**Production of TiB₂ by SHS and HCl Leaching at different Temperatures:
Characterization and Investigation of Sintering Behavior by SPS**

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Abstract

Sub-micron sized TiB₂ ceramic powders were prepared via self-propagating high-temperature synthesis (SHS) followed by HCl leaching at different temperatures. Purified powders obtained using optimum process parameters were consolidated by field assisted sintering technology / spark plasma sintering (FAST/SPS) technique. Phase and microstructural analyses of both the powder and sintered samples were carried out by X-ray diffractometer (XRD) and scanning electron microscope (SEM). The chemical analyses and particle size measurements of the specimen were conducted by inductively coupled plasma-mass spectrometry (ICP-MS) and dynamic light scattering (DLS) techniques. The final properties of the sintered sample were determined in terms of density and microhardness. The effects of different HCl leaching temperatures on the formation, microstructure, particle size, purity and sintering behavior of the SHS-produced TiB₂ powders were investigated. The SHS reaction of TiO₂-B₂O₃-Mg powders as a starting mixture yielded MgO, Mg₃(BO₃)₂ and Mg beside the desired phase TiB₂. All three magnesium containing by-products were completely removed by performing hot HCl leaching. TiB₂ powders after SHS reaction and leaching with 9.3 M HCl for 30 min at 80°C revealed a minimum purity of 98.4 % and a homogenous particle size distribution with an average particle size of 536 nm. In the ultimate SPS experiment which was conducted at 1500°C for 5 min under a pressure of 50 MPa, a relative density of 94.9 % and a micro-hardness value of 24.56 GPa were achieved.

Keywords: A. Powders: solid-state reaction; A. Sintering; B. Microstructure-final; D. Borides.

1. Introduction

Titanium diboride (TiB_2) is one of the technically most important advanced ceramics having high melting point, high strength, low density, high wear, corrosion and thermal shock resistance, excellent chemical stability, outstanding thermal and electrical conductivity [1-3]. According to the phase diagram of Ti-B binary system, TiB_2 is the most stable compound with a melting temperature of 3225°C [4]. Its extreme hardness arises from the presence of covalent B-B bonds and strong Ti-B interactions in the AlB_2 type of crystal structure [3-4]. Due to its superior mechanical, physical and chemical properties, TiB_2 is used as high temperature evaporation boats, ballistic armors, cutting tools, nuclear rods, wear resistant coatings, cathodes for electro-chemical processing of aluminum, grain refiner in aluminum castings, high temperature sleeves and reinforcement agents in ceramic or metal matrix composites [3, 5-8].

Many processes are available for the fabrication of TiB_2 ceramic powders such as high temperature methods using solid state reactions, borothermal and carbothermal reductions, fused-salt electrolysis, solvothermal reactions, gas phase combustion synthesis, chemical vapor deposition, ball milling and mechanochemical synthesis [1-2, 7-15]. However, most of these processes are not suitable for production in industrial quantities either due to the low yield and high cost of the reactants or requirement of expensive equipment [7]. Currently, titanium diboride is commercially accessible via carbothermal reduction of TiO_2 and boron oxide at temperatures between 1600 - 2100°C under Ar atmosphere [9]. The application of high temperatures, long reaction times and the use of complicated equipment are main restrictions for an efficient and simple fabrication of TiB_2 powders with high-purity and low particle size [1, 7]. Self-propagating high-temperature synthesis (SHS) or volume combustion synthesis (VCS) have been designated as alternative energy-saving methods which can be applied to the large scale production of many compounds [5, 16-21]. Compared to carbothermal technique, SHS has different advantages such as less energy loss, high efficiency, simple processing and equipment, and no need for extra processes to obtain finer product to be able to sinter easily [16-17]. During SHS, a highly exothermic combustion reaction occurs which is initiated by an electrical/chemical calorific device or a torch and the reaction becomes self-sustaining by utilizing the thermal energy released from the combustion reaction [19-20]. SHS technique has been reported in current literature as an economical and a novel route for the preparation of TiB_2 and TiB_2 -based ceramic powders [5, 16-23]: The typical combustion synthesis system is TiO_2 - B_2O_3 -Mg, where the chemical reaction processes affect the resultant phases [19-20]. The

effects of combustion process parameters such as compositions, particle size and shapes of the reactant mixtures or type and amounts of the diluent additives (KCl, NaCl etc.) on the synthesis of TiB₂ have been extensively investigated [5, 20-21]. Furthermore, the leaching procedure of the SHS samples was particularly discussed to eliminate by-products; however, there is still a lack of knowledge on determination of the reliable leaching parameters to obtain high-purity TiB₂ powders in the literature [22-23].

