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RESEARCH ARTICLE

SYNTHESIS and CHARACTERIZATION of MECHANICAL ACTIVATION ASSISTED BORON CARBIDE (B_4C) PRECURSOR POWDERS

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ABSTRACT

The study carries out the synthesis and characterization of the precursor to be converted to boron carbide (B_4C). For this purpose, starting materials are boric acid (H_3BO_3) and sodium citrate ($C_6H_5Na_3O_7$). Both starting materials' reactions formed a complex structure (precursor) consisting of B-O-C-Na elements. Phase and microstructure analyses and bond characteristics of the precursor powders perform using X-ray diffraction (XRD), scanning electron microscopy (SEM/EDS), and Fourier spectroscopy (FT-IR) methods, respectively. As a result, the heat treatment carried out at relatively low temperatures (1000 ^oC) and under an inert gas atmosphere resulted in XRD patterns of the B_4C phase. This study also investigated the possible reaction mechanism of the formation of the boron carbide phase and the effect of mechanical activation on the phase formation.

Keywords: *Boric Acid (H_3BO_3), Sodium Citrate ($C_6H_5Na_3O_7$), Boron carbide (B_4C), mechanical activation*

1. INTRODUCTION

In parallel with the rapidly advancing technology, the place and importance of advanced technology products are increasing daily [1]. Since the beginning of the 80s, developments in some sectors have increased the need for structural materials exposed to high temperatures and stresses at these temperatures, aerospace, space and satellite vehicles, advanced engines, and are resistant to temperature and radiation. The mechanical (strength, elastic modulus, hardness) and physical (density, electrical and electronic structure) properties of boron carbide (B_4C) have increased the choice of this material and expanded its usage area. Boron carbide can be used as an anode material in the nuclear field with its neutron absorption feature, in ballistics and automobile industries with its high strength, low specific gravity, and high elastic modulus, and also in supercapacitors due to its energy storage property [2-4].

63 % of the world's boron reserves, the primary raw material of boron carbide used in different advanced technology fields, are in our country. Therefore, studies on B_4C, a boron-based high-tech ceramic family member, are essential. An alternative method for producing boron carbide is by magnesiothermic reduction of boron oxide in the presence of carbon. The reaction products (boron

carbide) are processed by aqueous methods to remove them from magnesium oxide. Carbide still contains magnesium borides formed as stable compounds. This reduction technique is very suitable for manufacturing sintered products and produces fine amorphous powder [5-7].

The synthesis of boron carbide from the elements is uneconomical due to the high cost of elemental boron. Therefore, it is only used for special applications such as B10 enriched or pure boron carbide. Boron and carbon are mixed well, turned into pellets, and reacted at high temperatures for the synthesis of elements. B_4C production is carried out with boron-loaded organic compounds such as carburan, triphenylborane, polyvinyl pentaborane, and borazines [8-9]. Generally, this process is carried out in a vacuum or inert atmosphere in the temperature range of 1000-1500°C. Boron carbide is traditionally prepared by carbothermal reduction of boric acid. Carbon is used as a reducing agent. This process is carried out in electric arc or graphite resistance furnaces. The reaction temperature is > 2000 ^{o}C, and the boron carbide yield is low due to the evaporation of boron oxide. The production process is endothermic and requires 16800 kJ / mol of energy. Therefore, the disadvantages of this method are; high-temperature requirement, high energy requirement, low efficiency, and low homogeneity due to uneven temperature distribution in the reaction zone [10]. Synthesis of precursor powders (starting material that will turn into boron carbide) used in the production of B_4C is one of the alternative methods. The precursor elements are mixed homogeneously at the atomic scale offers many advantages. These; are due to short diffusion distance phase formation at low temperatures, high efficiency, low energy demand, prevention/reduction of the evaporation of components, and accordingly control of stoichiometry, small grain size, and poor agglomeration and high purity. Therefore, selecting and controlling the powder production process, which determines the starting powder properties for controllable properties and high performance in the final product, is a critical step [11-14]. The aim of this study is the synthesis and characterization of a precursor powder with conversion to boron carbide (B_4C) using native boric acid (H_3BO_3) and sodium citrate ($C_6H_5Na_3O_7$).

2. MATERIAL and METHOD

2.1. Preparation of Precursor Xerogel Powders

The starting chemicals used in synthesizing B_4C powders and their properties are given in Table 1. Sodium citrate synthesized compounds that homogeneously mixed boron, carbon, sodium, hydrogen, and oxygen (B-C-Na-H-O) elements were at the atomic level by forming a clamp/chelate with boric acid. Another task of sodium citrate is to provide a carbon source to take part in carbothermal reactions. Acetone was used as an anti-solvent "agent to precipitate the water-soluble compound formed between sodium citrate and boric acid.

Table 1. Starting chemicals used in boron carbide synthesis.

Chemical	**Chemical Formula**	**Aim of usage**	**Purity**
Boric acid	H_3BO_3	Boron source	%98
Sodium Citrate	$C_6H_5Na_3O_7.2H_2O$	Carbon source	≥ %98
Acetone	C_3H_6O	Anti-solvent	+%99

Sodium citrate (S) and boric acid (B) were used in two different molar ratios (S/B ratio 1:1 and 1:1.3). In Table 2, sample codes, mole ratios of components, and applied procedures are in table 2. While preparing xerogel precursor powders for B_4C synthesis, sodium citrate and boric acid were first added to 100 ccs distilled water, respectively, and mixed until a clear and homogeneous solution was obtained.

Table 2. Sample codes, mole ratios of components, and applied processes.

Sample Code	**$C_6H_5Na_3O_7.2H_2O$ [mole]**	**H_3BO_3 [mole]**	**Applied Process**
BC1	1	1	As synthesized
BC2	1	1.3	As synthesized
BC1-A	1	1	Mechanical activation
BC2-A	1	1.3	Mechanical activation

In order to concentrate the obtained solution, it is heated in a Heidolp brand rotary dryer device in a water pool with a temperature of 80 ^oC for approximately 90 minutes with a rotation speed of 137 cycles/min. During this time, 400 mbar vacuum pressure water was evaporated. 25 ml of acetone at -80 ^oC was added to the concentrated solution and mixed with a glass baguette stick, thus allowing a gel structure to precipitate from the solution. Xerogel was obtained by separating the gel part from the liquid it was in with the help of centrifugation and drying it completely in an oven at 80 ^oC for 48 hours. The characterization of the powder passed through a 125 µm sieve was made. This received product is defined as “precursor powder” in the following parts of the study.

2.1.1. Mechanical activation of precursor powders

Mechanical activation is the term applied to a powder synthesising method in which chemical reactions and phase transformations occur due to application of mechanical energy. In mechano-chemical synthesis, ball milling assistes the reaction in a mixture of reactive powders [15]. Mechanical activation was applied to the synthesized precursor powders with a Retsch PM 200 brand planetary mill. Powder and balls were placed in stainless steel crucibles under an argon atmosphere for this process. Mechanical activation parameters are given in Table 3.

