FORMATION OF BORON CARBIDE NANOFIBERS AND NANOBELTS FROM HEATED BY MICROWAVE

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Abstract. Boron Carbide (B_4C) is a ceramic material of technological application due to its extreme hardness and high chemical and thermal stability. To obtain homogeneous precursor for boron carbide, a suitable solvent is employed to form a dispersion of appropriate amounts of boron tri-isopropoxide, calcined sucrose and magnesium methoxide. The reactive mixture in the form of dispersion is performed under continuous stirring into a reactor system heated by microwave to promote the molecular agitation and the reaction rate, until a substantially dry reactive mixture is formed. After the precursor was calcined at 800 °C and mixed with amorphous carbon (1 wt.%), the mixtures were maintained under vacuum (10^{-4} atm) in a quartz capsule and heated in a microwave oven operating at 2.45 GHz and power levels of 1400 W until the reaction of the compounds is reached. A significant amount of nanotubes, nanoparticles and nanofibers was found in the samples and have been characterized by X-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectrum (FTIR).

1. INTRODUCTION

Boron carbide has various prominent properties, such as high melting point (2447 °C), high hardness (28-35 GPa Knoop), low density ($2.52 \cdot 10^3$ Kg/m^3), high corrosion and oxidation resistance, *etc* [1,2]. Recently, this material is receiving much attention in nanocomposites study due to its unique physical, chemical, and electronic properties which give it a leading role among materials that might have suitable potential for high performance applications [3].

A variety of precursors are available for the production of boron carbide powders, but the formation of film and fibers is difficult. A number of methods had been developed for their production [4-7]; carbon nanotubes (CNT´s) or some porous ceramic material are used as templates for the production of filled nanotubes and nanofibers [8,9]. The microwave radiation is another technique applied in the synthesis of fullerenes and nanostructures [10].

Due to their properties, boron carbide nanofibers are expected to be useful for the preparation of nanostructured ceramic materials. Zhang *et al.* reported the synthesis of $(BN)_xC_y$ filled nanotubes by a laser ablation method [11]. Han *et al.* demonstrated that a mass quantity of boron carbide nanowires encapsulated in $(BN)_xC_y$ nanotubes or BN nanotubes can be synthesized by a substitution reaction using carbon nanotubes as templates [8]. Recently Pender *et al.* reported the use of porous alumina template technique in combination with a single source molecular precursor synthesized by hydroboration reaction of decaborane to generate boron carbide nanofibers [12].

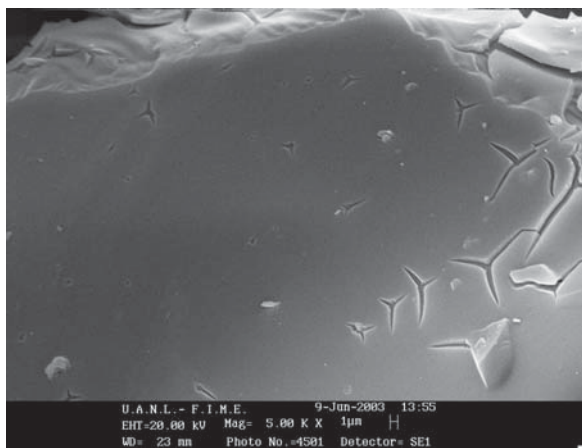Corresponding author: Oxana V. Kharissova, e-mail: okhariss@ccr.dsi.uanl.mx

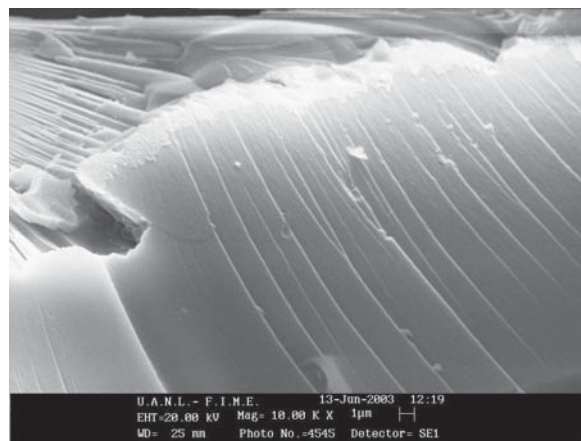**Fig. 1.** SEM image of gel obtained.

