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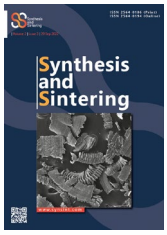
Synthesis and Sintering

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



Research article

Optimum temperature, time and atmosphere of precursor pyrolysis for synthesis of B_4C ceramics

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A B S T R A C T

In this paper, the variables of the pyrolysis operation such as temperature, time, and atmosphere were studied and optimized. At first, the effect of increasing pyrolysis time at lower temperatures was investigated to understand the mutual influence of pyrolysis time and temperature in enhancing the efficiency of B_4C synthesis. Then, three pyrolysis atmospheres were selected to find the optimal conditions: burial method in a box furnace (air), pyrolysis in a tubular furnace (argon), and pyrolysis in a box furnace (air). The pyrolyzed powders were finally located inside the tubular furnace at 1500 °C for 4 h under an argon atmosphere to synthesize B_4C ceramics. X-ray diffractometry (XRD) was employed to determine the optimal processing conditions. The temperature of 600 °C and the holding time of 2 h were selected as the optimal pyrolysis conditions. Meanwhile, the burial method was chosen as the best atmosphere despite having a higher percentage of impurity because of the much lower cost compared to the argon atmosphere.

KEYWORDS

Ceramics
B_4C synthesis
Process optimization
Pyrolysis
Atmosphere

OPEN ACCESS

1. Introduction

After diamond and cubic boron nitride, boron carbide (B_4C) is considered one of the hardest materials on planet earth [1–3]. This interesting property paves the way for the use of this ceramic in various applications, such as abrasives for polishing, blasting nozzles, cutting tools, lapping, and ceramic armor for the protection of civilians [4–7]. Several methods such as carbothermal reduction [8, 9], elemental synthesis [10, 11], chemical vapor deposition [12, 13], and magnesiothermic reduction [10] have been employed to synthesize ultrafine B_4C powders. The use of polymer materials as a source of carbon for the cheap and easy manufacture of B_4C ceramics has attracted the attention of a number of researchers [6, 14, 15].

A low-temperature synthetic route (~400 °C) has been reported for the production of orthorhombic B_4C powders via the reaction of polyvinyl alcohol and boric acid after pyrolysis at 400–800 °C [16]. Powders of B_4C have been synthesized via pyrolysis of polyvinyl borate, prepared by the condensation of boric acid and poly(vinyl alcohol), at 600 °C in the air followed by heat treatment at 1300 °C in an argon atmosphere. Pyrolysis of the polyvinyl borate precursor has led to the formation of submicron B_2O_3 distributed in a carbon matrix [17]. Crystalline B_4C powders have been synthesized by carbothermal reduction of three different carbonaceous sources (glucose, cellulose, and starch) with boric acid. The precursors obtained from cellulose have a fine homogeneous structure composed of carbon fibers and B_2O_3. The synthesis of B_4C using cellulose starts at ~1100 °C, which is 150–250 °C less than those for starch and glucose precursors, and is completed at 1200 °C [18]. Crystalline mesoporous powders of B_4C have been synthesized at 1200 °C by carbothermal reduction of boric acid and cellulose. The pyrolyzed cellulose at 400 °C has been composed of carbon fibers and B_2O_3 particles [19].

Submicron B_4C powders have been synthesized through a rapid heating carbothermal reduction of the mixture of carbon-B_2O_3 achieved from sucrose and boric acid [20]. Powders of B_4C have been synthesized via carbothermal reduction of ethylene glycol doped borate citrate. The addition of ethylene glycol enables the synthesis of B_4C at a

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Received 25 June 2022; Received in revised form 28 September 2022; Accepted 30 September 2022.

