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Sintering of TiB_2 ceramics

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ABSTRACT

Purpose: Titanium diborides (TiB_2) ceramic is particularly interesting because it exhibits high elastic modulus and hardness as well as high thermal conductivity. The interest in TiB_2 ceramic increased enormously due to these properties but applications seem to be limited due to difficulties during densification process. In the experiment the TiB_2 compacts was obtained using HP-HT method. The aim of this study is to work out and optimize the sintering densification process of TiB_2 ceramics.

Design/methodology/approach: The high temperature-high pressure (HT-HP) Bridgman type apparatus was used for densification method of TiB_2 powder. Ceramics were sintered at pressure of 7.2 ± 0.2 GPa and temperature at 1500-2300ºC ± 50ºC. The duration of sintering was 60 seconds. In order to investigate the structure changes, the optical and scanning electron microscope was used. Mechanical properties were determined by Vickers hardness. Young modulus measurements were carried out using ultrasonic method.

Findings: The TiB_2 ceramics was obtained without using sintering agents. The properties and structure of TiB_2 ceramics strongly depend on conditions of sintering process. The application of the temperature of 1500ºC±50ºC and pressure of 7.2 ± 0.2 GPa and time of 60 seconds permits to obtain the TiB_2 ceramics without cracks.

Practical implications: The TiB_2 ceramic might be used for production of composites. From a practical position it is important to optimize the sintering densification of TiB_2 ceramic.

Originality/value: The TiB_2 ceramics were formed using HP-HT technique without the use of additives. This method of sintering for TiB_2 ceramics is original one.

Keywords: Sintering; TiB_2 Ceramics; HT–HP technique

MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Non-oxide ceramics, in particular TiB_2, are candidate materials for high temperature applications due to their attractive properties like high melting point (3127°C), low density (4.451 g/cm^3), high electrical conductivity, high elastic modulus, good chemical stability as well as good thermal shock stability and good corrosion resistance. TiB_2 is also well known for its high hardness and outstanding tribological properties. Its Vickers hardness (34 GPa) is greater than that for more commonly used WC (20 GPa) and is almost as high as that of SiC (35 GPa). Furthermore, it has a high thermal conductivity (~110 Wm^{-1} K^{-1} at 25°C) and a significantly lower coefficient of thermal expansion (and ~7.2×10^{-6} K^{-1}) [1-3]. Such unique properties give TiB_2 materials a wide application area such as advanced engineering ceramics (cutting tools, wear-resistant parts, armour materials). Therefore, TiB_2 ceramic find application in aircraft, automotive, armaments and aerospace industry including production of the armour of land vehicles, ships, aircrafts, helicopters, aerospace parts and parts which are work in high temperature and are characterized by high abrasion resistance [4,5].

Limitation of wide application of TiB_2 ceramics arises from the sintering process itself and finally with obtaining the pure and compact TiB_2 ceramics. These difficulties among other like very high melting point of TiB_2 ceramics and presence of TiO_2 and B_2O_3 oxide layers had negative influence on the densification and reactions with metal matrix. Since TiB_2 is both an ionic and covalently bonded compound it can withstand high sintering temperatures. Temperatures above 2200°C are required for pressureless sintering, and density of the resultant sample can reach a value as high as 95% of theoretical density. In addition, the relatively low crystalline boundary diffusion coefficient of the TiB_2 decreases the densification speed, and prolongs the duration of sintering. Currently, the application of the sintering agents such as Ni, Fe, Co permit the decrease of the sintering temperature down to about 1530°C but they favour deterioration of the properties of TiB_2 ceramic [4-7].

The most popular method of the obtaining of the TiB_2 ceramics is applying sintering under pressure, for example hot isostatic pressing (HIP) or high temperature, high pressure (HT–HP) method. The application of high pressure during sintering causes:

- the acceleration of densification process,
- decrease of the sintering temperature,
- shortening of the duration of sintering,
- facilitation of the elimination process of pores in the sintering process.