Fig. 2. SEM image of the calcined precursor.

Some precursors are synthesized from organic or carbonaceous material complexes with boron oxide; they are stirred simultaneously until a molecular precursor is formed and then treated in electric furnaces, or a high temperature reactor system at 1450-1550 °C to get a boron carbide [13-16]. Recently Shi *et al.* reported the synthesis of crystalline B_4C ultrafine powders produced by co-reduction in an autoclave system; however nanofibers were not detected [17].

The objective of this work is to obtain homogeneous molecular reactive precursors for boron carbide nanofibers without a template using a vacuum heating by microwave radiation provide the reaction which forms nanocompounds and to perform the precursor characterization by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Fourier Transform Infrared Spectrum (FTIR).

2. EXPERIMENTAL

Preparation of the precursor was carried out using boron isopropoxide, magnesium methoxide and a colloidal suspension of calcined sucrose as carbonaceous material. These reagents were stirred together in a sol-gel-microwave heating system at 70 °C until the molecular mixing and the dehidratation of the compound was obtained. The process was carried out at the *p*H of the solution within the range of 7.5—8.5. Under this condition, a black gray color gel was formed; subsequently, the gel was calcined at a constant temperature in conventional furnaces (800 °C for 4 h) in a flow of inert atmosphere. The black brittle precursor mass obtained after the py-

rolysis of the gel was pulverized and mixed with 1 wt.% of amorphous carbon to promote directly the microwave heating. The mixtures were exposed under vacuum of 10^{-4} atm into a quartz capsule and then heated in a domestic microwave oven (power 1400 W and frequency 2.45 GHz.) from 6 hrs.

Both precursors and products obtained were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM) and Fourier transform infrared spectrum (FTIR).

3. RESULTS AND DISCUSSION

The SEM images of the weakly gel obtained (crude precursor), see Fig. 1, show a continuous flake morphology; a general packing architecture of plate-like particles was observed. This kind of general morphology is obtained when as less one of the reagents belongs to the colloidal type [18]. In this case it is the calcined sucrose.

When the precursor is calcined at 800 °C for 4 h in a flow of inert atmosphere, the general architecture is not changed, but SEM images of flakes show a fracture surface after calcination (Fig. 2); this is attributed presumably to a remove of volatile substances and water vaporization.

The X-ray diffraction of the calcined precursor (Fig. 3) shows a series of magnesium-boron-oxygen compounds, magnesium carbonate, carbon, and an amorphous zone.

Measurements of the absorption bands of boron carbide precursor and products in the IR spectrum (500 – 4000 cm^{-1}) were carried out in transmission
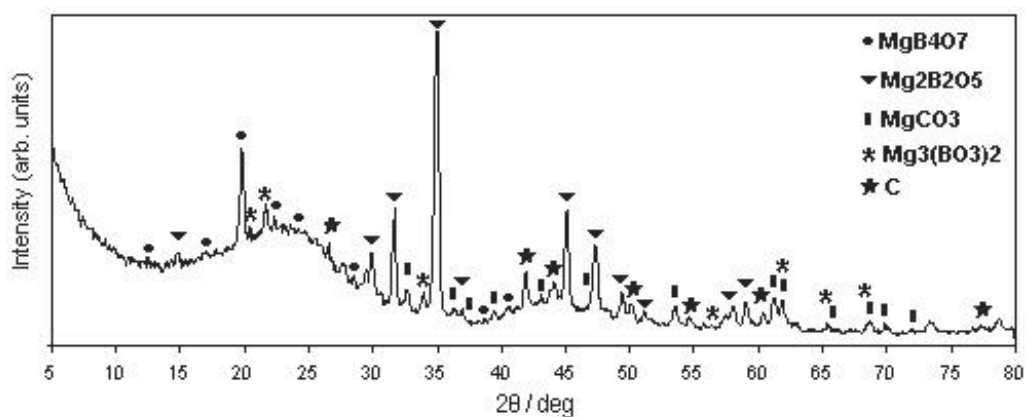
Fig. 3. XRD pattern of calcined precursor.

using a powder technique (potassium bromide pastilles), see Figs. 4 and 5, respectively.