The sinterability of TiB₂, which is the key issue for its technical application, is limited due to its covalent bonding, high melting temperature and low self-diffusion rate [3, 6]. Therefore, hot pressing (HP), hot isostatic pressing (HIP) or spark plasma sintering (SPS) techniques have been utilized to consolidate TiB₂ powders [24-29]. Some sintering aids such as Ni and Fe have been employed to improve the sintering behavior [30]. It has been also reported that purity and particle size play a crucial role during sintering and for obtaining high-dense final products [17, 27-29, 31]. Further studies revealed higher densification rates for the nano-crystalline TiB₂ powders prepared by the SHS technique compared to those from commercial powders [17, 24]. On the other hand, reports concerning the sintering of combustion synthesized TiB₂ ceramics using SPS technique are very limited [17].

In present study, sub-micron and high-purity TiB₂ ceramic powders were fabricated via SHS followed by HCl leaching at different temperatures. The sintering behavior of the powders obtained using optimum process parameters were investigated by SPS technique.

2. Experimental procedure

2.1. Powder processing

In this study, TiO₂ (Sigma Aldrich, > 99 % purity), B₂O₃ (Eti Maden, > 98 % purity) and Mg (Sigma Aldrich, > 99 % purity) powders were used as starting materials. Approximately 50 g of the powder mixtures containing stoichiometric amounts of the reactants were prepared according to the reaction given in Eq.(1). The mixtures of TiO₂ and B₂O₃ powders were mechanically mixed for 30 min by using a rolling mill. Then, Mg was added to the mixture and distributed homogenously by using a Turbula blender.

The SHS experiments were conducted in a very simple, self-constructed low-priced combustion system (i.e. a steel reactor placed in a water-cooled tank). The schematic representation of the SHS arrangement is shown in Figure 1. The as-prepared powder mixtures (Figure 1(h)) were loaded into a steel crucible (Figure 1(g)) which in turn was placed in the steel reactor (Figure

1(f)). After closing the reactor, Ar gas was loaded into the system (Figure 1(a)) with a flow rate of 10 l/min. Within 5 minutes, the air was replaced by the inert gas and the mixture was ignited by a Hydrogen torch (Figure 1(c)). The use of Ar during the SHS experiments is a must in order to prevent oxidation. Since the mixture of Mg and TiO_2 is a typical thermite, a very exothermic combustion reaction takes place propagating on its own and terminated in a very short time period of approximately 15 seconds. The cooling time by means of the water-cooled tank is comparatively longer lasting 45 - 60 min. The room temperature and hot HCl leaching processes were applied on the products in order to remove the undesired by-products MgO , $\text{Mg}_3[\text{BO}_3]_2$ and metallic Mg. Leaching was carried out in a 9.3 M HCl solution for 30 min at room temperature, 70 and 80°C.

2.2. Sintering

Purified powders obtained using optimum process parameters were consolidated by using a field assisted sintering technology / spark plasma sintering (FAST/SPS) system type HP D 25 (FCT Systeme GmbH, Germany). Powders were loaded in a graphite die with an inner diameter of 40 mm. After evacuation and application of an uniaxial pressure of 50 MPa, the powder compact was heated to 1500°C with a heating rate of 50 K/min. After a dwell time of 5 min, the pressure was released followed by natural cooling.

