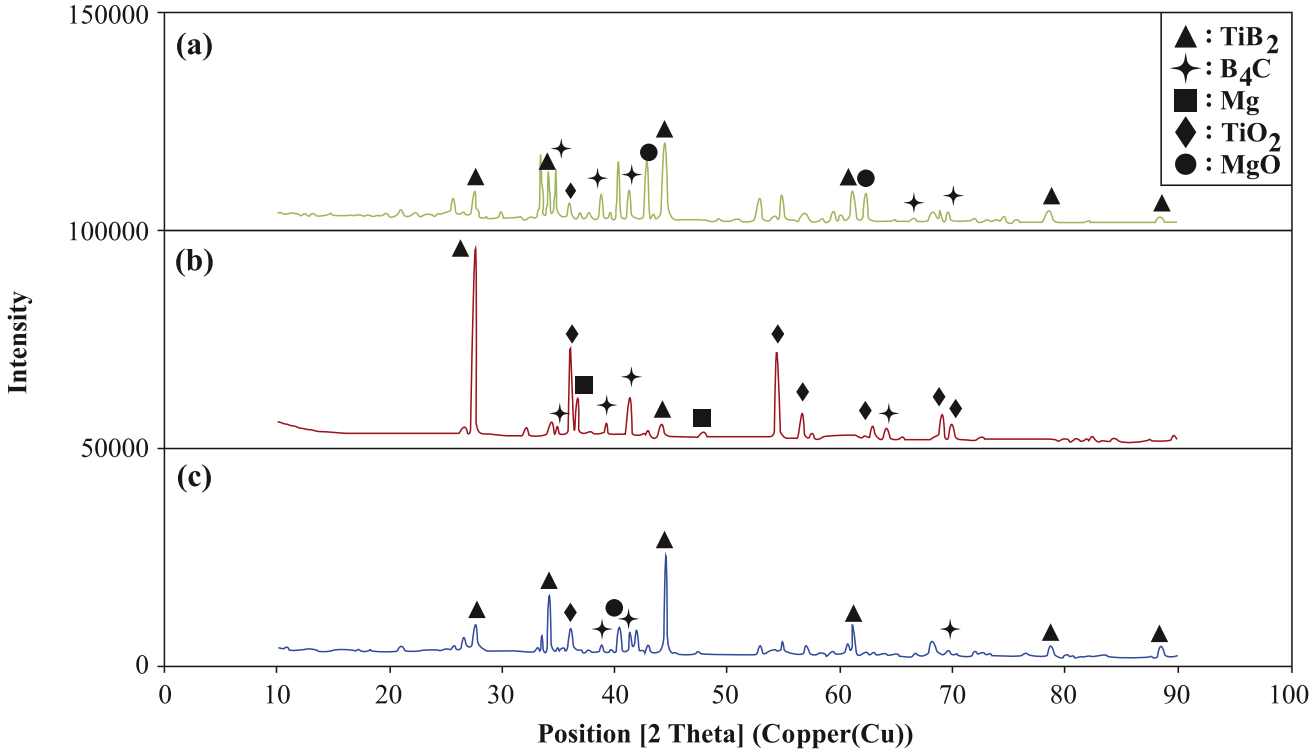

Fig. 9 XRD analysis results of leached products of (**a**) 75% B_4C-25% TiB_2, (**b**) 50% B_4C-50% TiB_2 and (**c**) 25% B_4C-75% TiB_2 samples

