Research article

Comparison of residual carbon content and morphology of B₄C powders synthesized under different conditions

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ABSTRACT

In this article, the impact of different B₄C synthesis methods on the amount of residual carbon and the final morphology of the prepared ceramic particles was investigated. The main materials for the synthesis of B₄C were glucose and boric acid, and the effects of adding tartaric acid and performing mechanical activation were studied. For this purpose, two methods of carbon dissolution and boron carbide oxidation were used to determine the amount of residual carbon in the ceramic products. The results of the investigations on the sample synthesized in optimal conditions showed that if additives and mechanical activation are not used, about 7 wt% of carbon will remain in the synthesized powder. The amount of carbon decreased to 5.7 wt% with mechanical activation, but the best result was obtained with the addition of tartaric acid, in which the amount of impurity dropped to 3.3 wt%. Finally, the size and morphology of B₄C particles and carbon impurities were observed and compared using a scanning electron microscope.

1. Introduction

Boron carbide (B₄C) is a member of non-oxide refractory ceramics that is of prodigious interest for numerous industrial applications [1–4]. This ceramic possesses a mixture of characteristics including high neutron absorption, high melting temperature, outstanding chemical stability, high hardness, high elastic modulus, and excellent resistance against wear [5–8]. Because of these unique and interesting features, B₄C is used in nuclear reactors, ballistic armors, abrasive materials, semiconductors, etc. [9–12].

There are various methods for the synthesis of boron carbide, but the production of this material at low temperatures is preferred [13–15]. In addition, the use of polymer precursors has received special attention from researchers in recent years due to their special advantages [16–18]. However, one of the biggest limitations of this approach is the residual amount of carbon left in the final powder produced by the synthesis with polymeric raw materials [18–20].

Krishnarao and Subrahmanyam [21] synthesized B₄C ceramic via carbothermal reduction of B₂O₃ with boric oxide and carbon black. That reaction was performed at 1300–1625 °C for 0.5 h under argon protection. The residual carbon was formed in the B:C mixture with a molar ratio of 4:2.66, but no residual carbon was seen using a molar ratio of 4:2. Crystalline B₄C material with a little amount of residual carbon was synthesized by Maqbool et al. [22] using cellulose precursor and boric acid at a low temperature of 1200 °C. Kenny et al. [19] showed that it is feasible to synthesize B₄C powder via a low temperature synthesis route. The synthesized powders were then densified by spark plasma sintering (SPS). Final products exhibited great purity with residual carbon contents of 0.61 wt% and 0.17 wt% before and after SPS, respectively.

Boron carbide was produced through a two-stage heat treatment of sol-gel obtained polymeric gel by Avcioglu et al. [18]. Replacing some proportion of boric acid with a nano-sized boron element, the kinetics and transformation of B₄C are boosted remarkably. They found that the

residual carbon content in the prepared product, processed at 1400 °C, is directly decreased proportional to the amount of nano boron additive. Crystalline B$_4$C with less than 1±5 wt% carbon was synthesized by replacing 50 mol% boric acid with nano boron at 1500 °C. Pilladi et al. [23] obtained nanocrystalline B$_4$C powders at 1500 °C for 3 h using sucrose and boric oxide as the gel precursors with a carbon impurity level of 3 wt%. Boron carbide nano-powders were synthesized by Vijay et al. [24] using sucrose and boron oxide at 1600 °C in a vacuum. Heated products for 10 min at 1600 °C contained less than 3 wt% carbon impurities.

We recently showed that glucose as a carbon source has an influential effect on B$_4$C synthesis by reacting with boric acid as a boron source [25]. Next, the effect of glucose pretreatment and the use of extra boric acid on B$_4$C synthesis was also studied [26]. In addition, the optimization of precursor pyrolysis parameters such as time, temperature, and atmosphere was also carried out [27]. Then, the parameters of the synthesis process including time, temperature, and atmosphere were optimized [28]. Meanwhile, the effects of tartaric acid addition and mechanical activation on B$_4$C synthesis performance were studied [29]. In this work, residual carbon content is measured with several methods, and the size and morphology of B$_4$C powders, synthesized under different conditions, are investigated.