2.3. Characterization

Phase analyses of the powders and sintered samples were carried out using a Bruker D2 Phaser powder diffractometer with $\text{CuK}\alpha$ radiation in the 2θ range of 20–90° at a step size of 0.02° and at a rate of 2°/min. Microstructural characterizations of the powders and sintered products were performed by using a Zeiss EVO LS15 Scanning Electron Microscope (SEM) coupled with an energy dispersive X-Ray spectrometer (EDS). The chemical analysis and particle size measurement of the powders were conducted by using an Agilent 7700x inductively coupled plasma-mass spectrometry (ICP-MS) and a Malvern ZS Zetasizer dynamic light scattering (DLS) techniques, respectively. The purity (% wt.) of the obtained powders was based on the calculations obtained from the elemental analysis of Ti, B and Mg by ICP-MS measurement. In order to achieve scratch-free mirror finish for SEM analyses and Vickers microhardness measurements, sintered samples were subjected to a typical metallographic preparation procedure (mounting, grinding and polishing). The SEM analyses of the sintered specimen were carried out after polishing and fracture. The densities were measured in ethanol using the Archimedes method and the results were reported as the arithmetic mean of three different measurements taken from the same sample. Vickers microhardness measurements were

conducted using a Shimadzu HMV Microhardness Tester under a load of 200 g for 15 s. Microhardness test results for each sample include the arithmetic mean of twenty successive indentations and standard deviations.

3. Results and discussion

3.1. Phase and microstructural analyses of the powders

Figure 2 shows the XRD pattern of the $\text{TiO}_2\text{-B}_2\text{O}_3\text{-Mg}$ powders after the SHS reaction. As seen from Figure 2, TiB_2 (ICDD Card No: 07-0275), MgO (ICDD Card No: 45-0946), $\text{Mg}_3(\text{BO}_3)_2$ (ICDD Card No: 04-008-3201) and Mg (ICDD Card No: 35-0821) phases are observed in the product. This indicates that a reaction took place between the starting materials of TiO_2 , B_2O_3 and Mg resulting in the TiB_2 and MgO as majority phases. Unlike the reaction given in Eq.(1) which yields the MgO phase as the only by-product, a small amount of $\text{Mg}_3(\text{BO}_3)_2$ phase formed and unreacted Mg remained in the microstructure. This is understandable since products of the actual reaction triggered by the SHS reactions which is away from the equilibrium conditions may not completely conform to those of the ideal case. On the other hand, there are no remaining TiO_2 and no additional compounds between Ti-Mg , B-Mg , Ti-Mg-O and Ti-B-O in the detection limit of XRD. The formation of magnesium borate phases arising from the reaction between MgO and B_2O_3 during ignition has already been reported in SHS of TiB_2 powders [18-19, 21-22]. It has been previously suggested that the addition of excess Mg starting powder could reduce the produced magnesium borate phases [20]. In the present case, however, the SHS sample comprises a minor quantity of unreacted Mg (Figure 2). Previous results showed that Mg_2TiO_4 phase was also formed by a parallel reaction between unreacted TiO_2 and MgO and remained as the main impurity even after acid leaching [18-19, 21]. Obviously, the complete consumption of TiO_2 during ignition process prevented the further formation of the acid resistant Ti -based by-products, such as Mg_2TiO_4 [20]. The absence of magnesium titanate phases in Figure 2 is very likely related to powder preparation stage where the starting materials were prepared by mechanical mixing/Turbula blending and a homogenous distribution of the reactants was obtained. Furthermore, the higher homogeneity, reactivity and contact area of powder particles provide a higher combustion temperature and decrease the reaction temperature and combustion speed [20].

The XRD pattern of the SHS sample after HCl leaching at room temperature is depicted in Figure 3 which shows that the unwanted by-product MgO was completely removed from the powder mixture after leaching with 9.3 M HCl . The preference of using highly concentrated hydrochloric acid (9.3 M) during leaching process is the considerable temperature increase in