Table 3. Parameters of mechanical activation.

Parameter	
Rotation speed of vial (rpm)	500
Milling Time (h)	2
Vial material	Stainless steel
Capacity of vial (ml)	125
Ball material	ZrO_2
Diameter of balls (mm)	5
Powder/ball ratio	1/20
Powder amount (g)	5

2.1.2. Heat treatment of precursor powders

For the purpose of improve formation of B_4C, the milled synthesized precursor powders were subjected to a heat treatment. Protherm brand high-temperature furnace was used for the heat treatment of the precursor powders. The prepared powders were placed in a graphite crucible and placed in an alumina tube furnace, and heat treatment was applied for 1 hour at a heating rate of 5 ^{o}C/min at temperatures of 800 – 1000 ^{o}C.

2.2. Characterization of Synthesis Powders

For the phase analysis of the powders, images were taken in Cu-Kα radiation at a scanning speed of 2 ^{o}/min using the Panalytical Empyrean brand X-ray device located in Kütahya Dumlupınar University Advanced Technologies Design Research Development and Application Center (ILTEM). FEI / NOVA NANOSEM 650 scanning electron microscope (SEM) was used to analyze the microstructure and elemental composition of the powders. Bruker brand Fourier Transform Infrared Spectroscopy (FT-IR) device was used to define the bonds within the atomic structure. The bandgap between 350 and 4000 cm^{-1} was examined in FT-IR analysis. The absorbance spectrum of the components in the solutions used to synthesize the precursor powders were determined with the SpectroStar nano UV-VIS spectrophotometer device. Quartz cuvettes with an optical path length of 2 mm were used for the measurements. Mettler Toledo brand instrument was used to measure the pH of the solutions. The instrument was calibrated before use. The pH value of the boric acid solution was measured as 3.97, and sodium citrate was 8.31. The pH value of the boric acid-sodium citrate solution is 7.5, and the pH measured after 2 hours at 80 ^{o}C is 7.9. When the pH of BC2 was measured, values close to those of the BC1 solution were obtained. According to the pH measurement results, the pH values of boric acid - sodium citrate solutions support the formation of a compound between these two chemicals.

3. RESULTS AND DISCUSSION

3.1. Wavelength of Solutions – Optical Density Results

Figure 1 – 3 shows the absorption characteristics corresponding to the wavelength of the solutions obtained with boric acid, sodium citrate, and boric acid - sodium citrate solution (boric acid: sodium mole ratio 1:1). The x-axis wavelength (nm); the y-axis represents the optical density (OD). The optical density of each solution measured at different wavelengths, that is, the measure of light absorption, will be other. Here, the UV-VIS spectrophotometer technique is used to observe the formation of a compound due to a sodium citrate-boric acid reaction. When the boric acid solution was examined, it was determined that while a high absorption value was obtained at low wavelengths, absorption decreased with increasing wavelength.

The wavelength-absorption relationship was obtained similarly for sodium citrate, and mixture solutions measured the highest absorbance value as 0.13 for the boric acid solution, 3 for sodium citrate, and 2.8 for boric acid - sodium citrate solution, respectively. 2.8 absorbance value obtained in boric acid – sodium citrate solution; It can be said that a new structure is formed as a result of the reaction of these two components (boric acid and sodium citrate) and affects the optical properties of the solution [1].

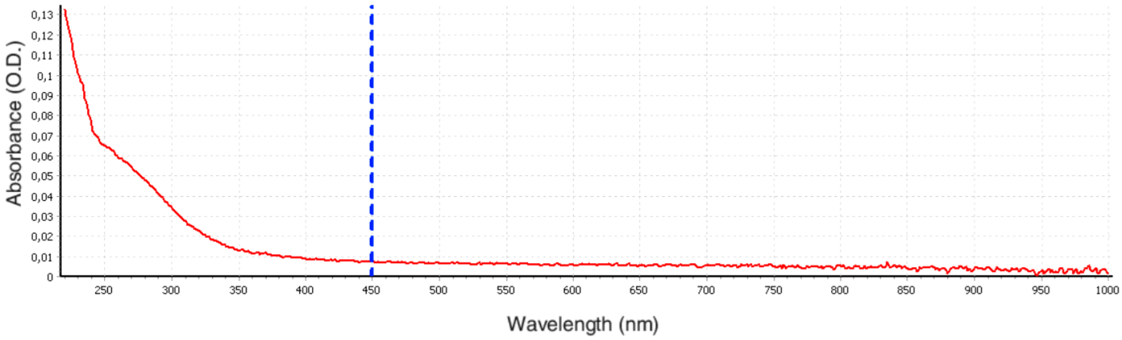


Figure 1. UV-Vis optical density graph of the boric acid solution prepared for the production of BC1 coded powder [1].

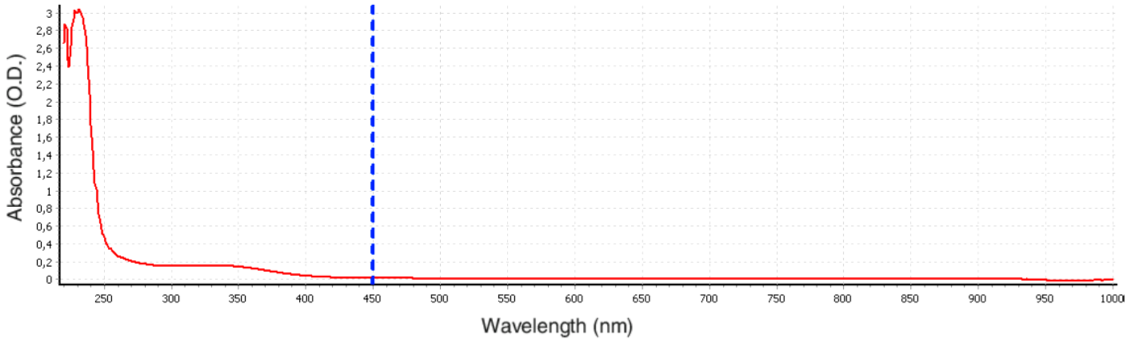


Figure 2. UV-Vis optical density graph of sodium citrate solution prepared for the production of BC1 coded powder [1].

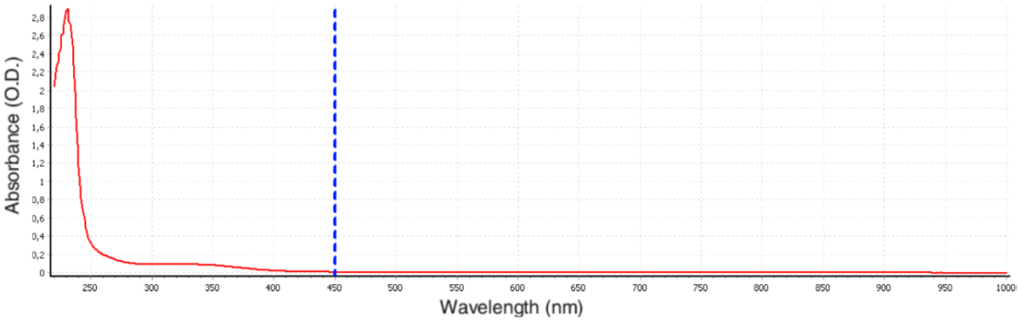


Figure 3. UV-Vis optical density graph of the boric acid-sodium citrate solution prepared for the production of BC1 coded powder [1].

