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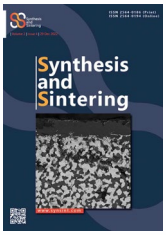

Research article

Synthesizability improvement of B_4C ceramics by optimizing the process temperature and atmosphere

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A B S T R A C T

In this research, the effects of synthesis temperature, holding time, and furnace atmosphere on the synthesizability of B_4C ceramics using glucose and boric acid as the starting materials were scrutinized. Three temperatures of 1300, 1400, and 1500 °C were selected as synthesis temperatures. The synthesis process was carried out in a tubular furnace for 4 h in Ar atmosphere. To scrutinize the interactive effect of synthesis temperature and holding time, three samples were synthesized at 1500, 1400, and 1300 °C for 4, 8, and 12 h, respectively. Moreover, two types of controlled atmospheres, traditional Ar and an innovative CO/CO_2 setup, were considered to optimize the synthesis process. X-ray diffraction (XRD) patterns were employed to determine the optimum synthesis temperature and atmosphere based on the detection of B_4C peaks as the desired product and undesirable hydrocarbon and carbon byproducts. The results showed that B_4C synthesized at 1500 °C for 4 h in Ar atmosphere contained the least byproduct impurities, so this temperature was chosen as the optimal choice. However, the sample fabricated at 1400 °C for 8 h is a good choice in cases where lower manufacturing temperatures are desired. The efficiency of the innovative setup was similar to the traditional one; therefore, considering the economic aspects, the CO/CO_2 atmosphere was chosen as an acceptable option for B_4C synthesis.

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KEYWORDS

Boron carbide
Synthesis
Optimization
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XRD analysis

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1. Introduction

Boron carbide is one of the most substantial non-oxide ceramics with noteworthy properties such as high hardness, low specific weight, high Young's modulus, high melting point, and excellent chemical stability [1–3]. Having such excellent features has caused this material to be used in various industries like abrasive and cutting tools [4–6]. In addition, due to its considerable boron content, B_4C is employed as neutron-absorbing material [7–10].

Several methods can be used for the synthesis of B_4C ceramics such as the solid-state elemental reaction of carbon and boron [11, 12], magnesiothermic reduction [13, 14], laser irradiation of boron in organic solvents [15], co-reduction in the autoclave [16], sol-gel [17], self-propagating high-temperature synthesis [18], microwave synthesis [19], and carbothermal reduction [20–22]. Reducing the temperature of the synthesis process, especially in heat-based methods, has always been one of the topics of interest to researchers in order to overcome the technological limitations caused by high temperatures and economic considerations caused by more energy consumption. Therefore, efforts have been made to lower and optimize the synthesis temperature.

Gubernat et al. [23] used a simple approach to produce B_4C powder by direct synthesis from expanded graphite and amorphous fine boron with a boron to carbon mass ratio of 10:1. A fine-grained B_4C powder with a crystallite size of 20–40 nm was obtained at 1550–1650 °C for holding time of 2 h under Ar protection. In fact, the B_4C synthesis reaction proceeds through the transportation of C towards B via the CO gas phase.

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The influence of the B_2O_3/carbon precursor arrangement on the low-temperature synthesis of B_4C was studied by Kakiage et al. [24]. Low-temperature heat treatment and air pyrolysis of polyvinyl alcohol and boric acid were used for the preparation of the condensed precursor. Crystalline B_4C powders with minimal free carbon were achieved at 1100 °C for 20 h under Ar protection using a homogeneously arranged nanometer-scale B_2O_3/carbon structure. Rafi-ud-din et al. [25] synthesized B_4C powder through carbothermal reduction of borate citrate with the addition of ethylene glycol. Such an additive reduced the required synthesis temperature to 1350 °C, which is about 100–300 °C less than the temperature needed for the additive-free sample. They also found that the use of 20% additive decreases the amount of residual carbon by about 4%.