the solution. Since leaching of MgO with HCl is fairly exothermic, increasing the acid concentration will also raise the solution temperature and enhance the dissolution of unwanted phases [22]. As seen from Figure 3, the acid treatment at room temperature is only partially successful, dissolving MgO exclusively while the impurities $\text{Mg}_3(\text{BO}_3)_2$ and a small amount of Mg are still present in the residue. These findings confirm that the utilized leaching parameters are suitable only for the removal of MgO but not adequate to remove magnesium borate and magnesium phases. Similar observations have also been made in previous studies related with the room temperature acid leaching of SHS products [22]. Therefore, the leaching of the powders was carried out using the same acid concentration and duration (i.e. 9.3 M HCl, 30 min) but at 70 and 80°C. Figure 4 shows the XRD patterns of the SHS samples after hot HCl leaching at different temperatures. Figure 4(a) and (b) reveal the effectiveness of hot HCl treatment for complete dissolution of magnesium borate and magnesium phases, since only TiB_2 was detected in both microstructures. The X-ray powder diagram of TiB_2 comprises ten peaks at values of 27.603°, 34.130°, 44.443°, 56.994°, 61.099°, 68.131°, 68.316°, 71.877°, 78.624° and 88.394° which are respectively indexed as (001), (100), (101), (002), (110), (102), (111), (200), (201) and (112) crystal planes (Figure 4(a) and (b)). Furthermore, the peak intensities of TiB_2 phase on the XRD pattern increased when the leaching temperature was raised from 70 to 80°C, which could be as a result of the reduction of the average crystallite size and an increase in lattice strain. The positive effect of hot HCl leaching on the yield of TiB_2 produced by SHS reaction has also been reported according to which pure TiB_2 powders were obtained after hot leaching of SHS samples in 5 M HCl solution at 75°C for 15 h [18].

The SEM images and EDS analysis of the SHS sample after HCl leaching at room temperature are illustrated in Figure 5. Figure 5(a) and (b) represent irregular agglomerates having sizes in the range of 200 nm and 2 μm . The general EDS measurement (Figure 5(c)) taken from the region in Figure 5(b) reveals that the microstructure comprise the elements Ti, Mg, B and O. Due to the absence of MgO in the XRD pattern in Figure 3, the detection of the elements Mg and O in the EDS analysis can only be explained by the presence of magnesium borate and magnesium in the sample. Similarly composed polycrystalline TiB_2 powders obtained after acid leaching were also observed and reported in current literature [5].

Figure 6 illustrates the SEM images and EDS analysis of the SHS samples after hot HCl leaching at different temperatures. As seen from Figure 6(a) and (b), after removal of impurities from TiB_2 powders, the blurred microstructure with adherence and agglomeration of the particles (Figure 5(a)-(b)) are disappeared. The SEM images of the hot leached powders (Figure

6(a) and (b)) contain polygonal, equiaxed and spheroidal-shaped particles ranging in sizes between 400 nm and 1 μm . Furthermore, hot leached samples do not consist of perfect spheroidal-shaped particles throughout the structure due to the high adiabatic temperatures and cooling rate of the SHS reaction [5, 22]. It can be seen from Figure 6(b) that specimen treated at 80°C consist of distinct particles with relatively clear boundaries which are more homogenous than those leached at room temperature (Figure 5(a)-(b)). The general EDS measurement (Figure 6(c)) taken from the region in Figure 6(b) reveals that the samples are composed of only Ti and B, which is in good agreement with the result of the XRD analysis from the hot leached powders in Figure 4(b). The related EDS analyses revealed no detectable peaks for Mg and O which is a clear proof for the complete removal of all unwanted phases after HCl leaching at 80°C.

3.2. Particle size analyses and purity of the powders

Figure 7 and Table 1, respectively, present the particle size measurements and the values of average particle size/purity of the SHS samples after HCl leaching at different temperatures. As it is evident from Figure 7(a) and (b), more homogeneous particle size distribution was obtained for the hot leached powders than those leached at room temperature. This finding harmonizes also well with the SEM images of the leached powders in Figure 5(a) and 6(b) in which an uneven size distribution of the particles was observed. On the other hand, the average particle size of powders leached at room temperature slightly increased from 487 to 645 and 536 nm after hot leaching at 70 and 80°C, respectively (Table 1). Agglomerated particles observed in SEM images in Figure 5(a)-(b) and 6(a)-(b) prevents the observation of the smaller ones. Therefore, particle size measurement carried out after homogenization of the powder mixtures gave more accurate results as depicted in Figure 7 and Table 1. It has been reported that the addition of SHS diluents (NaCl, KCl, CaCl_2) to the reaction mixture reduced the grain growth of particles possibly by reducing the adiabatic temperatures and giving a coating on TiB_2 particles [5, 17]. The production of TiB_2 powders with an average particle size of around 100 nm was achieved in literature by adding NaCl diluent (20-45 wt. %) to the reaction mixture during SHS reaction [17, 21]. On the other hand, the sizes of the SHS'ed and leached TiB_2 powders produced without adding any SHS diluents were reported as between 9 and 65 μm [5, 22]. It was also claimed that the effect of initial size and green density of the starting particles was more pronounced than the effect of the addition of SHS diluents [21]. Thus, in the present study, leached TiB_2 particles in average sizes lower than 650 nm were achieved without using any SHS diluents. This is most likely due to the initial powder preparation step which provided

