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IMPACT OF PLANETARY BALL MILLING PARAMETERS ON THE PARTICLE SIZE OF TIB_2 POWDERS

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Abstract: *Titanium diboride (TiB_2) is a hard compound with good strength at elevated temperatures. The experimental activities, presented in this paper, were aimed to develop some TiB_2 composite materials as close as possible to the nanometric range. These small particles assure high mechanical properties after sintering process. The initial powders of TiB_2, with particles of about 1 micron, were milled in wet environment in a planetary ball mill with different milling parameters. Two important parameters were 3:1[25] and 5:1 ball-to-powder mass ratios and milling time 2 and 3 hours. The working technology was by collision. Particles size distribution, scanning electron microscopy and energy-dispersive X-ray spectroscopy were done to characterize the samples. The results show that with increasing of milling time and ball ratio to powder decreases the particle size of TiB_2 with about 60 %, reaching in the nanometric range.*

Key words: *mechanical milling, particle size, TIB_2, powder, nanometric.*

1. INTRODUCTION

Titanium diboride (TiB_2) is an anisotropic polycrystalline material and has been widely used in many fields as cutting tools, wear-resistant parts, armour materials, crucibles etc. TiB_2 is characterized by a high melting point, high hardness, low density and high wear and corrosion resistance. This material also reveals a high electrical conductivity and good chemical stability [1-16]. The properties that recommend TiB_2 as an appropriate material for armour with good behaviour at ballistics tests are high elastic modulus and high compressive strength [4]

Because of the high sintering temperature, the risk of the grain growth rate of TiB_2 is significantly higher, even if the sintering process takes place in a short period of time [17-19]. The sintering temperature significantly affects the TiB_2 properties and therefore the monitoring of the sintering temperature is of the utmost importance. From previous research work, it has been observed that the best properties of TiB_2 were obtained when the size of the grains was in the nanometric range.

The aim of this research is to develop TiB_2 powders with particle sizes as small as possible (nanometric range). In order to obtain powders in this range, the ball milling technique (BM) both in a wet and dry environment was employed [20-24].

Ball milling (BM) is a solid-state powder process involving phenomena of the bonding and strengthening of the composites enhancing their properties after the sintering process [25].

High-speed planetary ball milling has been an effective physical technique used to refine ceramic particles.

Compared with general ball milling, high-speed planetary ball milling has the advantage of producing a more homogeneous microstructure and improving the mechanical properties of sintered ceramics [26]. This ball milling process is also used in other fields of work such as the production of materials for biomedical applications [27- 29].

During the high-speed planetary milling process, the grinding environment is accelerated at a much larger velocity than the one achieved in traditional ball milling. In this way, a high transfer of kinetic energy is transferred from the balls to the sample creating conditions for obtaining a powder with smaller grain size (nanometric range) [30].

In the present study, a high-speed planetary ball milling process was used to reduce the particle size of TiB_2 powders up to the nanometric range.

An important parameter of planetary ball milling is the ball-to-powder mass ratios. In this paper it was analyzed, the 5:1 ball-to-powder mass ratio and two milling times of 2 and 3 hours in a wet environment. This paper also reports comparative results of this 5:1 ratio with a 3:1 ratio, from another research [31].

It was found that the particle size of TiB_2 powders decreased more for the 5:1 ball-to-powder mass ratio compared to the 3:1 ratio.

2. MATERIALS AND METHODS

Commercially TiB_2 powder, from Sigma-Aldrich, about 1 micron and a purity > 99 %, was used as the raw material.

Ti>67.5

B>30.5

C<1.5

O<1

Fe<0.2

- molar mass: 69,489 g / mol
- density: 4.52 g / cm3
- melting point: 3,230 ° C

Fig. 1. Commercial TiB_2 powder specifications

Raw materials were dosed with an analytical balance and then subjected to the mechanical milling process, using a planetary ball mill (Fritsch P4 type) in dry and wet environment.

Planetary ball milling parameters are presented below:

- volume of milling bowls: 250 ml;
- material of milling bowls: stainless steel;
- ball diameter: Φ = 10 mm;
- number of balls: 50 pieces;
- ball material: stainless steel;
- balls / material ratio: 3/1[25], 5/1;
- working technology: by collision;
- milling environment: dry and wet;
- milling time: 2 and 3 hours.
- speed of the main disk: 300 rpm
- speed of the planets: -700 rpm

All the 50 balls were inserted in the milling bowls (dry milling environment) and the powder was placed over. Milling was set for two hours with a three minutes break after every ten minutes of milling. Milling was performed in cycles because during the milling period a significant amount of heat is released, which causes a significant increase in the temperature of the milling bowl, being necessary to interrupt the process for a certain period of time necessary to cool the bowl.