Finally, the samples with high density close to the theoretical one and practically limited to phenomena of the grain growth [4,8-12] were obtained. Several studies were reported on the use of the various techniques for the fabrication of TiB_2 ceramics such as the hot isostatic pressing (HIP) [4,13,14], self-propagating high-temperature synthesis (SHS) [8,15] and Pulse Plasma Sintering (PPS) [16,17]. W. Weimin *et al.* [4] produced the titanium diboride ceramics by the hot pressing sintering method. A hot pressing furnace was used with a flowing argon atmosphere, was used temperature at 1500–1900°C, applied pressure was 30 MPa, duration of sintering was 30–120 min. The sintering temperature and duration of sintering have remarkable influence on mechanical properties, *e.g.* at proper sintering parameters, the bending strength, fracture toughness and hardness reach 558 MPa, 5.7 $MPam^{1/2}$ and 93 HRA, respectively. Authors affirmed that quick hot pressing sintering at high temperature is the best sintering processing for TiB_2 ceramics (short duration of sintering and high temperature). Konigshofer *et al.* [13] obtained the titanium diboride ceramics by the hot pressing sintering applied at different pressures and temperature of 1800°C. In this experiment the addition of 0.5 wt.% of various sintering aids such as CrB_2 or Cr_2N were applied which caused the increase of densities. This material had very high hardness as well as Young's modulus, heat conductivity and electrical conductivity. Jaroszewicz *et al.* [16] produced the TiB_2 compacts using a mixture of titanium and boron powders by the Pulse Plasma Sintering (PPS) method. The compacts containing the TiB_2 phase alone were obtained from the mixture with the Ti/B ratio = 1:2.6 and consolidated at a temperature of 1400°C for 900s. The Vickers hardness of the sintered material produced this way was 22.6 GPa and its density was 3.5 g/cm^3.

2. Experimental procedure

The titanium diboride powders (Atlantic Equipment Engineers) had particles below 10 µm and 99.9% chemical purity. The powders were formed into discs (15 mm in diameter, 5 mm high) by pressing in a steel matrix under pressure of 200 MPa. Samples were heated using a ceramics gasket provided with an internal graphite heater. For the densification of TiB_2 powder the high temperature–high pressure (HT–HP) Bridgman type apparatus was used. Figure 1 shows a cross-section of this apparatus. Compacts were obtained at pressure of 7.2 ± 0.2 GPa and at temperatures of 1500 °C, 2000°C, 2200°C and 2300°C ± 50°C. Samples were the HT-HP sintered for 60 seconds. The high temperature–high pressure (HT–HP) Bridgman type apparatus is characterized by the ability of the sintering of compacts having relatively high volume (usually 0,3-1 cm^3). Depending on the volume of the chamber it generated the pressure up to about 9-12 GPa, thus the smaller the chamber the bigger the pressure can be obtained. This method assured the optimal distribution of the pressure and obtaining the high temperatures of the sintering.

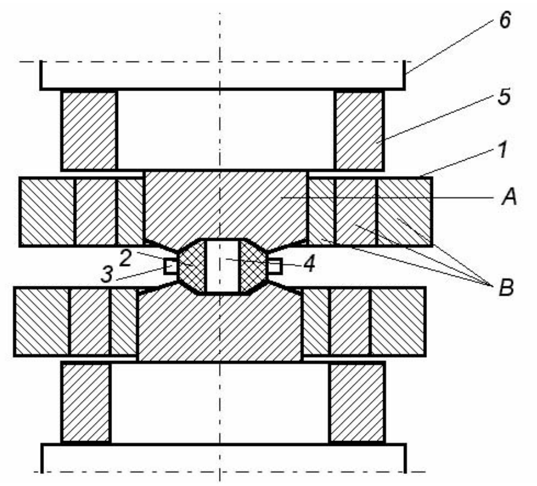

Fig. 1. Cross-section of the high pressure–high temperature Bridgman type apparatus; 1 – cell pressure (A – carbide anvil, B – set of steel rings), 2 – pyrophyllite gasket, 3 – pyrophyllite ring, 4 – assembly for sintering, 5 – carbide backing block, 6 – bottom platen [18]

Samples for Vickers hardness measurements and microstructure analysis were prepared through lapping on a cast iron plate with diamond paste. The Vickers indentation tests were performed on compacts using FM-7 microhardness tester. The applied load for non-graded materials was 0.98 N. Density was measured by hydrostatic method. Uncertainty of measurements was 0.02 g/cm^3. Young's moduli of the samples obtained by the HPHT sintering were measured basing on the velocity of the ultrasonic waves transition through the sample using ultrasonic flaw detector Panametrics Epoch III. The microstructures were observed using Olympus GX-51 optical light microscopy with SIS2.3 programme and JEOL ISM-6460 LV scanning electron microscopy.