https://doi.org/10.53063/synsint.2022.23119

temperature of 1350 °C, which is about 100–300 °C lower compared to the temperatures needed for the additive-free samples. The optimal additive amount is 20 mol%, which reduces the amount of residual carbon to 4% [21]. Rod-like crystalline powders of B_4C with a low amount of free carbon (0.8 wt%) have been synthesized successfully at a low temperature of 600 °C choosing aromatic poly(resorcinol borate) as the polymeric precursor [22]. Crystalline and irregular B_4C powders have been synthesized by heat treatment of industrial-grade reactants, sol-gel derived B_2O_3 particles distributed in the carbon matrix from the polyvinyl borate, at 1400 °C [23]. A modified sol-gel technique, via utilization of nano-sized elemental boron particles for modification of polymeric gel network, has been reported to synthesize morphology-controlled submicron B_4C powders without residual amorphous carbon or boron oxide [15]. Mechanical modification (ball milling) of a sol-gel prepared polymeric reactant, consisting of carbon and B_2O_3, and consequent heat treatment at 1400–1700 °C in an argon atmosphere results in the synthesis of non-agglomerated B_4C powders [24].

Recently, boron carbide has been synthesized in our laboratory after pyrolyzing saccharide polymers (glucose, cellulose, and sucrose) and boric acid as starting materials. The synthesis using glucose as the carbon source has led to the production of the purest B_4C with minimum hydrocarbon impurities [14]. Additionally, it has been observed in our laboratory that heat-treated glucose, caramelized by heating, shows the best synthesis efficiency Also, the studies have disclosed that boric acid with an excess of 30% more than the stoichiometric amount had a better result [25]. In this research article, continuing previous studies, the effects of temperature, time, and atmosphere of pyrolysis for the synthesis of B_4C ceramics were surveyed.

2. Materials and method

Our recent research has shown that among the family of saccharide materials as the carbon source, glucose has the best efficiency in the synthesis of B_4C by reacting with boric acid, which has been selected as a component containing boron [14]. The reaction that has been assumed for this synthesis is as follows:

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

In another paper and in continuation of the above research, we have investigated the effect of pretreatment on glucose as well as the excess percentage of boric acid on the better synthesis of boron carbide [25].

2.1. Determining the optimal temperature and time for pyrolysis

After the complete study of the effective parameters in the preparation of the precursors, which has been previously published in the form of two papers [14, 25], in this research, the variables of the pyrolysis operation were investigated. In order to understand the mutual effect of pyrolysis time and temperature in increasing the reaction efficiency of B_4C synthesis, the influence of increasing pyrolysis time at lower temperatures was investigated. Therefore, three experiments were performed at different temperatures and times, as described in Table 1, as conditions for performing the pyrolysis process.

Table 1. Selected temperatures and times for pyrolysis to conduct experiments.

Parameter	Experiment 1	Experiment 2	Experiment 3
Pyrolysis temperature	400 °C	500 °C	600 °C
Pyrolysis time	6 h	4 h	2 h

2.2. Determining the optimal pyrolysis atmosphere

To find the optimal atmosphere for the pyrolysis process, the precursors were first prepared. In the next step, three types of atmospheres were used for the pyrolysis of the precursors.

- Burial method in a box furnace with air atmosphere.
- Pyrolysis in a tubular furnace with an argon atmosphere.
- Pyrolysis in a box furnace with an air atmosphere.

In the powder burial method, the precursor was poured into a small alumina crucible and filled with pressed alumina powder. Then, the primary crucible was placed in another large crucible and its surroundings were filled with a mixture of graphite and alumina powders and it was completely covered with silicon powder. In the last stage, to reduce the concentration of oxygen in the space of the box furnace and prevent oxygen from penetrating and reaching the powder, the entire large crucible was filled with graphite and activated carbon powders. The schematic view of the placement of materials and precursors in this method is shown in Fig. 1.

In the second set, the powder precursor was placed in an alumina crucible inside the tubular furnace. To control the atmosphere and prevent oxygen entrance, the interior of the furnace was filled with a gentle flow of argon during the pyrolysis process. In the third set, the precursor was poured into the alumina crucible and placed directly in a box furnace. In this case, the pyrolysis process was carried out in the furnace without a protective atmosphere (in the vicinity of air).