For the other type of milling, distilled water was used as the wet environment.

After 2 and 3 hours of effective milling, the obtained slurry was air dried. Powders were morphologically characterized by determining the appearance of the powder granules by SEM microscopy and particle size distribution using BROOKHAVEN BI-MAS equipment. The technique employed - photon correlation spectroscopy (PCS) of quasielastically scattered light (QELS) - is based on correlating the fluctuations about the average, scattered, laser light intensity. Samples were also analyzed by energy-dispersive X-ray spectroscopy (EDXS).

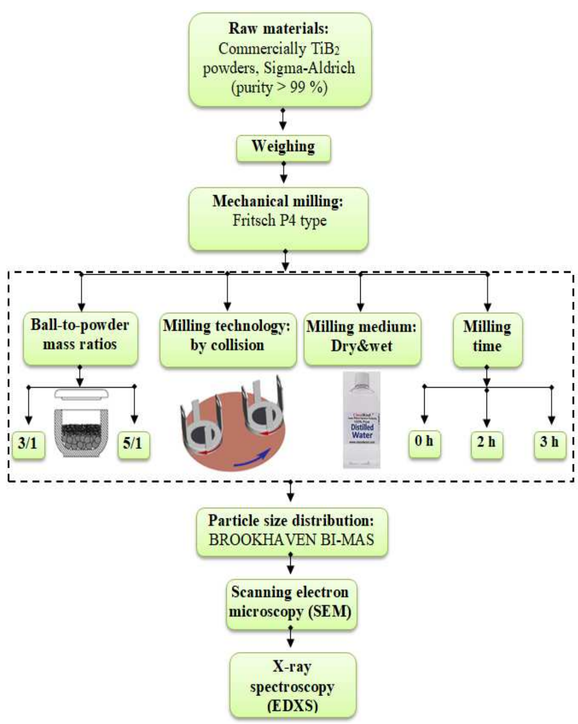

Fig. 2. Flow chart for research activities

Flow chart of all the research activities is presented in figure 2.

3. RESULTS AND DISCUSSIONS

Titanium diboride powders with particle sizes of about 1 micron were mechanically milled in dry environment for ball-to-powder mass ratio of 5:1. During milling, the powder is subject to high deformation by the impact generated between the balls and particles or between the balls, particles and the bowl wall.

The mechanical milling cycles are presented in the figure 3.

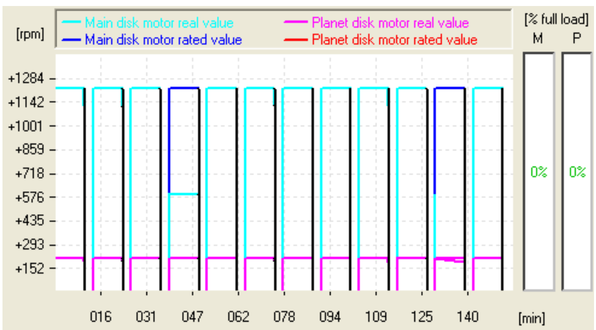

Fig. 3. Mechanical milling cycles in dry environment

It is observed that the milling in dry environment was finished after two hours, according to the figure 3.

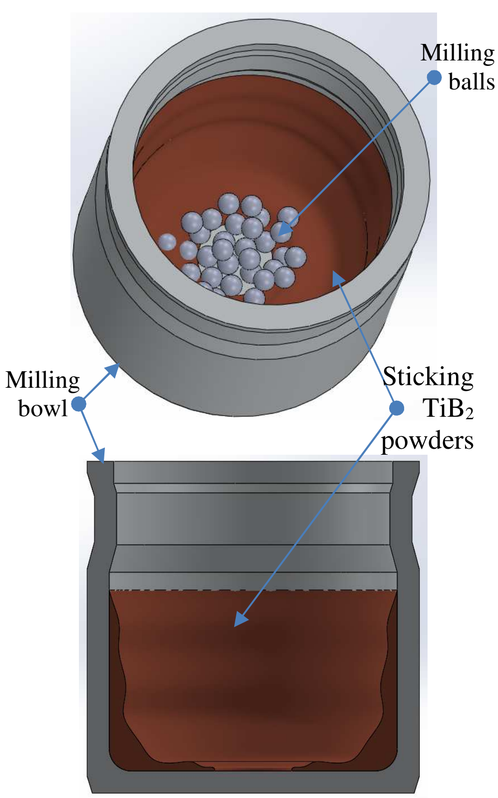

Fig. 4. TiB_2 powders-balls-milling bowl subassembly

After finishing the dry milling process, it was found that all the powder from the milling bowl was sticking to the wall of the bowl. An image of this process is presented in the figure 4.