Carbothermal reduction of a mixture of glycerin and boric acid resulted in the synthesis of crystalline B_4C powders with no residual carbon at 1250 °C for 5 h under Ar protection. The initial mixture was condensed via dehydration of equimolar glycerin and boric acid followed by air pyrolysis to get a precursor without excess carbon [26]. Wang and coauthors [27] explored a low-temperature technique for the synthesis of rod-like B_4C crystals with negligible undesirable carbon using the aromatic poly(resorcinol borate) precursor with a high char yield. Due to the extensive contact between carbon and B_2O_3, a relatively low temperature of 600 °C was sufficient for the successful synthesis of B_4C.

Among the group of saccharides, a research recently conducted by our group showed that glucose as the carbon source has the best performance in B_4C synthesis, via reacting with boric acid as the boron source [28]. In continuation of that research, the roles of glucose pretreating and the extra boric acid addition on the synthesizability of B_4C were also investigated [29]. Meanwhile, the pyrolysis variables such as time, temperature, and atmosphere were also scrutinized and optimized [30]. According to the experiences gained in the above research works as well as the obtained information and data, in this research, the optimization of the variables of the synthesis process such as the temperature, the time, and the atmosphere was put on the agenda.

2. Materials and methods

2.1. Determining the optimal synthesis temperature

In order to increase the efficiency of the synthesis process, changeable parameters were investigated. For this purpose, the raw material was prepared under optimal conditions, and pyrolysis was also performed on the powders in optimum conditions. The details were reported elsewhere [28–30]. Then, to investigate the effect of temperature on the efficiency of the synthesis process, the prepared powders were synthesized at three different temperatures of 1300, 1400, and 1500 °C for 4 h under Ar protection. XRD analysis was used to determine the optimal synthesis temperature.

2.2. Investigating the interaction of time and temperature

In order to understand the mutual effect of processing time and temperature in reducing the residual carbon content and increasing the synthesis reaction efficiency, the influence of decreasing the synthesis temperature on the reaction efficiency in exchange for prolonging the processing time was investigated. For this purpose, the conditions mentioned in Table 1 were considered. Finally, XRD analysis was used to compare the results.

Table 1. Process variables for investigation of the interaction of time and temperature.

Parameter	Experiment 1	Experiment 2	Experiment 3
Synthesis temperature	1300 °C	1400 °C	1500 °C
Synthesis time	12 h	8 h	4 h

2.3. Determining the optimal synthesis atmosphere

In order to get the optimal synthesis conditions, two types of atmospheres were considered for the synthesis furnace. For this purpose, the precursor was prepared in optimal conditions and then pyrolyzed. The processed powders under the following conditions were compared:

1. Synthesis of powders in the form of tablets in a tubular furnace with Ar atmosphere,
2. Synthesis of powders in the form of tablets under CO and CO_2 controlled atmospheres.

An alumina cylinder was used to provide the controlled atmospheric conditions of CO and CO_2. For this, the alumina cylinder with a diameter of 5 cm and a length of 25 cm was completely blocked on one side with the help of a round alumina lid and cement glue, and both ends of the cylinder were filled with active carbon powder tablets. Then, a tablet prepared from the pyrolyzed materials was placed in the middle of the cylinder on a flat alumina substrate, and finally, the beginning of the cylinder was closed and secured with the help of another round alumina lid. It should be noted that the second lid is never blocked with cement glue because during the synthesis process due to the formation of CO and CO_2 gases inside the cylinder, there is a possibility of excessive accumulation of gas and explosion of the cylinder inside the furnace. The schematic image of this setup is shown in Fig. 1.

The prepared cylinder was placed in the tubular furnace. The furnace was closed on one side with a compressed glass wool insulating cap, and from the other side, it was connected to a water container through a narrow hose to maintain the pressure inside the tubular furnace and to prevent the pressure from increasing too much inside the furnace. It should be noted that during the entire synthesis process, a very small amount of Ar gas was passed through the tube several times to remove possible oxygen from the environment. Similarly, the XRD technique was employed to analyze the outcomes.