After performing the above-mentioned steps, the pyrolyzed powders were synthesized in a tubular furnace with a heating rate of 10 °C/min up to the final temperature of 1500 °C under the argon protection for 4 h, and the obtained boron carbide was compared with each other. X-ray diffractometry (XRD) analysis was used for this purpose.

3. Results and discussion

3.1. Interaction of temperature and time in pyrolysis

In investigating the effect of pyrolysis parameters on the efficiency and final product of the boron carbide synthesis reaction, a lot of research

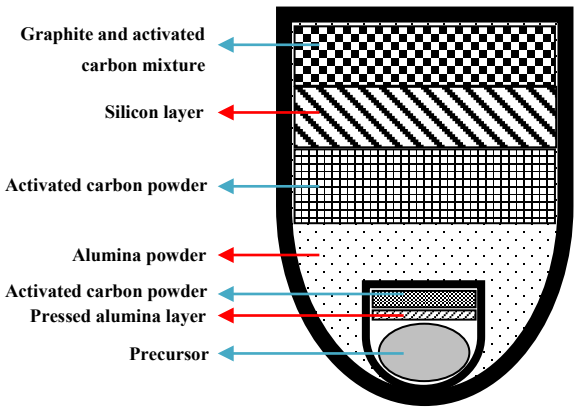

Fig. 1. Schematic of pyrolysis by powder burial method.

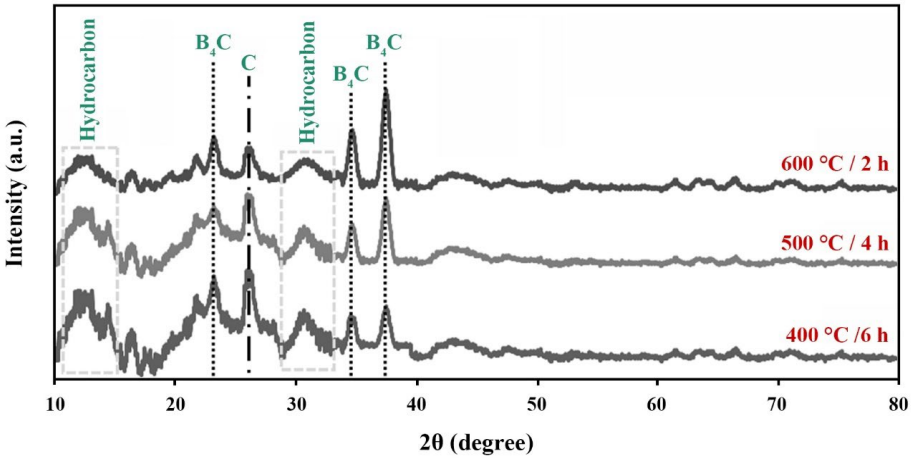

Fig. 2. XRD results of the synthesized B_4C ceramics after pyrolysis at different temperatures/times.

works have been done on various polymers. Since the temperature and time required for the pyrolysis process are almost the same in most of the published literature, the detailed investigation of these parameters was omitted and the interaction between time and temperature was studied instead. As regards the temperature of pyrolysis has been reported in different sources to be around 500–600 °C [26–29], the base temperature in this research was chosen to be 600 °C. Also, to check the possibility of performing pyrolysis at a lower temperature, two experiments with lower temperatures but longer times were also performed, as presented in Table 1.