The causes of sticking powder on the walls of the bowl can be various, so in the following we will present some:

- high temperature inside the bowl may cause powder to stick on the surface of the balls and also on inner wall;
- the milling time is too long;
- not enough liquid medium during milling;
- high speed during milling;
- number too large of milling ball inside the mill;
- too many powders in the bowl.

The sticking of the powders on the walls of the bowls makes the milling process not carry out properly.

The sticking powder was removed from the wall of the bowl and analyzed for particle size distribution point of view.

The logarithmic curve of the granulometric analysis of the TiB_2 sample, mechanically milled in dry environment for 2 hours, is shown in figure 5.

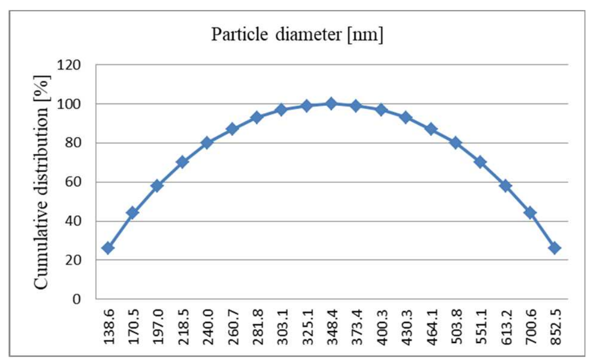

Fig. 5. Particle size distribution of the TiB_2 powders, milled for 2h in dry environment

The figure above presents a particle size range of the sample between [0.13-0.85 μm]. A large volume of particles with a size of 0.34 μm is also observed.

If we compare these results with those from the particle size distribution of the commercial TiB_2 powders [25], it is found that after two hours of dry milling, in not very good conditions, the dimensions of the powder particles are close to those of commercial (initial), presented in another research [25].

Although there are a number of elements that help to prevent powder from sticking to the wall of the bowl and milling balls, this type of milling has still been abandoned in this paper.

In subsequent research, this type of dry milling will be analyzed in detail in order to avoid the inconveniences that appeared in this experimental activity.

The process of mechanical milling continued, but in a wet environment. There were used the same milling cycles for wet milling, as in figure 3.

The particle size distribution of TiB_2 powders, mechanically milled for 2 hours, with a ball-to-powder mass ratio of 5:1 is presented in figure 6.

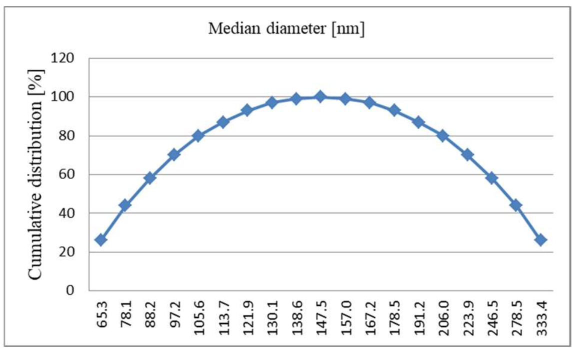

Fig. 6. Particle size distribution of the TiB_2 powders, milled for 2h in a wet environment

Scanning electron microscopy for the TiB_2 powders, milled for 2h in a wet environment is presented in figure 7 and the X-ray spectroscopy for the same sample, in figure 8.