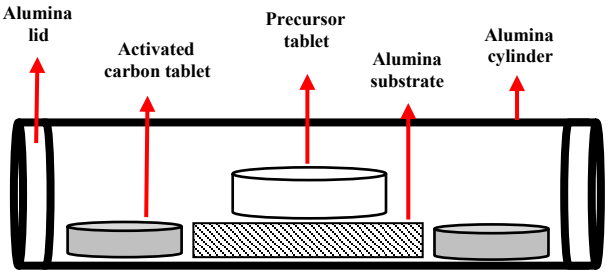

Fig. 1. Schematic of CO and CO_2 controlled atmosphere system.

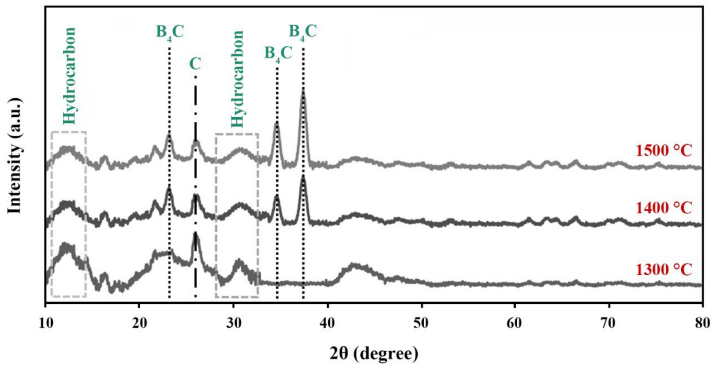

Fig. 2. The results of XRD analysis related to the effect of synthesis temperature.

3. Results and discussion

3.1. Influence of synthesis temperature

Since the main approach in carbide synthesis processes is carbothermal reactions, temperature plays a very critical and vital role in this regard. Synthesis of B_4C also depends on temperature due to having the highest activation energy among carbides. For this purpose, different temperatures were selected to investigate this effect, and experiments were carried out in Ar atmosphere for 4 h.

The results of XRD analysis, which can be seen in Fig. 2, show that the synthesis at higher temperatures leads to greater efficiency and higher purity. Additionally, performing synthesis at low temperatures can hardly cause boron carbide synthesis, and no trace of B_4C peaks can be observed in the diffraction pattern.

By examining the reactions that take place in the synthesis process and their mechanism, it is concluded that the main factor in the formation of B_4C is the diffusion mechanism. Therefore, according to the diffusion equations, it can be claimed that the effect of temperature is very considerable in the reaction progress. It has been reported that the rate of reaction at temperatures lower than 1377 °C is significantly low [31]. Therefore, almost no B_4C was observed in the sample synthesized at 1300 °C for 4 h. This observation shows that in the case where B_2O_3 is present in liquid form in the environment, the reaction speed is low, and this amount of time was not enough for effective diffusion reaction and B_4C formation. With the increase in temperature, B_4C peaks in the final product increased and carbon and polymer peaks decreased in the same proportion. Increasing the synthesis temperature causes B_2O_3 to gradually turn into vapor in the reaction medium. Since diffusion-based reactions have much higher rates and efficiency in the gas-solid system than those in the liquid-solid system, it seems logical to enhance the reaction efficiency with increasing temperature. The results verify that the synthesized product at 1500 °C has the lowest amount of carbon impurities and is more efficient. Therefore, this temperature was selected as the optimal synthesis temperature.

3.2. Interaction of time and temperature

From the thermodynamic and kinetic points of view, increasing temperature raises the rate and efficiency of chemical reactions, especially endothermic ones. Therefore, the fact that increasing the synthesis temperature will boost its efficiency is a proven and confirmed issue. From an economic viewpoint, enhancing production efficiency depends on reducing the cost and required energy. Therefore, it is very important to investigate solutions to reduce the temperature required for the synthesis of a material such as B_4C.

