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AN EXPERIMENTAL INVESTIGATION OF B_4C PREPARATION FROM BORIC ACID – POLYMERIC GEL PRECURSORS AT LOW TEMPERATURE

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ABSTRACT

In this study, boron carbide (B_4C) has been effort prepared by using boric acid (H_3BO_3) as a boron source, and three types of polymer materials as carbon source (glucose, polyvinyl alcohol (PVA) and corn starch) by developing the carbothermal process using reduced gas (H_2) flow. Aqueous solutions of boric acid in presence one of the polymers forms astable gel. Pyrolysis temperature 350°C was used after getting the gel. Then, the pyrolysed product is calcined at a range of (600 – 900)°C for 2 hours. XRD analyses showed that B_4C could be produced by using boric acid and PVA as raw materials after calcination at 800°C. Also, the addition of magnesium sulfate into the mixture reactants promoted the reaction and resulted in an increase in the boron carbide content. The SEM images and particle size distribution tests showed that the prepared B_4

دراسة عملية لتحضير كاربيد البورون من حامض البوريك ومواد بوليميرية عند درجة حرارية واطئة

الخلاصة :-

في هذه الدراسة تم محاولة تحضير كاربيد البورون (B_4C) باستخدام حامض البوريك كمصدر للبورون وثلاثة انواع من البوليمرات (كلوكوز، بولي فينيل الكحول (PVA) و نشأ الذرة) كمصادر للكاربون بواسطة تطوير عملية الكربوالحرارية (Carbothermal) باستخدام جريان غاز مختزل (H_2). محاليل مائية من حامض البوريك مع واحد من البوليمرات شكلت مادة هلامية. استخدمت درجة حرارة التحلل الحراري 350 درجة مئوية بعد الحصول على المادة الهلامية. بعدها تم كلسنة ناتج التحلل الحراري ضمن المدى (600 – 900) درجة مئوية لمدة ساعتين. أظهرت تحليلات حيود الأشعة السينية أن كاربيد البورون يمكن أن ينتج عن طريق استخدام حامض البوريك و PVA كمواد اولية عند الكلسنة بدرجة حرارة 800 درجة مئوية. ايضا ان اضافة كبريتات المغنيسيوم الى خليط التفاعل ادى الى تعزيز التفاعل ونتج زيادة في محتوى كاربيد البورون. أظهرت اختبارات صور المجهر الماسح والتوزيع الحجمي للدقائق ان كاربيد البورون المحضر يمتلك متوسط حجم حبيبي 460نانومتر.

1. INTRODUCTION :-

Boron carbide (B_4C) is an attractive material because ofits extreme hardness, low density(2.52 g/cm^3), high chemicalstability and good wear resistance**[Moshtaghioun et al, 2013]**. Its hardness comesthird after diamond and cubic boron nitride, but with theadvantage of being stable at very high temperatures**[Ma et al, 2010]**. Italso has high cross section for neutron capture and excellenthigh-temperature thermoelectric properties**[Kakiage et al, 2011]**. Thecombination of these properties consequently makes it anattractive material for numerous applications in microelectronic,nuclear, military, space and medicalapplications**[Chang et al, 2006]**.

Boron carbidepowder can be prepared by a variety of methods. Forexample, commercial boron carbide powders can easily bemade by carbothermal reduction of boron oxide (B_2O_3), forwhich the overall reaction is given by reaction (1), owing to the low cost ofthe raw materials (boric acid (H_3BO_3) or B_2O_3 as the boron source andgraphite or petroleum coke as the carbon source)**[Kakiage et al, 2011 and Bigdelooand and Hadian, 2009]**.

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO \qquad (1)$$

However, this process requires a high synthesis temperature of approximately 2000°C.A low-temperature synthesis of B_4C by carbothermal reductionis expected to be developed by improving the dispersion of theB_2O_3 and carbon components. Carbothermal reduction using a condensed product as a precursor that is made up of boric acid/boric oxide and a polymer precursor is attractive as a low-temperature method of preparation boron carbide. The condensed product forms a borate ester (B–O–C) bond by the dehydration condensation reaction between boric acid and polymers.The B–O–C bond forming reaction accelerates the dispersion of boron and carbon sources. Thus the temperature of synthesis is reduced owing to the enlarged surface-active area between the boric oxide and carbon components with superior reactivity **[Tahara et al, 2013 and Kakiage et al, 2012]**.

Borate esters with B–O–C bonds of various polyols, such as glycerin, citric acid, cellulose, saccharides and poly vinyl alcohol (PVA) have recently been studied as promising precursors of B_4C powders **[Kakiage et al, 2011]**. These classes of precursors were prepared by a hydrothermal treatment to promote esterification, and the heat treatment of those precursors in an inert atmosphere at 1500–1600°C led to the preparation of carbon-free boron carbide microcrystals. On the other hand, the heat treatment of borate ester of glycerol as a precursor above 1300°C in Ar flow yielded a small amount of boron carbide, which contained a considerable amount of free-carbon residue even after heat treatment at 1400°C **[Yanase et al, 2009]**.

Studies have researched several different types of polymer precursors because they have many advantages. For example, the use of polymer precursors will allow for precise control of ceramic composition, it can be formed into a desired shape and converted to a ceramic with possible retention of form, and it can undergo decomposition at lower temperatures allowing ceramic formation under milder conditions. These advantages all contribute to reducing costs **[Mondaland and Banthia, 2005 and Usluand and Tunc, 2012]**.

The objective of the present work is to prepare boron carbide powder from boric acid – polymeric gel precursors at low temperatureby using reduced gas (H_2) flow during calcination process with catalyst addition.

2. EXPERIMENTAL WORK :-

The raw materials used in this research with its manufacturing origins are presented in **Table 1**.Boron carbide prepared by using boric acid as a boron source and used three types of polymericmaterials as carbon source (glucose, polyvinyl alcohol (PVA) and corn starch). A general flow diagram for the preparation of B_4C powder is shown in **Fig. 1**.

