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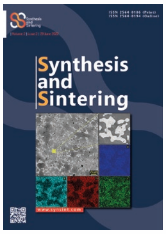
Synthesis and Sintering

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



Research article

Effects of glucose pretreatment and boric acid content on the synthesizability of B_4C ceramics

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ABSTRACT

Synthesis of boron carbide (B_4C) as one of the hardest materials on planet Earth is of particular importance due to its wide range of industrial and engineering applications. For this purpose, boric acid and polymers can be used as the boron and carbon sources, respectively. From the family of saccharides in polymeric materials, glucose has shown the best performance for the synthesis of B_4C. In this research, untreated and pretreated (caramelized by heating) glucose precursors were selected and mixed with boric acid for subsequent pyrolysis and synthesis processes. X-ray diffractometry and Fourier transform infrared spectroscopy confirmed that heat-treated glucose is a better carbon precursor for B_4C synthesis. In order to evaluate the effect of the amount of boric acid, more than its stoichiometric ratio, additional amounts of boric acid (10–40%) were also examined and the excess amount of 30% was determined as the optimal value.

KEYWORDS

B_4C
Synthesis
Glucose
Boric acid
Pretreatment

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1. Introduction

Boron carbide is widely employed in strategic industrial applications due to its fascinating characteristics such as low density (2.5 g/cm^3), high hardness and wear resistance, high melting temperature (2445 °C), and inertness against chemicals [1–6]. Synthesis from its elemental constituents [7, 8] or polymeric raw materials [9–11], magnesiothermal [12, 13] or carbothermal reduction [14, 15], and chemical vapor deposition [16–18] are the main manufacturing processes for the production of B_4C ceramics. Although the B_4C is usually synthesized through the high temperature carbothermal reduction of B_2O_3, the evolution of the carbothermal reduction for organic precursors to synthesize B_4C is receiving considerable curiosity [19]. Due to its convenience in fabrication of single-source reactants for low-temperature synthesis of B_4C, the sol-gel method is preferred in polymeric precursors production [10, 20–22].

Open structure polymers can be used as a carbon source to bond to a boron source such as boric acid. It should be noted that the use of such carbonaceous sources improves the synthesizability of B_4C compared to pure carbon, but the final product may not be completely pure. Hence, in-depth research on synthesis parameters is essential to reduce residual carbon or other impurities from the final product. [23, 24]. The amount of B_4C in the synthesized material depends on the polymer, the synthesis temperature, and the precursor preparation route [19, 25–27].

Microcrystals of B_4C were synthesized by 1 h treatment at 1500–1600 °C under argon atmosphere using saccharide-prepared precursors such as cellulose and glucose. Despite the small amount of remained carbon in the final product, this is an interesting methodology because of inexpensive raw materials, simple precursor preparation, and non-hazardousness of the process [28]. Crystalline B_4C ceramic was synthesized via carbothermal reduction of glucose, cellulose, and starch as carbon sources together with boric acid. The precursors achieved by thermal decomposition of cellulose had finer and more homogeneous structure composed of carbon fibers and B_2O_3. The synthesis of B_4C using the cellulose precursor began at ~1100 °C, around 200 °C less than that for starch or glucose precursors, and completed at 1200 °C within a short time [29].

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Received 17 May 2022; Received in revised form 24 June 2022; Accepted 25 June 2022.

https://doi.org/10.53063/synsint.2022.22115

Rod-like crystalline B_4C with less than 1 wt% free carbon was successfully synthesized at 600 °C using poly(resorcinol borate) with a high char yield and aromatic structure as the polymeric precursor. In fact, the pyrolysis temperature adjusted the amount of carbon in the synthesized B_4C, which resulted in the enlarged contact between carbon and B_2O_3 [9]. Powders of B_4C were synthesized via carbothermal reduction of borate citrate precursors doped with ethylene glycol. Addition of ethylene glycol to borate citrate simplified the synthesizability of B_4C at 1350 °C, about 100–300 °C less than the undoped sample. The amount of residual carbon decreased to 4% by the addition of 20% ethylene glycol. The morphology of synthesized B_4C was transformed from polyhedral rod-like particles to needle/blade-like structure with further ethylene glycol additions [30].

