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Synthesis and Sintering

ISSN 2564-0186 (Print), ISSN 2564-0194 (Online)



Research article

Performance of glucose, sucrose and cellulose as carbonaceous precursors for the synthesis of B₄C powders



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ABSTRACT

Boron carbide is the third hardest material in the world after diamond and cubic boron nitride, which is one of the most strategic engineering ceramics in various industrial applications. The aim of this research is to synthesize B₄C by reacting boric acid as boron source with polymers from the saccharide family as carbon sources, and to determine the best saccharide as precursor. For this purpose, glucose (monosaccharide), sucrose (disaccharide), and cellulose (polysaccharide) were used and examined. The samples were prepared by appropriate mixing of the starting materials, pyrolysis at 700 °C, and synthesis at 1500 °C. The results of Fourier transform infrared (FT-IR) spectroscopy and X-ray diffractometry (XRD) showed that among the studied saccharide polymers, glucose is the best carbon source candidate for the synthesis of B₄C. To describe precisely, the specimen prepared with glucose and boric acid had more boron carbide and less hydrocarbon.

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KEYWORDS

Synthesis
Boron carbide
Saccharide
Boric acid
Glucose
Precursor



1. Introduction

Boron carbide has interesting combination of properties such as high melting point (2445 °C), low density (2.5 g/cm³), high hardness, good resistance against chemical agents, high wear resistance, good modulus of elasticity, high neutron absorption and high impact resistance [1–4]. This material is widely used in industry and has become one of the most important and strategic engineering ceramics [5–7]. Therefore, acquiring the technical knowledge of B₄C production, achieving its manufacturing technology from available raw materials, as well as using cost-effective fabrication methods are of special importance [8–10]. There are various techniques for synthesis of B₄C ceramics including carbothermal reduction [11, 12], synthesis from its elemental constituents [13, 14], magnesiothermal reduction [15, 16], chemical vapor deposition (CVD) [17–19], and synthesis from polymeric raw materials [20–22].

Among the above methods, the synthesis using constituent elements is not cost-effective due to the expensive pure raw materials required and is merely a research-based methodology for synthesis in the laboratory

[23]. The CVD method, despite its advantages such as very high purity of the final product and the ability to precisely control the size and amount of materials in the composition of solid B₄C, due to the high cost of needed equipment and low production volume at each run of synthesis process, cannot be used as a universally accepted industrial route [24, 25]. Among other methods, the carbothermal reduction is a relatively easier and less expensive technique in terms of materials and equipment required, but the main drawback of this method is the need of ultrahigh temperatures for the synthesis of B₄C. Another limitation with this method is the relatively low purity of the final product because the carbon used as the starting material is not completely consumed during the process and remains as an impurity in the synthesized B₄C. This causes the product to eventually become contaminated with carbon, which is a major limitation of this method [26, 27]. Numerous studies and researches in this field have been done to increase the efficiency of the carbothermal process. The help of mechanical and chemical methods to encourage raw materials to be synthesized at lower temperatures is one of the investigations of researchers to increase the process efficiency. The use of high-energy

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Received 2 March 2022; Received in revised form 24 March 2022; Accepted 25 March 2022.

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<https://doi.org/10.53063/synsint.2022.21108>

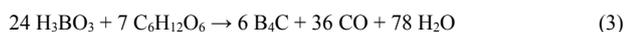
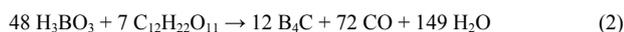
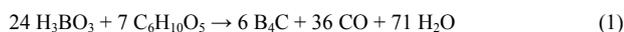
and fast agitators for the preparation of raw materials [28, 29] as well as the stimulants such as microwave energy are among these efforts [30, 31]. Attempts have been made to employ materials with high reactivity and high combustion heat such as magnesium to provide the energy needed for synthesis and to reduce the process temperature, which have led to the invention of the magnesiothermal method for the synthesis of B₄C [32, 33].

Commendable efforts have been done to employ other carbon sources, and researchers have tried to use materials that are more reactive and require less activation energy than activated carbon or graphite [34]. These substances include organic acids such as citric and acetic acid; alcohols such as polyvinyl alcohol; and other polymers such as glycerin and saccharides [35]. Polymers have been considered as a source of carbon with an open structure and susceptible to bonds with other materials such as boric acid as a source of boron. This methodology is performed in a neutral or vacuum atmosphere and is a suitable solution for B₄C synthesis due to the cheapness of raw materials and precise composition control. The use of such materials has caused the synthesis reaction temperature to drop sharply from 1800–2100 °C [36] to 1200–1600 °C [37]. So far, studies have been conducted on the synthesis of B₄C using polymeric raw materials such as glycerin [37, 38], polyvinyl alcohol [39], cellulose and sucrose [40], citric acid [41] and carbon waste [42]. Although the use of carbonaceous sources instead of carbon itself has improved the synthesis efficiency, the final product may not be of high purity and residual carbon may be observed. Therefore, careful study of processing conditions and parameters to reduce carbon in the final product seems to be essential [36, 43].

