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Spark plasma sintering of monolithic TiB_2 ceramics

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Spark plasma sintering is a promising technology particularly on the sintering of covalently bonded boride based ceramics. In the present study, effects of sintering temperature, sintering pressure and pressure application mode were tried to be determined for the spark plasma sintering of monolithic TiB_2 ceramics. The hardest compact (17.46 GPa) was obtained in the experiment which was conducted at 1780 ºC under a pressure of 50 MPa (applied when die reached to 1500 ºC). The relative density value of the sample was achieved as 79.44%. X-Ray diffraction spectrometry, scanning electron microscopy, Vickers micro hardness and Archimedes density measurement techniques were mainly used for the characterization.

Key words: Titanium diboride, Spark plasma sintering.

Introduction

TiB_2 is a transition metal boride with remarkable mechanical, physical and chemical properties such as high strength, durability, high melting point, hardness and wear resistance [1]. Its extreme hardness arises from covalently bonded atomic structure and its crystal structure has been reported as hexagonal in space group P6/mmm [1, 2]. Impact resistant armors, cutting tools, crucibles, wear resistant coatings and aluminum electrolysis cathodes are between the most important application areas [1].

Sintering of TiB_2 powders with high relative densities is a hard process due to its atomic bonds and its high melting point reaching up to 3250 ºC (for Kelvin conversion; ºC + 273.15 = K) [3]. Several studies were conducted to explain the sintering behavior of TiB_2 ceramics through hot pressing techniques. Wang et al. were investigated the effects of hot press and sintering parameters on the mechanical and microstructural properties of monolithic TiB_2 ceramics. Thus, they determined that short soaking time (60 minutes) and high temperature (1800 ºC) were the most suitable for the sintering of TiB_2 powders having an average grain size of 1.5 μm [4]. In 2005, TiB_2 powders with various grain size values (D50; 1.59, 3.09, 5.51 μm) were sintered using hot press technique by Königshofer et al. A powder activation process, which was conducted by milling, prior to the sintering process was also applied for some powders. Relative density value of 99.9% was achieved from the experiment conducted with activated TiB_2 powders under a pressure of 45 MPa at 1800 ºC for 60 minutes of soaking time [5]. Murthy et al. carried out a study on the tribological properties of hot pressed TiB_2 compacts in 2006 [6].

A study which was conducted using (High Temperature-High Pressure) Bridgman type apparatus was reported by Sulima et al. in 2007 in addition to the experiments where hot press was used. In that study, 1500 ºC ± 50 ºC sintering temperature under a pressure of 7.2 ± 0.2 GPa and 60 seconds of soaking time were chosen as the optimum parameters to obtain TiB_2 ceramic compacts without cracks with 98% relative density and 10.6 GPa hardness. It was remarked that an increase in the sintering temperature caused crack formation although density and hardness values increased [7].

The reported studies concerning the sintering of monolithic TiB_2 ceramics using spark plasma sintering (SPS) are very limited. Zhang et al. studied the effects of spark plasma sintering parameters on the sintered TiB_2 ceramics. The starting powder grain size was ranging between 1-2 μm. The experiments were conducted under a sintering pressure of 50 MPa at temperatures between 1200 ºC and 1800 ºC with a heating rate of 150 ºC · min^{-1} and under vacuum atmosphere. Thus, consolidated samples were obtained with a relative density of 97.6% and the micro hardness was achieved to be 29.6 ± 2.5 GPa for the experiment sintered at 1800 ºC. Related sintering conditions were reported to provide the optimum combination of dense microstructure and excellent mechanical properties [8]. In 2013, Mukhopadhyay et al. released the results of a comparative study containing the outputs of hot pressing and SPS experiments of TiB_2. That study suggests that hardness and density values of spark plasma sintered TiB_2 compacts are inferior than hot pressed samples,

