Contents lists available at ScienceDirect

Open Ceramics

Dynamic / thermochemical method: A novel approach in the synthesis of B$_4$C powder

Hamza Boussebha [a],[*], Sinan Bakan [b], Ali Osman Kurt [c]

[a] *Sakarya University, Research and Development Center (SARGEM), Powder Research and Development Group, Esentepe Campus, 54187, Sakarya, Turkey*
[b] *Fatih Sultan Mehmet Vakif University, Haliç Yerleşkesi, Sütlüce Mah. Karaağaç Cad. No:12 Beyoğlu, İstanbul, Turkey*
[c] *Sakarya University, Department of Metallurgy and Materials Engineering, Esentepe Campus, 54187, Sakarya, Turkey*
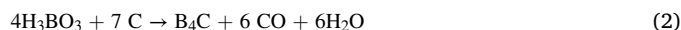
ARTICLE INFO

ABSTRACT

The synthesis of high quality B$_4$C powders with high purity, uniaxial shape and homogeneous size distribution, has been hard to obtain. Current production methods take place at temperatures above 1800 °C, yielding high free carbon and large particle size. In this study, using a novel and patented approach, a reaction temperature of 1500 °C for 1 h was sufficient to synthesize fine B$_4$C powders from boron oxide (B$_2$O$_3$) and carbon black (C). This technique is based on the dynamic/thermochemical method (DTM), in which B$_2$O$_3$ and C powders are granulated before being charged into an atmosphere-controlled rotary type furnace. The granulation process and parameters of raw materials were the key to obtain high purity B$_4$C powders, with equiaxed-grains and homogenous distribution with an average size of 10 μm.

1. Introduction

With the title of "black diamond" bestowed upon it, boron carbide (B$_4$C), possesses a low density (2.52 g/cm^{-3}) [1], high hardness (29.1 GPa) [2], high elastic modulus (470 GPa) [3], high melting point (2540 °C) [4], an outstanding chemical resistance [5] and a high neutron absorption cross-section (^{10}B$_X$C, x > 4) [6]. These properties promote B$_4$C as an excellent choice for armor and abrasive applications. Boron carbide is commonly obtained via magnesiothermic [7] or carbothermic (also named carbothermal) reduction (CR) [8], mechanothermal synthesis [5], synthesis from boron (B) and carbon mixture [9], synthesis from polymer precursors [10], besides vapor phase reactions, ion beam synthesis and vapor liquid solid (VLS) growth, usually desired in the synthesis of B$_4$C for surface coating [2]. Although there exist multiple approaches to synthesize B$_4$C powder, the carbothermic reduction of either boric acid (H$_3$BO$_3$) or boron anhydride/boron oxide (B$_2$O$_3$), which are both inexpensive starting materials, is the commercially preferred method, due to its simplicity and economic advantages. The general reactions of boron carbide synthesis are given in Equations (1) to (5) [8] [11]. Despite being the widely used method, carbothermic reduction, has the major disadvantage of boron loss in form of its oxides [9]. Hence, the powders synthesized in this way, usually contain a high amount of free carbon, which has a detrimental effect on the mechanical properties of the

sintered boron carbide products. The presence of free carbon is based on the binary phase diagram B–C. Since B$_4$C is in equilibrium with carbon in a range that enlarges at high temperature to the carbon-rich side, a super-saturation can take place during the cooling process, causing a precipitation of free carbon [8].

$$2 \text{ B}_2\text{O}_3 + 7 \text{ C} \rightarrow \text{B}_4\text{C} + 6 \text{ CO} \tag{1}$$

$$4\text{H}_3\text{BO}_3 + 7 \text{ C} \rightarrow \text{B}_4\text{C} + 6 \text{ CO} + 6\text{H}_2\text{O} \tag{2}$$

Latter reaction proceeds in three steps:

$$4\text{H}_3\text{BO}_3 \rightarrow \text{B}_2\text{O}_3 + 6\text{H}_2\text{O} \tag{3}$$

$$\text{B}_2\text{O}_3 + 3 \text{ CO} \rightarrow 2 \text{ B} + 3 \text{ CO}_2 \tag{4}$$

$$\text{C4 B} + \text{C} \rightarrow \text{B}_4\text{C} \tag{5}$$

The carbothermic reduction is extremely endothermic requiring 16,800.00 kJ/mol or 9.10 kWh/kg of B$_4$C [12]. In the commercial method, the process takes place in an electrical arc furnace where B$_2$O$_3$/C mixture is heated above 2000 °C, resulting a volatilization of boron, and subsequently precipitation of free carbon. Some studies have suggested that the presence of a controlled small amount of free carbon can be useful during sintering. Chen et al. [13]. reported that a carbon excess enhances the densification and inhibits grain growth. Nevertheless, Yong

---

* Corresponding author.

E-mail address: hamza.boussebha@ogr.sakarya.edu.tr (H. Boussebha).

Gao et al. [8]. explained that the enhancement that occurs in the case of carbon addition as a sintering aid, differs from carbon existence as precipitates, due to the fact that some of the latter are entrapped within boron carbide particles making it hard to be removed during sintering. Moreover, as B_4C precipitates during cooling in the CR process via electric arc furnace, large dross-like shapes are formed due to the high temperature reached. Consequently, a further milling is required, resulting powders of coarse size and sharp-edged particles with flat surfaces.