An enhanced carbothermal process was developed for synthesis of uniform and fine-grained B_4C particles employing cellulose as the carbon source. To increase the precursors homogeneity in this process, not only immiscible hexane/water solvents were used to get high-dispersed boric acid that boosted the esterification of acid with carbon, but also the sources of carbon and boron oxide were sufficiently ground before carbonization at high temperature. An excellent photoelectrocatalytic hydrogen production activity in water reduction was exhibited by the synthesized B_4C microparticles [31].

Pyrolysis and carbothermal processes were used for synthesis of B_4C by heating a gel precursor prepared through the condensation reaction of polyvinyl alcohol and boric acid with the addition of different glycerine contents. A remarkable drop occurred in the amount of free carbon in the produced B_4C due to the introduction of glycerine via boosting the condensation reaction, which led to the finer B_2O_3 distribution in the carbon matrix. The addition of glycerine had also a great impact on the morphology of the synthesized B_4C particles [32].

Nanocrystalline B_4C was synthesized employing a precursor got ready via the thermal decomposition of a condensed material made by microwave-assisted heating of mannitol and boric acid. The prepared precursor was heat treated for 10–240 min at 1000–1600 °C to optimize the time and temperature of heating to synthesize B_4C with minimal free carbon. The B_4C synthesis was found to happen even at ~1000 °C temperature. In the sample synthesized at 1600 °C, the amount of the free carbon was lower than 0.5 wt% [33].

In addition to B_4C ceramic, several in-situ synthesized composites such as B_4C–SiC, B_4C–ZrB_2, and B_4C–TiB_2 were fabricated using organic–inorganic hybrid precursors through a simple bottom-up method. A sucrose-based precursor and boric acid as well as silicon, zirconium, and titanium powders were selected as the starting materials. In fact, the introduction of Si, Zr, or Ti particles into the precursor solutions led to the synthesis of SiC, ZrB_2, or TiB_2 phases along with the B_4C ceramic. Such an in-situ composite making approach resulted in more uniform size distribution and finer particles [34].

Recently, B_4C ceramics were synthesized in our laboratory using boric acid and saccharide polymers (glucose, sucrose, and cellulose) at 1500 °C after proper mixing and pyrolysis. Glucose was selected as the best source of carbon among the investigated saccharides due to the maximum content of B_4C in the synthesized product with the minimum hydrocarbon impurities [35]. Continuing previous research, in the current work, the effect of glucose pretreatment on the efficiency of B_4C synthesis will be investigated. In addition, because boric acid is considered as the source of boron in the current study, the effect of the amount of this precursor and its excess contents on the synthesizability improvement will be surveyed.

2. Materials and methods

In this study, boric acid was used as the source of boron for the synthesis of B_4C through reaction with glucose as the carbon source, the best saccharide precursor based on our previously published findings [35]. The expected chemical reaction between boric acid and glucose for the synthesis of B_4C is given in Eq. 1:

$$7\,C_6H_{12}O_6 + 24\,H_3BO_3 \rightarrow 6\,B_4C + 78\,H_2O + 36\,CO \qquad (1)$$

In order to increase the probability of B–O–C bond formation in the precursor and enhance the efficiency of B_4C synthesis, in addition to the sample containing liquid glucose without any initial treatment, a sample was prepared by performing a pretreatment on glucose. For this purpose, liquid glucose was stirred for 5 h at 150 °C with a high-speed stirrer. The resulting polymer was a pasty substance with very high viscosity, light brown color, and caramel-like odor.

In addition, in order to find the optimal ratio of polymer/acid (or carbon/boron) for the synthesis of B_4C, different ratios of glucose and boric acid were determined and compared with each other. To do this, first the amount of glucose and boric acid was considered as a stoichiometric ratio according to Eq. 1. Afterwards, to study the effect of the boric acid content on the synthesis efficiency, samples with additional amounts of 10%, 20%, 30%, and 40% boric acid were prepared.