2. Materials and methods

After investigating the most influential parameters, treatments, and synthesis conditions of B$_4$C ceramics, the outcomes of which were previously published by our group [25–29], in this work, some techniques were employed to quantitatively measure the residual carbon in the synthesized powders.

2.1. Determination of residual carbon

To determine the exact reaction efficiency of B$_4$C synthesis as well as the quality of the final product, it is necessary to check the amount of residual carbon in the final product. For this purpose, two methods were used.

- Carbon dissolution method

In this method, the final product resulting from the synthesis process is dissolved in a suitable solution that has the ability to dissolve free carbon and remove it from the environment. In this case, the obtained solid powder does not contain any free carbon. For this purpose, sulfochromic acid was used. First, 2 grams of synthesized B$_4$C powder was poured into 50 ml of sulfochromic acid solution and kept at 140 °C for 30 min. In order to prevent acid from evaporating, a reflux system was used under the hood. Finally, the remaining deposits after filtering, washing, and drying in an oven at a temperature of 150 °C were considered pure B$_4$C powder. Based on this, the residual carbon is obtained from Eq. 1, where M1 is the initial weight of the powder and M2 is the weight of the powder after dissolving the carbon.

$$C(\%) = \frac{M1 - M2}{M1} \times 100 \tag{1}$$

- Boron carbide oxidation method

In this method, the oxidizing trick is used to determine the residual carbon percentage. For this purpose, carbide powder was first placed in air at a temperature of 700 °C with a heating rate of 10 °C/min. Then the powder was weighed after cooling and its weight loss was

calculated. The heated powders were washed several times in boiling water to remove the boron oxide remaining on them. Finally, the powder was dried and weighed. The amount of residual carbon in the carbide was determined based on the following equations:

$$M4 = M2 - M3 \tag{2}$$

$$M5 = M4\left(\frac{55.2}{139.2}\right) \tag{3}$$

$$M6 = M5 + M3 \tag{4}$$

$$M7 = M1 - M6 \tag{5}$$

where M1 is the weight of impure B$_4$C (B$_4$C plus carbon), M2 is the weight of the heated powder (B$_4$C plus oxidized B$_4$C), M3 is the weight of the sediment remaining after washing (B$_4$C), M4 is the weight loss due to washing (oxidized B$_4$C), M5 is the actual weight of oxidized B$_4$C, M6 is the total weight of B$_4$C in the initial powder, and M7 is the total weight of carbon in the initial powder.

2.2. Investigation of the morphology of synthesized powders

The synthesized powders were subjected to scanning electron microscope (SEM) imaging to investigate the microstructure and size of B$_4$C particles, as well as possible impurities and the distribution of particles. Since the final product of the synthesis process is a porous and solid mass, it should be crushed. For this purpose, a high-energy planetary mill was used for 3 h. In order to prepare the samples, before placing the samples in the microscope chamber, a thin gold coating was applied on them.

3. Results and discussion

Since the results obtained from X-ray diffractometry, reflected in the previous papers of our group [25–29], are analytical and qualitative, it is not possible to accurately calculate the amount of impurities in the final products using XRD analysis. This point is important in cases where the impurity level is low, and the synthesis efficiency is more or less optimal. Therefore, it is necessary to use a quantitative tool to obtain the exact amount of residual carbon and make a more detailed comparison. In order to carefully examine the synthesis process of B$_4$C, the efficiency of different methods of reducing the residual carbon, and their quantitative comparison, a number of the final products of the synthesis process were tested to determine the percentage of remaining carbon. For this purpose, the following three samples were selected:

-Sample 1: synthesized without mechanical activation and without additives.

-Sample 2: synthesized from activated powders.

-Sample 3: synthesized from the materials doped with tartaric acid.

The results of the amount of residual carbon in the samples are reported in Table 1. According to the results obtained from two measurement methods, it can be concluded that the sample that has not undergone any purification operations and is formed only in optimal synthesis conditions (sample 1) has about 7 wt% of free carbon. It is also evident that mechanical activation (sample 2) has a minor role in the reduction of impurities as the percentage of carbon is decreased to about 5.7 wt%. The addition of tartaric acid (sample 3) has an excellent performance in terms of purification and increasing the efficiency of B$_4$C synthesis because it reduces the impurity content to about 3.3 wt%.