a high homogeneity, reactivity and contact area of powder particles [20]. Furthermore, high acid concentration and utilized temperatures during leaching process may provide TiB_2 structures in the absence of any impurity resulting smaller network grains having high surface areas [22].

The purity (%) of TiB_2 powders was calculated based on the Ti:B ratio obtained from the elemental analysis by ICP-MS. The results are presented in Table 1 confirming that the purity of the TiB_2 powders produced after HCl leaching at room temperature is considerably increased from 90 to 96.5 % for those leached at 70°C. The highest purity (> 98.4 %) was achieved for SHS'ed TiB_2 samples obtained after HCl treatment at 80°C. Chemical analyses of the HCl leached samples at different temperatures are compatible to their XRD and SEM/EDS analyses given in Figure 3, 4, 5(c) and 6(c). On the basis of these results, the optimal leaching conditions for the production of high-purity (> 98.4 %) and sub-micron scale (536 nm) SHS'ed TiB_2 powders with homogeneous particle size distribution were determined to be in 9.3 M HCl solution for 30 min at 80°C. These powders obtained using optimum process parameters will be further named as optimized powders.

3.3. Phase and microstructural analyses of the sintered product

Optimized powders were consolidated by SPS technique at 1500°C for 5 min under a pressure of 50 MPa. In order to determine the probable contaminations or phase formations occurred during SPS, sintered samples were subjected to XRD analyses which confirm that the specimen are free of any detectable contamination, secondary or other undesired phases. The XRD pattern of the spark plasma sintered sample originated from optimized powders is presented in Figure 8 which shows that the obtained sample contains solely mono-phase TiB_2 . In contrast to the present findings, there are two similar studies reporting on the formation of secondary TiB phase after SPS of TiB_2 powders and the negative effect of TiB on the microstructural and mechanical properties of the sintered products [29, 32].

The SEM images of the spark plasma sintered sample originated from optimized powders taken from their polished and fractured surfaces are given in Figure 9. Figure 9(a) illustrates that SPS of pure TiB_2 powders provides a fine microstructure without any observable pore and segregation in the SEM image. In addition, the fracture surface in Figure 9(b) indicates a nearly complete densification of the sample. This shows the effectiveness of SPS technique even at relatively low temperature (1500°C) due to factors, such as the application of pressure and the presence of pulsed direct electric current through powders [29, 33]. The applied high electric current provides a local increase in the temperature at the particle contacts which significantly

enhances the diffusivity of the powders and accelerates the densification [29, 33]. Similar SPS conditions (1500°C for 15 min under pressure of 60 MPa) were employed for the consolidation of mechanochemically synthesized niobium boride powders; however, a complete densification could not be obtained [34]. This is most likely due to the phase transformation occurred during SPS after which unstable and secondary phases of niobium borides were formed [34]. Thus, the phase stability during the SPS of metal boride powders may be the key factor for high densification rates [34]. Non-porous microstructures of the polished and fractured sample (Figure 9(a) and (b)) promote the effect of the obtained phases (Figure 8) during SPS on the densification of TiB₂ powders. Furthermore, a closer look at the fractured surface of the sample in Figure 9(c) shows that there is no aggregates along the grain boundaries and triple point corners by means of the absence of any secondary phase in the microstructure. In a related study, it was reported that the TiB clusters occurred during SPS of TiB₂ powders were pulled out during the fracture process indicating the weak bonding between the matrix (TiB₂) and secondary phase (TiB) [32]. Figure 9(b) and (c) also reveal that the grain sizes of spark plasma sintered SHS'ed TiB₂ vary between 500 nm and 5 μm. This non-uniform size of grains throughout the microstructure of fracture surface could result from the partial formation of big platelets during sintering which might occur due to the high defect concentrations in SHS samples [17].