The boric acid with different contents was introduced to glucose materials and mixed at 85 °C for 3 h, and then, the mixtures were put in an oven to achieve dried masses at 150 °C. The masses were crushed and pyrolyzed inside a box furnace at 600 °C for 2 h under argon atmosphere. The pyrolyzed powders were crushed again and several pellets were made with hydraulic cold pressing. Finally, the synthesis process was completed in a tubular furnace at 1500 °C for 4 h with 10 °C/min heating rate under the protection of argon gas.

To study the possible formed bonds, the Fourier transform infrared (FT-IR) spectroscopy was employed. Phase analysis was also carried out employing the X-ray diffractometry (XRD) technique.

3. Results and discussion

3.1. Effect of glucose pretreatment

The results of FT-IR tests of glucose and precursors prepared from untreated glucose and pretreated glucose shown in Fig. 1. Accordingly, the preheated glucose precursor at the wavenumber range of 3200 to 3500 cm^{-1}, which is related to the hydrated n(OH) bonds of water, has almost no strong peak and is significantly reduced compared to the glucose precursor. Such an observation is due to the caramelization reaction in glucose. This process consists of many different stages, one of the most basic of which is its structural water outflow. In addition, an enolization reaction occurs over the caramelization process. During this reaction, the ketone agent, which is attached to a carbonyl group with two other carbon atoms, is converted to enol, which contains a hydroxyl group attached to a double-bonded carbon atom.

Caramelized glucose has specific peaks at the wavenumbers of 922, 896 and 864 cm^{-1} [36], two of which are shown in Fig. 1. Alteration of caramelized glucose peaks compared to glucose indicates the loss of ketone bonds and their conversion to alkenol double bonds. Another point that can be deduced from Fig. 1 is the increase in peak intensity at the wavenumber range of 1430–1450 cm^{-1}, which belongs to the B–O

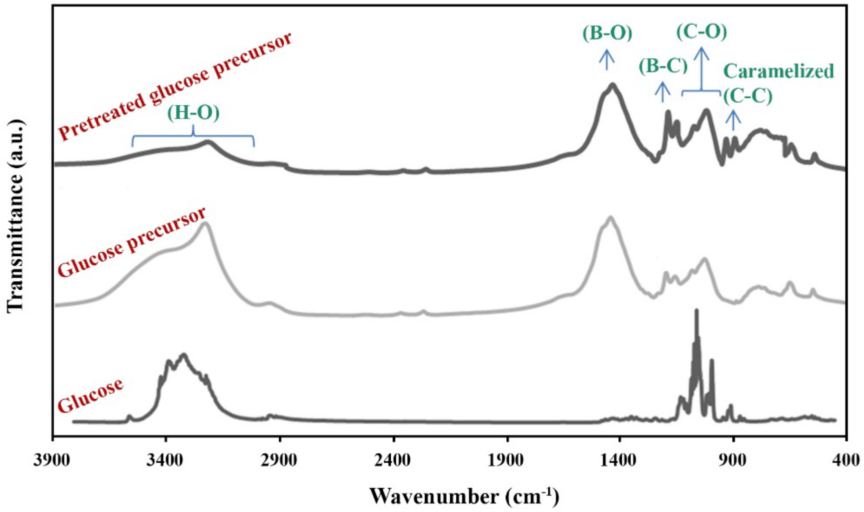

Fig. 1. FT-IR analyses of glucose, glucose precursor and pretreated glucose precursor (Some data have been reused with permission from Ref. [35]).

bond. The peak at the wavenumber of 1190 cm^{-1} has also intensified, which is related to the B–C bond. Such observations indicate the formation of a stronger bond between boron and the polymer. In fact, it can be concluded that pretreatment on glucose increases the susceptibility of the polymer to react with boric acid and form a bond with boron.