Since the challenges of B₄C synthesis by conventional methods have limited the production of this industrially and strategically important material, use of polymeric materials for easier and cheaper fabrication of B₄C ceramics has been considered in this research. The polymers selected in this study are glucose (monosaccharide), sucrose (disaccharide), and cellulose (polysaccharide), all of which belong to the saccharide family.

2. Materials and methods

In this study, boric acid (H₃BO₃) was used as boron source for B₄C synthesis. Also, cellulose (C₆H₁₀O₅), sucrose (C₁₂H₂₂O₁₁) and glucose (C₆H₁₂O₆) saccharides were used separately as carbon sources. The chemical reactions that are expected to occur between boric acid with cellulose, sucrose and glucose, leading to the formation of B₄C, are given in Eqs. 1–3, respectively:



Three samples were prepared based on their stoichiometric ratios in the above reactions under similar conditions. First, the saccharide materials were separately dispersed in distilled water at 60 °C for 2 h at 500 rpm, whereby glucose and sucrose were dissolved in aqueous medium, but the cellulose remained suspended. Then, according to the stoichiometric ratios of each saccharide, solid boric acid was added to them and mixed for 4 h at 85 °C. Each mixture of polymer and boric acid was then placed in an oven at 150 °C to remove surface moisture and obtain a solid mass. At this step, Fourier transform infrared (FT-IR) spectroscopy was performed on the prepared precursors to compare with the raw polymers and to investigate possible formed bonds.

In the next step, after crushing, the masses were pyrolyzed for 3 h at a rate of 10 °C/min in the air atmosphere in a box furnace at 700 °C. The pyrolyzed powders were then crushed and came in the shape of pellets by hydraulic pressing inside a metal mold. They finally synthesized in a tubular furnace under the argon atmosphere at 1500 °C and heating rate of 10 °C/min. The synthesized powders were subjected to X-ray diffractometry (XRD) after crushing to determine the optimal saccharide for B₄C synthesis by comparing the results of phase analyses.

3. Results and discussion

The approach of current research is based on increasing the efficiency of the synthesis reaction and also decreasing the percentage of remained carbon impurity in the synthesized B₄C powders. In the following, the results obtained from these efforts will be discussed.

Since boric acid has been used as the source of boron, it is expected that the H⁺ can react with the carboxyl group in the saccharides to form a bond. For this purpose, single, double and multiple polymers of saccharides are used as raw material. As the amount of carboxyl (–OH) increases with increasing carbon content, the initial expectation is that the polysaccharide (cellulose) not only will react more and better with boric acid but also the precursor made from this polymer will be more stable. Another expectation is that boric acid can structurally alter the polymer molecule to introduce the boron into the polymer structure. In fact, a suitable polymer should be able to establish stronger bonds between the polymer and boron.

3.1. Performance of cellulose (polysaccharides)

According to FT-IR spectra presented in Fig. 1, raw cellulose has a peak at the wavenumber range of 3100–13600 cm^{–1}, which is related to the n(OH) bond and the hydrated water bonds. These peaks are almost eliminated in the precursor after the drying operation due to the release of water from the polymer structure during the drying process. Also, the wavenumbers of 1360 to 1410 cm^{–1} are related to CH₂ cellulose bonds that are not disappeared in the precursor but are slightly shifted due to the reaction with boric acid [44, 45].

In addition, the relatively high peak of cellulose at the wavenumber of 1210 cm^{–1} is related to the C–OH bond, which is destroyed by reaction with boric acid. In fact, as previously expected, boric acid has been able to neutralize basic sites of cellulose molecule and bind to the polymer via (–OH) heads. The peaks in cellulose spectrum at the wavenumbers of 1030 and 1080 cm^{–1} correspond to the C–O cyclic bonds, the so-called C6. The absence of peak shifts indicates that boric acid has not been able to disintegrate the cyclic structure of cellulose. Since there is no evidence of a connection between boron and cellulose structure, it can be concluded that boric acid is only able to form a weak bond with the polymer.