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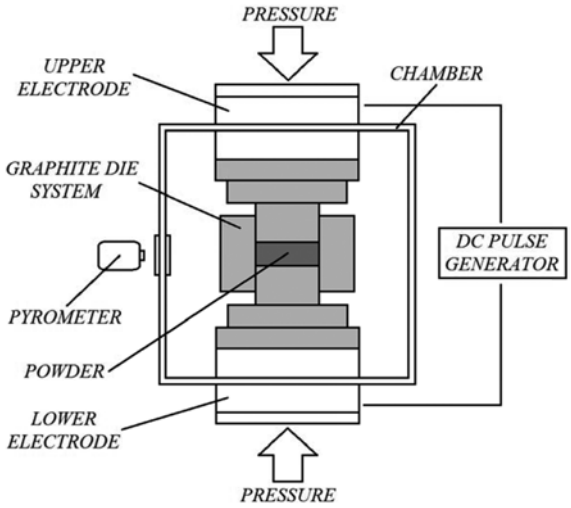

Fig. 1. A sketch showing the SPS system.

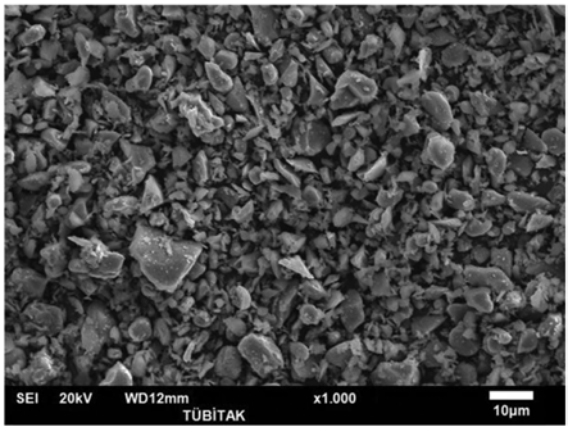

Fig. 2. SEM micrograph of TiB_2 powders.

despite of the short processing times and lower sintering temperatures of SPS technique [9]. High oxidation tendency of TiB_2 is the most important limitation for the sintering of TiB_2 ceramics. Therefore sintering processes are usually performed under vacuum or inert gas atmosphere (e.g. Ar and He). A study indicating the oxygen affinity of TiB_2 at lower temperature was conducted in 2006. Monolithic TiB_2 based hot pressed compacts were examined in a tube furnace at 850 °C under air atmosphere for 64 hours of soaking time. The formation of TiO_2 and glassy B_2O_3 based phases were observed using scanning electron microscopy (SEM) and X-Ray diffraction (XRD) technique in an increasing proportion with increasing time [10].

SPS is one of the newest approaches for the sintering of ceramics and metallic powders. It provides an internal heating by the formation of spark plasma, which is generated from direct current electricity discharge, between powders. Shorter sintering times at relatively lower temperatures are the most important features of the process. An SPS system is roughly the combination of graphite die system, electrodes, pressure mechanism, chamber to work under vacuum or gas atmosphere, pyrometers, water cooling unit, DC generator and a control unit [11, 12]. A schematic figure of the SPS system can be seen in Figure 1.

Determination of the optimum SPS sintering parameters of monolithic TiB_2 was the objective of the present study. TiB_2 powders were sintered at various temperatures under vacuum atmosphere with different pressure values for this purpose. XRD, SEM, micro hardness and Archimedes density measurement techniques were applied to the sintered compacts for the characterization.

Experimental Procedure

In this study, H. C. Starck-Grade D TiB_2 powders, having a D50 particle size of 5.68 μm, were used. The content of the powder was determined by using chemical analysis methods as 68.45% Ti, 0.05% Fe, 0.008% Mg, 0.16% C, 0.002% S, 0.80% O, 0.16% N and 30.00% B. SEM micrograph of TiB_2 powders can be seen in Figure 2. TiB_2 powders were mixed in ethanol media for further homogenization. TiB_2 containing ethanol suspension was dried and related powders were granulated. Afterwards, TiB_2 powders were loaded into a graphite die. The graphite die system which has an inner diameter of 50 mm and graphite sheet between powders-punches and inner sides of die was employed. Moreover, the die was covered with a carbon heat insulator blanket to eliminate the heat loss. SPS Syntex (SPS-7.40MK-VII) brand spark plasma sintering apparatus was used for the sintering experiments. Detailed information concerning the system can be found elsewhere [13]. DC pulse sequence of the SPS was fixed to be 12 : 2 (3.3 ms each). The constant parameters of SPS stage were chosen as heating rate of 150 °C · min^{-1} and 5 minutes of soaking time.