3. Results and discussion

In case of the HT-HP method, simultaneous action of pressure and temperature influences the faster course of sintering (only a few minutes) in comparison with the free sintering which progress for even a dozen hours. The result of sintering process was presented for TiB_2 compacts depending on the sintering temperature (1500°C-2300°C ± 50°C). It is worth emphasizing, that the TiB_2 ceramics were sintered without the use of sintering agents. The obtained ceramics were characterized by very high density and isotropy of properties.

Table 1.
Properties of the TiB_2 ceramics obtained by HP-HT methods

Samples	T [°C]	Density [g/cm³]	Poisson's ratio	Young's modulus E [GPa]	$\frac{E}{E_0}$ [%]
TiB_2 (1)	1500	4.37	0.11	261	47
TiB_2 (2)	2000	4.42	0.12	492	90
TiB_2 (3)	2200	4.42	0.15	495	90
TiB_2 (4)	2300	4.45	0.14	514	93

Table 2
The hardness HV1 results for TiB_2 ceramics

Samples	Microhardness			
	HV1 [GPa]	HV1 average [GPa]	Standard deviation ± S	Uncertainty of measurement ± U [%]
TiB_2 (1)	9.6	10.6	0.54	1.49 ~15%
	11.1			
	11.7			
	11.6			
	9.1			
TiB_2 (4)	28.5	25.2	0.87	2.4 ~10%
	25.0			
	24.6			
	24.4			
	23.4			

The selected properties of the TiB_2 compacts are summariesed in Table 1. The measured hardness values of selected compacts are presented in Table 2. The TiB_2 specimens which were the HT-HP sintered at temperature of 1500°C ± 50°C reached density of 4.37 g/cm³ corresponding to 98% of theoretical density (4.451 g/cm³) [2]. However, the Young's modulus, Poisson's ratio and average Vickers hardness for these ceramics are 261 GPa and 0.11 and 10.6 GPa, respectively. Figures 2 and 3 illustrate the characteristic microstructure of TiB_2 ceramics which were obtained at 1500°C ± 50°C. These results of the examinations indicate that the applied conditions of sintering process (temperature of 1500°C ± 50°C, pressure of 7.2 ± 0.2 GPa, time of 60 seconds) permit the achievement of the compact TiB_2 ceramics.

In the case of the TiB_2 specimens which were sintered at temperatures of 2000°C ± 50°C, 2200°C ± 50°C, 2300°C ± 50°C, the density received values 4,42 g/cm³ and 4,45 g/cm³ (Tab.1), respectively.

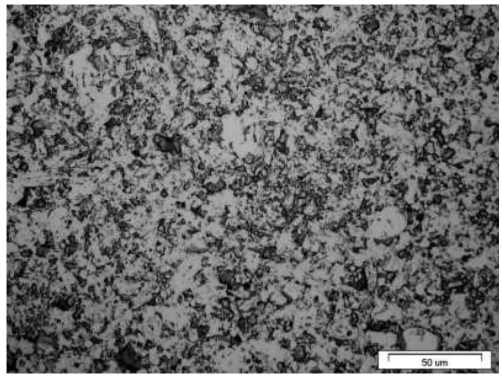

Fig. 2. Microstructure of the TiB_2 ceramic (number 1) after sintering at temperature of 1500°C ± 50°C

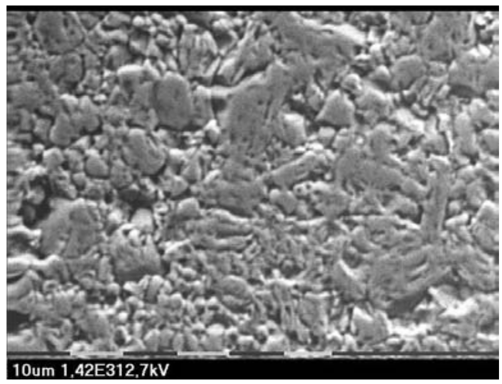

Fig. 3. SEM microstructure of the TiB_2 ceramic (number 1) after sintering at temperature of 1500°C ± 50°C