Figures 4 - 6 show the absorption characteristics corresponding to the wavelength of the solutions obtained by boric acid, sodium citrate, and boric acid - sodium citrate solution (mole ratio of boric acid: sodium citrate 1:1.3). We measured the highest absorbance value as was 0.095 for the boric acid solution, 2.8 for sodium citrate, and 2.6 for boric acid - sodium citrate solution, respectively. Similarly, it can state that a new structure is formed by the reaction (chelation) of these two components in boric acid and sodium citrate solution [1].

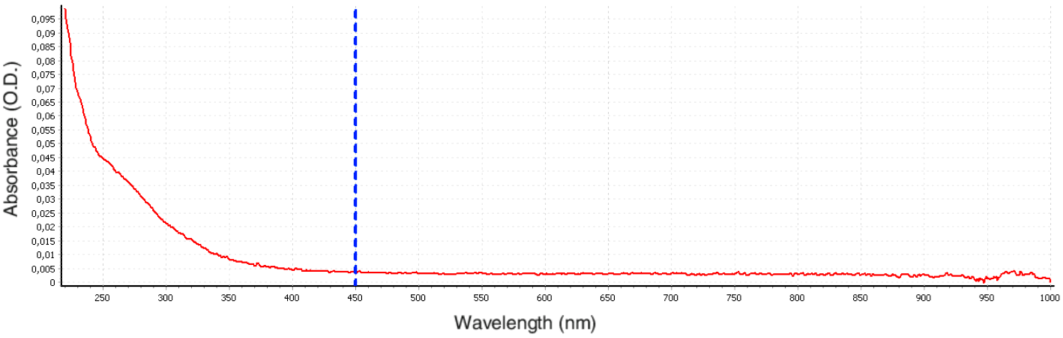


Figure 4. UV-Vis optical density graph of the boric acid solution prepared for the production of BC2 coded powder [1].

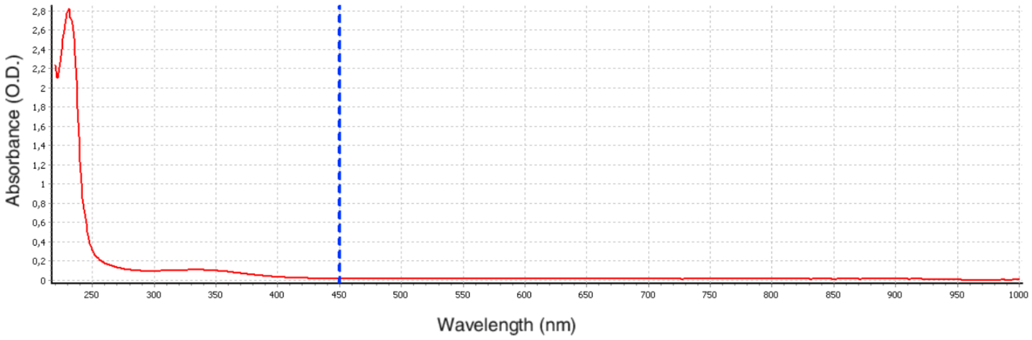


Figure 5. UV-Vis optical density graph of sodium citrate solution prepared for the production of BC2 coded powder [1].

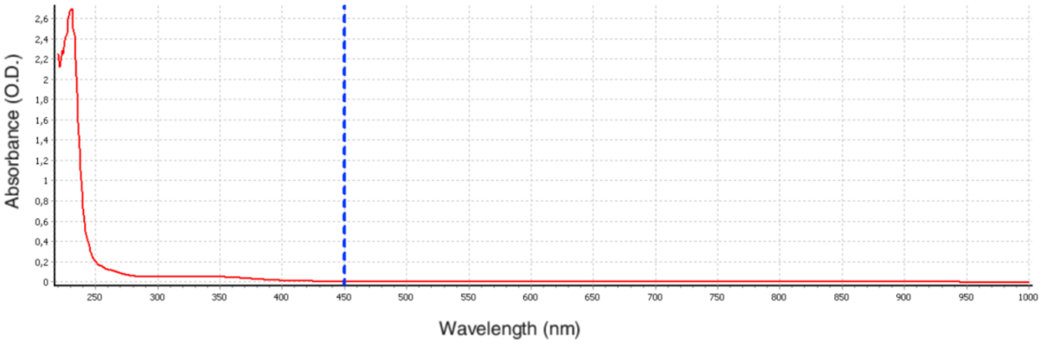


Figure 6. UV-Vis optical density graph of the boric acid-sodium citrate solution prepared for the production of BC2 coded powder [1].

Sodium citrate and boric acid were dissolved in distilled water at room temperature. The resulting solution was stirred at 80 ^oC, and the water evaporated. Then, 25 ml of acetone was added to the solution at -80 ^oC. As a result of this process, it was observed that a gelled phase precipitated. This event resulted in a water-soluble compound formed between sodium citrate and boric acid, and this compound precipitates with the addition of acetone. According to this result, acetone acted as an anti-solvent. The images of the precipitated phase with the addition of acetone and dried at 90 ^oC and ground in agate mortar are given in Figure 7, respectively [1].

Figure 7. The gel product precipitated by the addition of acetone and the precursor powder obtained by drying the gel product [1].

3.2. Phase (XRD), Microstructure (SEM/EDS) and Bond Characteristic (FT-IR) Analysis Results of Powders

XRD phase analysis results of BC1 coded raw powders (as-synthesized) were given in Figure 8. When the mole ratio of sodium citrate: boric acid was 1:1, peaks of sodium and sodium borate-based compounds were observed. These phases are; disodium dodecahydroxo-dodecaborate tetrahydrate (indexed #1), disodium tecto-octaborate (#2), and trisodium heptaborate (#3). It was also observed in the diffraction of the aqueous sodium hydroxide (#4) phase. The formation of single-phase compounds of Na and B elements has been interpreted as the homogeneous coexistence of these elements at the atomic level [1].