In the first set, TiB_2 powders were sintered at various temperatures between 1600-1800 °C under vacuum atmosphere and under 50 MPa pressure which was applied before the beginning of heating stage.

In the second experimental set, 50 MPa sintering pressure was applied after the die reached to 1500 °C and maximum sintering temperature was achieved to be 1780 °C. It was proposed that removing the glassy boron film (formed around the grains) by sparks was possible up to 1500 °C without applying pressure [10]. Furthermore, because of 20 °C lower sintering temperature is that at 1800 °C sintering temperature melting started to occur under these experimental conditions as it was already experienced.

In the third experimental set, powders were sintered between 1600 °C and 1780 °C under vacuum atmosphere and under an initial sintering pressure of 70 MPa.

Obtained ceramic compacts were cut by using diamond coated blade and polishing stage was performed

to the samples which would be characterized using XRD and SEM. XRD patterns were obtained by using Rigaku Miniflex (Cu-Kα) XRD and SEM was used for obtaining micrographs (JEOL JSM 6510LV for TiB_2 powder, JEOL JSM 7000F for TiB_2 compacts). Archimedes principle was used for obtaining density values. Hardness tests were practiced by using the Vickers indentation technique (Leica VH-MOT). Applied load of 2000 g was chosen for the hardness tests.

Results and Discussion

Relative density values notably increased with the increase in sintering temperature for all experiments. The highest relative density value was obtained as 80.17% at sintering temperature of 1780 °C under the initially applied pressure of 70 MPa (Figure 3, Table 1). Also, the experimental set which 50 MPa initial pressure applied had a remarkable relative density value as 80.05% at 1800 °C.

Hardness values indicated that hardness of the sintered compacts increased with increasing temperature. The hardest sample (17.46 GPa) was obtained in the experiment under 50 MPa sintering pressure applied after 1500 °C at 1780 °C. 70 MPa pressure applied experimental set also provided high hardness values (16.59 GPa at 1780 °C). The relationship between hardness and sintering temperature can be seen in Figure 4 and Table 1.

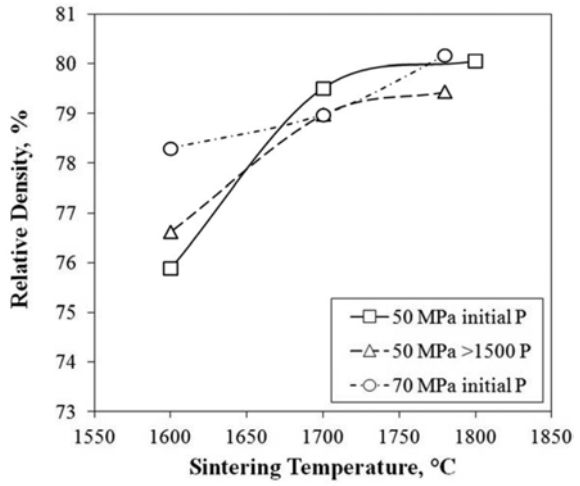

Fig. 3. Relative density values of the sintered TiB_2 ceramics with increasing sintering temperature.

Table 1. Relative density (d_{rel}, %) and Vickers micro hardness (HV, GPa) results of sintered TiB_2 ceramics.