3.2. Performance of sucrose (disaccharides)

Raw sucrose has n(OH) hydrated bonds of water at the wavenumber range of 3100–3500 cm^{–1}, which almost disappeared in the dried precursor. This is due to the breaking of such bonds due to heating of the precursor, which is shown in Fig. 2. The CH–CH₂ bond in raw sucrose is seen at the wavelength of 1032 cm^{–1}. In the precursor, these wavenumbers are slightly changed and their intensity is reduced, which indicates the stresses applied to these bonds and their partial deformation during the precursor-making process [46, 47].

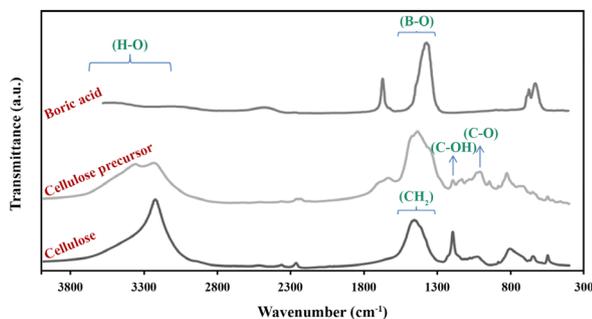


Fig. 1. FT-IR analyses of raw materials and precursor made of cellulose.

Sucrose has a strong characteristic peak corresponding to C–O–C bonds at the wavenumber of 1170 cm^{-1} . The mentioned bond is present in two regions of the sucrose molecule, one of which is known as glycoside linkage that binds two glucose monomers to form the sucrose molecule. The decrease in the intensity of this peak may be due to the breaking of the disaccharide bond. Boric acid has been shown to break down some disaccharides into monosaccharides. Also, the wavenumber of 1052 cm^{-1} , which has a relatively high peak in sucrose, is related to $\text{CH}_2\text{-OH}$ in alcohols. This C–O stretch peak indicates that the main constructive bonds of the sucrose have been changed by reacting with boric acid [48]. In fact, it can be stated that boric acid has been able to decompose sucrose to some extent but has not been able to do so completely. Evidence of this claim is the presence of a small peak at the wavenumber of 1030 cm^{-1} related to the B–O–C bond and low-intensity peaks at the wavenumbers of 1430 to 1450 cm^{-1} attributed to the B–O bond in the precursor. The low intensity of these peaks along with the much higher intensity of the main cellulose peaks indicate that the reaction of boric acid and polymer could not proceed completely and boron was not connected to the hydrocarbon structure [40].

3.3. Performance of glucose (monosaccharides)

Glucose, as the smallest member of the saccharides, has the simplest molecular structure in this family. Raw cellulose has $n(\text{OH})$ hydrated bonds of water at the wavenumber range of 3200 – 3500 cm^{-1} . As shown in Fig. 3, after drying in the furnace, the intensity of these bonds in the precursor is slightly reduced but does not disappear. CH-CH_2 bonds in raw glucose are found at the wavenumbers of 924 and 940 cm^{-1} , but these numbers are slightly shifted in the precursor and their intensity is reduced, indicating the applied stresses on these bonds and their partial deformation during the precursor preparation. Meanwhile, glucose at the wavenumber of 1133 cm^{-1} has a strong characteristic peak, which is related to C–O–C bonds of aliphatic ether type [49]. Of course, the intensity of this peak has not changed much and has only shifted slightly. Such an observation indicates that glucose has not decomposed and remained stable in response to boric acid. Another important phenomenon seen in glucose precursor is the relatively sharp peak at the wavenumber range of 1430 – 1450 cm^{-1} , which belongs to the B–O bond.

There is also a characteristic peak at the wavenumber of 1190 cm^{-1} , related to the B–C bond, in the precursor that was not seen in any of the previous precursors. This new peak indicates a stronger bonding between boric acid and glucose than other saccharides. The wide and sharp peaks at the wavenumber range of 1430 to 1450 cm^{-1} , which belong to the B–O bond, can also support this claim [40].

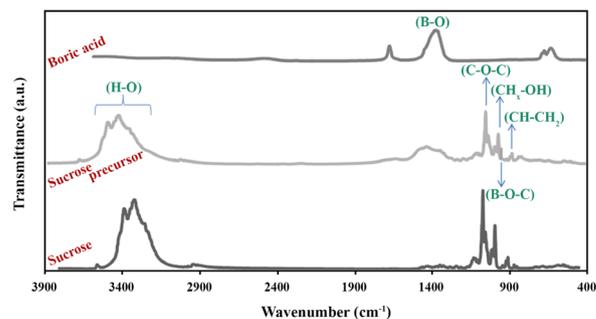


Fig. 2. FT-IR analyses of raw materials and precursor made of sucrose.