The following steps were carried out for preparing of B_4C:

2.1 Preparing Solutions:

- Boric acid solution (2.5 M) was prepared by dissolving boric acid in distilled water at 85°C.
- Glucose solution was prepared by dissolving glucose (10 g) in (100 ml) of distilled water at 85°C.
- PVA solution was prepared by dissolving PVA (5 g) in (100 ml) of distilled water at 85°C.
- Corn starch solution was prepared by dissolving corn starch (10 g) in (100 ml) of distilled water at 85°C.

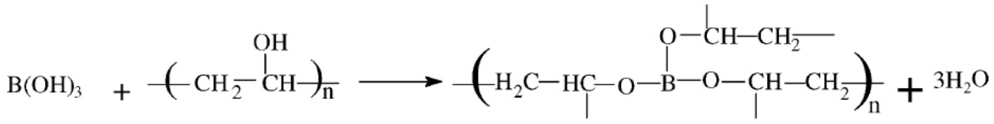
2.2. Mixing Solutions:

- Glucose solution was added to the boric acid solution in hot condition with constant stirring (250 rpm) in magnetic stirrer for 1 hour. Boric acid and glucose were taken in the weight ratio of 1.2:1 since this mixture could yield B_2O_3 and carbon required for the formation of B_4C in the subsequent step shown in reaction (1). The overall reaction between boric acid and glucose could be represented by reaction (2).

$$24H_3BO_3 + 7C_6H_{12}O_6 \rightarrow 6B_4C + 36CO + 78H_2O \qquad (2)$$

The temperature increased during the stirring to 110°C to remove excess water. During evaporation, the temperature of the solution was constantly monitored with the help of a thermometer placed within the solution through a test beaker. The pH of the solution, during evaporation, was maintained within the range of 4–5 by adding ammonia solution. A transparent golden yellow colored gel material was formed.

- PVA solution was added to the boric acid solution in hot condition with constant stirring (250 rpm) in magnetic stirrer for 1 hour. The weight ratio of boric acid to PVA was 1:2. The temperature increased during the stirring to 110°C to remove excess water. A white floppy and rubbery material was obtained. The possible reaction pathway between boric acid and PVA is represented as follows **[Mondaland Banthia, 2005]**.



- Corn starch solution was added to the boric acid solution in hot condition with constant stirring (250 rpm) in magnetic stirrer for 1 hour. The weight ratio of boric acid to corn starch was 1:1. The temperature increased during the stirring to 110°C to remove excess water. A thick white colored gel material was formed.

2.3. Drying and Pyrolysis:

The formed materials from mixing process have been dried in programmed electrical oven at temperature 80°C for 3 hours. Then the fragile product was crushed by mortar and pestle to get powder. In this stage, the obtained powder was pyrolyzed. For this purpose, the powderswere put in alumina crucibles and heated in a furnace to 350°C and were kept at this temperature for 6 hours; a heating rate of 5°C/min was applied during the process. After pyrolysis, a black precursor powders were obtained.

2.4. Calcinations:

The calcination process was done at two conditions:

- **First Calcination Condition:**

The pyrolysed powders were placed in alumina crucible. The crucible was covered from top using Kaolin clay. The clay cover contained a small hole for gases releasing. The crucible was then placed into vacuum tube furnace as shown in figure (2-a). Before starting to heat, the furnace was evacuated up to 10^{-2} bar. Argon (Ar) gas was then flushed through the furnace until reach the pressure in the furnace to the atmospheric pressure. Then the furnace was evacuated again up to 10^{-2} bar. The powders were then heated at different temperatures (600, 700, 800 and 900)°C, at heating rate 5°C/min for 1 hour. After the reaction was finished at the desired temperature, the furnace was cooled down to room temperature. During this process, the pressure in the furnace was maintained at 10^{-2} bar.

- **Second Calcination Condition:**

The pyrolyzed precursor powders were compacted at pressure of 20 MPa in a stainless steel cylinder (40 mm diameter with 100 mm height) as shown in figure (3). The cylinder was covered from top and bottom using two stainless steel lids. The lids contained a central hole of 10 mm diameter (to ensure inter and release the gases during the calcination process). The schematic of the used stainless steel cylinder is shown in figure (4). Then the cylinder was placed in a tube furnace as shown in figure (2-b). Before start to heat, the furnace was evacuated up to 10^{-3} bar. Ultrahigh purity hydrogen (H_2) and argon (Ar) gases were then flushed through the furnace (H_2 was used as reducing gas while Ar was used as buffer gas). H_2/Arflux was kept constant at 100/100 ml/min. The precursor powders were then heated at (800 and 900)°C, at heating rate 10°C/min for 2 hours under H_2/Ar flowing and the total pressure in the furnace was kept at 10^{-3} bar during the heating process. After the reaction was finished at the desired temperature, the furnace was cooled to room temperature. During this process, the pressure in the furnace was maintained at 10^{-3} bar.

2.5. Catalyst Addition:

Magnesium sulfate heptahydrate ($MgSO_4.7H_2O$) has been added as catalyst to the mixture solution (2). 10 wt% of $MgSO_4.7H_2O$ from total weight of the mixture solution was dissolved in the minimum volume of deionized water and then added to boric acid solution during the stirring before adding PVA solution. After addition PVA solution to the solution of boric acid with magnesium sulphite in the hot condition, the followed processes will repeated that consist both of drying, crushing, pyrolysis and then heated in the second heating condition.

2.6. Milling and Cleaning:

After completion of the reaction, the resultant product was removedfrom the stainless steel cylinder and then grounded by ball mill to form fine B_4C powders. The product was then washed with absolute ethanol, dilute hydrochloric acid (10 % HCl aqueous solution) and distilled water, respectively assisted by magnetic stirrer, to remove impurities such as

$Mg_3(BO_3)_2$, B_2O_3, etc. After drying in vacuum at 60°C for 3 hours, the final gray powder product was obtained.