To verify this claim, untreated and pretreated glucose precursors were used for synthesis of B_4C ceramic, and the results demonstrated that this claim is true. Fig. 2 shows the XRD patterns of synthesized B_4C powders using both glucose precursors**.** As the phase analysis discloses, B_4C synthesized from caramelized glucose has sharper peaks. Also, unreacted raw materials, which generally contain residual carbon and heavy polymer compounds, are much lower in the caramelized-glucose-induced B_4C. During the caramelization reaction, the structural water of saccharide is removed and thus, the carbon content in this carbon source increases. As the reaction continues, the saccharide begins to decompose, releasing light and reactive aromatic compounds. These substances, which have a characteristic caramel odor, have a relatively good affinity for substitution reactions [36]. Continuation of this reaction leads to further oligomerization of sucrose and formation of long-branched and heavy polymers. This reaction also releases H^{+} and increases the pH of the reaction medium. The caramelization reaction seems to be effective in amplifying glucose to form boron and ultimately synthesizing boron carbide [37–39].

3.2. Effect of boric acid content

In this section, according to the results of the previous section, pretreated and caramelized glucose was used as the source of carbon. Based on Eq. 1, the stoichiometric ratios of the synthesis reaction components (boric acid and polymer) can be determined. In addition to the stoichiometric amount, to investigate the effect of adding excess boric acid as the source of boron, several samples were prepared in which the amounts of boric acid were considered 10, 20, 30, and 40%

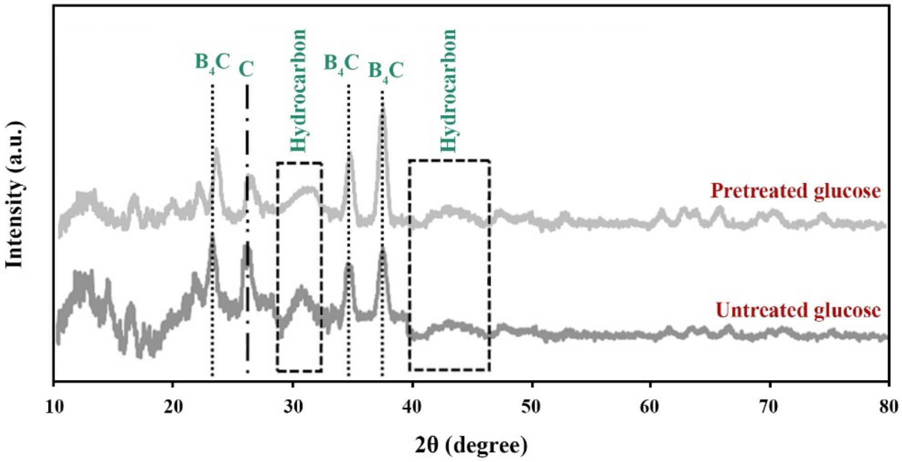

Fig. 2. XRD patterns of B_4C powders synthesized using untreated and pretreated glucose precursors (Some data have been reused with permission from Ref. [35]).