Table 1. Measured residual carbon content in the synthesized B_4C powders.

Sample No.	Amount of residual carbon (wt%)	
	Carbon dissolution method	B_4C oxidation method
1	6.8	7.2
2	5.5	5.8
3	3.2	3.5

According to the mentioned results, since the carbon impurities are separated from the main product during the washing with acid, this method can be used to purify the synthesized powders as much as possible. Finally, it can be disclosed that adding tartaric acid is a more suitable method to increase the efficiency of the synthesis process, and washing the final product with an acid solution makes it possible to prepare a purer product.

In order to study the morphology of the synthesized powders and measure their particle size, the final B_4C powders were photographed with a scanning electron microscope (SEM). For this purpose, two samples were used:

-Sample (i): synthesized in the presence of tartaric acid (sample 3 of the previous step).

-Sample (ii): synthesized under optimal conditions with no residual carbon reduction processing.

It should be noted that the final products obtained from the synthesis processes are usually porous and solid masses and have an integrated structure. Therefore, in order to achieve more accurate and specific images, as well as to compare the particle size of the powders, the synthesized products are crushed by a high-energy planetary mill before imaging. This causes the agglomerated masses that are stuck to each other during the synthesis process at high temperatures for a long time to be separated so that the actual particle size of B_4C powder shows itself better and clearer.

Fig. 1a shows the microstructure at low magnification of sample (i), the synthesized B_4C powders optimized by the addition of tartaric acid, in which the washing method with the acid solution was used to remove the carbon impurities from the product. In Figs. 1b and 1c, images with higher magnifications, the B_4C particles are clearly visible. The uniform size of boron carbide particles, along with their purity and the absence of visible impurities, indicate high synthesis efficiency and suitable processing conditions. The average particle size in the sample (i) is 28.9 μm, measured by the Digimizer Image Analysis Software, which can be seen in Fig. 1d.

For a better and more accurate comparison of sample (i) with sample (ii) synthesized in optimal conditions but without additives and without activation, that sample was also investigated by SEM. Fig. 2a is an image with an overview of the particles present in the sample (ii). Figs. 2b–e show that next to the main B_4C particles, there are small and irregular particles and aggregates, which are probably impurities. According to the investigations in the previous step, these impure materials are made of carbon and the result of incomplete synthesis of raw materials during the process. The average particle size in the sample (ii) is 16.6 μm, which can be seen in Fig. 2f.

Based on these images, it can be claimed that the performed processes are effective in increasing the synthesis efficiency of B_4C ceramics. By examining the scattered impurities in samples (i) and (ii), it is clear that the acid washing operation removes carbon impurities from the material and provides a more uniform product. Also, in the examination of the particle size, it can be said that considering that both powders have undergone the same crushing operation after synthesis and have experienced similar conditions, the relatively smaller size of the particles in the sample (ii) can indicate that it is more brittle than the sample (i).
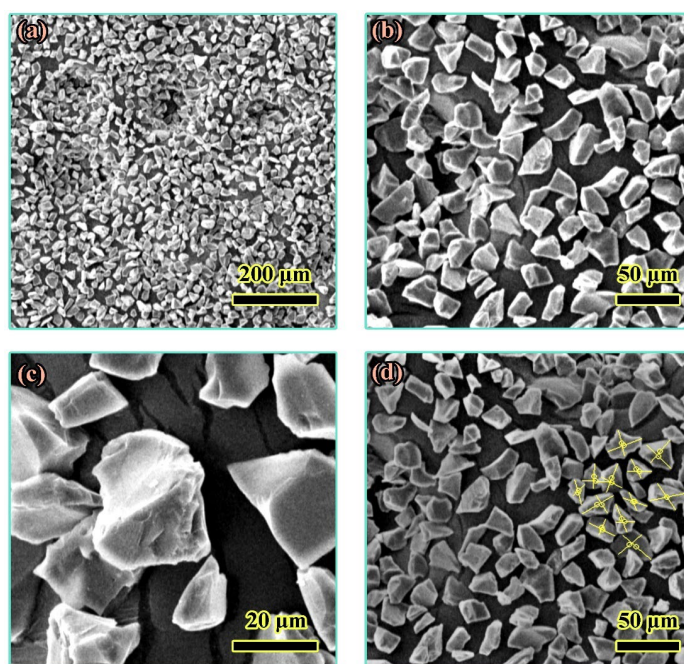