Parameters	T, °C	1600	1700	1780	1800
50 MPa Initial P	d_{rel}, %	75.88	79.51		80.05
	HV, GPa	5.61	6.25		11.54
50 MPa P >1500 °C	d_{rel}, %	76.62	78.98	79.44	
	HV, GPa	5.98	6.00	17.46	
70 MPa Initial P	d_{rel}, %	78.3	78.98	80.17	
	HV, GPa	12.79	14.89	16.59	

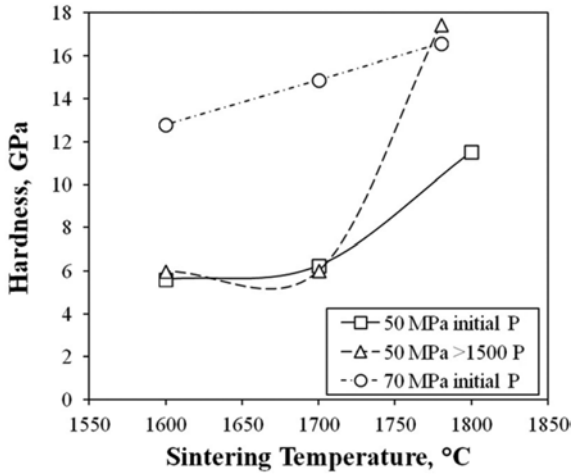

Fig. 4. Hardness values of the sintered TiB_2 ceramics with increasing sintering temperature.

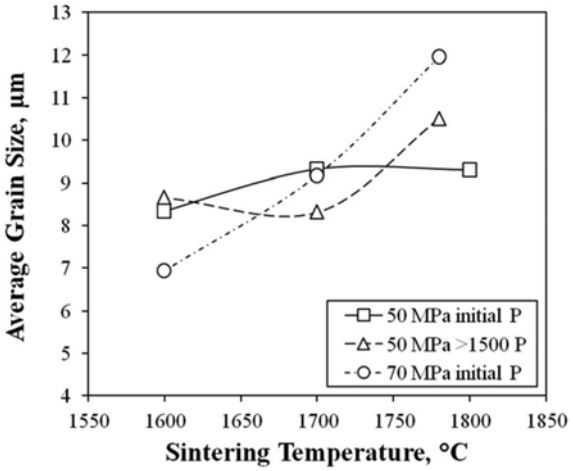

Fig. 5. Average grain size values of the sintered TiB_2 ceramics with increasing sintering temperature.

It is clear to see in Figure 5, higher sintering pressure and the application of pressure after 1500 °C cause formation of larger grain size on sintering as a result of neck formation. The highest average grain size was calculated as 11.96 µm in the experiment conducted under a pressure of 70 MPa.

Polished and fractured surface SEM micrographs of the sintered samples were given in Figure 6. XRD patterns of the samples which were sintered at the highest temperatures of per experimental set are shown in Figure 7. The XRD patterns indicate that there are not any phase transformation and the formation of another phases such as B_2O_3 and TiO_2 during sintering experiments. Toughness values could not be measured due to the porous structure of SPS products as seen in Figure 8.

Conclusions

In summary, sintering parameters of monolithic TiB_2

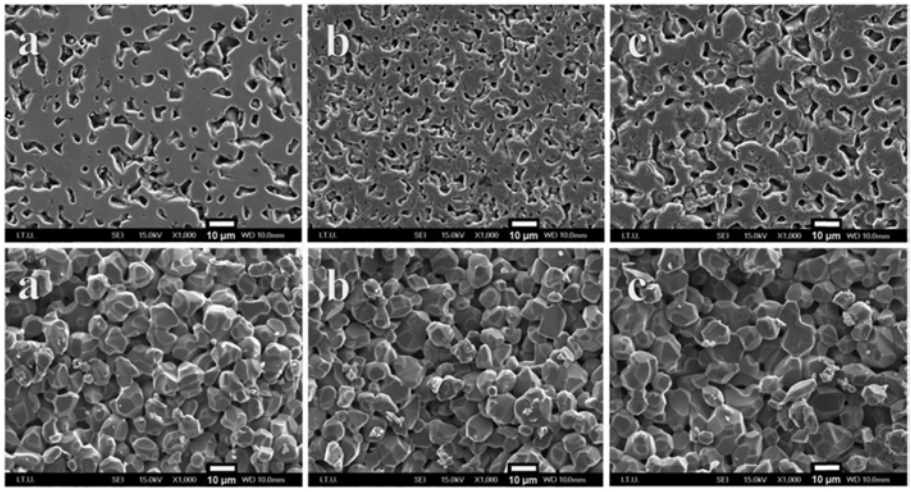

Fig. 6. SEM micrographs of polished (above) and fractured (below) TiB_2 samples (a: 50 MPa initial pressure at 1800 °C, b: 50 MPa pressure applied after 1500 °C at 1780 °C, c: 70 MPa initial pressure at 1780 °C).