Since the carbothermal reduction is the commercially desired method, many studies focused on its optimization as to achieve a better B_4C powder quality, via lowering the total amount of free carbon and obtaining uniform equiaxed particles. It was suggested that precursor homogeneity, reactant materials' particle size and the amount of boron in the precursor are the main factors that control the presence of free carbon [8]. Alizadeh et al. [11]. reported that a boric acid to carbon ratio of 3.3 and 3.5 decreased the amount of free carbon in B_4C after a heat treatment of 5 h at 1470 °C. Furthermore, it has been found that an addition of 0.5% reactants' total weight fraction, of commercial B_4C to the starting mixture, enhances the reaction, producing powders with homogenous morphology [14]. In spite of the improvement of B_4C powder quality reported by the previously mentioned studies, limitations in terms of purity, grain size and size distribution, invoke further optimization of the CR method or an alternative approach in order to reach a better-quality product.

In this paper, we propose a dynamic/thermochemical method (DTM) to synthesize B_4C powders. This is a novel approach in the synthesis of B_4C that is based on the patented process by Kurt [15]. In this process, fine equiaxed powders are synthesized in a rotating reactor system allowing the reaction to take place at a relatively lower temperature and in a shorter time compared to the conventional carbothermal reduction (CR). DTM method was experimentally successful in achieving high purity and homogeneous size distribution along with ready to use final product powders of TiN and Si_3N_4 ceramics, which compared to other product, were achieved in a shorter time with a better particle morphology [16–18]. Additionally, the powders obtained via DTM, can readily be used in their as-synthesized form, occasionally after soft grinding using agate mortar and pestle.

In the present study, aiming to optimize the powder quality, high purity fine equiaxed B_4C powders were synthesized from non-stoichiometric B_2O_3 and carbon black mixture. Furthermore, the effect of nucleant addition, as well as different mixing parameters were investigated.

2. Experimental procedure

The raw material used as a boron source for the synthesis of B_4C was B_2O_3 (Alfa Aesar) with a purity over 99% (1% comes from boric acid, having no adverse effect on the DTM or the final product), and an average particle size of 300 μm. XRD pattern and SEM image corresponding to B_2O_3 powder are given in Fig. 1. Carbon black (coded as ISAF-N220) of high purity and an average particle size of 5 μm (Körfez Petrochemical Refinery, Turkey) was used as carbon source. Commercial B_4C powder, with an average particle size of 20 μm obtained via milling (Coded as 10 F from a Chinese origin, obtained from NUROL Technology, Turkey), were used in some experiments as nucleating agent. XRD pattern and FESEM image (FEI Quanta FEG 450 model) of the commercial B_4C are given in Fig. 2.

Initially, B_2O_3 and C powders at different molar ratios were mixed using an agate mortar and pestle, then manually granulated using ethanol with an added 5% glycerol (as to not affect the stoichiometry with carbon excess), via a wood spatula in a flat plastic cup. To investigate the effect of mixing, some samples were mixed and granulated using EIRICH EL1 laboratory mixer, in a stainless-steel container at 2000, 4000 and 6000 rpm for 10 min (no balls were involved in the process). Ethanol and 5w.% glycerol mixture, was as well used as a binder in the granulation via spraying it on the raw powder mixture of B_2O_3 and C. The granules were later sieved to 1–3 mm size range. The reason behind targeting this exact size range of granules, is the optimum efficiency, observed in previous studies [14–16,18], considering both the rotary tube furnace and the graphite reactor sizes, to allow smooth rotation during the synthesis process. Following sieving, the granules were dried at 80 °C for 24 h then 15 g were charged into a cylindrical graphite reactor (φ 45 mm, L 300 mm) with centered little vents on both sides, to allow gases to leave the reaction zone.

In order to investigate the effect of nucleation, a very small molar fraction of B_4C powder was added to the mixture before the granulation processing. The B_4C fraction, which has been reviewed previously [14], was added as 0.5% of the total weight fraction of the reactants. Due to the volatilization of boron, a non-stoichiometric reaction, given in Eq. (6), was adapted, to compensate for the boron loss. The molar ratio of the B_4C to be used as seeding agent was calculated using equation (7)

$$X \, B_2O_3 + Y \, C + Z \, B_4C \rightarrow N \, B_4C + R \, CO \qquad (6)$$
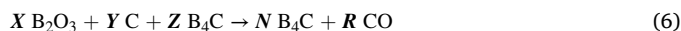
N stands for final molar weight of B_4C. R stands for the value of carbon monoxide, whereas, the value of Z is calculated as follows:

$$Z = \frac{((X \, x \, Molar \, Weight_{B_2O_3}) \ + \ (Y \, x \, Molar \, Weight_C)) * \left(\frac{5}{1000}\right)}{Molar \, Weight_{B_4C}} \qquad (7)$$

The molar fraction of carbon to boron oxide was selected as 2 instead of the 3.5 in the stoichiometric equation (Eq. (7)). The adapted recipes are given in Table 1.

Prior to syntheses, Factsage 7.0 program has been used for a thermodynamic modelling of the non-stoichiometric reaction adapted in our process (Recipe R2), in order to determine the temperature range in which the formation of B_4C takes a place. Fig. 3 illustrates the obtained graph.
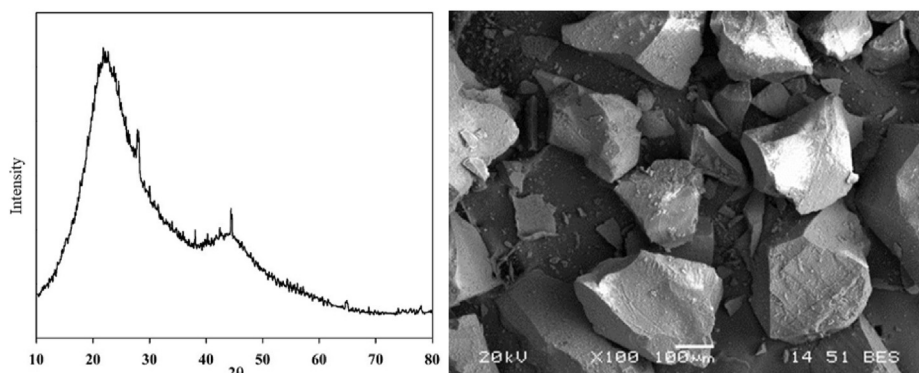