Fig. 1. SEM images of sample (i) doped with tartaric acid with the lowest amount of residual carbon at a) X100, b) X300, and c) X1000 magnifications and d) notations for calculating the average particle size.
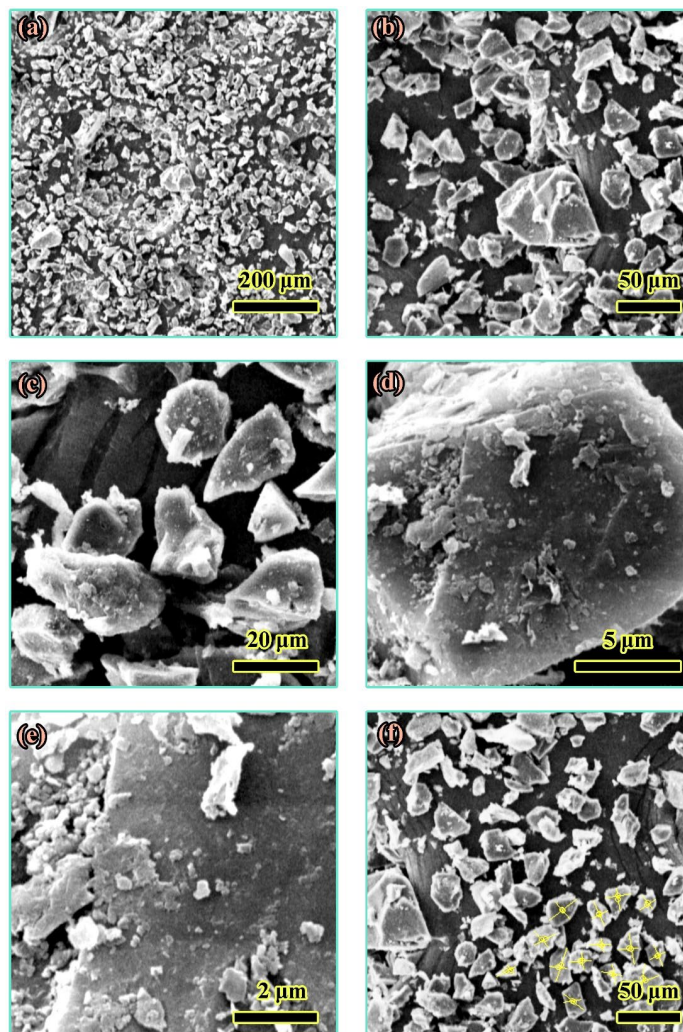
Fig. 2. SEM images of the sample (ii) synthesized under optimal conditions with no residual carbon reduction processing at a) 100, b) 300, c) 1000, d) 5000, and e) 10000 magnifications, and f) notations for calculating the average particle size.

It should be reminded that B_4C is a solid solution with a relatively wide area in the boron-carbon phase diagram, and the percentage of carbon in the boron carbide solid solution has a direct relationship with its hardness and strength. In fact, it can be claimed that tartaric acid causes more uniformity and creates optimal synthesis conditions to finally produce B_4C with higher quality and properties.

4. Conclusions

One of the important challenges in B_4C synthesis is the effort to reduce the amount of residual carbon in the final product. In this research, boric acid and glucose were used as starting materials for the synthesis of boron carbide. The type of treatments that were considered for the synthesis of B_4C not only affected the amount of impurity but also the size and morphology of ceramic powder particles to some extent. In fact, the effect of mechanical activation and the addition of tartaric acid on the amount of residual carbon were investigated. Because phase analysis with XRD is not quantitatively accurate enough, methods of carbon dissolution and boron carbide oxidation were used to determine the amount of carbon impurities more accurately in the final powders. Performing mechanical activation reduced the amount of residual carbon from 7 wt% to 5.7 wt%, but the effect of adding tartaric acid was more significant, which decreased the impurities to 3.3 wt%. The size and morphology of the particles of the synthesized powders were finally checked and compared with scanning electron microscopy.

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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