2.7. Characterizations:

The prepared B_4C powder was characterized via X-ray diffraction (XRD) using a Phillips PW3830 (Cu-Kα) powder diffractometer, scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) and particle size distribution.

3. RESULTS AND DISCUSSION :-

3.1 X-Ray Diffraction (XRD) of Boric Acid - Corn StarchMixture

Fig. 5-a,b,c and d show XRD patterns of the pyrolyzed powders from boric acid with corn starch that are prepared in the first calcination condition at temperatures ranged between (600 – 900)°C. It has been shown at 600°C there are no diffraction peaks appear in XRD pattern. At calcination temperature of 700°C, only one peak of cubic boron oxide (B_2O_3) at $2\theta = 27.7°$ (310) was observed, corresponding to Joint Committee on Powder Diffraction Standards (JCPDS) card No. (06-0297). With increasing the calcination temperature until 900°C some peaks will appear due to increasing crystallinity. All the diffraction peaks in the patterns match with more the standards peaks of cubic B_2O_3, 2θ values as (14.5°, 27.7° and 39.9°) and notice some of graphite phase at $2\theta = 26.4°$ (002) corresponds to JCPDS card No. (41-1487).

Fig. 6 shows XRD pattern of the pyrolyzed powder from boric acid with corn starch that was prepared in the second calcination condition at 900°C. The diffraction peaks appear coincide with those of cubic B_2O_3 with new peak at $2\theta = 57.4°$ (620) and graphite with hexagonal structurer but with high diffraction intensities, because increase the crystilinity of the phases is due to lower the atmospheric pressure of the furnace 10^{-3} bar and flowing the Ar/H_2 gases. In this figure, the peak at $2\theta = 32.1°$ (102) is more coincide with that of hexagonal B_2O_3 according to JCPDS card No. (44-1085). From all XRD patterns of the pyrolyzed powders from boric acid with corn starch noticed there are no formation of B_4C from this powder at these conditions. This pyrolyzed powder may be needs more temperature for complete the chemical reaction rate.

3.2 X-Ray Diffraction (XRD) of Boric Acid - Glucose Mixture

XRD patterns of the pyrolyzed powders from boric acid with glucose that are prepared in the first calcination condition in temperature ranges between (600 – 900)°C are shown in **Fig. 7-a,b,c and d**. All diffraction peaks can be indexed for two phases: cubic B_2O_3 phase with its peak at 2θ values as 14.5° (111), 27.7° (310), 30.6° (222), 39.9° (420) and 54.6° (442), and hexagonal graphite phase with its peak at 2θ values as 26.4° (002) and 44.4° (101). The intensity of all diffraction peaks increased with increasing the temperature, this satisfies that the crystallization is obtained at high temperature.

Fig.8 shows XRD pattern of the pyrolyzed powder from boric acid with glucose that was prepared in the second calcination condition at 900°C. It has been shown that there are three phases were appeared cubic B_2O_3, hexagonal graphite and small peaks of orthorhombic boron carbide (B_8C) at $2\theta = 19.8°$ (800) and 22.2° (820) according to JCPDS card No. (26-0232). B_8C appearance in XRD pattern indicates either that the amount of carbon was insufficient to form rhombohedral boron carbide (B_4C) or the pyrolyzed powder needs more high temperature for completing the reaction.

3.3 X-Ray Diffraction (XRD) of Boric Acid - PVA Mixture

Fig. 9-a,b,c and d show XRD patterns of the pyrolyzed powders from boric acid with PVA that are prepared in the first calcination condition in temperature range between (600 – 900)°C.

It is clear from calcination temperatures (600 – 800)°C that, samples consist of B_2O_3 as the main phase, with small amount of graphite phase. At 900°C, in addition to the presence of both phases B_2O_3 and graphite, small peaks of rhombohedral B_4C phase are observed at $2\theta = 19.7°$ (101), 23.4° (012), 34.9° (104) and 37.8° (021), corresponds to JCPDS card No. (35-0798).

In the second calcination condition, the XRD patterns for the pyrolyzed powders from boric acid with PVA are shown in **Fig.10-a and b** at temperatures of (800 and 900)°C. The figures show that only three phases B_2O_3, graphite and B_4C were appeared. Furthermore, it was found that the diffraction peaks intensities of both graphite and B_4C were increased while B_2O_3 decreased with increasing calcinations temperature from (800 to 900)°C. In addition to increase the reaction rate between B_2O_3 and graphite at 900°C, it was seen that B_2O_3 decreased with comparison with graphite, this refers to volatile of boron at this calcination condition.

Diffraction peaks intensities of B_4C were increased and absence of B_2O_3 phase after addition magnesium sulfate ($MgSO_4.7H_2O$) as catalyst to the boric acid and PVA mixture as shown in XRD pattern **Fig. 11-a**. It can be seen that the addition of magnesium sulfate into the powder reactants resulted in an increase in the formation of boron carbide because addition of metallic sulphates as catalyst has been found to reduce the reaction temperature of B_4C formation **[Suri et al, 2011]**. It is believed that the $MgSO_4.7H_2O$ acts as a catalyst and promotes the reaction by providing the Mg element in the structure of reactant powders that hasten the reaction rate between boron and carbon. The chemical reaction might occur of the mixture of B_2O_3 and C reacted with Mg to produce B_4C as indicated in thefollowing reaction ($2B_2O_3 + 6Mg + C \rightarrow B_4C + 6MgO$). The formation of MgO may be reduced by H_2 to produce Mg again as in the following reaction ($MgO + H_2 \rightarrow Mg + H_2O$) **[Kumar, 2012 and Alkan et al, 2012]**.

It is clear from **Fig. 11-a**, that the formed B_4C contains B_2O_3 and magnesium borate ($Mg_3(BO_3)_2$) as impurities. $Mg_3(BO_3)_2$ phase appears at $2\theta=33.5°$ (121), 40.3° (211) and 41.4° (131), corresponds to JCPDS card No. (38-1475). For removing any impurities and achieves pure B_4C particles, purification was carried out by washing the product powder with absolute ethanol, dilute hydrochloric acid and distilled water, respectively and assisted by magnetic stirrer.