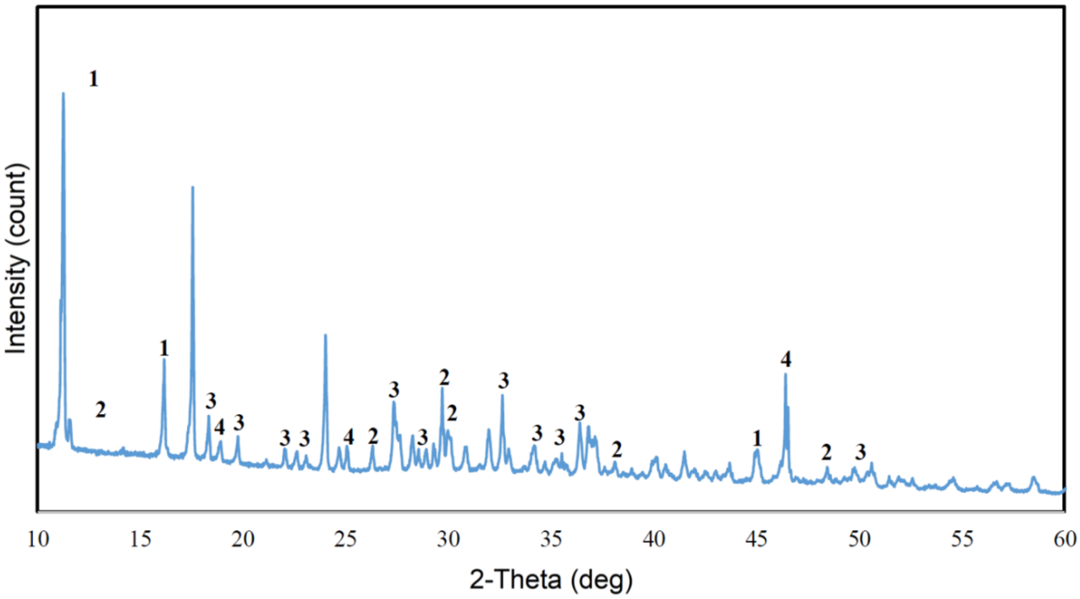


Figure 8. XRD diffraction pattern of BC1 coded powder [1].

In Figure 9, the phase contents of BC2 coded raw powders (as-synthesized) were obtained by X-ray diffraction. In the case where the mole ratio between sodium citrate: and boric acid is 1:1.3, the amount and intensity of the crystalline phase in the structure decreases, while it was observed that the powder has an irregular (amorphic) phase content. Observed sodium-boron-based phases; trisodium heptaborate (#1) and disodium octaborate (#2). It was also observed in the diffraction of the aqueous sodium hydroxide (#3) phase. Due to the amorphic structure of the powder, it may turn into a crystalline structure at relatively lower temperatures [1].

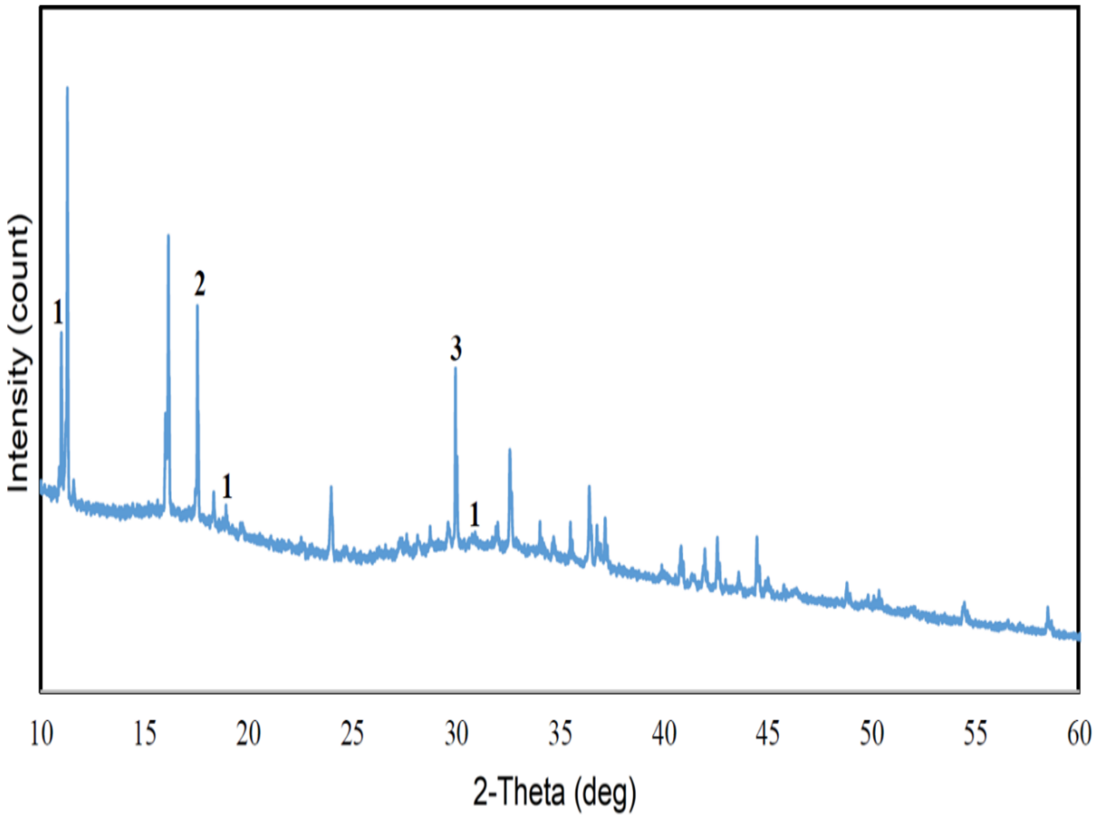


Figure 9. XRD diffraction pattern of BC2 coded powder [1].

FT-IR analysis results of BC1 and BC2 coded powders are given in Figures 10 and 11, respectively. The FT-IR spectrum characteristics obtained from both powders are similar. According to FT-IR analysis; peaks of 1071.47 cm^{-1}, 1296.98 cm^{-1} and 1527.22 cm^{-1} belong to B-C, 1632.98 cm^{-1} B-OH, 2413.33 cm^{-1} C-C, 2986.85 cm^{-1} O-H bonds determined as peaks. Here, the B-C bond, boron, and carbon coexist at the atomic scale, and the boron carbide phase is thought to occur in the formation reactions.

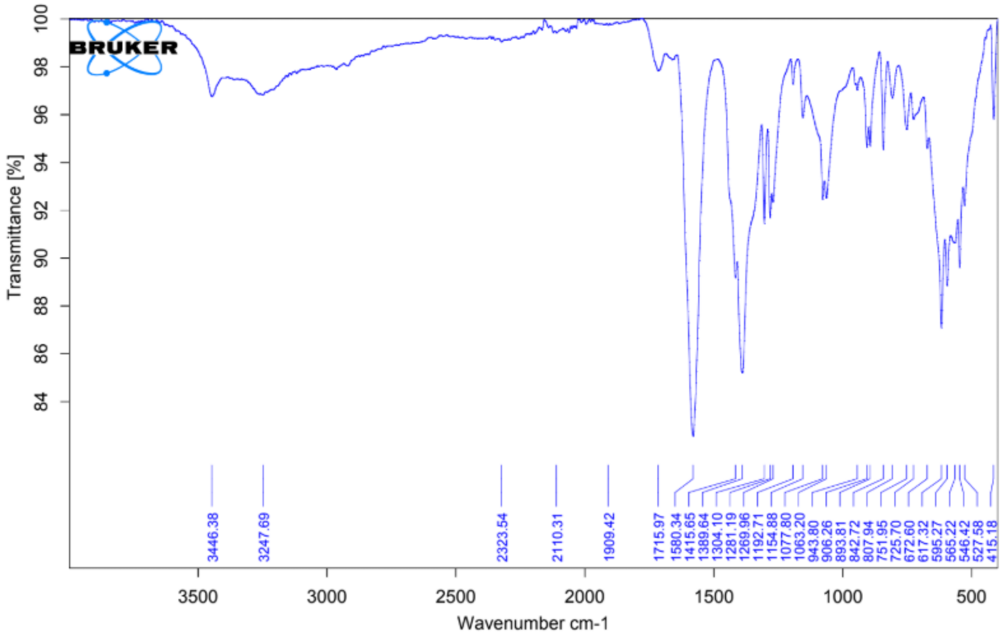


Figure 10. FT-IR spectrum of BC1 coded powder [1].

