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Synthesis of boron carbide powder by a carbothermic reduction method

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Abstract

Carbothermic reduction process is an economic method to produce boron carbide powder. In the present article this method was utilized to produce a boron carbide powder using commercial purity raw materials. Boric acid as a source of boron, and carbon active and petroleum coke as reducing agents were used. Mixtures of boric acid and carbon bearing material with a particle size of less than 44 μm were placed in a graphite crucible and heated under a flow of argon atmosphere in a tube furnace to 1400–1550 °C for 1–5 h. This resulted in the formation of boron carbide powder with or without un-reacted starting raw materials. It was found that the optimum weight ratio of boric acid to carbon bearing material was 3.5 and 3.3 for petroleum coke and carbon active, respectively. Heat treatment of these blends at 1470 °C for 5 h resulted in the synthesis of boron carbide powders, which contained 0.82 and 0.59 weight percent free carbon, respectively.

Keywords: Boric acid; B_4C; Carbon active; Carbothermic reduction; Petroleum coke; Powder preparation

1. Introduction

Boron carbide has found many applications due to its extreme hardness, low density and good neutron absorption cross-section. It is used as an abrasive material in polishing and grinding media.[1] It is also well known as an ideal control and shielding material in nuclear industry.

Its extreme hardness and low density have been made it to be used in the development of lightweight armor ceramic composites.[2]

Its usage as sintered article is finding wide applications in sand blasting nozzles, ceramic bearing and wire drawing dies.[3] In the aerospace industry, boron carbide powder is finding use as a rocket propellant due to its capacity to generate an intense amount of heat when combined with oxygen.[4,5]

Boron carbide powder can be synthesized from elemental boron and carbon directly. The high cost of these elements has made this method economically unattractive.[6] Metallothermic and carbothermic processes, which are inexpensive, have been widely used to produce boron carbide powder. Boric acid (H_3BO_3) and boron oxide (B_2O_3) are inexpensive starting materials, which can be reduced by using carbon to produce boron carbide. The powder prepared by this method has morphology and surface characteristics suitable for hot pressing and hot isostatic pressing.[1,7]

The overall carbothermic reduction reaction can be presented as the following:

$$4\ H_3BO_3 + 7C = B_4C + 6\ CO + 6H_2O \qquad (1)$$

This reaction proceeds in three steps:

$$4\ H_3BO_3 = 2\ B_2O_3 + 6\ H_2O \qquad (2)$$

$$B_2O_3 + 3\ CO = 2B + 3CO_2 \qquad (3)$$

$$4\ B + C = B_4C \qquad (4)$$

The reduction of B_2O_3 with carbon monoxide, step 3, becomes thermodynamically feasible above 1400 °C.[1,8] The temperature is usually maintained beyond 2000 °C to enhance the rate of overall reaction. The quality of produced boron carbide is widely dependent upon the

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techniques used for the reduction. In the tube furnace, a boron carbide powder with less than 1 wt.% free carbon can be produced.[1]

In the present investigation, carbothermic method has been used to produce boron carbide powder from the commercial purity raw materials such as boric acid, carbon active and petroleum coke.

2. Experimental procedure

The materials used were boric acid, carbon active and petroleum coke. The first powder was used as a source of boron and the last two powders were used as reducing agents. The chemical analyses of powders used are given in Table 1. The particle size of all powders was less than 44 μm.

A number of powder mixtures were prepared from boric acid and a carbon bearing material with different ratios. Powder mixtures were mixed in a laboratory ball mill for 1 h. They were then formed into specimens with 20 mm diameter and 5 mm thickness by cold pressing under a pressure of 1000 kPa. The specimens were heated up to 1400–1550 °C with a heating rate of 100 °C/min in a tube furnace, held for 1–5 h, and finally cooled to room temperature with a rate of 5 °C/min. During heating and cooling of specimens, an argon gas flow was injected with a rate of 1 l/min into the furnace. The specifications of the processed powder specimens are given in Table 2. The powder specimens were first washed with hot water to remove any un-reacted B_2O_3. They were then washed by hot chloridric acid and caustic soda to remove metallic impurities and un-reacted oxides, respectively. They were then dried in a dryer at 110 °C.