Fig.11-b shows XRD pattern prepared B_4C after purification process. The later XRD pattern of B_4C powder will use in followed process in this work. In this work, the B_4C powder was prepared at temperature less than 500°C comparing with previous literatures **[Yanase et al, 2009 and Usluand and Tunc, 2012]**, that prepared B_4C from the same raw materials (H_3BO_3+PVA) but different heating conditions.

3.4 Scanning Electron Microscope (SEM) of Powders

Scanning electron microscopy imaging was conducted for the B_4C powder, in order to observe the morphology of the powder. The resulting SEM image of the prepared B_4C powder (as from XRD pattern **Fig. 11-b**), may be seen in **Fig. 12** at different magnifications. As seen in this figure, the morphology of the B_4C powder particles, however, appears to be much more evenly distributed. The form seems to be fairly blocky with a few rectangular particles being scattered throughout.

3.5 Energy-Dispersive X-ray Spectroscopy (EDX) of B_4C Powders

EDX composition analysis of the prepared B_4C is shown in **Fig. 13**. The composition mainly contains carbon and boron and a very small amount of oxygen, magnesium and silicon. Oxygen is probably from B_2O_3 on the B_4C particles. It is well known that B_4C absorbs oxygen very easily and forms B_2O_3 on the particle surface. The atomic percentage of B/C of prepared

B_4C in this work was 3.43, while the right atomic percentage, according to molecular weight, should be 3.6, so there is some of free carbon. The presence of free carbon in the product suggests that some boron has been lost during reaction. In this case the amount of free carbon was measured to be about 1.1 at %. The free carbon in the product may have a beneficial effect on further processing of the powder. It has been reported in the literature that very fine graphite in B_4C powder can act as a sintering aid during consolidation of the powder into high density particles**[Sinha et al, 2002]**.

3.6 Particle Size Distribution

A particle size distribution analysis is a measurement designed to report information about the size and range of a set of particles representative of a material.The particle size distribution of the prepared B_4C powder is shown in **Fig. 14**. The result of the B_4C particle size distribution showed that particles are consisted of (Dv 10 = 0.276), (Dv 50 = 0.460) and (Dv 90 = 0.675) microns.

4. CONCLUSIONS :-

The following remarks are concluded from the preparing of B_4C powder which is:

1. Submicron size boron carbide (B_4C) powder can be prepared from using boric acid (H_3BO_3) and polyvinyl alcohol(PVA) as raw materials at low temperature (800°C) for 2 hours by developing the carbothermal process using a mixture of gases flow (Ar/H_2) during the calcination process.
2. The obtained B_4C powder from this work is composed of particles are nearly equiaxial with somewhat narrow size distribution having a median size of 460 nm.
3. XRD analyses showed that the boron carbide could be produced after calcination at 800°C and the addition of magnesium sulfate (10 wt% $MgSO_4.7H_2O$) into the mixture reactants promoted the reaction and resulted in an increase in the boron carbide content and synthesis of crystalline boron carbide powder with little free carbon.
4. B_4C cannot be produced from using boric acid as boron source with corn starch or glucose as the carbon source at low temperature from using a mixture of gases flow (Ar/H_2) during the calcination process**.**

Table 1:The used raw materials.

Raw materials	Formulation	Molecular weight-g/mol	Purity %	Physical state	Origin
Boric acid	H_3BO_3	61.83	99	Solid	Panreac, Spain
Glucose	$C_6H_{12}O_6$	180.16	99.5	Solid	Panreac, Spain
Polyvinyl alcohol	$(C_2H_4O)_n$	44.5	99	Solid	M.O.H, Germany
Corn starch	$C_6H_{10}O_5$	162.14	99.8	Solid	Panreac, Spain
Magnesium sulfate	$MgSO_4.7H_2O$	246.48	99+	Solid	Alfa Aesar, England
Hydrochloric acid	HCl	36.46	10% HCl	Liquid	Alfa Aesar, England
Ethanol absolute	C_2H_5OH	46.07	99.8	Liquid	Alfa Aesar, England