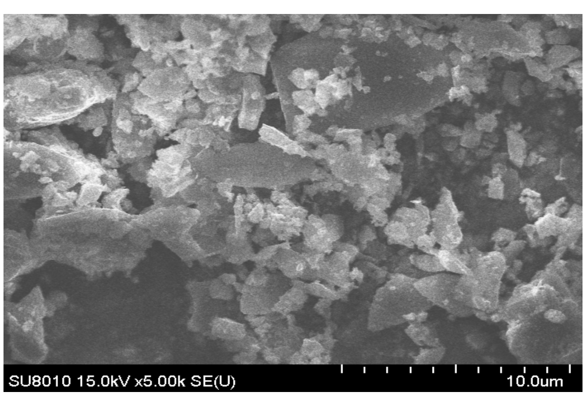

Fig. 7. SEM images of the TiB_2 powders milled for 2h in a wet environment

From SEM image and logarithmic curve of the granulometric analysis it can be seen the shape of the TiB_2 powder particles after milling and the particle size range between [0.06-0.33 µm]. A large volume of particles around 0.14 µm was recorded. There is an area with a smaller volume of particles in the nanometric range close to 65 nm, but there is another area where a small volume of larger particles in the submicron range appears, namely 0.33 µm.

There was a significant decrease in the particle size of TiB_2 powders for the 2-hour mechanically milled sample, which shows a 60% decrease compared to the initial, unmilled sample presented in [25].

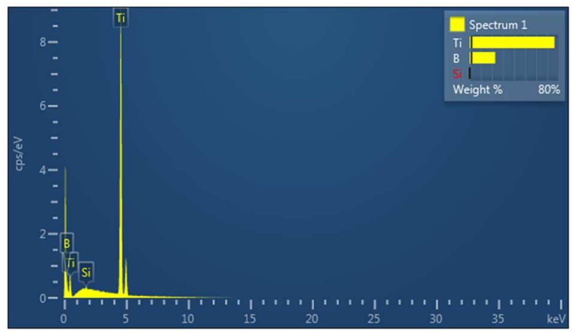

Fig. 8. X-ray spectroscopy of the TiB_2 powders milled for 2h in wet environment

Ti and B elements of the TiB_2 compound, are presented in figure 8.

The mechanically milled TiB_2 sample in wet environment for 3 hours presents the logarithmic curve of the granulometric analysis in figure 9.

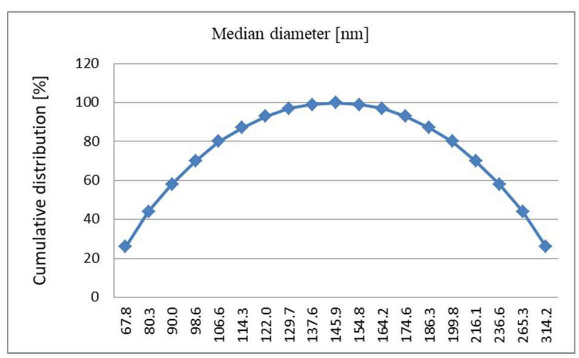

Fig. 9. Particle size distribution of the TiB_2 powders, milled for 3h in a wet environment

For the 3 hours mechanically milled sample, similar particle sizes of TiB_2 powders were recorded as in the 2 hours mechanically milled sample, indicating this way that the powders are beginning to agglomerate.

SEM image and X-ray spectroscopy for the TiB_2 powders, milled for 3h in the wet environment are presented in figures 10 and 11.

It is observed from the SEM analysis of this sample milled for 3 hours that the dimensions of the powder particles are smaller than the sample milled for 2 hours and thus strengthens the ones mentioned earlier, namely, the agglomeration of TiB_2 powder particles.

The agglomeration of TiB_2 powders was visible in both milling ratios, indicating this way that mechanical milling should be stopped at 3 hours.

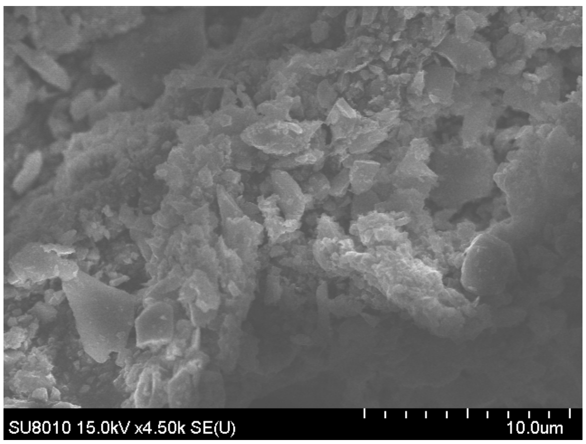

Fig. 10. SEM images of the TiB_2 powders milled for 3h in a wet environment

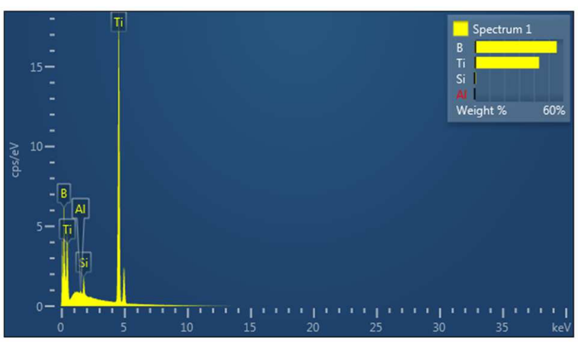

Fig. 11. X-ray spectroscopy of the TiB_2 powders milled for 3h in a wet environment