It seems that one of the tricks to reduce the synthesis temperature is to increase the holding time in the synthesis environment. Therefore, the effect of increasing time on reducing the required synthesis temperature was investigated. Three identical samples of the precursor were pyrolyzed and then subjected to synthesis under different temperatures and times as presented in Table 1. According to the XRD results shown in Fig. 3, as previously announced, the first sample synthesized at 1500 °C for 4 h has sharp characteristic peaks of B_4C. The amounts of impurities, mainly caused by carbon residues and decomposed polymers, are low.

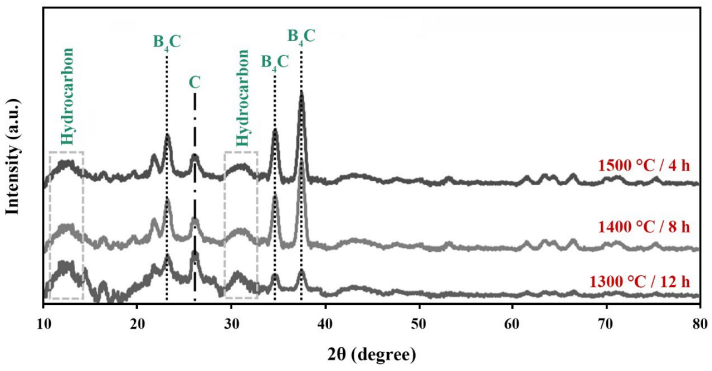

Fig. 3. The results of XRD analysis related to the interactive effect of temperature and time.

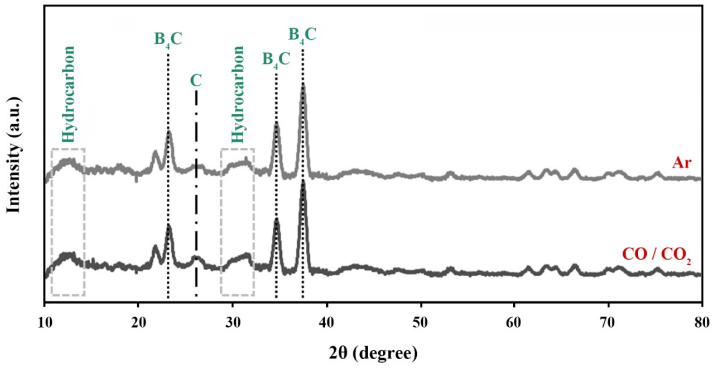

Fig. 4. The results of XRD analysis related to the effect of synthesis atmosphere.

In the second sample, which was synthesized at a lower temperature (1400 °C) and a longer time (8 hours), the characteristic peaks of B_4C have not dropped much. In addition, the amount and intensity of impurity peaks have not significantly changed compared to the sample synthesized at 1500 °C for 4 hours. In fact, it can be stated that the durability for 8 h has been able to compensate for the decrease in temperature to some extent and the synthesis efficiency has not decreased much.

In the third sample which was synthesized at 1300 °C, despite the relatively long holding time of 12 hours, the amounts of characteristic peaks of impurities have increased remarkably; hence, it seems that the quality of the final B_4C product has decreased.

According to the results obtained from this section, it can be concluded that although the temperature of 1500 °C is an appropriate temperature for B_4C synthesis, the temperature of 1400 °C can be a useful choice in cases where lower manufacturing temperatures are considered.

3.3. Influence of synthesis atmosphere

The synthesis reaction is actually the main stage of the B_4C preparation process and plays the most important role in the quality and purity of the final product. Since this reaction takes place at a relatively high temperature, the atmosphere of such reaction plays an influential role in the progress and fate of the final product. In this part of the research, two different atmospheres were evaluated for the synthesis reaction. Since the air atmosphere was used in the pyrolysis process in the previous research of our group and it did not yield acceptable results [30], and also considering the fact that the synthesis reaction temperature is much higher than the pyrolysis temperature, the air atmosphere was removed from the options to be considered. Instead, in order to reduce the amount of Ar required for the synthesis process and to control the reaction atmosphere as much as possible, an innovative method was used.