X-ray diffraction analyses of the synthesized B_4C ceramics after pyrolysis at different temperatures and times are shown in Fig. 2 to be a comparison to investigate the interactive effect of time and temperature on the pyrolysis process. The obtained results show that lowering the pyrolysis temperature has a relatively direct and significant effect on the purity of the final boron carbide and has greatly affected the impurity content. The peaks in the angle of 26 ° are related to graphite and the roughness in the ranges of 10–20 ° and 30–35 ° is clear evidence of the presence of heavy hydrocarbon materials and carbon residues. Due to the fact that these peaks have become more and more intense in pyrolyzed samples at a lower temperature, it can be concluded that the decrease in temperature has a great impact on the level of impurities in the final product. It can also be noted that increasing the duration of the pyrolysis operation did not have much effect on the efficiency. In fact, lowering the pyrolysis temperature cannot be compensated by a longer holding time.

The reason for the mentioned phenomenon can be found in the nature of reactions and events that took place at this stage. In the pyrolysis stage, the polymer is subjected to a thermal decomposition reaction, during which the chain structure of the polymer is broken and while its interstructural water is released, it is decomposed into simple carbon compounds. In addition, boric acid, which has structural water, is converted into boron oxide during this reaction. Since both of these reactions are of the decomposition type and require almost certain activation energy to start the reaction, therefore the materials start to decompose at a certain temperature and do not get the necessary energy for decomposition at lower temperatures [27]. Since lengthening the heating time has no effect on the amount of energy applied to the

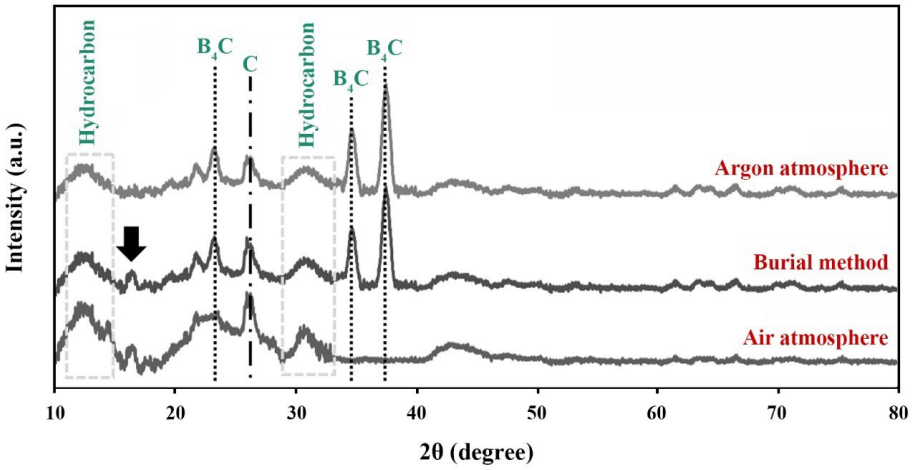

Fig. 3. XRD results of the synthesized B_4C ceramics after pyrolysis under different processing atmospheres.

material, the influence of temperature is greater than that of time. Accordingly, the temperature of 600 °C and the time of 2 h were selected as the optimal pyrolysis conditions.

3.2. Effect of processing atmosphere on the pyrolysis

In this section, the pyrolyzed precursors in three different atmospheres were subjected to XRD analysis after the final synthesis process. The results of the analysis (Fig. 3) show the fact that in the pyrolysis method in the air atmosphere; the final product does not have boron carbide peaks. Also, pyrolysis in an argon atmosphere has caused the final product to have the lowest relative amount of residual materials and unreacted carbon in the synthesized ceramic, and in other words, a purer boron carbide has been obtained. Using the method of burying the precursor in alumina is very useful and effective, and unlike the sample pyrolyzed in air, it has been able to produce boron carbide in the synthesis stage. However, it seems that this method has more carbon impurity and lower synthesis efficiency than the pyrolysis method in an argon atmosphere.

By paying close attention to the peaks corresponding to the angle of ~16 °, it can be seen that the impurity in the sample pyrolyzed by burial method, which is indicated by the arrow symbol in Fig. 3, has been removed in the sample pyrolyzed in the argon atmosphere. Also, the shortening of the carbon peak at an angle of 26 ° in the sample processed under an argon atmosphere compared to the burial method sample is another proof of this claim.