The spectrum from figure 11 also shows the presence of Ti and B elements from the titanium diboride synthesis.

4. CONCLUSION

The aim of the research was to develop TiB_2 powders with particle size in the nanometric range, using planetary ball milling. Due to some important parameters of planetary ball milling such as milling technology, milling ratios, different milling times and milling environment the aim was achieved. The impact of planetary ball milling parameters on the particle size of TiB_2 powders is presented in figures 12 and 13.

TiB_2 comercial powders [µm] [25]		
Minority fraction	Majority fraction	Minority fraction
0.14	0.35	0.86

3:1 ball-to-powder mass ratio [25]

TiB_2 powders, milled 2 h [µm]		
Minority fraction	Majority fraction	Minority fraction
0.084	0.19	0.44

TiB_2 powders, milled 3 h [µm]		
Minority fraction	Majority fraction	Minority fraction
0.076	0.17	0.38

5:1 ball-to-powder mass ratio

TiB_2 powders, milled 2 h [µm]		
Minority fraction	Majority fraction	Minority fraction
0.065	0.14	0.33

TiB_2 powders, milled 3 h [µm]		
Minority fraction	Majority fraction	Minority fraction
0.067	0.14	0.31

Fig. 12. Comparative results of TiB_2 particle size distribution

For the same mechanical milling time, the fineness of the TiB_2 powders of the 5:1 ratio is lower compared to that of the powders with the 3:1 milling ratio.

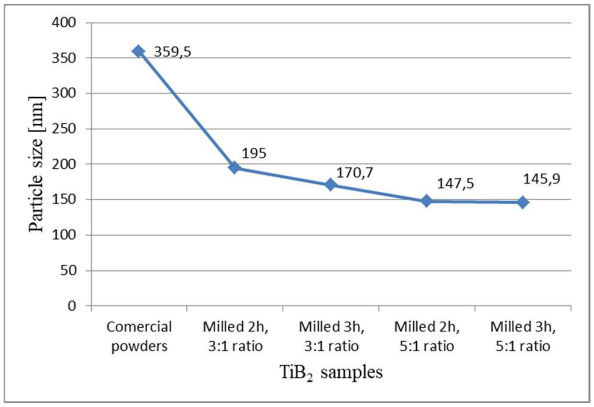

Fig. 13. Values of comparative majority fractions of TiB_2 particle size

It is visible that there is not a very big difference between 2 and 3 hours, not at all in the samples within the milling ratio 5:1. This is due to the fact that the powders become finer and thinner and tend to crowd.

5. ACKNOWLEDGEMENTS

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Impactul parametrilor de măcinare planetară cu bile asupra dimensiunilor particulelor pulberilor de TiB_2

Rezumat: TiB_2 este un material dur cu rezistență bună la uzură și la temperaturi ridicate. Activitățile experimentale, prezentate în această lucrare, au avut ca scop dezvoltarea unor materiale compozite (TiB_2) cât mai apropiate de intervalul nanometric. Aceste particule mici asigură proprietăți mecanice ridicate, după procesul de sinterizare. Pulberile inițiale de TiB_2, cu particule de aproximativ 1 micron, au fost măcinate în mediu umed într-o moară planetară cu bile cu diferiți parametri de măcinare. Doi parametri importanți au fost raportul de masă bile-pulbere 3:1 şi 5:1 şi timpii de măcinare de două şi trei ore. Tehnologia de lucru a fost prin coliziune. Distribuția dimensiunii particulelor, microscopia cu scanare electronică și spectroscopia cu raze X cu dispersie de energie au fost efectuate pentru a caracteriza probele. Rezultatele arată că odată cu creşterea timpului de măcinare și a raportului bile-pulbere scade dimensiunea particulelor de TiB_2 pana la 60 %, ajungând în domeniul nanometric.

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