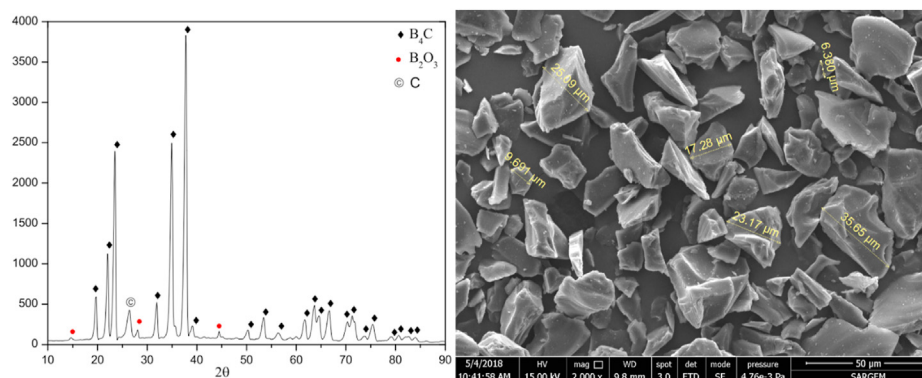**Fig. 1.** XRD pattern (left) and SEM image (right) of B_2O_3 used as raw material.

Fig. 2. XRD pattern (left) and FESEM image (right) of commercial B$_4$C powders used for nucleation.

Table 1
Molar weight of the adapted recipes.

Recipes	X B$_2$O$_3$ (mole)	Y Carbon (mole)	Z B$_4$C (mole)
R1	3	6	0
R2	3	6	0.03

It can be seen in the model analysis that apart from the transition of boron oxide from solid to liquid state (represented in green and blue respectively), up to 1200 °C, no change takes place. With the increase of temperature, B$_2$O$_3$ and carbon decrease gradually, whereas an increase of both B$_4$C and CO takes a place referring to the initiation of the reaction. The amount of B$_4$C phase continues to increase until approximately 1550 °C at which B$_4$C reaches an optimum level. Hence 1500 °C was adapted in our work for B$_4$C synthesis.

Subsequent to sieving and drying of granules, 15 g were charged into the graphite reactor, then heated in a Protherm tube furnace with heating and cooling rate control capability. The furnace was modified in order to introduce a rotary system into it by installing a 3 V DC servo-motor externally to rotate the alumina tube using pinion gears installed on the furnace's exterior. In order to assure the stability of the reactor in the heat center of the furnace, graphite pipes were placed on both sides of the reactor, inside the alumina tube. A schematic representation of the overall process is given in Fig. 4.

The granules were heated to 1500 °C at a rate of 5 °C/min, held for 1 h under flowing argon (Ar) of 99.95% purity (ARTOK Ltd. Turkey) at a constant rotation speed of 4 rpm, then cooled at the same rate of heating (5 °C/min). The kiln rotation speed of 4 rpm was chosen based on a previous study in which this speed provided optimum results in matters of spherical powder shape and a reduced reaction time [19]. Following synthesis, the collected granules, which seemed to maintain their shape and size during the DTM process, were softly hand-grinded to homogenize the powders, then characterized with XRD (Rigaku D/Max-2200/PC) and SEM (JEOL 6060 LV). Powder size distribution was measured using MICROTRAC S3500 size characterization device.

3. Results and discussion

The loss of boron in form of its oxides has always been related to B$_4$C synthesis [9]. The decrease in boron loss with commercial boron carbide addition, originated with Yıldızlı's work [14], who observed a certain decrease in the loss of B$_2$O$_3$, with a low amount of commercial B$_4$C involvement in the starting mixture. The depletion of boron is linked to its loss in form of gases (usually B$_2$O$_2$ and BO forms [9]), which at high temperatures, and under the effect of the flowing Ar gas, escape from the reactor's vents causing a reduction of productivity. In our study, boron loss has been observed similarly to other studies. However, this loss, was found to decrease when the raw materials prepared via automated mixing, were used instead of that prepared by hand. Furthermore, the amount of powder collected subsequent to syntheses, increased proportionally to mixing speed, suggesting an improvement of the productivity comparing to manual mixing and granulation.
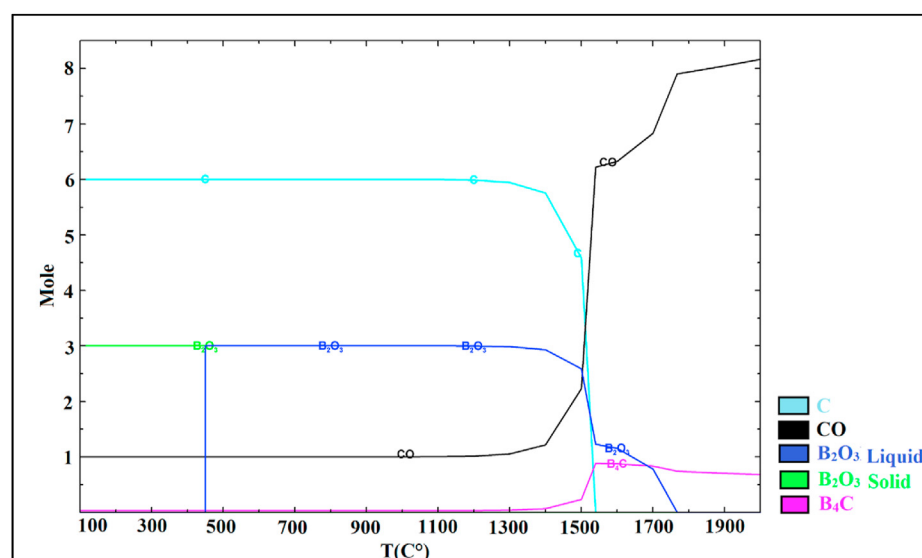