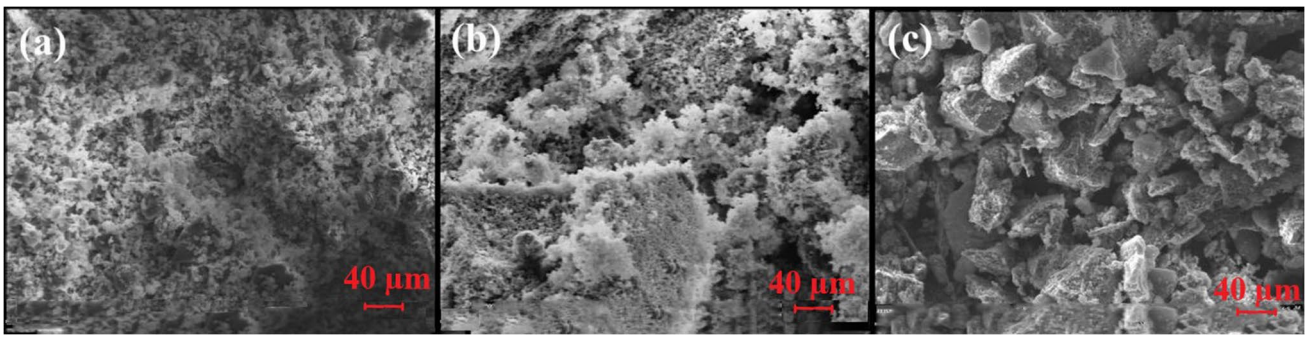

Fig.10 SEM micrographs of leached products (**a**) 100% B_4C, (**b**) 50% B_4C-50% TiB_2 and (**c**) 100% TiB_2 samples (Mag = 500×)

product given in Fig. 11b and c are compared, agglomeration of nanoparticles was observed to be higher after modified leaching.

Conclusions

Synthesis of composite powders is of great importance in order to combine the superior properties of advanced ceramic materials. In this study, B_4C-TiB_2 composite powders could successfully be synthesized by leach-assisted SHS method using oxide raw materials. It has been demonstrated in some studies that processes such as mechanical activation, use of argon gas and vacuum atmosphere for the production of similar ceramic powders increase the product quality. However, in this study, it is aimed to increase the product quality by improving the processes without carrying out these processes that increase the production cost. For this purpose, stoichiometric optimization of reactants and charge stoichiometry optimization were performed for the SHS process. In addition to optimizing the acid concentration for the leaching process, time-dependent pH and temperature