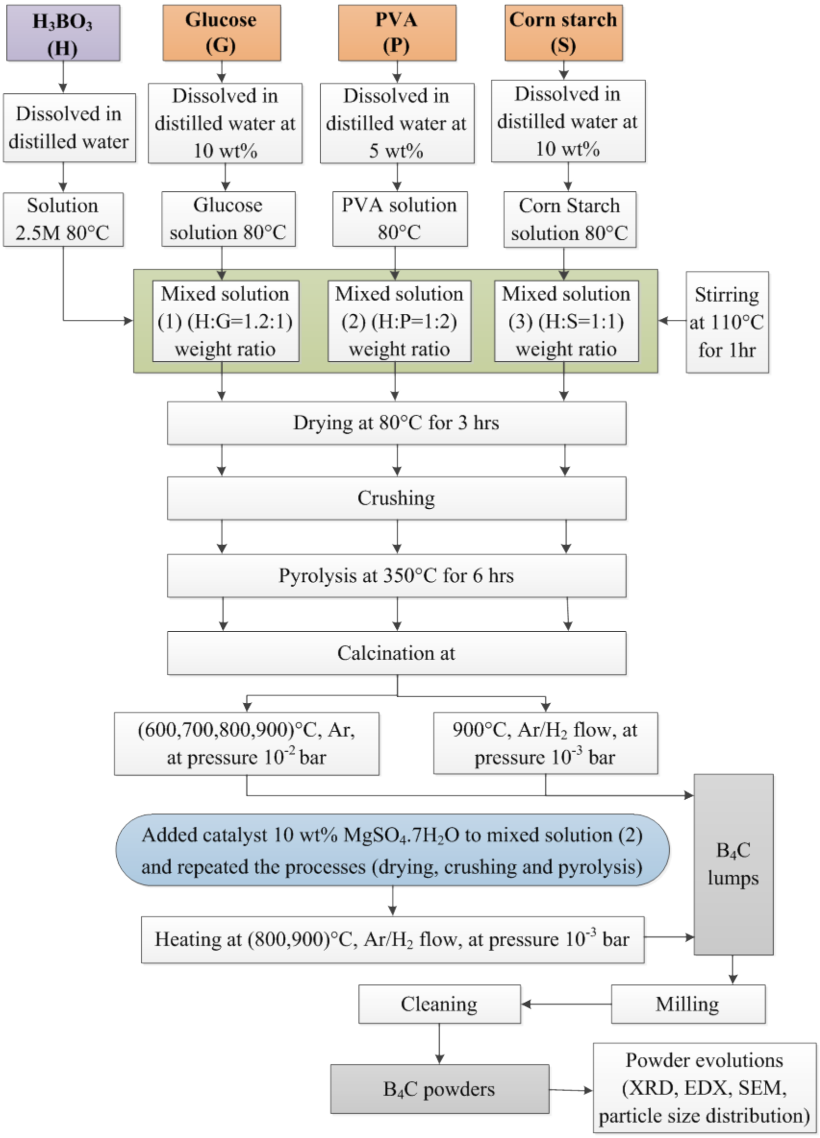


Figure 1:A general flow diagram for the preparation of B_4C powder.

(a) (b)

Figure 2:Vacuum tube furnace that is used in the,
(a) first calcination condition and
(b) second calcination condition.

Figure 3: the used stainlesssteel cylinder with lids.

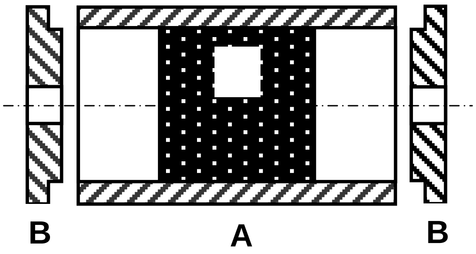


Figure 4: schematic of the stainless steel cylinder (A) with lids (B) and compact powder (C).

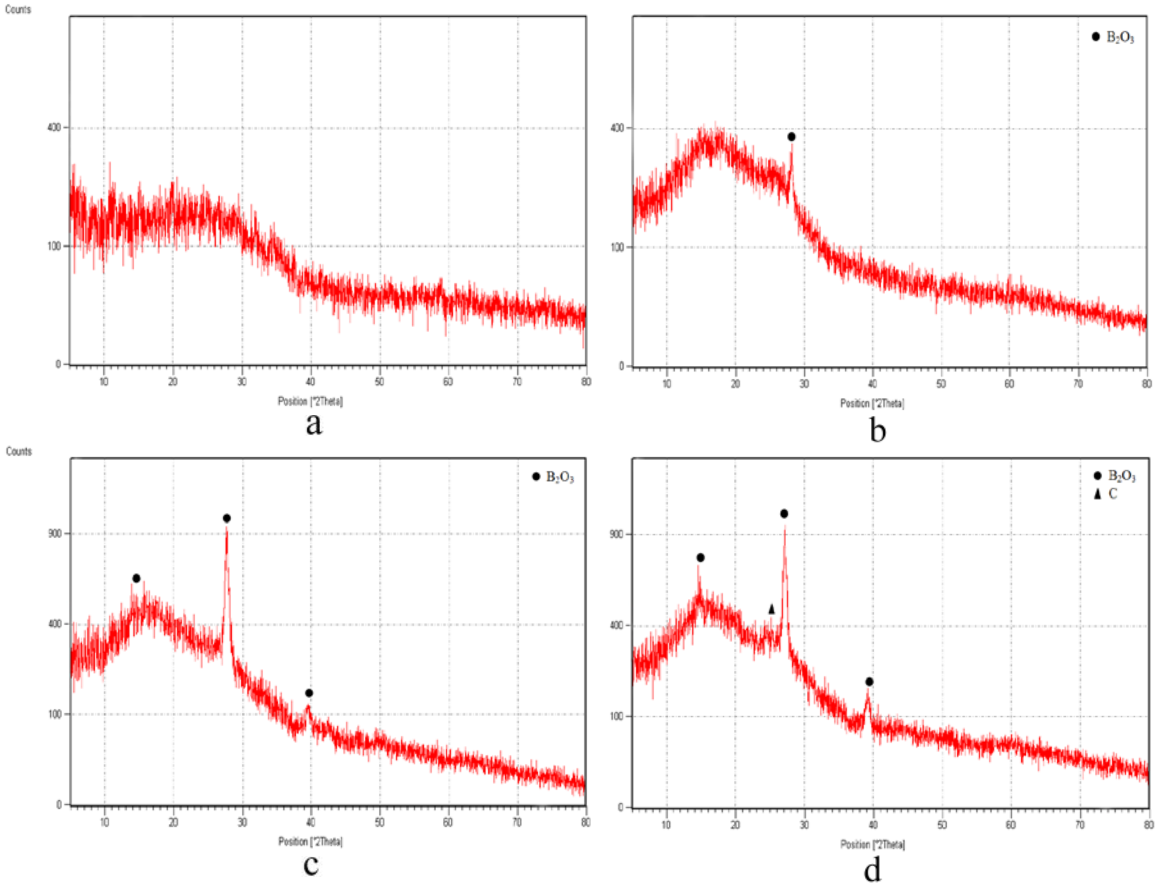


Figure 5: XRD patterns of samples from (H_3BO_3+corn starch) produced under Ar flow and pressure 10^{-2} bar at temperature: (a) 600°C, (b) 700°C,(c) 800°C and (d) 900°C.

