

ELABORATION AND CHARACTERIZATION OF THE NANOMETRIC TITANIUM DIBORIDE POWDERS BY THE MECHANICAL MILLING METHOD

I. Stefan*, G. C. Benga, A. Olei

University of Craiova, Faculty of Mechanics, Romania

*Corresponding author's e-mail address: stefan_iuly@yahoo.com

ABSTRACT

The research activities are oriented towards elaborating and characterizing nano-sized powders by powder metallurgy technologies based on wet milling in a planetary mill. For the elaboration of the TiB_2 powders, a wet milling regime of initial powders was used up to nano size with the following parameters: milling technology by collision, milling times, rotational speed. The characterization of the TiB_2 material will include particle size distribution analysis. EDXS and SEM analysis were used to study the structural evolution of the powder after ball milling. The mechanical milling technology, by its milling regimes, proved to be very efficient, obtaining a reduction of the titanium diboride powders particle size up to 50% compared to the initial unmilled powders.

KEYWORDS: TiB_2 , mechanical milling, nanometric, particle size, powder

1. INTRODUCTION

TiB_2 is well known as a ceramic material with hexagonal crystal structure and it has been widely used in various industrial and military applications due to its high melting temperature, hardness and thermal diffusivity, excellent refractory properties and chemical inertness [2], [6]-[8]. Titanium diboride is the most stable of the intermetallic compounds between the titanium (Ti) and boron (B) system [7].

Figure 1 shows the lattice parameters of TiB_2 which have slightly quadratic dependence, and $a=b=302.9 \text{ \AA}$, $c=322.9 \text{ \AA}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$. The prevalent covalent bonding determines the low ductility, high hardness and high melting point [4].

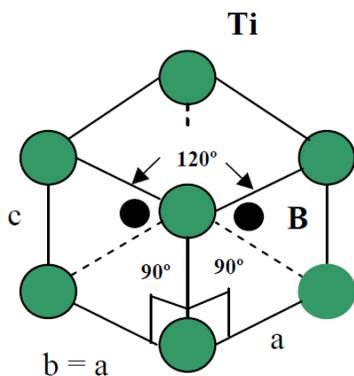


Fig. 1. The crystal structure of TiB_2 [3], [4], [9]

There are different methods mentioned in the literature that may be used to obtain nanocrystalline materials. Several researchers have used the mechanical milling method to obtain a reduction of TiB_2 powder particles [1], [5].

When comparing the energy-consuming reduction processes, one of the advantages of this method is that it is a simple method for producing nanocrystalline materials, at room temperature [8].

In the present study, a high-energy ball milling process, named mechanical milling, was used.

Titanium diboride powders, with a particle size of about 1 micron, were used in the present research. The aim was to reduce the powder particle size using a milling ratio of balls/powder and different milling times. The work technology by collision in the milling process was used.

The research conducted in this paper shows that the work technology by collision, the milling ratio and time significantly influence the reduction of TiB_2 powder particle sizes.

These materials, developed in this paper, will be used in future studies, as armouring materials. It is necessary that their mechanical properties be high performance. It is known that the mechanical properties of TiB_2 compound depend on grain size and become harder as the grain size decreases. The particle size of the TiB_2 powders should be as small as possible so that, during sintering, the grain size shall not exceed 1 micron.

2. MATERIALS AND METHODS

The raw materials used in this study were TiB_2 commercial powders (purity > 99 %, Sigma-Aldrich). Raw materials were mechanically milled in a vario-planetary mill (FRITSCH - Pulverisette 4 type) in a wet medium (distilled water). Figure 2 shows the planetary mill parameters used for the research.

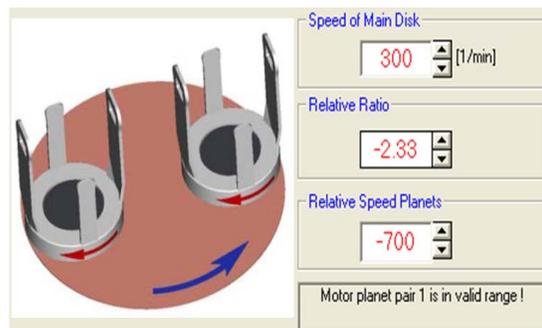


Fig. 2. Planetary mill parameters

Figure 2 shows that the speeds used for milling by collision are: the speed of the main disk 300 rpm and the speed of the planets equal to -700 rpm, respectively. The reason why the rotation direction of the planets is opposite to that of the main disk is that the authors chose to use the working technology by collision. The steel bowl was hardened steel of 250 ml volume that was filled with 50 steel balls that were 10 mm in diameter. The experiments were carried out in a wet medium. A ball-to-powder mass ratio of 3:1 was used. The milling times were 0 hour, 2 hours and 3 hours in order to optimize the ball milling process and obtain the finest particles of titanium diboride. Time 0 means that the powders are in the initial state.