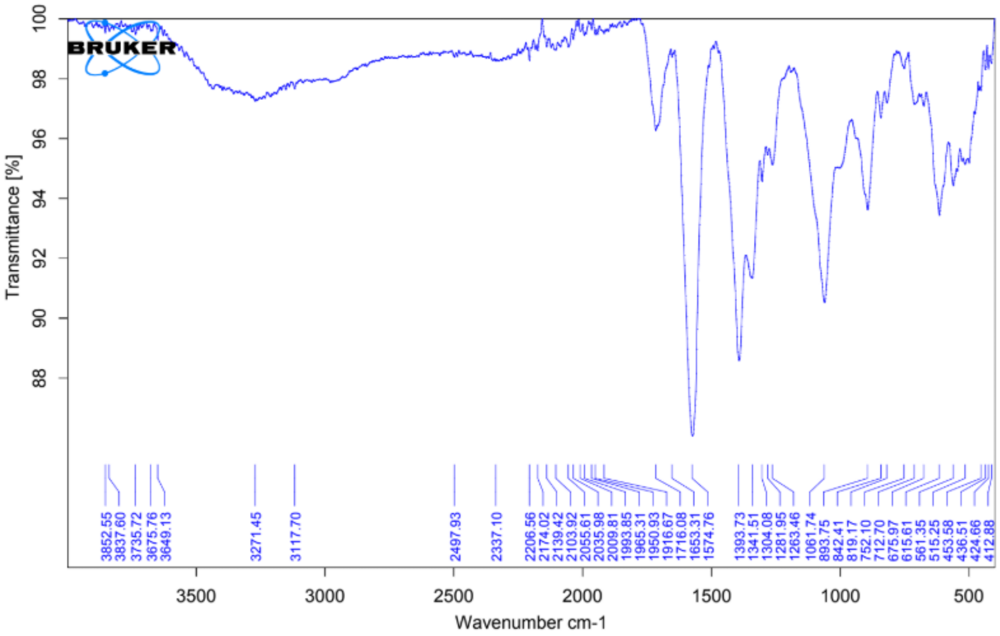


Figure 11. FT-IR spectrum of BC2 coded powder [1].

Figure 12-a and b show microstructure images of BC1 coded powder obtained from a scanning electron microscope (SEM). SEM microstructure images showed that the powder size has a wide

range (~50 µm – nano level). The powders were generally irregular and observed broken shapes with sharp corners. In addition, the particles are dense and do not contain pores [1].

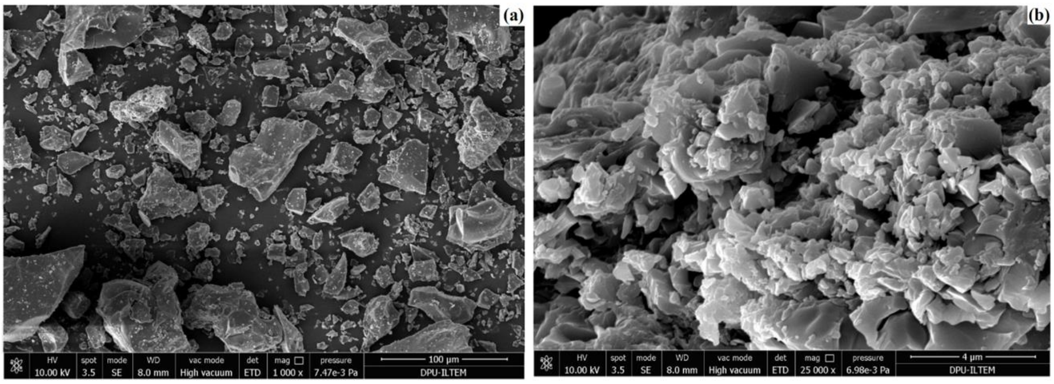


Figure 12. SEM microstructure images of BC1 coded powder (a) X 1000, (b) X 25000 [1].

Microstructure images of BC2 coded powder obtained from scanning electron microscope (SEM) were given in Figure 13-a and b. Compared to the BC1 coded powders, coarser grains were observed. The structure does not have a homogeneous size distribution. It has been determined that small-sized grains come together to form coarse and irregular powder agglomerations [1].

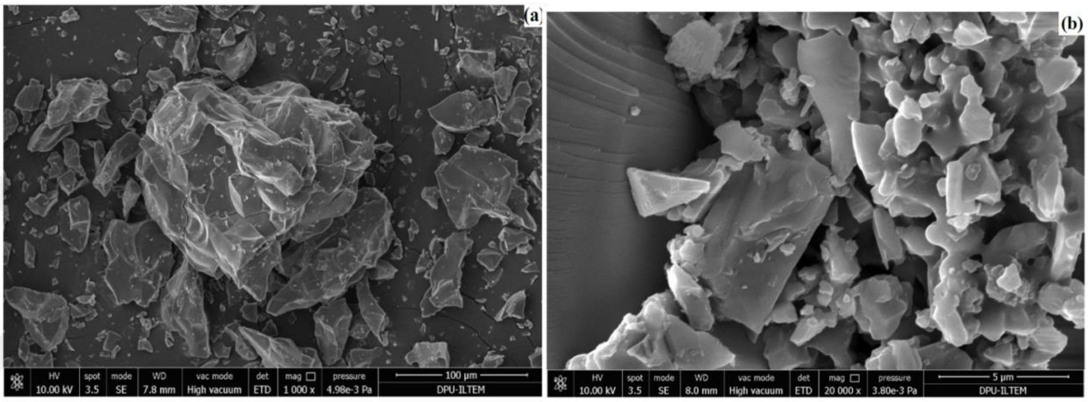


Figure 13. SEM microstructure images of BC2 coded powder (a) X 1000, (b) X 25000 [1].