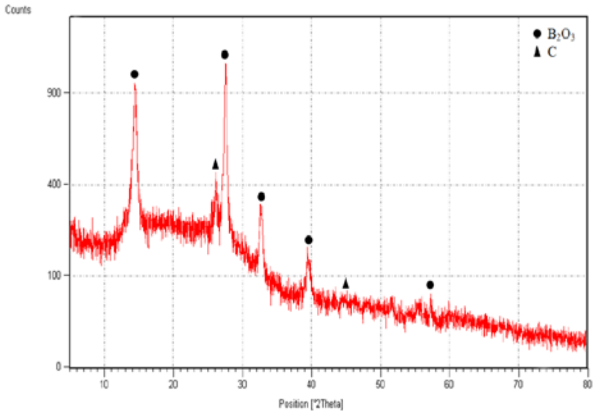
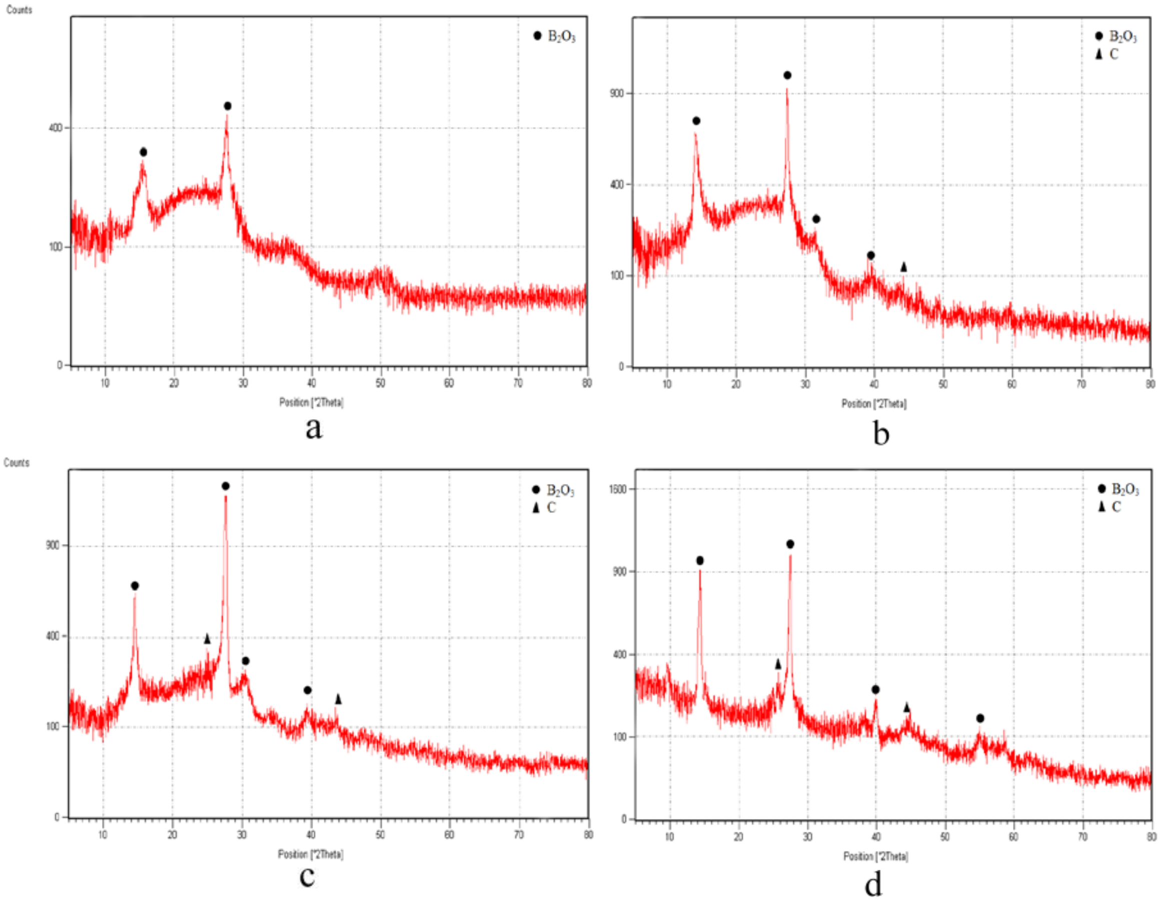


Figure 6: XRD pattern of sample from (H_3BO_3+corn starch) produced under Ar/H_2 flow and pressure 10^{-3} bar at 900°C.



a b c d

Figure 7: XRD patterns of samples from (H_3BO_3+glucose) produced under Ar flow and pressure 10^{-2} bar at temperature: (a) 600°C, (b) 700°C,(c) 800°C and (d)900°C.

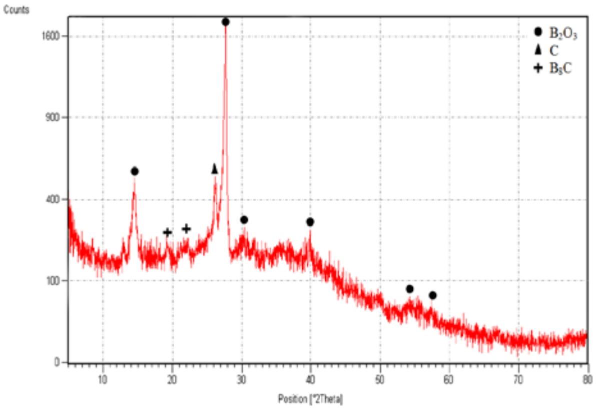


Figure 8: XRD pattern of sample from (H_3BO_3+glucose) produced under Ar/H_2 flow and pressure 10^{-3} bar at 900°C.