The transmittance bands at 2200-2400 cm^{-1} in the FTIR spectra of the initial gel and calcined gel, see Figs. 4a and 4b, appear due to C-O stretching of the CO_2 molecule or due to the noise coming from the equipment; the broad absorption band at 2800-3700 cm^{-1} was attributed to the stretching band of O-H from the moisture present in the medium [19]. All these bands were also registered in the FTIR spectrum of the products, see Fig. 5.

The residual solvent and humidity contained in the gel make difficult the identification of the vibrational mode of the compounds since the information provided is not so clear; therefore, the spectrum of the calcined gel was used to identify the peaks of the principal compounds detected by XRD.

Most of the showed bands in the spectrum of the calcined precursor correspond to the stretched mode of vibration of magnesium-boron, boron-oxygen, boron-carbon or magnesium-boron-oxygen compounds.

The narrow peak at 836 cm^{-1} shows the vibration of boron magnesium [20], the bands at 1450-1490 cm^{-1} and 1190 cm^{-1} correspond to a carbon-carbon and carbon-boron clusters [21], or boron carbon compound [22]. The vibrational band at 1450-1490 cm^{-1} is observed to be overlapped in this region by the band at 1380 cm^{-1} assigned to magnesium-boron and magnesium-boron-oxygen [20]. The narrow peaks observed at 704 cm^{-1}, 680 cm^{-1}, 628 cm^{-1}, and 606 cm^{-1} are related to the bending vibration of boron-oxygen-hydrogen and boron-hydrogen bonds [23,24]; the band at 1262 cm^{-1} is due to the asym-
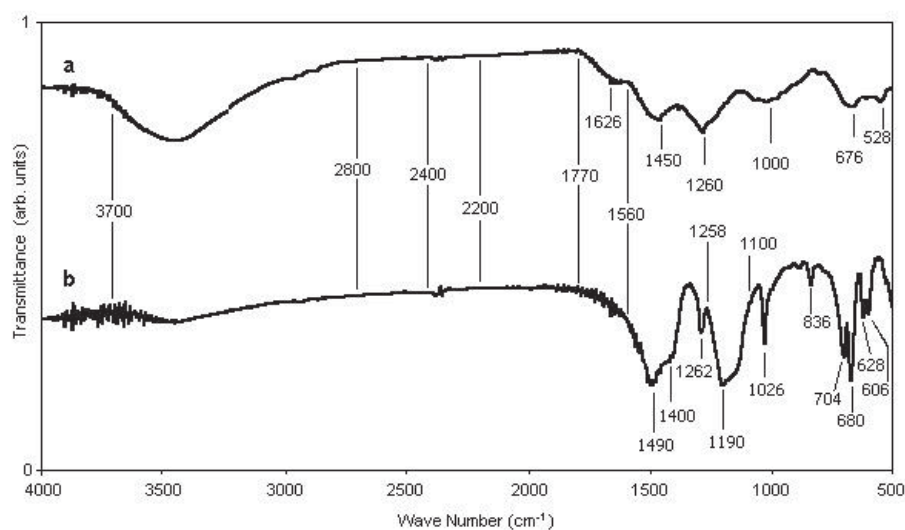