3.4. Phase analysis of synthesized products

The results of XRD analysis of the synthesized products with precursors prepared from different saccharides are shown in Fig. 4. Based on these outcomes, no trace of B_4C formation is observed in the material synthesized with the cellulose precursor. In contrast, the product synthesized with sucrose precursor has weak peaks of B_4C along with sharp peaks of hydrocarbon and graphite. Under the same processing conditions, the sample prepared using glucose has much more B_4C peaks than other saccharides and also has a lower hydrocarbon phase. This trend indicates that glucose is a more suitable option for the synthesis of B_4C than cellulose or sucrose, which is consistent with the results of FT-IR analyses. In addition to having sharper B_4C peaks, glucose also has fewer hydrocarbon peaks. This claim is clearly seen in the XRD pattern that the hydrocarbon peaks in glucose are much lower than in sucrose and cellulose. Hence, glucose is suggested as the best saccharide for synthesis of B_4C .

The results of this study showed that contrary to the initial expectation of better reactivity of the acid with the polymer having higher molecular weight and chain size, monosaccharide such as glucose reacted more effectively with boric acid and established a much stronger bond with it. In the case of sucrose, although boric acid was able to react with the polymer to some extent and decompose it, and introduce boron into the polymer structure, the bond strength was weak and not significant. On the other hand, cellulose underwent minimal bond changes, indicating its high resistance to acid. Why a molecule with a long chain and high ($-\text{OH}$) groups such as cellulose reacts much less than glucose with acid can be attributed to its spatial geometry and three-dimensional arrangement. The spatial barrier arising from multiple chains causes the groups in the cellulose molecule not to have effective access and enough space to react with the acid molecules. Also, the cyclic structures of cellulose and sucrose are less reactive than the linear structure of glucose and provide weaker bonds [50, 51].

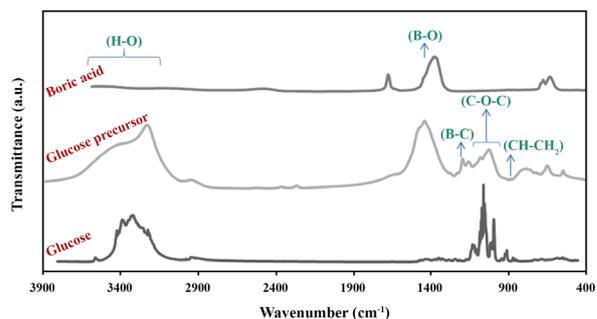


Fig. 3. FT-IR analyses of raw materials and precursor made of glucose.

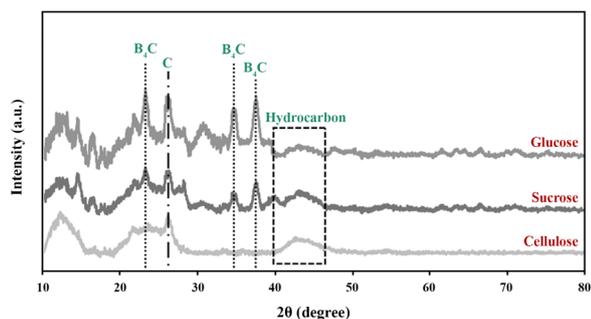


Fig. 4. XRD patterns of final synthesized products from different saccharides.

Finally, it can be concluded that by increasing the molecular weight of saccharides and their complexation, the conditions for effective reaction with boric acid become more difficult and the possibility of boron bonding with the polymer during the precursor preparation is reduced. Therefore, the synthesis conditions of B_4C will be equally more complicated and require a higher temperature [52].

4. Conclusions

The challenges of boron carbide synthesis by conventional methods have limited the production of this industrially and strategically important material. Therefore, using the polymer sources can make B_4C synthesis easier and cheaper. For this purpose, three saccharides (glucose, sucrose, and cellulose) were selected as the carbon sources to react with boric acid as the boron source for the ultimate goal of B_4C production. The fabricated samples by mixing, pyrolysis and synthesis were investigated by FT-IR and XRD analyses. The results showed that the substance prepared with glucose and boric acid had the best performance from the viewpoint of B_4C synthesis.

CRedit authorship contribution statement

Syed Faridaddin Feiz: Methodology, Writing – original draft.

Leila Nikzad: Conceptualization, Supervision, Resources.

Hudsa Majidian: Project administration, Funding acquisition, Writing – review & editing.

Esmail Salahi: Supervision, Project administration, Funding acquisition.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

Funding and acknowledgment

The content of this article originates from a segment of the master's thesis of the first author, bearing the project number 371394069. The authors wish to express their deep appreciation to the Materials and Energy Research Center (MERC) for their invaluable financial assistance. Their support has been instrumental in shaping the outcome of this research, and the authors are grateful for their support and encouragement.

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