XRD phase analyses of mechanically activated and heat-treated BC2 powders are shown in Figure 14. In general, when the phase analysis results of the powders obtained after both processes are examined, it is seen that there is no significant difference. In the powder heat-treated only at 1000 ^{o}C, the peaks are sharper and of higher intensity, suggesting better crystallization. However, characteristic diffractions of B_4C were found at 2θ:23.4 and 34 angles [1].

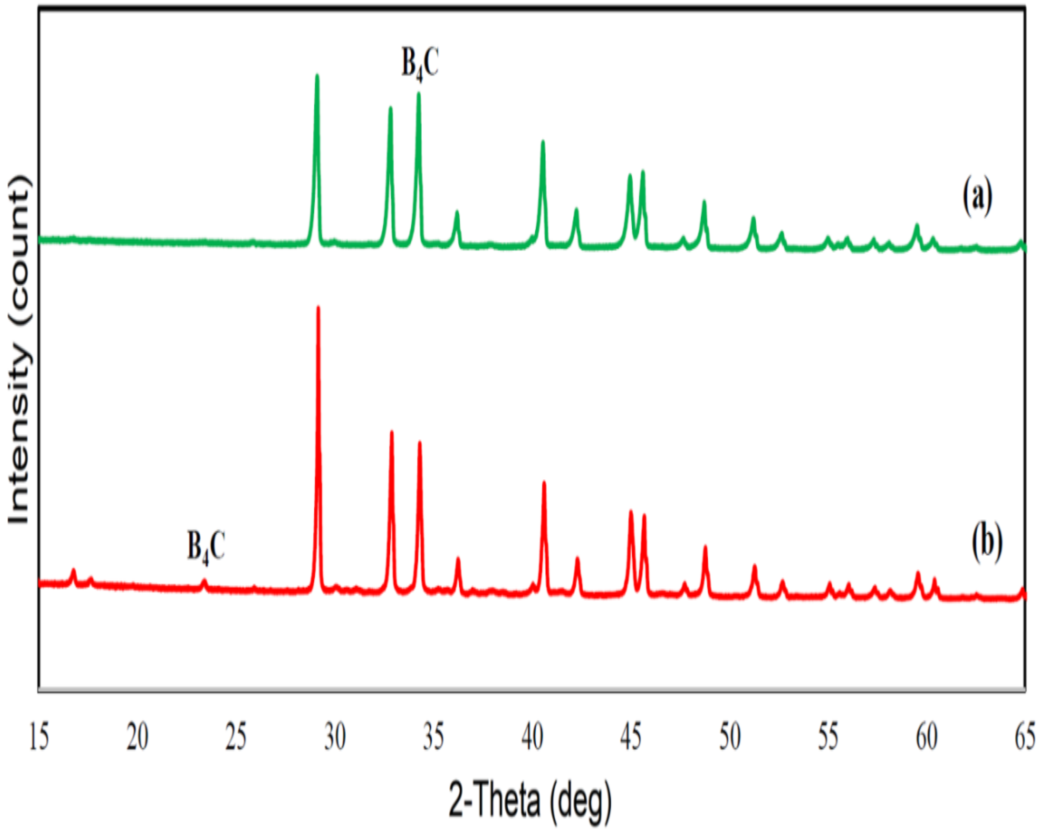


Figure 14. XRD pattern of BC2 coded powders (a) mechanical activation and heat treatment at 1000 °C, (b) heat treatment at 1000 °C [1].

The result of FT-IR analysis of the BC2 coded powder raw (as ground), heat-treated at 1000 °C, and heat-treated after activation was given in Figure 3.15. The peaks observed in 1061 - 675 cm^{-1} bands were defined as B-C bonds, 1575 - 1304 cm^{-1} B-O-C bonds, 2200 - 1900 cm^{-1} C-C bonds, and 3270 - 3117 cm^{-1} bands were defined as O-H bonds. According to the FT-IR results, the B-C bonds will be the precursors for the nucleation of the B_4C phase by heat treatment. In addition, the presence of C-C bonds indicates that there is a free carbon phase in the structure [1].

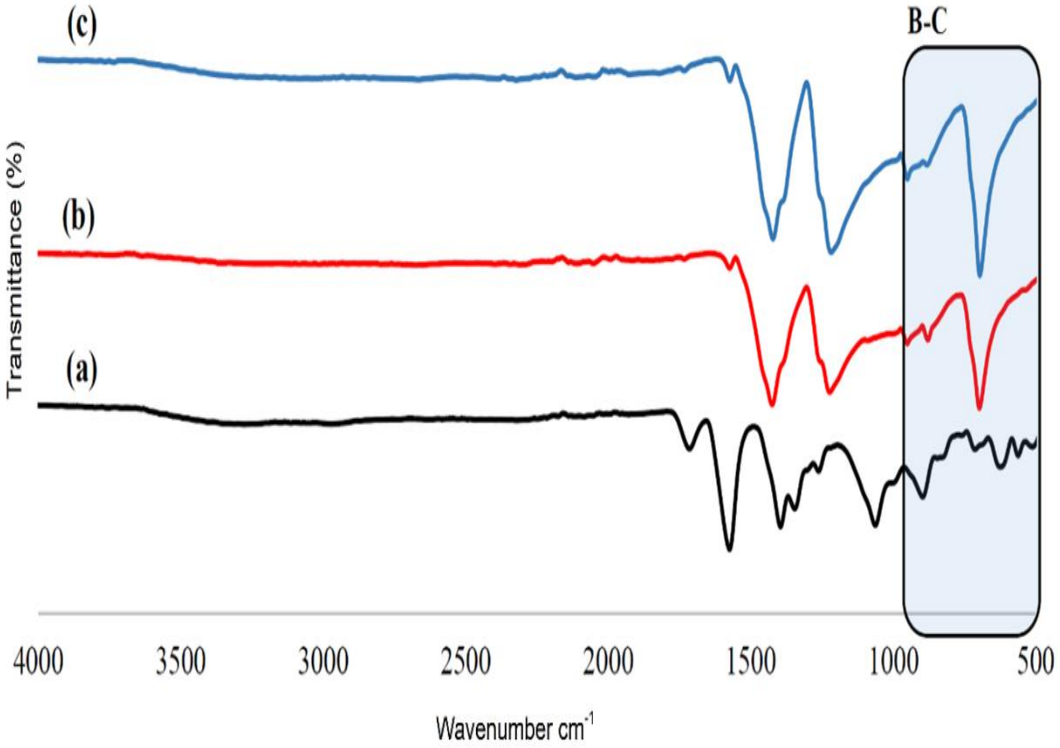


Figure 15. FT-IR spectrum graph of BC2 coded powders (a) raw powder, (b) powder heat-treated at 1000 °C, (c) activated and heat-treated powder [1].

The microstructure images obtained from a scanning electron microscope (SEM) of BC1 coded powder heat-treated at 1000 °C are given in Figure 3.16. It was observed that the size distribution in the powder mass varies in the range of ~ five μm – nanoscale. In addition, the grains exhibit a morphology close to spherical. It is thought that the dust lumps formed in the structure are created by the melting of the oxide components consisting of sodium - oxygen (Na-O) or sodium - boron - oxygen (Na-B-O) elements and bonding the grains together. For this reason, the powders need to be removed by dissolving these molten phases by washing them with pure water, which has weak acidic properties, after the heat treatment.