Fig. 4. (a) FTIR spectrum of the dried precursor, (b) spectrum of the calcined precursor.
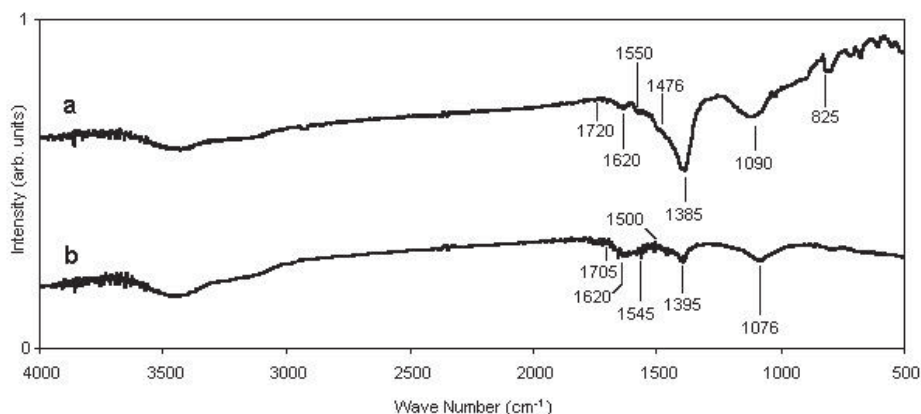
Fig. 5. (a) FTIR spectrum of the nancompounds products in the sample, (b) spectrum of the leached products.
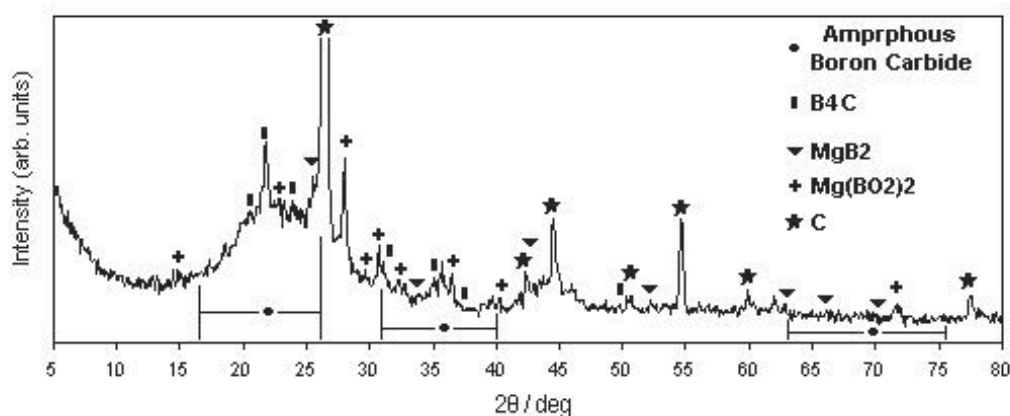

Fig. 6. XRD pattern of products of the precursor heated for 8 h in a microwave oven at vacuum of 10^{-4} atm.

metric stretch of oxygen atoms which link the trigonal boron atoms contained in different tetraborate structure units. The band at 1022 cm^{-1} is attributrd to the asymmetric B-O stretch of B-O-B bonds between primary units which link one trigonal and one tetrahedral boron atom [23].

After the heating of this compound in a microwave oven at vacuum, the products were analyzed by XRD (Fig. 6). Amorphous and crystalline boron carbide, magnesium diboride and a boron-magnesium-oxygen compound were detected.

SEM observation of the products allowed to determine the formation of nanoparticles (Fig. 7). The TEM image (Fig. 8) shows that the principal structures are nanofibers, nanobelts, and nanoparticles.

The infrared spectrometry analysis (FTIR) of the products shows two principal peaks at 1385 cm^{-1} and 825 cm^{-1} that correspond to magnesium diboride (Fig. 5a); the spectrum is in agreement with that reported in [20]. Since some of the bands are observed to be overlapped by the other products (in