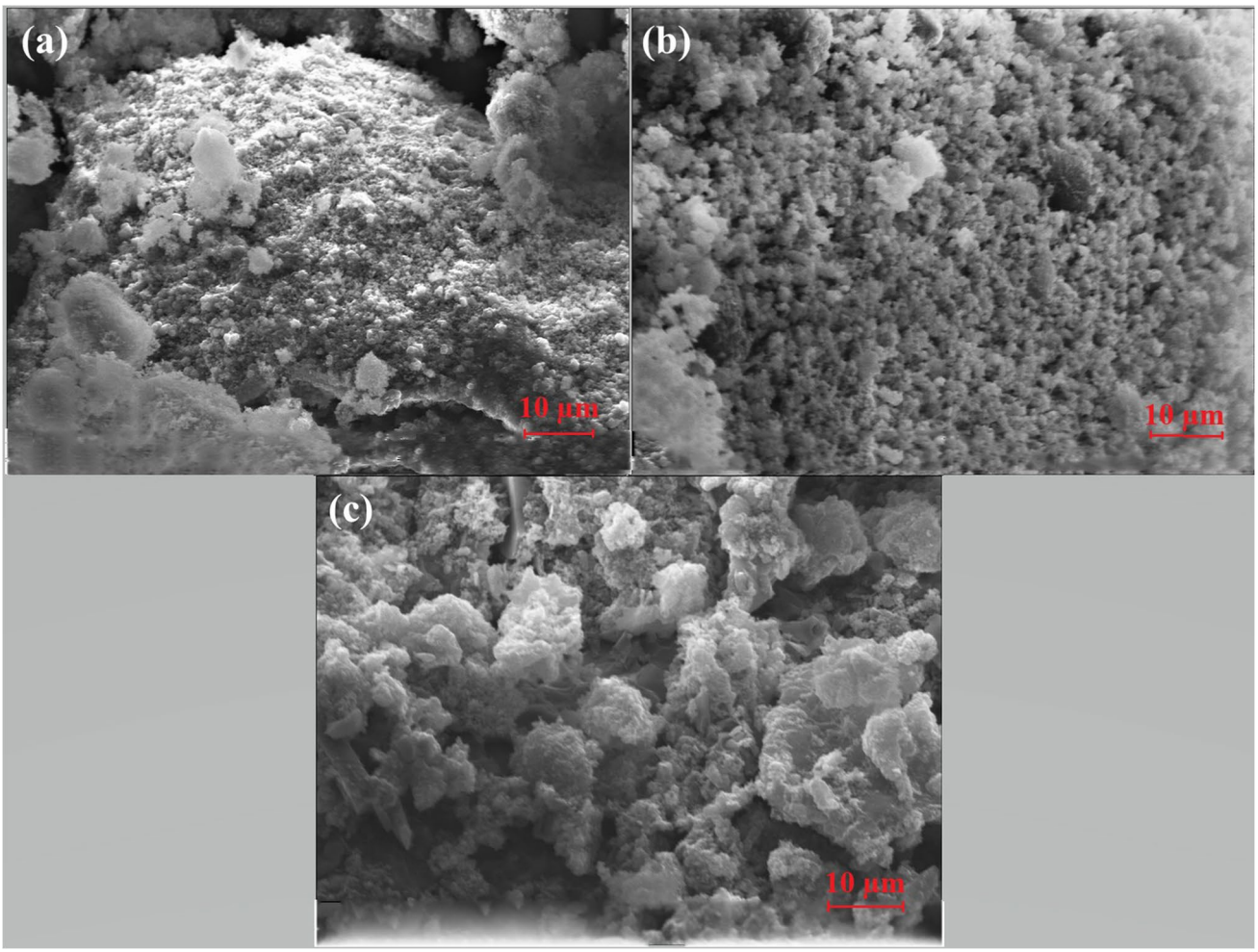

Fig. 11 SEM micrographs of 50% B_4C-50% TiB_2 sample (**a**) SHS product, (**b**) leached product and (**c**) modified leached product (Mag = 2500×)

Table 6 BET analysis results of 50% B_4C-50% TiB_2 sample

Product	BET surface area (m^2/g)	Average particle size (nm)	Pore volume (cm^3/g)
SHS product	1.6133	3719	0.0128
Leached product	28.8037	208.3	0.1551
Modified leached product	15.9747	375.5	0.0419

changes were controlled during the process. In addition, it is aimed to improve the process by adding chemicals to the HCl leaching process. According to the results obtained:

1. As a result of stoichiometric optimization performed by thermochemical analysis, the optimum molar ratios were determined as TiO_2:B_2O_3:Mg:C = 1:3:12:1.6.
2. It has been determined that the SHS efficiency has increased and the undesired phases have decreased significantly as a result of performing the combined SHS process rather than separately. Charge stoichiometry for the production of B_4C-TiB_2 composite was optimized after leaching. It was observed that the product with the least undesired phase could be obtained with 50% B_4C-50% TiB_2 charge stoichiometry. It was observed that good results were obtained in 25% B_4C-75% TiB_2 charge stoichiometry, but the amount of undesired phase increased with the increase of B_4C stoichiometry (Fig. 9).
3. Acid concentrations have been optimized both individually and for the production of B_4C-TiB_2 composite. Accordingly, 12 M for B_4C synthesis, 9 M for TiB_2 and 10.5 M for B_4C-TiB_2 were determined as optimum values.
4. The effect of adding carbonic acid and H_2O_2 at appropriate moments for dissolution of TiO_2 was investigated by examining the pH change depending on time during the leaching process. According to the results obtained, TiO_2 was completely removed with this method, which is expressed as modified leach. However, it caused an

increase in the amount of MgO and magnesium borate (Fig. 8). Increase in the pH value during carbonic acid addition can be the reason for that. It is predicted that higher purity could be obtained by performing the second acid leaching process.

5. As a result of SEM and BET analysis, it was determined that HCl leaching after SHS significantly reduced the particle size, increased the surface area and porosity, as well as provided the removal of undesired phases (Fig. 11, Table 6). After the leaching process, a product with high surface area of 28.80 m^2/g was obtained. SEM micrographs also revealed that synthesizing B_4C-TiB_2 composite instead of synthesizing separately provided binding of circular fine particles of B_4C and angular and sharp-edged agglomerates of TiB_2 (Fig. 10). This would lead to increase in sintering ability of both B_4C and TiB_2 powders.

When the results are evaluated briefly, the B_4C-TiB_2 composite powder, which has an average particle size of 208.3 nm, has a surface area of 28.8 m^2/g, but whose residual TiO_2 needs to be removed with carbonic acid and H_2O_2 added second leach and could be synthesized by SHS method.

Acknowledgements The authors would like to thank Dr. Amir Motallebzadeh from Koç University Surface Science and Technology Center (KUYTAM) for BET Surface Area Analysis.

Declarations

Conflict of interest The authors declare no competing interests.

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