Fig. 3. Temperature dependency in the reaction of 3 B$_2$O$_3$ + 6 C + 0.03 B$_4$C, drawn using Factsage 7.0.
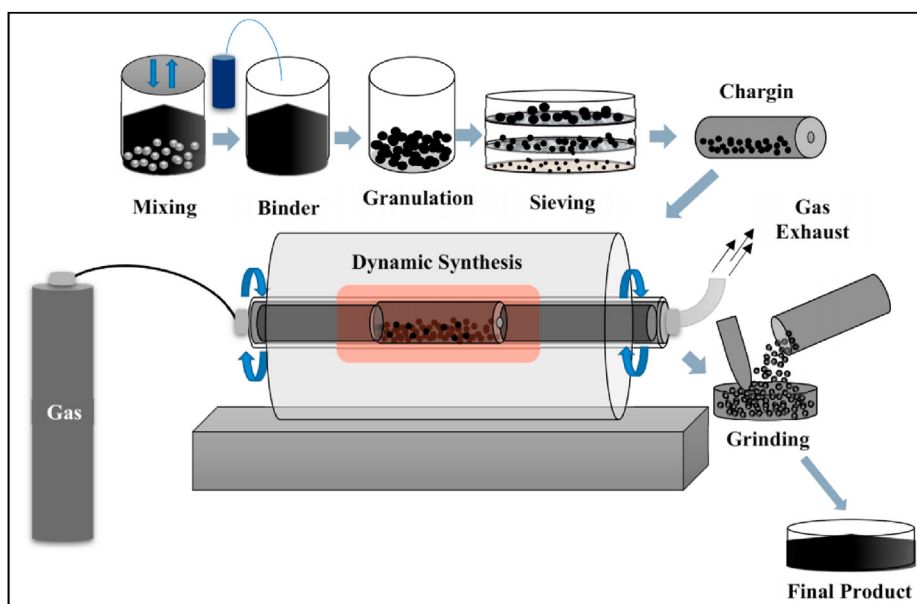
Fig. 4. Schematic representation of the DTM process.

Fig. 5 demonstrates XRD patterns of B$_4$C powder synthesized from differently mixed raw powders prepared from recipe R2 (B$_2$O$_3$ and carbon with a very low amount of B$_4$C added as a seeding agent). When the powder was hand-mixed and granulated, a considerable amount of unreacted C and B$_2$O$_3$ was observed with certain amorphous phase (seen in Fig. 5 "Manual"). However, when mixing and granulation took place in the machine, both amorphous C and B$_2$O$_3$ decreased gradually with the increasing mixing speed. At 4000 rpm and 6000 rpm, a complete conversion of B$_2$O$_3$ to B$_4$C was achieved, with the a very small amount of free carbon, as it is evident from the typical amorphous carbon dome at around 26–27° 2θ. The dynamic nature of the system is thought to be the main reason to activate the reaction, due to the constant movement of the reactor. The amount of free carbon in the synthesized B$_4$C powder was relatively reduced to a minimum level for those reactants mixed and granulated at 4000 rpm and 6000 rpm (Fig. 5). Hence, it can be said that a good mixing of raw materials is required to obtain a complete dispersion of carbon and B$_4$C seeds within B$_2$O$_3$. Moreover, 4000 rpm can be considered as the optimum mixing condition for uniform and fine B$_4$C powder synthesis.

In order to show the effect of seeding agent addition, the synthesis from both recipes R1 and R2 (Table 1) was considered. Preparation and synthesis conditions for both recipes were identical. The raw materials were mixed and granulated at 4000 rpm, then maintained at 1500 °C for

1 h at 4 rpm reactor rotation speed under 1 L/min flowing argon. The XRD patterns and SEM micrographs of the obtained B$_4$C powders are given in Figs. 6 and 7, respectively.

In the absence of B$_4$C in the B$_2$O$_3$–C starting mixture (Fig. 6-a), a full conversion to B$_4$C was not recorded, as it is shown with the unreacted B$_2$O$_3$ remains in the final product. In the case of 0.03 M weight addition of commercial B$_4$C powders in the starting mixture, a nearly complete conversion of boron oxide to B$_4$C was achieved, with a little amount of residual carbon (Fig. 6-b). It is worth mentioning here that a minor amount of in-situ carbon residues in B$_4$C powders, can be tolerable in further sintering processes [9].

Fig. 7 reveals a morphology difference between B$_4$C powders, with and without seeding agent addition, both synthesized at 1500 °C for 1 h at 4 rpm reactor rotating speed under 1 L/min flowing argon.