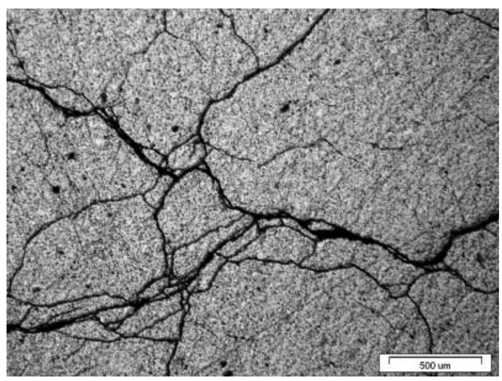

Fig. 4. Microstructure of the TiB_2 (number 4) ceramic after sintering at temperature of 2300°C ± 50°C

These values present almost 99% and 100% of theoretical density (4.451 g/cm³) [2]. Moreover, the Young's modulus is 492-514 GPa, Poisson's ratio is 0.12-0.14. Average Vickers hardness is 25.2 GPa for TiB_2 compacts (number 4). Figures 4-6 show the typical microstructure of TiB_2 ceramics after sintering at temperature of 2300°C ± 50°C. This microstructure is characterized by the numerous cracks (Fig.4). Some cracks were observed in all TiB_2 compacts which were obtaine d at temperature of 2000°C ± 50°C, 2200°C ±

50°C, 2300°C ± 50°C. The HP–HT technique always introduces strong structural stresses in the compacts, which might result in cracks and even their self-fragmentation. The applied conditions of sintering process (temperatures of 2000-2300°C ± 50°C, pressure of 7.2 ± 0.2 GPa, time of 60 seconds) cause the obtaining of the unfavourable microstructure of TiB_2 compacts.

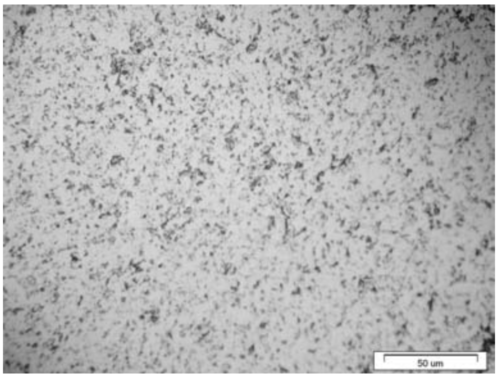

Fig. 5. Microstructure of the TiB_2 ceramic (number 4) after sintering at temperature of 2300°C ± 50°C

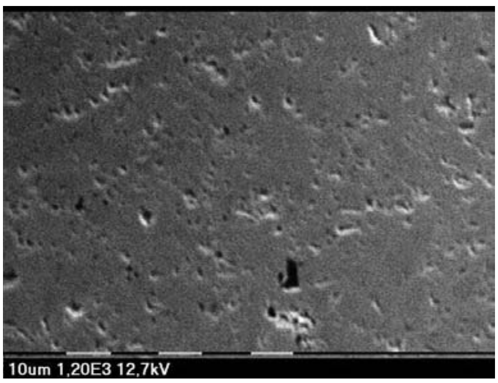

Fig. 6. Microstructure SEM of the TiB_2 ceramic (number 4) after sintering at temperature of 2300°C ± 50°C

4. Conclusions

The HT-HP technique is effective and the best sintering method for TiB_2 ceramics (short duration of sintering and high temperature). The TiB_2 ceramics were obtained without the use of sintering agents. The examinations indicate that the properties and microstructure of TiB_2 ceramics strongly depends on conditions of sintering process (temperature, duration of sintering, pressure).

The conditions of sintering proposed in this work (temperatures of 1500°C ± 50°C, pressure of 7.2 ± 0.2 GPa, time of 60 seconds) allow to obtain the TiB_2 ceramics without cracks.

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