this case, with the bands of boron carbide), the reaction products were leached, first with benzene, and next with hydroclhloric acid at 60 °C, and finally with distilled water and acetone. This procedure was applied to obtain only boron carbide
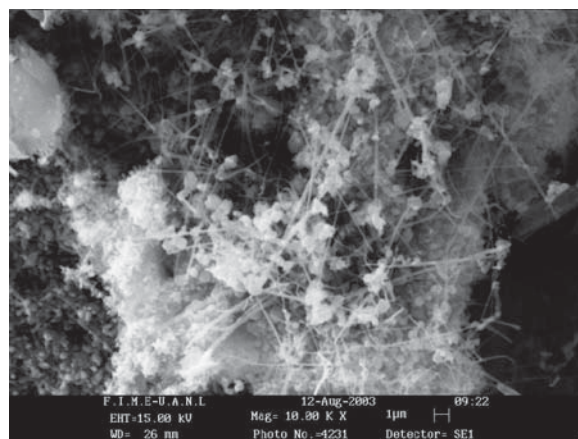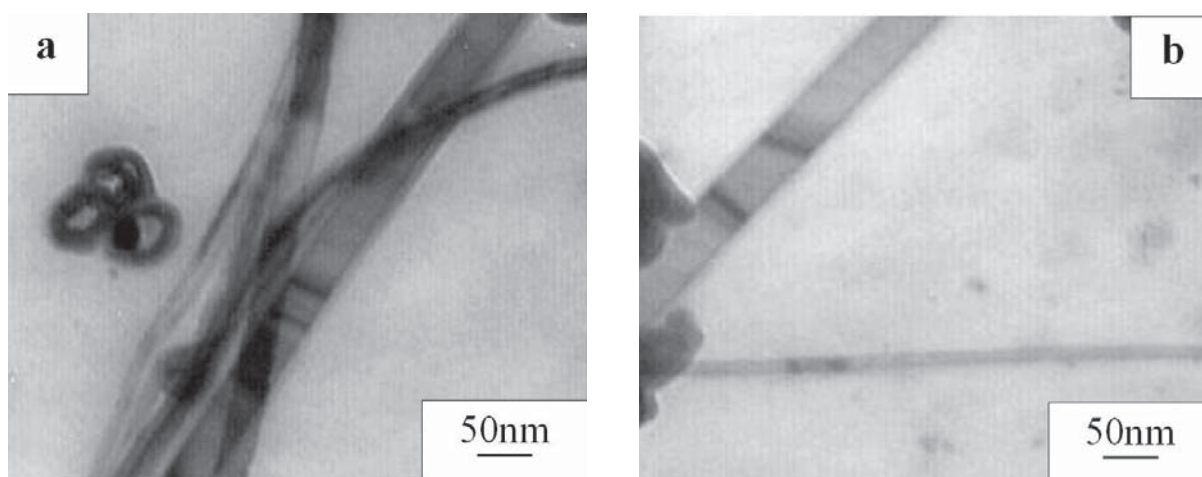

Fig. 7. SEM image of the products.

Fig. 8. TEM image of a CNT´s, boron carbide nanofibers, and nanoparticles of magnesium diboride (400,000X).

nanofibers in the products, see the respective spectrum in Fig. 5b.

The peaks in the range of 1075 cm^{-1} and 1620 cm^{-1} correspond to the stretching mode of vibration of the central atom of the three-atom chain in the unit cell of boron carbide (C-^{11}B-^{10}B; C-^{10}B-C; C-^{10}B-^{11}B; C-^{10}B-^{10}B), where C-^{10}B-C are the principal chain, see [25,26] for more detail.

4. CONCLUSIONS

The results of this study can be summarized as follows.

- The use of one colloidal compound among the reagents (calcined sucrose) promotes a general packing architecture of platelike particles formation in the gel.
- The identification of the boron-carbon, magnesium-boron, trigonal boron and tetrahedral boron stretching mode of vibration in the calcined gel points out that the molecular mixing degree has been reached.
- The precursor synthesized is not a well microwave absorbing material, so a 1 wt%. of carbon amorphous was added to promote directly the microwave heating.
- Boron carbide nanofibers, magnesium diboride nanoparticles and carbon nanotubes can be synthesized by rapid carbothermal reduction by microwave heating from the homogeneous precursor, without the use of template technique.
- The calcined sucrose and the amorphous carbon assist the formation of boron carbide and the magnesium diboride.
- The microwave heating assists the rapid heating and the formation of nanoparticles.

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