It can be seen that the morphology of B$_4$C obtained from raw powders to which a nucleating agent was add (Fig. 7-b) is by far better in terms of powder shape and size than that corresponding to seeding agent free raw powders (Fig. 7-a), in which coarse and longitudinal grains are present. Seeding helped achieve a better purity as well as homogeneity of the product, which is in line with the results reported in similar systems [20]. The addition of B$_4$C seeds to the starting mixture, allowed more B$_2$O$_3$ and C to be consumed in the reaction yielding homogeneous grains of boron carbide as seen in Fig. 7-b.
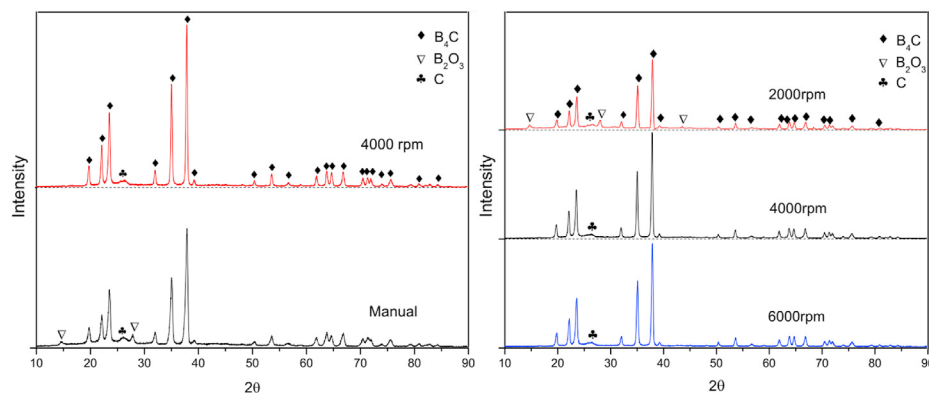

Fig. 5. XRD Patterns of B$_4$C synthesized at 1500 °C for 1 h at 4 rpm, from R2 mixed manually and automatically at different speeds (2000 rpm, 4000 rpm and 6000 rpm).

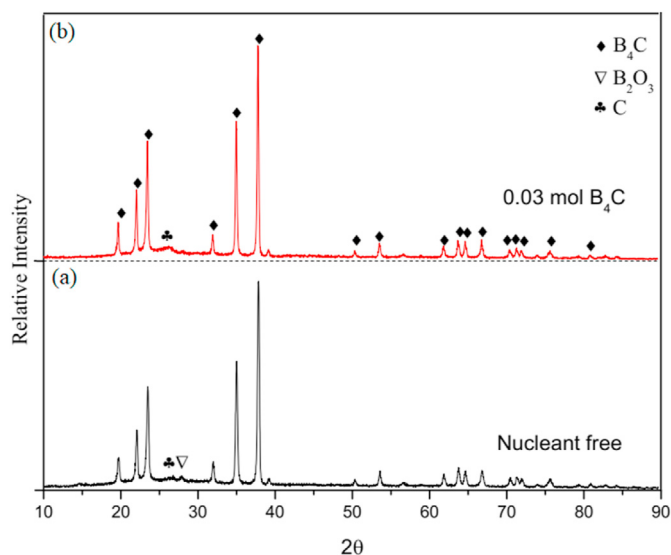**Fig. 6.** XRD patterns of B$_4$C powders synthesized via DTM process from B$_2$O$_3$/C mixture. a) R1, nucleate free and b) R2, mixed with 0.03 mol commercial B$_4$C as a seeding agent.

is a result of gas phase synthesis, since B$_4$C can be obtained from the reaction of boron suboxides with carbon monoxide [22]. The absence of the needle shaped product in the off-reactor synthesis, comparing to the product collected from the reactor (Figs. 7b and 9a), can as well support the argument of a gas phase synthesis, since that shape, which can only take a place inside the reactor, had been linked to a solid-gas reaction [21].

SEM results demonstrates the effect of the mixing quality of the reactants (Fig. 10). When the powder was synthesized from manually mixed and granulated reactants, a slight improvement was observed (Fig. 10-a), comparing to the nucleant free samples R1 (Fig. 7-a). Nonetheless, the difference of morphology is not clear since the amount of the needle shaped structure is considerably high. This can be explained with the bad distribution of B$_4$C seeds due to a poor mixing of the raw powder, enforcing our suggestion that a good mixing is mandatory in order to obtain homogeneous equiaxed grains. Mixing and granulation carried out using the machine at 2000 rpm enhanced the morphology of B$_4$C powders (Fig. 10-b). Yet, B$_4$C in form of blocks (encircled in white) of a size exceeding 10 μm are apparent in the image which cause a non-uniformity of the powder. The formation of these blocks has been reported to be linked to the nucleation effect where a non-uniform distribution of nuclei results a non-uniform growth [20].

In the case of mixing at 4000 rpm and 6000 rpm (results after DTM process given in Fig. 10-c and 10-d, respectively), relatively fine powders were observed with a complete absence of blocks or needle shaped
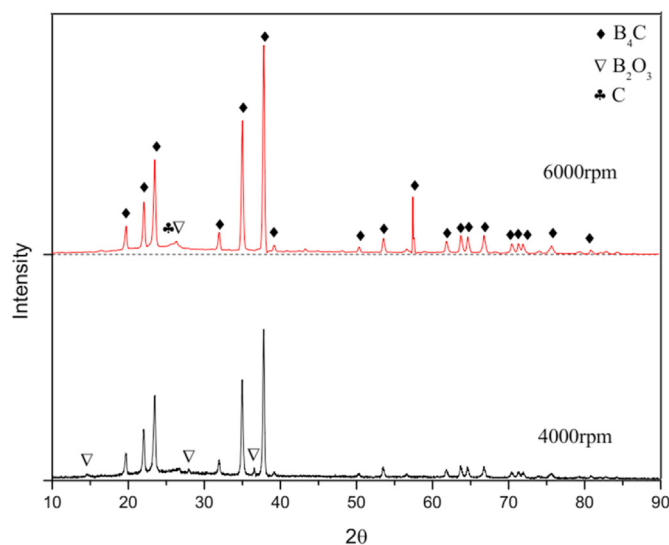
Thus, it is possible to say that the addition of B$_4$C seeds, if not eliminated totally, significantly decreased the amount of the needle shaped structure giving a relative uniformity to the synthesized powder. The nucleation has been reported to have a key role in the homogeneity of the product. Temperatures exceeding 1800 °C, were deemed necessary to favor nucleation over growth, resulting a uniform fine B$_4$C, whereas intermediate temperatures (such as 1450 °C for 2 h) are more likely to result a non-uniformity of the synthesized powder due to a simultaneous nucleation and growth [20]. Alternatively, in our case, the existence of nuclei allowed growth to be favored resulting fine powders with less needle shaped structures, in comparison with Fig. 6-a corresponding to B$_4$C obtained without seeding agent addition.