The size and particle size distribution of the milled powders were determined by the laser light scattering method, using a BROOKHAVEN 90 PLUS BI - MAS device. Energy-dispersive X-ray spectroscopy (EDXS) and scanning electron microscopy (SEM) were used to study the structural evolution of the TiB_2 powder.

3. RESULTS AND DISCUSSION

The mechanical milling of the TiB_2 powder particles is a process that takes place with great intensity and has visible effects, namely changing the size of powder particles. TiB_2 powders were mechanically milled in a high energy ball mill in order to bring the powder particles as close as possible to the nanometric range. Both mechanically milled and unmilled powders were analyzed in order to determine the morphology. So, figures 3 and 4 show the particle size distribution and scanning electron microscopy SEM for the initial TiB_2 powder and figure 5 shows the X-ray spectroscopy for these unmilled powders.

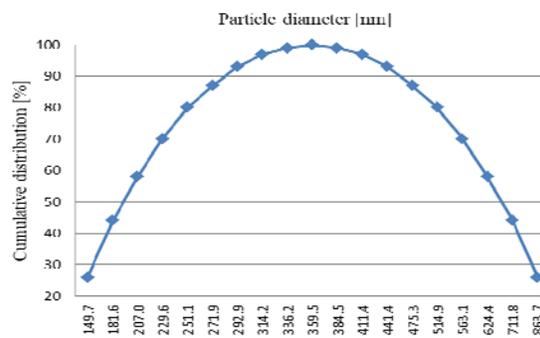


Fig. 3. Particle size distribution of the unmilled TiB_2 powders

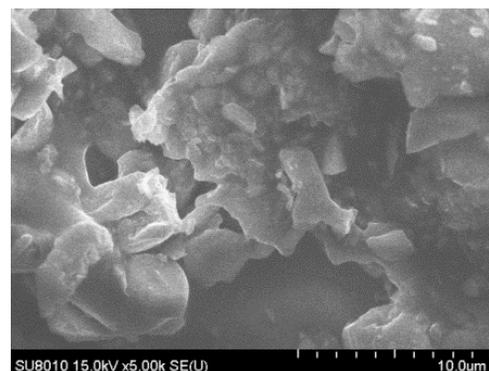


Fig. 4. SEM images of the unmilled TiB_2 powders

The figures above show the shape of the TiB_2 powder particles and the particle size range of the sample, namely [0.1-0.8 µm]. It is also observed that there is a large volume of particles with a size of 0.35 µm, but there are also two areas where the particles are smaller and larger than 0.35 µm, as seen in the SEM micrograph in figure 4.

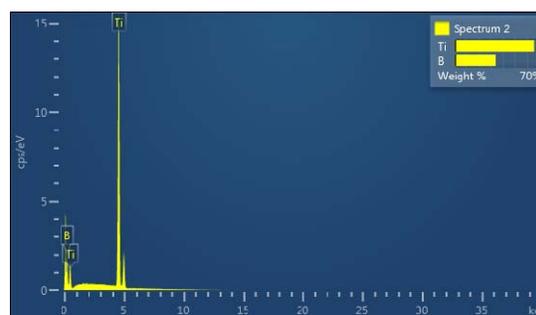


Fig. 5. X-ray spectroscopy of the unmilled TiB_2 powders

The spectrum in figure 5 highlights the presence of the Ti and B elements in the form of the TiB_2 compound.

Furthermore, figures 6 and 7 show the particle size distribution and scanning electron microscopy SEM for the TiB_2 powders, milled for 2h.