Activated carbon powder tablets inside the alumina cylinder at high temperatures (Fig. 1) have a high tendency to react with oxygen, so they quickly consume all the oxygen in the cylinder and make the environment free of oxygen. On the other hand, with the burning of carbon, the concentration of CO and CO_2 in the environment of the cylinder increases sharply. This event makes carbon in the gaseous form more and accessible to boron atoms, and even at lower temperatures, the diffusion phenomenon takes place through the gas-gas or gas-liquid systems [32]. This may increase the reaction rate and synthesis efficiency at lower temperatures. In fact, creating an atmosphere containing carbon monoxide and dioxide around raw materials increases the amount of carbon available for boron without increasing the carbon/boron ratio, which increases the probability of boron/carbon atoms coming together and promotes the B_4C formation reaction.

The XRD analysis results shown in Fig. 4 disclose that by creating an atmosphere containing carbon oxides, B_4C peaks can be detected, but impurity peaks are almost negligible. In fact, the quality of the final product does not decrease by reducing the amount of Ar consumed in the synthesis process, which verifies the efficiency and proper performance of the designed innovative setup. This trick, in addition to saving about 85% in Ar consumption, has not caused any noticeable change in the quality of the product. Finally, considering the economic aspects of greater productivity, the innovative atmosphere of CO and CO_2 was determined as the optimal atmosphere for the synthesis of B_4C.

4. Conclusions

The synthesizability of B_4C ceramics was improved by optimizing the synthesis temperature, holding time, and furnace atmosphere. The sample obtained at 1500 °C was the best among the samples synthesized at 1300–1500 °C for 4 h in Ar atmosphere due to the least byproduct impurity. Decreasing the synthesis temperature to 1400 °C in exchange for prolonging the holding time up to 8 h did not have much effect on the reaction efficiency. Therefore, synthesis at 1400 °C for 8 h can be a good option in cases where a lower manufacturing temperature is needed. Meanwhile, the performance of the innovative CO/CO_2 atmosphere was comparable to the traditional synthesis under Ar protection, which seems to be attractive for B_4C synthesis from an economic point of view.

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.

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References

[1] W. Zhang, A novel ceramic with low friction and wear toward tribological applications: Boron carbide-silicon carbide, Adv. Colloid Interface Sci. 301 (2022) 102604. https://doi.org/10.1016/j.cis.2022.102604.

[2] H. Biçer, M. Tuncer, Conventional and two-step sintering of boron carbide ceramics with a sintering additive, J. Aust. Ceram. Soc. 58 (2022) 21–27. https://doi.org/10.1007/s41779-021-00661-7.

[3] M. Jansen, High Performance Non-Oxide Ceramics I, Springer, Berlin, Heidelberg. (2002).

[4] C. Liu, Z. Zhang, G. Yang, A. Zhou, G. Wang, et al., Finite element analysis and wear mechanism of B4C–TiB2 ceramic tools in turning AISI 4340 workpieces, Ceram. Int. 48 (2022) 5459–5467. https://doi.org/10.1016/j.ceramint.2021.11.090.

[5] A. Arumugam, P. Lakshmanan, S. Palani, Micro groove cutting on the surfaces of Cu-B4C nanocomposites by fiber laser, Surf. Topogr. Metrol. Prop. 9 (2021) 035023. https://doi.org/10.1088/2051-672X/ac1c7f.

[6] M. Pul, S. Yağmur, Examination of the effect of B4C and GNP reinforcements on machinability in the machining of Al 6061 matrix B4C/GNP reinforced hybrid composites, J. Braz. Soc. Mech. Sci. Eng. 44 (2022) 469. https://doi.org/10.1007/s40430-022-03776-5.