Despite the improvement of the powder morphology with nuclei addition, the needle shaped structure did not completely disappear. Jung et al. [21]. suggested that this shape is linked to a Gas-Solid (GS) reaction. In our work, it may be argued that the needles, were the product of a gas phase reaction, since a considerable amount of powder, which appeared to be similar to boron carbide, was found at the frontal vicinity of the reactor, on the gas exhaust side. Corresponding XRD patterns and SEM images of reactor vicinity powder synthesis from the recipe R2, are given in Figs. 8 and 9, respectively (only powders mixed at 4000 rpm and 6000 rpm were given as examples here, since optimum results were recorded at these two mixing speeds).

The XRD analyses revealed powders, not dissimilar to that synthesized inside the reactor (Fig. 5). It is suggested that the obtained product

Fig. 8. XRD patterns of B$_4$C collected from the frontal vicinity (gas exhaust side). Following synthesis at 1500 °C for 1 h at 4 rpm, from R2, for granulation carried out at 4000 rpm and 6000 rpm.
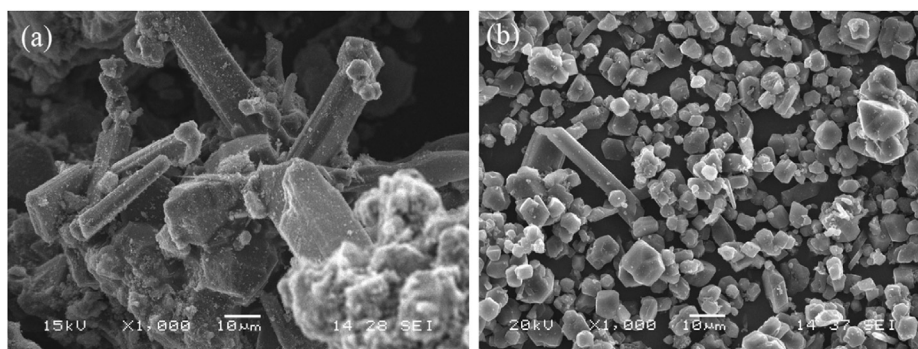

Fig. 7. SEM images of B$_4$C powders synthesized at 1500 °C for 1 h at 4 rpm, from B$_2$O$_3$ and C mixture (mixed and granulated at 4000 rpm):a) nucleate free and b) 0.03 mol commercial B $_4$C powders.

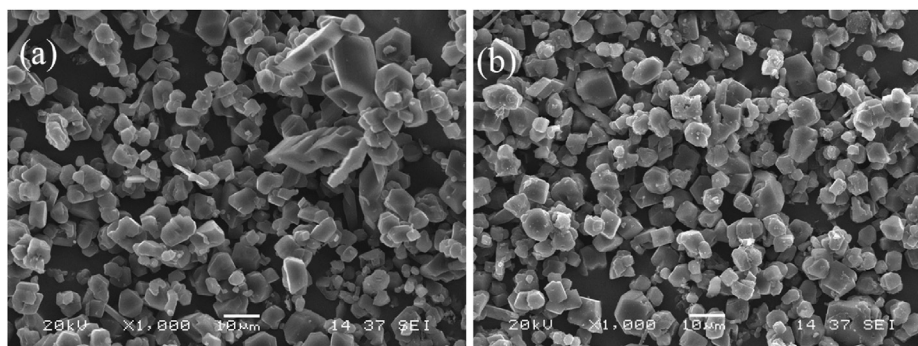**Fig. 9.** SEM images of B$_4$C collected from the frontal vicinity (gas exhaust side), following synthesis at 1500 °C for 1 h at 4 rpm tube rotation, from R2, mixed at: (a) 4000 rpm, (b) 6000 rpm.
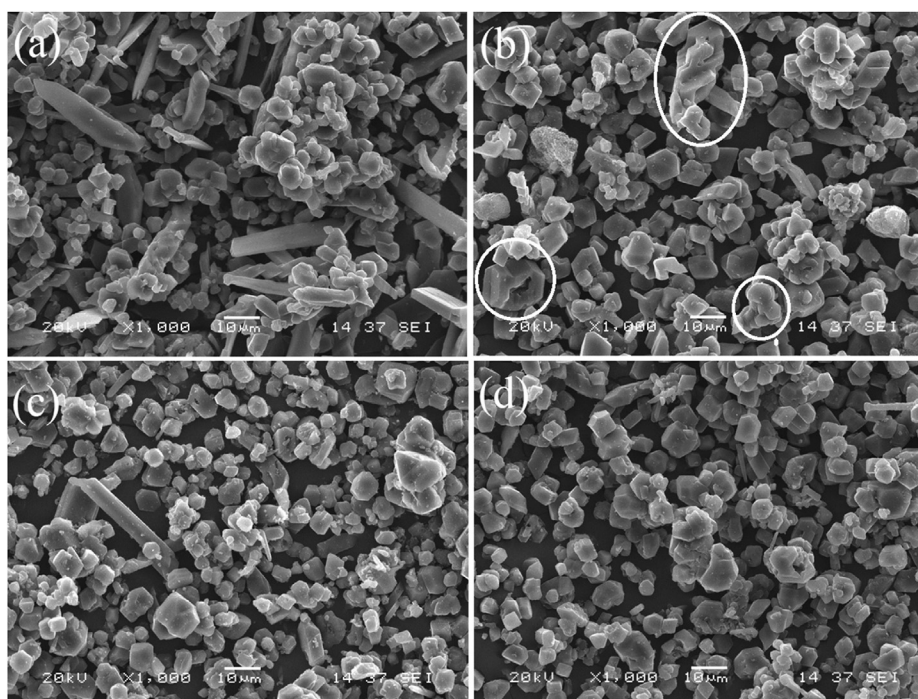