The possible reaction in the pyrolysis process is mainly the breaking of the polymer chains and the transformation of the polymer into simpler and smaller compounds, as well as the exit of interstructural water from the polymers. In addition to these reactions, the thermal decomposition of boric acid and its transformation into boron oxide is also a possible reaction in this process. Considering the nature of the mentioned reactions and the fact that they do not need oxygen to be carried out, and also considering the fact that hydrocarbon substances at high temperatures, if exposed to oxygen, have a relatively high tendency to burn and combine with oxygen, it can be concluded that the most suitable conditions for the pyrolysis process are oxygen-free conditions. This is clearly visible in the pyrolyzed sample in an argon environment. In this situation, the synthesized boron carbide has the highest purity and the best efficiency. On the other hand, performing the pyrolysis reaction in the air causes the polymers to combine with the oxygen in the furnace space and leave the environment before they have the opportunity to decompose and form lighter and smaller compounds. This causes the release of the carbon source needed for the synthesis of boron carbide from the environment. During this reaction, the hydrocarbons that underwent minor changes during the precursor preparation process and turned into semi-heavy polymers that are prone to react with boron, react with oxygen, and leave the environment, and instead, heavy polymers that react with boron have less to remain in the environment. This has caused the pyrolyzed precursor to not contain boron carbide in the air atmosphere after the synthesis process. The drastic decrease in the amount of precursor in this case in the pyrolysis reaction is also evidence of the burning of a significant percentage of the polymer during this process.

The outcome that pyrolysis in the argon atmosphere gives the best results in the synthesis of boron carbide and improves the reaction efficiency was somewhat predictable. However, heavy costs in providing a suitable atmosphere and continuous injection of argon during pyrolysis reaction are a big problem in achieving boron carbide with high purity and reasonable and competitive price. Also, the supply of argon in high volume for the mass production of boron carbide is also a problem that cannot be ignored. Therefore, a new method for performing pyrolysis operation was proposed, which can be done with a lower cost and a more accessible method of pyrolysis reaction in the absence of oxygen. For this purpose, the burial method was suggested that prevent the polymer from burning at high temperatures by creating a physical barrier against oxygen. Covering the surface of the crucible with fine-grained silicon powder prevents oxygen from entering the crucible containing the precursor powder, and the graphite and carbon placed in different layers of the larger crucible react with possible oxygen and prevent oxygen from reaching the precursor. The result obtained from the synthesis of the pyrolyzed precursor material from this methodology shows that this technique has largely prevented oxygen from entering the pyrolysis environment and the final product is largely similar to the pyrolyzed product in the argon environment.

Therefore, as a summary, the burial method in the air atmosphere was selected as the optimal process despite having a higher percentage of impurity. The reason for this choice can be considered the much lower cost of this method compared to the argon atmosphere technique, as well as the reasonable percentage of impurity. On the other hand, the treatments that can be used to reduce the percentage of carbon are far less expensive than the method of using argon, which will be investigated in the future research works of this group.

4. Conclusions

Several variables of the pyrolysis process were investigated and optimized in this research work. Not only the mutual effect of pyrolysis time and the temperature was scrutinized to enhance the B_4C synthesis efficiency, but also three various pyrolysis atmospheres (burial method in box furnace in air, pyrolysis in tubular furnace in argon, and pyrolysis in box furnace in air) were studied. Synthesis of B_4C ceramics was completed inside an argon-protected tubular furnace at 1500 °C for 4 h using the as-pyrolyzed powders. Determination of the optimal processing conditions was carried out using X-ray diffractometry results as the criterion. Finally, by reviewing and analyzing the results, the optimal conditions of the pyrolysis process were chosen as follows: the temperature of 600 °C, the holding time of 2 h, and the atmosphere provided by the burial method based on economic considerations despite the presence of more impurities.

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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