[7] S. V. Klinkov, V.F. Kosarev, V.S. Shikalov, T.M. Vidyuk, Optimization of cold spraying of neutron-absorbing (Al+B4C) composite coatings, J. Appl. Mech. Tech. Phys. 63 (2022) 279–288. https://doi.org/10.1134/S0021894422020110.

[8] A.S. Larionov, L.V. Chekushina, E.E. Suslov, Development and investigation of high-strength neutron-absorbing composite coatings based on borides of metals, Mater. Sci. Forum. 945 (2019) 660–664. https://doi.org/10.4028/www.scientific.net/MSF.945.660.

[9] C. Li, X. Xia, J. Cai, Z. Zhang, J. Wang, et al., Influence analysis of B4C content on the neutron shielding performance of B4C/Al, Radiat. Phys. Chem. 204 (2023) 110684. https://doi.org/10.1016/j.radphyschem.2022.110684.

[10] Y. Jung, Y. Lee, J.H. Kim, S. Ahn, Accelerated corrosion tests of Al-B4C neutron absorber used in spent nuclear fuel pool, J. Nucl. Mater. 552 (2021) 153011. https://doi.org/10.1016/j.jnucmat.2021.153011.

[11] A. Chakraborti, N. Guignot, N. Vast, Y. Le Godec, Synthesis of boron carbide from its elements up to 13 GPa, J. Phys. Chem. Solids. 159 (2021) 110253. https://doi.org/10.1016/j.jpcs.2021.110253.

[12] A. Chakraborti, N. Vast, Y. Le Godec, Synthesis of boron carbide from its elements at high pressures and high temperatures, Solid State Sci. 104 (2020) 106265. https://doi.org/10.1016/j.solidstatesciences.2020.106265.

[13] M.K. Zakaryan, A.R. Zurnachyan, N.H. Amirkhanyan, H.V. Kirakosyan, M. Antonov, et al., Novel pathway for the combustion synthesis and consolidation of boron carbide, Materials (Basel). 15 (2022) 5042. https://doi.org/10.3390/ma15145042.

[14] P. Asgarian, A. Nourbakhsh, P. Amin, R. Ebrahimi-Kahrizsangi, K.J.D. MacKenzie, The effect of different sources of porous carbon on the synthesis of nanostructured boron carbide by magnesiothermic reduction, Ceram. Int. 40 (2014) 16399–16408. https://doi.org/10.1016/j.ceramint.2014.07.147.

[15] Y. Ishikawa, Q. Feng, N. Koshizaki, Growth fusion of submicron spherical boron carbide particles by repetitive pulsed laser irradiation in liquid media, Appl. Phys. A. 99 (2010) 797–803. https://doi.org/10.1007/s00339-010-5745-6.

[16] L. Shi, Y. Gu, L. Chen, Y. Qian, Z. Yang, J. Ma, A low temperature synthesis of crystalline B4C ultrafine powders, Solid State Commun. 128 (2003) 5–7. https://doi.org/10.1016/S0038-1098(03)00627-6.

[17] A. Najafi, F. Golestani-Fard, H.R. Rezaie, Sol-gel synthesis and characterization of B4C nanopowder, Ceram. Int. 44 (2018) 21386–21394. https://doi.org/10.1016/j.ceramint.2018.08.196.

[18] I.D. Kovalev, V.I. Ponomarev, S.V. Konovalikhin, D.Y. Kovalev, V.I. Vershinnikov, SHS of boron carbide: Influence of combustion temperature, Int. J. Self-Propagating High-Temp. Synth. 24 (2015) 33–37. https://doi.org/10.3103/S1061386215010045.