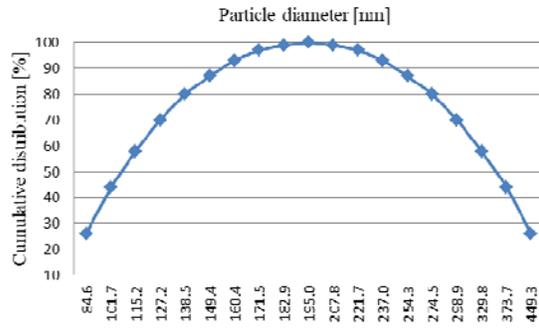


Fig. 6. Particle size distribution of the TiB₂ powders milled for 2h

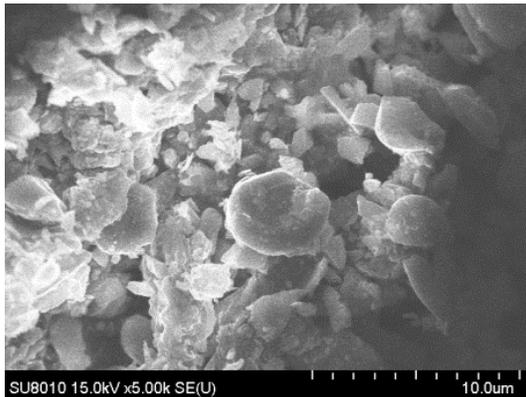


Fig. 7. SEM images of the TiB₂ powders milled for 2h

After two hours of mechanical milling, a particle size range between [0.08-0.4 μm] was recorded. The large volume of particles is now situated at 0.19 μm and it is observed that some particles are placed in the nanometric domain, more precisely at 84 nm. The particles in the coarser area also decreased a lot, up to 0.44 μm. The SEM image shows this decrease in the particle size of titanium diboride powders and the hexagonal shape of the particles is better observed.

The last sample seen in figures 8 and 9 exhibits the particle size distribution for the TiB₂ powders, milled for 3h, and the analysis by scanning electron microscopy (SEM).

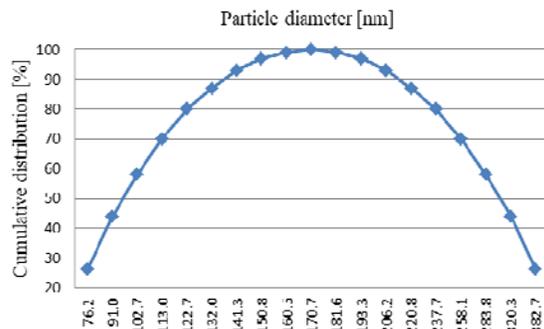


Fig. 8. Particle size distribution of the TiB₂ powders milled for 3h

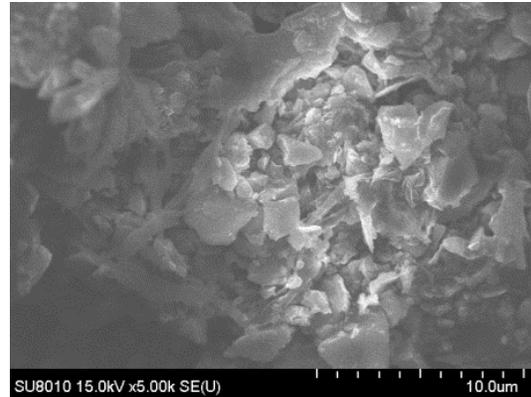


Fig. 9. SEM images of the TiB₂ powders milled for 3h

A particle size range between [0.07-0.3 μm] was recorded for the final sample. The majority of TiB₂ particles decreased up to 0.17 μm. With the increase of the mechanical milling time up to 3 h, several nanometric particles of titanium diboride appeared. However, the size of the powder particles did not decrease too much compared to the sample milled for 2 hours. This happened mainly because the very small powder particles were agglomerated, as it can be seen in the SEM image in figure 9.

4. CONCLUSIONS

In this paper, the research activities were carried out in order to develop materials based on titanium diboride powders, with dimensions as close as possible to the nano field, by the mechanical milling method.

The results of the experimental activities are shown in table 1, and allow for drawing the following conclusions:

Table 1. Results of experimental activities

No.	Samples	Particle size ranges [μm]	Median diameter [μm]
1.	TiB ₂ unmilled powders	[0.14 – 0.86]	0.35
2.	TiB ₂ powders milled for 2h	[0.08-0.4]	0.19
3.	TiB ₂ powders milled for 3h	[0.07-0.3]	0.17

- a significant decrease of the TiB₂ powder particles size was recorded for the sample that was mechanically milled for 2 hours, which ensures a percentage decrease of 46% as compared to the initial sample, which was unmilled.
- the largest decrease of the TiB₂ powder particles size is recorded for the sample that was

mechanically milled for 3 hours, which ensures a percentage decrease of 53% as compared to the initial unmilled sample.

- there is a decrease of about 13% for the sample that was mechanically milled for 3 hours as compared to the sample that was mechanically milled for 2 hours, which leads to the conclusion that the latter case allowed for a smaller particle size distribution in comparison to the former one.

As a general conclusion, it can be evinced that the milling regimes of the mechanical milling method proved to be very efficient, allowing the obtention of TiB₂ nanometric powders in a very short milling time, up to 2 or 3 hours.

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