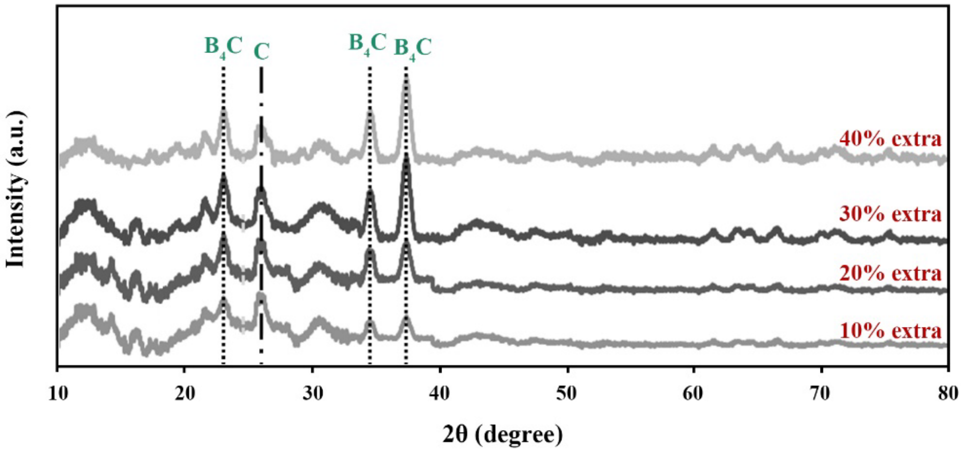

Fig. 3. XRD patterns of B_4C powders synthesized from pretreated glucose and different extra amounts of boric acid.

higher. In fact, the pretreated glucose precursors with different percentages of boric acid were mixed and prepared for the synthesis of B_4C.

The results of XRD analysis of B_4C ceramics synthesized using different amounts of excess boric acid are shown in Fig. 3. It is observed that by increasing the amount of boric acid from 10% to 30%, the synthesized boron carbide has a higher purity, and the amount of carbon impurities decreases. In fact, the weakening in the intensity of carbon and hydrocarbon peaks and the increase in the intensity of B_4C peaks support this hypothesis.

The main peak intensities of B_4C (about 38 °) in the samples with 30% and 40% extra boric acid are high and significant. The intensity of this peak in the sample with 20% excess boric acid has decreased sharply. This decreasing trend can also be seen in the sample containing 10% extra boric acid. Since the melting and boiling temperatures of boron oxide are 450 °C and 1860 °C [40, 41], respectively, part of it may become gaseous during the synthesis process at high temperatures and leave the furnace before it has a chance to react with carbon. On the other hand, due to the nature of the B_4C formation process, boron atoms may not be effectively placed next to carbon atoms in some areas and cannot be able to synthesize boron carbide even if the reaction conditions are met. Therefore, the addition of excess boric acid can compensate for the lack of boron due to evaporation and also by increasing the chance of effective association between carbon and extra boron.

The presence of more acid causes a more effective reaction with the polymer and increases the likelihood of bonding between boron and carbon. This trend is true in all samples under study and with increasing of excess boric acid, product purity and synthesis efficiency has increased. However, it is observed that the intensity of B_4C peaks in the sample containing 30% and 40% of excess boric acid is almost the same. In fact, the results show that the addition of excess boron is somewhat effective and adding more does not have a significant effect on the quality of the synthesized product.

Since B_4C is a solid solution with a relatively wide concentration range and covers a wide range of carbon/boron ratios, and boron carbides with different boron percentages have almost identical characteristic peaks in the X-ray diffraction test, it can be concluded that the addition of more boron changes the composition of B_4C and enriches the carbide with boron. Due to the role of boron concentration on the mechanical properties of B_4C, it has been reported that excessive addition of boron will reduce the mechanical properties of manufactured ceramic [42].

Since boron-rich boron carbides have lower mechanical properties than stoichiometric boron carbide (B_4C), the addition of excessive amounts of extra boric acid does not seem appropriate. According to all the mentioned discussions, the sample with 30% excess boric acid is recommended as the optimal composition for the B_4C synthesis.

4. Conclusions

Despite the widespread use of boron carbide in industry, overcoming the synthesis challenges of this engineering ceramic still requires in-depth research to make the production of this material economical. Therefore, the use of boric acid as a source of boron and polymers such as saccharides as a source of carbon has become important. Among the saccharides, glucose has shown better function than sucrose or cellulose for the synthesis of B_4C. The results of this study showed that the caramelized glucose has better synthesizability, with the aim of producing B_4C, than the untreated one. Meanwhile, the role of boric acid content in the synthesis of B_4C was investigated and the excess amount of 30% than the stoichiometric ratio was obtained as the optimal value.

CRediT authorship contribution statement

Seyed Faridaddin Feiz: Methodology, Writing – original draft.
Leila Nikzad: Conceptualization, Supervision, Resources.
Hudsa Majidian: Project administration, Funding acquisition, Writing – review & editing.
Esmaeil 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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