Table 1
Chemical analysis of raw materials used

	Wt.% element										
Raw material	Al	Fe	Ca	Cu	As	Pb	Zn	C	S	N	Mg
Boric acid	0.4	0.03	0.01	0.01	–	–	–	–	–	–	–
Carbon active	–	0.05	–	–	0.0005	0.005	0.15	–	–	–	–
Petroleum coke	–	–	–	–	–	–	–	98.5	0.5	0.02	–

The powder products were characterized by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). They were also analyzed to determine boron and free carbon contents. Boron content was determined by using atomic absorption spectroscopy (AAS). The progressing of the overall reduction reaction in the specimens was determined by comparing the I_{B4C}/I_G ratio in all the specimens, where I_{B4C} and I_G denote the intensity of peak 100 of B_4C ($2\theta = 37.8$) and the intensity of peak 100 of graphite ($2\theta = 26.5$) respectively. It is obvious that the higher the I_{B4C}/I_G ratio, the higher the volume fraction of formed boron carbide and the lower the free carbon.

For determination of residual free carbon content two different methods were utilized. In the first method, an amount of boron carbide powder containing some free carbon was weighed and taken as W_1. It was then heated to 700 °C for 30 min in air. It was assumed that all free carbon and a part of boron carbide powder are oxidized during this heat treatment. So, the remaining

Table 2
Composition of powder mixtures, their processing conditions and analyses

Spec. no.	Type of carbon	H_3BO_3/C ratio	Temp. (°C)	Holding time (h)	Catalyst (wt.%)	I_{B4C}/I_G ratio[a]	Total boron (%)[b]	Free carbon(%) method I[e]	Free carbon(%) method II[f]
1	CA[c]	2.9	1470	5	–	12.1	69.2	3.1	–
2	CA	3.1	1470	5	–	14.5	73.4	2.2	–
3	CA	3.3	1470	5	–	25	76.8	0.59	0.8
4	CA	3.3	1470	5	1.5	29	77.1	0.47	0.62
5	CA	3.3	1470	1	–	12.9	73	–	–
6	CA	3.3	1470	2	–	15	74.2	–	–
7	CA	3.3	1400	1	–	–	–	–	–
8	CA	3.3	1550	1	–	23.2	76.5	0.73	0.9
9	PC[d]	3.3	1470	5	–	9.46	70.3	–	–
10	PC	3.5	1470	5	–	23.23	76.5	0.82	1
11	PC	3.5	1470	1	–	1.5	48.2	11.81	12.1
12	PC	3.5	1470	1	1.5	–	62	6.51	6.83
13	PC	3.5	1470	2	–	3.72	60.7	–	–
14	PC	3.5	1400	1	–	–	–	–	–
15	PC	3.5	1550	1	–	17.17	75.2	–	–

[a] Intensity ratio of peak 100 of B_4C ($2\theta = 37.8$) to peak 100 of graphite ($2\theta = 26.5$).

[b] Atomic Absorption Spectroscopy.

[c] Carbon active.

[d] Petroleum coke.

[e] Method I. The method used in the present study.

[f] Method II. The sulpho-chromic oxidation method.

powder, W_2, was washed with hot water to remove the oxidized part of boron carbide, namely B_2O_3. The resulting powder was then dried and weighed as W_3. The different $W_2-W_3=W_4$ yields the amount of B_2O_3 and therefore the oxidized boron carbide (W_5). The sum of $W_3+W_5=W_6$ gives total boron carbide and therefore the different $W_1-W_6=W_7$ yields the amount of residual free carbon.

In the other technique, sulphochromic oxidation method was used for determination of free carbon in the produced boron carbide.[9] In this method one gram of boron carbide powder was leached with 100 ml of sulphochromic solution (40 g $K_2Cr_2O_7$–900 ml H_2SO_4). The solution was agitated with a magnet to hold the temperature of 140 °C for 30 min. During this treatment, the free carbon is oxidized and removed from the solution, so that the remaining precipitation gives boron carbide.

The particle size distributions of the carbon active, petroleum coke and boron carbide powders were measured by the laser diffraction technique.