Fig. 10. SEM images of B$_4$C synthesized at 1500 °C for 1 h at 4 rpm, from R2 mixed:(a) manually, (b) at 2000 rpm, (c) 4000 rpm and (d) 6000 rpm.

structures in the case of 6000 rpm. It is believed that the extensive mixing enhances the dispersion of B$_4$C seeds within the granulates, which maintain their solid form, whereas B$_2$O$_3$ passes to a liquid state after 450 °C. As the reaction temperature increases above 1100 °C, boron carbide forms at the contact interface of high viscosity sticky form of liquid boron oxide with solid carbon particles and B$_4$C nuclei, via a liquid-solid (LS) phase synthesis process. The presence of B$_4$C seeds, enhances the formation of boron carbide allowing the synthesis to achieve completion in 1 h.

In order to better observe the particle size homogeneity, particle size measurement was held for the as-synthesized product from DTM, prepared at 4000 rpm, together with that of the commercial B$_4$C (Fig. 11).

B$_4$C synthesized via DTM had a size ranging from 3.27 μm to 74.00 μm, with an average of 10.78 μm. It can be clearly seen that an improvement of the morphology, took place with an average size of 10 μm. Hence, not only does this novel approach in the synthesis of B$_4$C, provide powders with a minimum free carbon, but also, it allows the synthesis of homogenous powders and better size distribution, so that they can be directly used without any need for further processing.

4. Conclusion

Boron carbide powders with fine particle size and very low free carbon were synthesized using non-stoichiometric composition of carbon to boron oxide via dynamic/thermochemical reduction (DTM) at 1500 °C for 1 h. High velocity mixing and granulation of the reactants was effective in providing a good distribution of the raw materials that helped producing a uniform particle size and shape of B$_4$C powders. The addition of 0.03 mol commercial B$_4$C into the reactants was found to enhance the reaction and promote the synthesis of homogenous powders. Following the DTM process, high purity B$_4$C powders, with equiaxed grains, fine particle size and homogenous size distribution, were obtained. DTM is a possible substitute to the commercial arc plasma method for the synthesis of B$_4$C powders, offering the possibility to synthesize large powder quantities that can be used without any need for further processing. Additionally, this method can be effective in the synthesis of nitride, carbide, boride and other types of technical ceramic powders and their composite forms.
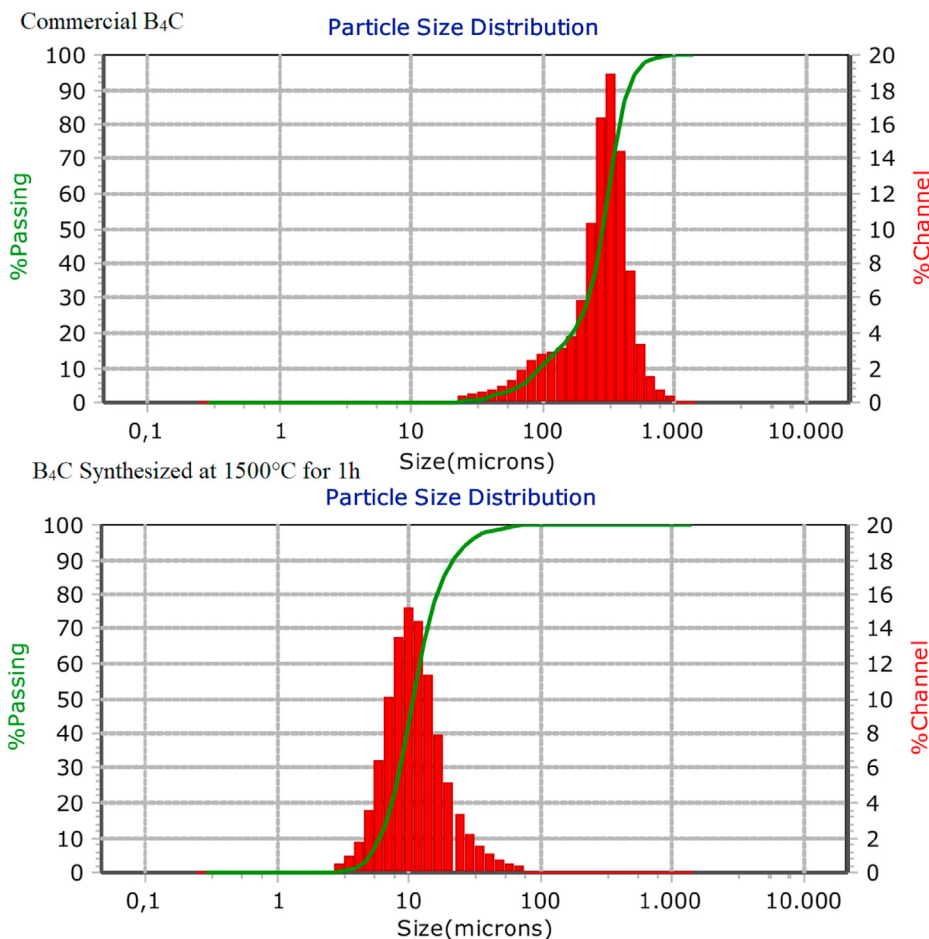
Fig. 11. Particle size distribution of:(a) B $_4$C synthesized at 1500 °C for 1 h at 4 rpm from R2 mixed at 4000 rpm, (b) Commercial B$_4$C used as nucleant.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https ://doi.org/10.1016/j.oceram.2021.100133.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] S. Gao, X. Li, S. Wang, P. Xing, J. kong, G. Yang, A low cost, low energy, environmentally friendly process for producing high-purity boron carbide, Ceram. Int. 45 (2019) 3101–3110.