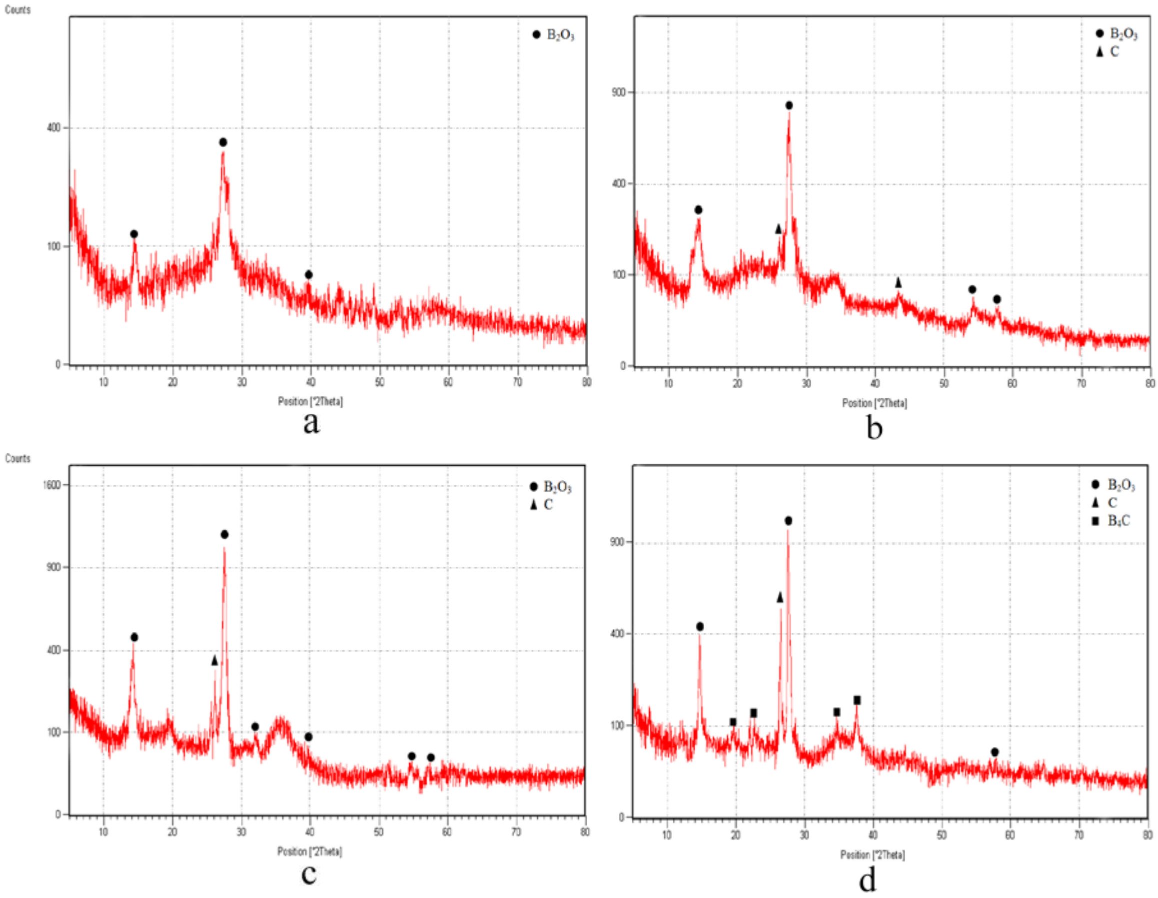


Figure 9: XRD patterns of samples from (H_3BO_3+PVA) produced under Ar flow and pressure 10^{-2} bar at temperature: (a) 600°C, (b) 700°C,(c) 800°C and (d) 900°C.

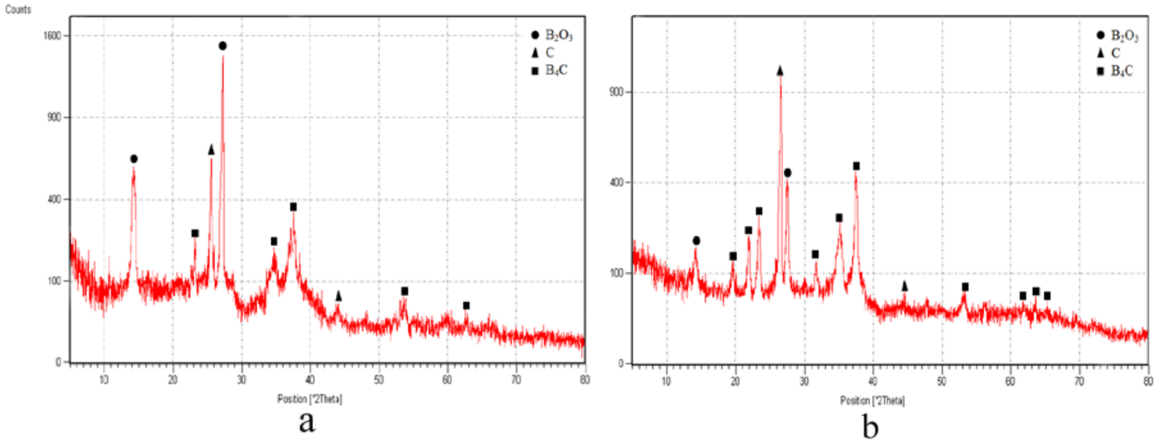


Figure 10: XRD patterns of samples from (H_3BO_3+PVA) produced under Ar/H_2 flow and pressure 10^{-3} bar at temperature:(a) 800°C and (b) 900°C.