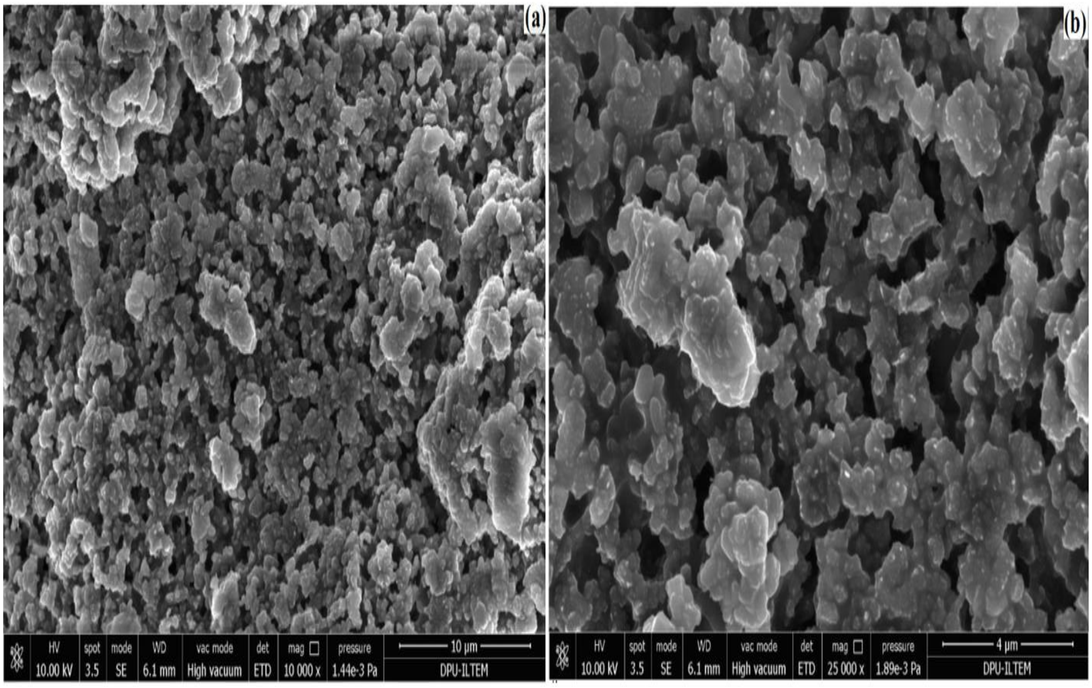
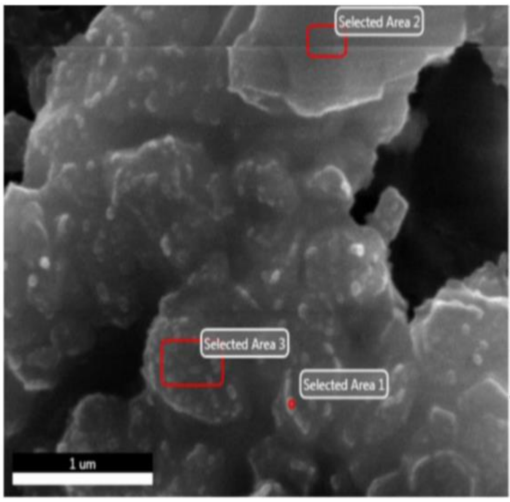


Figure 16. SEM microstructure images of BC1 coded powder heat treated at 1000 ^{o}C (a) X 10000, (b) X 50000 [1].

Figure 17 shows the SEM/EDS analysis results of the BC1 coded powder heat-treated at 1000 ^{o}C. Boron (B), carbon (C), nitrogen (N), oxygen (O) and sodium (Na) elements in the structure were analysed according to the EDS results on different regions. Boron content varies between 12.02 – 7.99 wt.%, carbon 10.93 – 6.73 wt.%, nitrogen 1.53 – 0.91 wt.%, oxygen 39.32 – 32.40 wt.% and sodium content between 47.55 – 40.66 wt.%. The results support the formation of boron-based (BxCy, BxNayOz) oxide and non-oxide phases and sodium-based (NaxOy, NaxByOz) oxide phases. Soluble phases can be removed from the structure by washing with pure water with weak acidic properties [1].



	Zone 1		Zone 2		Zone 3	
Element	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
B	11,76	18,17	7,99	12,70	12,02	18,42
C	6,73	9,37	10,83	15,49	10,93	15,07
N	1,53	1,83	1,23	1,50	0,91	1,07
O	39,32	41,07	32,40	34,78	33,68	34,86
Na	40,66	29,56	47,55	35,52	42,46	30,58

Figure 17. SEM/EDS analysis of BC1 coded powder heat treated at 1000 ^{o}C [1].

Microstructure images obtained from scanning electron microscope (SEM) of BC2 coded powder heat-treated at 1000 ^{o}C were given in Figure 18, and SEM/EDS analysis results were shown in Figure 19. Dense grains with rod-like morphology and ~1 µm in size were observed in the powder mass. Observed Boron (B), carbon (C), nitrogen (N), oxygen (O), and sodium (Na) elements in the SEM/EDS analysis performed on different regions of these grains. Boron content is 14.89 – 12.44 wt.%, carbon is 3.91 – 3.32 wt.%, nitrogen is 2.11 – 1.94 wt.%, oxygen is 49.45 wt.% and sodium is 32.67 – 29.83 wt.%. The results support the formation of boron-based (BxCy, BxNayOz) oxide and non-oxide phases and sodium-based (NaxOy, NaxByOz) oxide phases.