[2] S.K. Vijaya, R. Krishnaprabhu, V. Chandramouli, S. Anthonysamya, Synthesis of nanocrystalline boron carbide by sucrose precursor methodoptimization of process conditions, Ceram. Int. 44 (2018) 4676–4684.

[3] S. Hayun, V. Paris, M.P. Dariel, N. Frage, E. Zaretzky, Static and dynamic mechanical properties of boron carbide processed by spark plasma sintering, J. Eur. Ceram. Soc. 29 (2009) 3395–3400.

[4] D.D. Radev, E. Ampaw, Classical and contemporary synthesis methods of boron carbide powders, C. R. Acad. Bulg. Sci. 68 (2015) 945–956.

[5] A.S. Ramos, P. Simone, E. Taguchi, C. Ramos, V.L. Arantes, S. Ribeiro, High-energy ball milling of powder B–C mixtures, Mater. Sci. Eng. 422 (2006) 184–188.

[6] F. Thevenot, Laboratory methods for the preparation of boron carbide, The Physics and Chemistry of Carbide, Nitride and Boride 185 (1990) 87–96.

[7] G. Sun, Y.W. Li, Q.K. Hu, Q.H. Wu, D.L. Yu, Non-stoichiometric boron carbide synthesized in moderate temperature conditions, Materials Science-Poland 27 (4/1) (2009) 1033–1039.

[8] Y. Gao, A. Etzold, T. Munhollon, W. Rafaniello, R. Haber, Processing factors influencing the free carbon contents in boron carbide powder by rapid carbothermal reduction, Diam. Relat. Mater. 61 (2016) 14–20.

[9] A.K. Suri, C. Subramanian, J.K. S, T.C. Murthy, Synthesis and consolidation of boron carbide: a review, Int. Mater. Rev. 55 (1) (2010) 4–40.

[10] Rafi-ud-din, G.H. Zahid, E. Ahmad, M. Maqbool, T. Subhani, W.A. Syed, S.Z. Hussain, Effect of cellulose-derived structural homogeneity of precursor, J. Inorg. Organomet. Polym. Mater. 25 (4) (2015) 995–999.

[11] A. Alizadeh, E. Taheri-Nassaj, N. Ehsani, Synthesis of boron carbide powder by a carbothermic reduction method, J. Eur. Ceram. Soc. 24 (2004) 3227–3234.

[12] G. Goller, C. Toy, A. Tekin, C. Gupta, The production of boron carbide by carbothermic reduction, High Temp. Mater. Process. 15 (1–2) (1996) 117–122.

[13] M.W. Chen, J.W. McCauley, J.C. LaSalvia, K.J. Hemker, Microstructural characterization of commercial hot-pressed boron carbide ceramics, J. Am. Ceram. Soc. 88 (7) (2005) 1935–1942.

[14] Z. Yıldızlı, «SYNTHESIZING TiB2, B4C and BN CERAMIC POWDERS USING DYNAMIC/THERMOCHEMICAL METHOD,» Masters Thesis, Sakarya University, 2019.

[15] A.O. Kurt, «A Production Method of High-Tech Ceramic Raw Materials in Atmosphere-Controlled Rotary Kiln», Patent: TR 2011 02804 B, Sakarya, Turkey, 2011.

[16] N. Canikoğlu, B. Özdemir, Y.Y. Özbek, A.O. Kurt, Synthesis of TiN powders using dynamic CRN method, SAU JOURNAL OF SCIENCE 22 (5) (2018) 1438–1443.

[17] A.O. Kurt, Y.G. Vardar, Synthesis of α-Si3N4 Ceramic Powders via Dynamic CRN, Afyon Kocatepe University JOURNAL OF SCIENCE, 2003, pp. 125–130.

[18] E.B. Türker, A.O. Kurt, TiN Powder Synthesis Using Dynamic CRN Method, Afyon Kocattape University FEMÜBİD, 2014, pp. 565–569, 14.

[19] B. Özdemir, Production of TiN and ZrN Powder by Dynamic Carbothermal Reduction Method, Sakarya University, 2018.

[20] P. Foroughi, Z. Cheng, Understanding the morphological variation in the formation of B4C via carbothermal reduction reaction, Ceram. Int. 42 (2016) 15189–15198.

[21] C.-H. Junga, M. Leeb, C. Kim, Preparation of carbon-free B4C powder from B2O3 oxide by carbothermal reduction process, Mater. Lett. 58 (2004) 609–614.

[22] B.Z. Dacic, V. Jokanovic, B. Jokanovic, M. Dramicanin, Thermodynamics of gas phase carbothermic reduction of boron-anhydride, J. Alloys Compd. 413 (2006) 198–205.