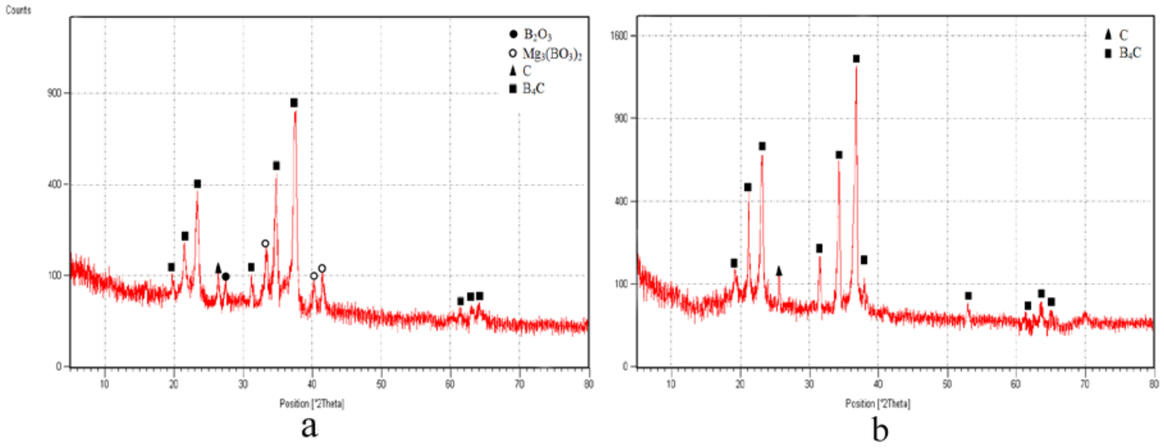


Figure 11: XRD patterns of samples from (H_3BO_3+PVA+$MgSO_4.7H_2O$) produced under Ar/H_2 flow and pressure 10^{-3} bar at800°C, before (a) and after (b) purification process.

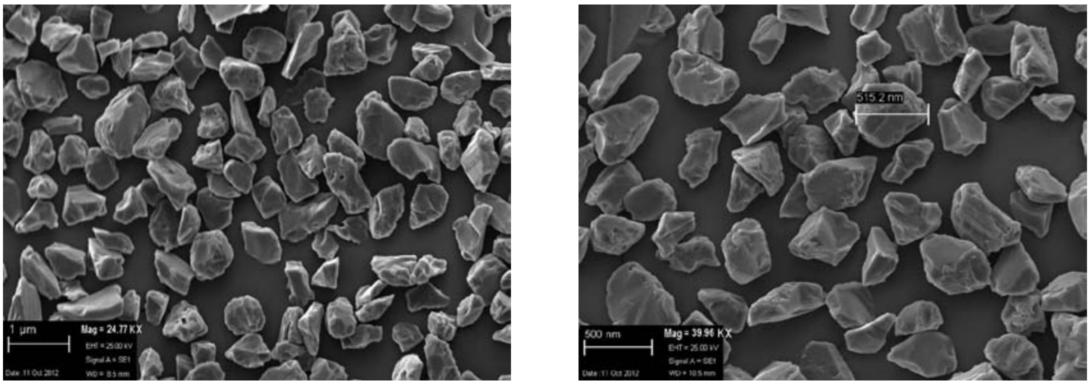


Figure 12: SEM images with different magnifications of the prepared B_4C powder.

Element	Weight%	Atomic%
B	74.45	76.75
C	24.12	22.40
O	0.92	0.64
Mg	0.18	0.08
Si	0.33	0.13
Totals	100.00	

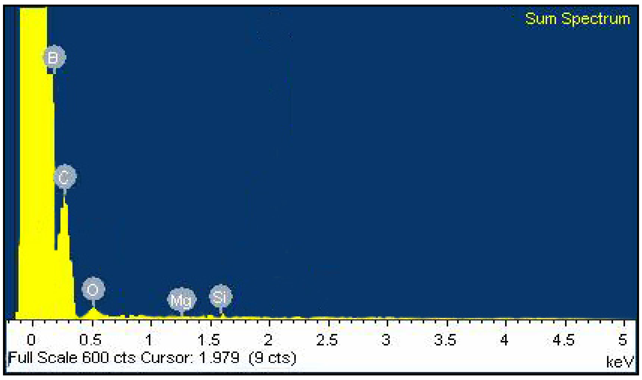
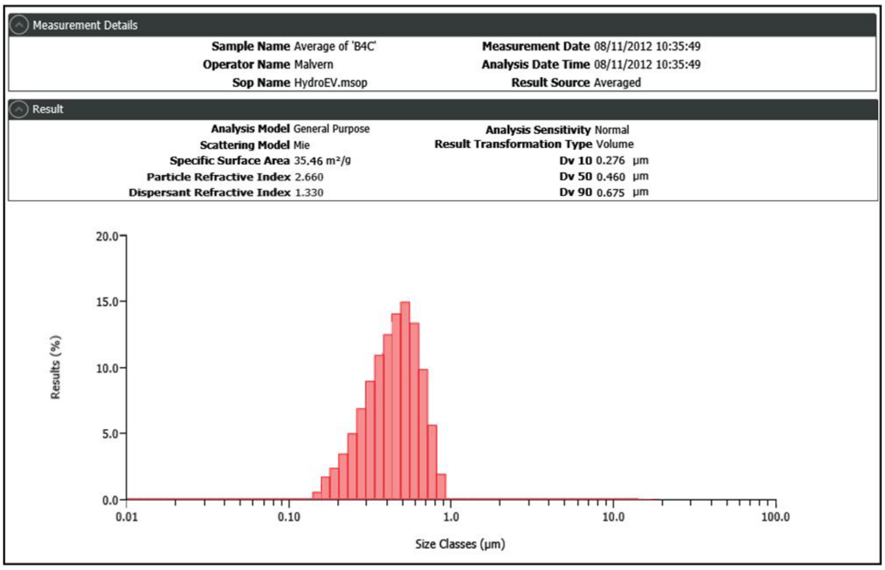


Figure 13: EDX of the prepared B_4C powder.


Measurement Details

Sample Name Average of 'B4C'
Operator Name Malvern
Sop Name HydroEV.msop
Measurement Date 08/11/2012 10:35:49
Analysis Date Time 08/11/2012 10:35:49
Result Source Averaged

Result

Analysis Model General Purpose
Scattering Model Mie
Specific Surface Area 35.46 m²/g
Particle Refractive Index 2.660
Dispersant Refractive Index 1.330
Analysis Sensitivity Normal
Result Transformation Type Volume
Dv 10 0.276 µm
Dv 50 0.460 µm
Dv 90 0.675 µm

Figure 14:Particle size distribution of the prepared B_4C powder.

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