3.4. Density and microhardness measurements of the sintered product

Table 2 presents the density, relative density and microhardness values of the spark plasma sintered sample originated from optimized powders. Relative density (%) of the sintered sample was calculated by taking into account the theoretical density of TiB₂ and the measured Archimedes density of spark plasma sintered TiB₂ powders. As seen from Table 2, sintered product exhibits a relative density of 94.9 % and a microhardness value of 24.56 GPa. The high relative density value of 94.9 % conform well to the non-porous microstructures presented in the SEM images (Figure 9(a)-(c)). The considerably high density and microhardness values (Table 2) are attributed to the high purity (Table 1) and homogenous particle size distribution (Figure 7(b)) of the optimized powders. It is well known that the impurities in the microstructure of the precursor powders prevent the complete densification during SPS process. The results confirm that high-purity and homogeneous size distribution of precursor TiB₂ particles play a crucial role in consolidation process, microstructure and hardness of the resultant samples. They further give evidence of the essential effect of acid leaching process on the SHS'ed TiB₂ powders for obtaining the desired powder properties with enhanced sintering behavior.

A comparative pressureless sintering study of TiB_2 powders revealed that SHS-produced powders showed 97 % densification at 1950°C , whereas the identically sintered commercial powder could only be densified to 86 % at the same temperature [17]. Sintered micron-scale TiB_2 powders exhibited a relative density of 96.1 % and a microhardness of 18.3 GPa by SPS at 1500°C for 10 min under a pressure of 40 MPa [32]. A similar study also reported on the SPS of micron-scale TiB_2 powders according to which a relative density of 79.44 % and a microhardness of 17.46 GPa were achieved at 1780°C under a pressure of 50 MPa [28]. On the other hand, higher microhardness values (~ 26 GPa) of the sintered TiB_2 products with high relative density (> 92 %) were obtained by hot pressing at temperatures above 1800°C with long holding times (> 2 h) [6, 27]. Thus, comparing the reported density and hardness values of TiB_2 ceramics with those of the present study, it can be stated that the achieved relative density (94.9 %) and microhardness values (24.56 GPa) are remarkably high for the utilized consolidation processes and parameters (SPS at 1500°C for 5 min under a pressure of 50 MPa).

4. Conclusions

In this study, sub-micron sized TiB_2 ceramic powders in high purity were successfully synthesized from stoichiometric $\text{TiO}_2\text{-B}_2\text{O}_3\text{-Mg}$ powder mixtures by SHS and subsequent HCl leaching at different temperatures. The consolidation of the optimized powders was performed by SPS technique. The results were discussed regarding the effect of different leaching temperatures on the formation, microstructure, particle size, purity and sintering behavior of the SHS-produced TiB_2 powders. They allow following conclusions:

- The SHS reaction of $\text{TiO}_2\text{-B}_2\text{O}_3\text{-Mg}$ powder mixtures yielded TiB_2 and MgO , as main phases while $\text{Mg}_3(\text{BO}_3)_2$ and Mg formed as by-products. The unwanted MgO could be completely removed after leaching with 9.3 M HCl at room temperature, leaving $\text{Mg}_3(\text{BO}_3)_2$ and also very small amount of Mg in the residual powder. High-purity TiB_2 powders without any impurities were obtained after hot HCl leaching at 70 and 80°C .
- Pure TiB_2 powders -i.e. without detectable foreign phases in XRD patterns- with a minimum purity of 98.4 %, an average particle size of 536 nm and a homogenous particle size distribution were obtained after SHS and hot leaching in 9.3 M HCl for 30 min at 80°C .
- After SPS at 1500°C for 5 min under a pressure of 50 MPa, TiB_2 was the only observable phase in the microstructure of the sintered product originated from optimized powders.

Polished and fractured surfaces of the spark plasma sintered sample showed nearly full densification.

- TiB₂ ceramics having a relative density of 94.9 % and a microhardness value of 24.56 GPa were obtained by FAST/SPS of TiB₂ powders prepared by SHS and hot HCl leaching at 80°C. The remarkably high density and hardness values are related to the purification degree and homogenous particle size distribution of the powders achieved at optimum process conditions.

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