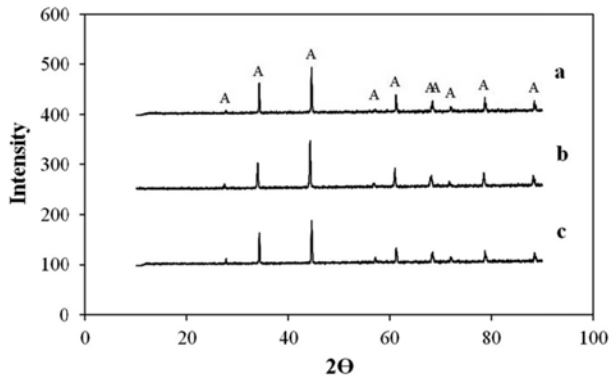

Fig. 7. XRD patterns of sintered TiB_2 samples (a: 50 MPa initial pressure at 1800 °C, b: 50 MPa pressure applied after 1500 °C at 1780 °C, c: 70 MPa initial pressure at 1780 °C).

ceramics which have a D50 particle size of 5.68 μm were investigated by using SPS. Effects of sintering temperature between 1600 °C and 1800 °C, sintering pressure of 50 MPa and 70 MPa and sintering pressure mode as initial and after 1500 °C were among the parameters to be investigated. The constant parameters of SPS were heating rate of 150 °C · min^{-1} and 5 minutes of soaking time. The experiments were conducted under vacuum atmosphere.

It was clearly observed that increase in sintering pressure from 50 MPa to 70 MPa and the application of sintering pressure after 1500 °C (to prevent the negative effects of the oxide films surrounding ceramic grains) beneficially influenced the hardness values. The highest hardness values were obtained in the experiments as 17.46 GPa at 1780 °C under 50 MPa pressure applied after 1500 °C and as 16.59 GPa at 1780 °C under initially applied pressure of 70 MPa. Relative density values of the compacts which were produced in these experiments were 79.44% and 80.17% respectively. Also the increase in the average grain sizes of sintered samples was determined in accordance with higher hardness and relative density values due to the increase in diffusion between the grains.

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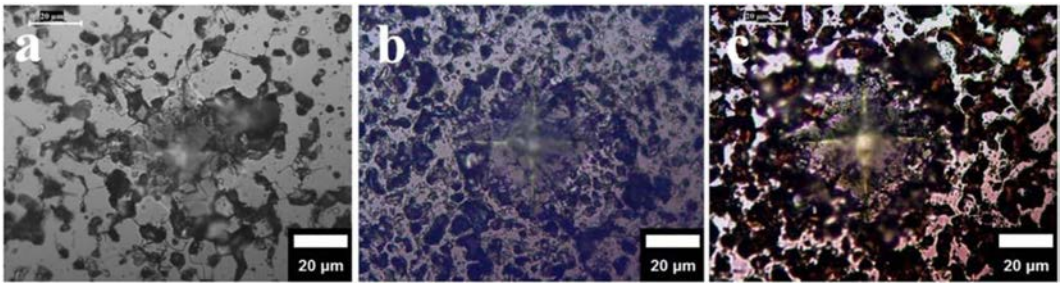

Fig. 8. Micrographs of sintered TiB_2 ceramics after indented by Vickers hardness apparatus (a: 50 MPa initial pressure at 1800 °C, b: 50 MPa pressure applied after 1500 °C at 1780 °C, c: 70 MPa initial pressure at 1780 °C).

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