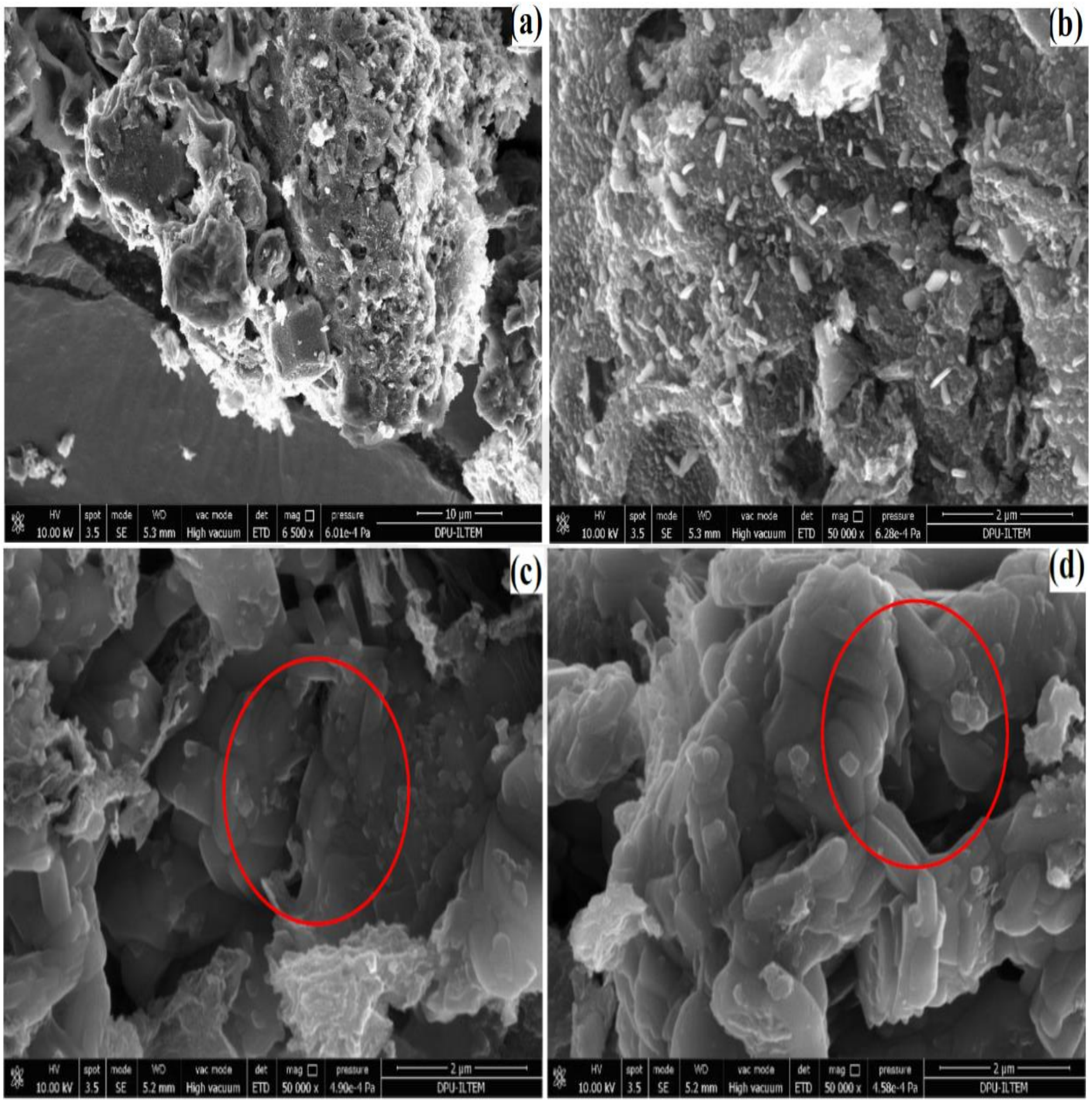
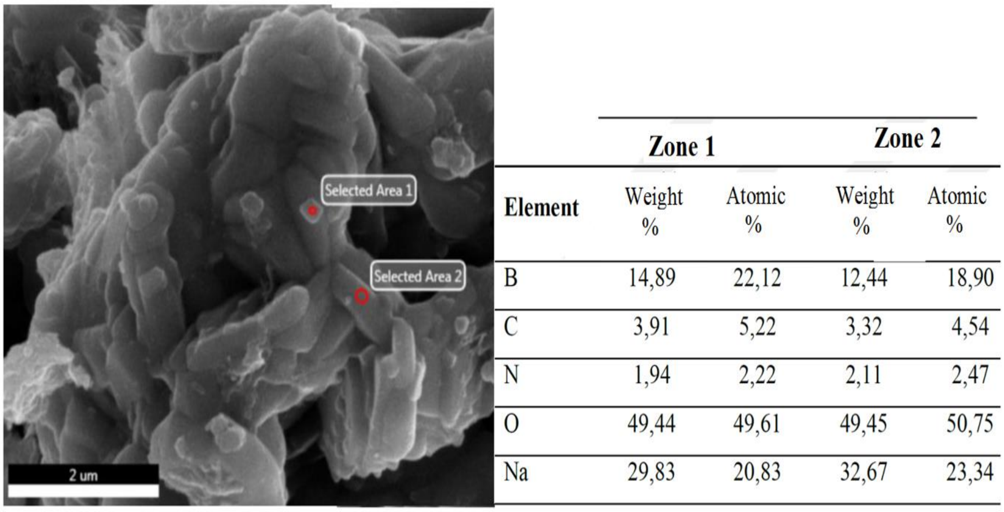


Figure 18. SEM microstructure images of BC2 coded powder heat treated at 1000 ^{o}C (a) X 6500, (b) X 50000, (c) X 50000, (d) X 50000 [1].



	Zone 1		Zone 2	
Element	Weight %	Atomic %	Weight %	Atomic %
B	14,89	22,12	12,44	18,90
C	3,91	5,22	3,32	4,54
N	1,94	2,22	2,11	2,47
O	49,44	49,61	49,45	50,75
Na	29,83	20,83	32,67	23,34

Figure 19. SEM/EDS analysis of BC2 coded powder heat treated at 1000 °C [1].

A complex structure consisting of B-O-C-Na elements occurs between boric acid (H_3BO_3) and sodium citrate ($C_6H_5Na_3O_7$). This structure is the precursor that will later be converted to boron carbide (B_4C) by heat treatment. With increasing temperature, sodium reacted with oxygen and boron and formed oxide phases. At high temperatures, these oxide components melted to form a liquid phase. This liquid phase triggered B_4C nucleation by reducing the diffusion distance and allowing the boron (B) and carbon (C) to react at low temperatures. Possible reactions to the interaction of B-O-C-Na elements are given below [1].

x mole Na + y mole O $\rightarrow$ Na_xO_y (oxide phase) (1)

x mole Na + y mole B + z mole O $\rightarrow$ $Na_xB_yO_z$ (oxide phase) (2)

$C + O_2 \rightarrow CO_2$ (gas phase) (3)

X mole B + y mole C $\rightarrow$ z mole B_4C (Nucleation of the B_4C phase) (4)

4. CONCLUSION

B_4C phase nucleation was observed by the anti-solvent precipitation method using sodium citrate and boric acid.

Sodium citrate was used as a source of sodium and carbon. Sodium (Na) acted as the mineralizer that would allow the designed phase to form at low temperatures. In other words, the liquid B_4C phase formed by sodium with oxygen created an environment that allowed nucleation at relatively low temperatures (1000 °C). These soluble oxide compounds must be removed from the structure by washing.

Scanning electron microscopy (SEM) analyses showed micron-level, agglomerated particles that did not exhibit a specific morphology.

The optical density values of the solutions at different wavelengths are characterized. Different absorbance (OD) values were obtained depending on the solutions' light diffraction and absorption characteristics; different absorbance (OD) values were obtained.

After the BC2 coded sample @ 1000 ^{o}C heat treatment, regions with dense grains were observed. The SEM/EDS chemical analysis carried out in this region showed that the B-O-N-Na elements exhibited a homogeneous distribution. Low-intensity diffraction of B_4C nucleation was observed in XRD analysis.

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