[19] D. Davtyan, R. Mnatsakanyan, L. Liu, S. Aydinyan, I. Hussainova, Microwave synthesis of B4C nanopowder for subsequent spark plasma sintering, J. Mater. Res. Technol. 8 (2019) 5823–5832. https://doi.org/10.1016/j.jmrt.2019.09.052.

[20] C.-H. Jung, M.-J. Lee, C.-J. Kim, Preparation of carbon-free B4C powder from B2O3 oxide by carbothermal reduction process, Mater. Lett. 58 (2004) 609–614. https://doi.org/https://doi.org/10.1016/S0167-577X(03)00579-2.

[21] A. Sudoh, H. Konno, H. Habazaki, H. Kiyono, Synthesis of boron carbide microcrystals from saccharides and boric acid, TANSO. 2007 (2007) 8–12. https://doi.org/10.7209/tanso.2007.8.

[22] I. Yanase, R. Ogawara, H. Kobayashi, Synthesis of boron carbide powder from polyvinyl borate precursor, Mater. Lett. 63 (2009) 91–93. https://doi.org/10.1016/j.matlet.2008.09.012.

[23] A. Gubernat, W. Pichór, D. Zientara, M.M. Bućko, Ł. Zych, D. Kozień, Direct synthesis of fine boron carbide powders using expanded graphite, Ceram. Int. 45 (2019) 22104–22109. https://doi.org/10.1016/j.ceramint.2019.07.227.

[24] M. Kakiage, N. Tahara, S. Yanagidani, I. Yanase, H. Kobayashi, Effect of boron oxide/carbon arrangement of precursor derived from condensed polymer-boric acid product on low-temperature synthesis of boron carbide powder, J. Ceram. Soc. Jpn. 119 (2011) 422–425. https://doi.org/10.2109/jcersj2.119.422.

[25] Rafi-ud-din, G.H. Zahid, Z. Asghar, M. Maqbool, E. Ahmad, et al., Ethylene glycol assisted low-temperature synthesis of boron carbide powder from borate citrate precursors, J. Asian Ceram. Soc. 2 (2014) 268–274. https://doi.org/10.1016/j.jascer.2014.05.011.

[26] M. Kakiage, N. Tahara, I. Yanase, H. Kobayashi, Low-temperature synthesis of boron carbide powder from condensed boric acid–glycerin product, Mater. Lett. 65 (2011) 1839–1841. https://doi.org/10.1016/j.matlet.2011.03.046.

[27] S. Wang, Y. Li, X. Xing, X. Jing, Low-temperature synthesis of high-purity boron carbide via an aromatic polymer precursor, J. Mater. Res. 33 (2018) 1659–1670. https://doi.org/10.1557/jmr.2018.97.

[28] S.F. Feiz, L. Nikzad, H. Majidian, E. Salahi, Performance of glucose, sucrose and cellulose as carbonaceous precursors for the synthesis of B4C powders, Synth. Sinter. 2 (2022) 26–30. https://doi.org/10.53063/synsint.2022.21108.

[29] S.F. Feiz, L. Nikzad, H. Majidian, E. Salahi, Effects of glucose pretreatment and boric acid content on the synthesizability of B4C ceramics, Synth. Sinter. 2 (2022) 78–83. https://doi.org/10.53063/synsint.2022.22115.

[30] S.F. Feiz, L. Nikzad, H. Majidian, E. Salahi, Optimum temperature, time and atmosphere of precursor pyrolysis for synthesis of B4C ceramics, Synth. Sinter. 2 (2022) 146–150. https://doi.org/10.53063/synsint.2022.23119.

[31] A.W. Weimer, Carbide, nitride and boride materials synthesis and processing, Springer Science & Business Media. (2012). https://doi.org/10.1007/978-94-009-0071-4.

[32] J.A. Puszynski, Thermochemistry and kinetics, carbide, nitride and boride materials synthesis and processing, Springer Netherlands, Dordrecht. (1997) 183–228. https://doi.org/10.1007/978-94-009-0071-4_9.