3. Results and discussion

The analysis of boron carbide powder produced in different conditions is given in Table 2. It may be seen from the data presented in this table that the products obtained by reaction between boric acid and carbon active with the ratios of 2.9 (specimen No. 1) and 3.1 (specimen No. 2) contained high levels of free carbon, whereas the stoichiometric ratio of H_3BO_3/C is 2.94 in the reaction 1. This may be due to the deficiency of boric acid caused by its volatilization during heating.[4,9] Therefore some excess of boric acid were added to both carbon active and petroleum coke in the mixtures. As can be seen from the data shown in Table 2 and Fig. 1 that the H_3BO_3/C ratio of 3.3 (specimen No. 3) was found to be optimum to yield the higher amount of boron carbide, when carbon active was used as reductant. According to Fig. 2 (a), (b) and Table 2 this ratio was found to be 3.5 (specimen No. 10) to produce the highest amount of boron carbide, when petroleum coke was used as reductant. Therefore, the required excess boric acid was lower when carbon active (12.24 wt.%) was used instead of petroleum coke (19.05 wt.%). This is because carbon active is oxidized at lower temperature due to its higher reactivity compared to petroleum coke. It should be mentioned that the carbon active is an amorphous form of carbon with a more fine particles, so it has a high tendency to react. Fig. 3(a), (b) show the particle size distribution of petroleum coke and carbon active respectively. It is shown that the carbon active powder is finer (<20 μm) than petroleum coke. Moreover, the particle size distribution of petroleum coke (<70 μm) is wider than that of carbon active (<40 μm).

It can be seen from the data shown in Table 2 and XRD patterns presented in Figs. 1, 2(a) and (b) that an increase in the H_3BO_3/C ratio resulted in decreasing free carbon and increasing boron and I_{B4C}/I_G ratio. According to the data presented in the Table 2 the

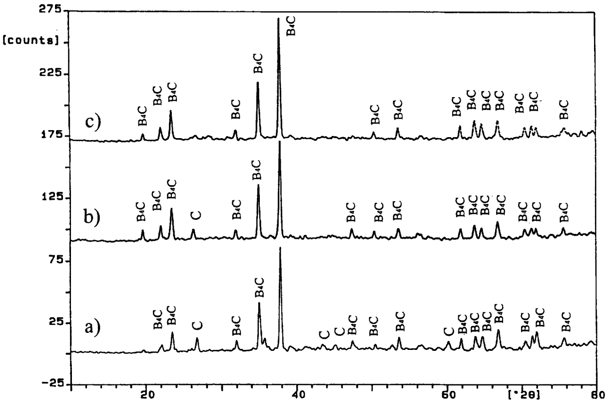


Fig. 1. XRD patterns of the boron carbide powder produced from the mixtures of (a) H_3BO_3/carbon active = 2.9 (specimen No. 1), (b) H_3BO_3/carbon active = 3.1 (specimen No. 2) and (c) H_3BO_3/carbon active = 3.3 (specimen No. 3) at a temperature of 1470 °C for 5 h.

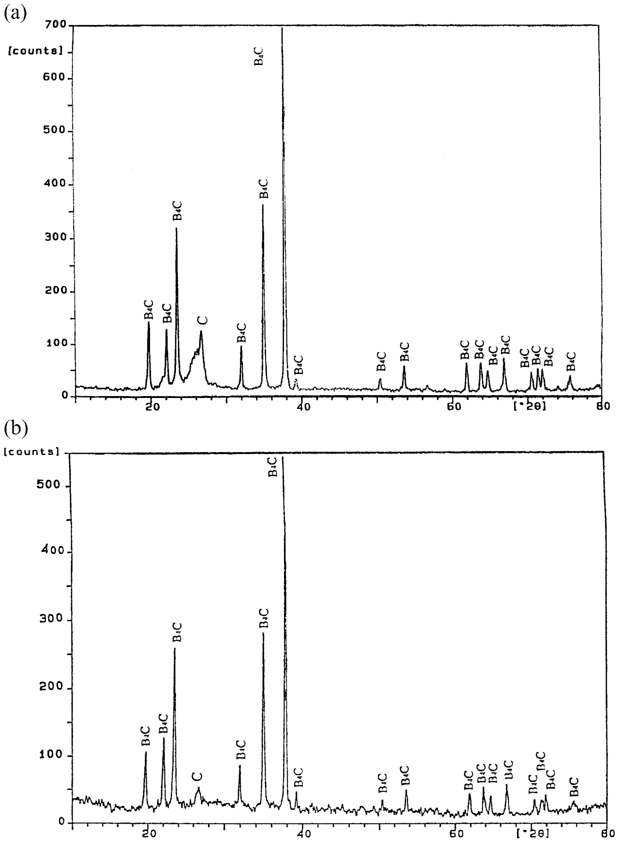


Fig. 2. XRD pattern of the boron carbide powder produced from the mixture of (a) H_3BO_3/petroleum coke = 3.3 (specimen No. 9) and (b) H_3BO_3/petroleum coke = 3.5 (specimen No. 10) at a temperature of 1470 °C for 5 h.

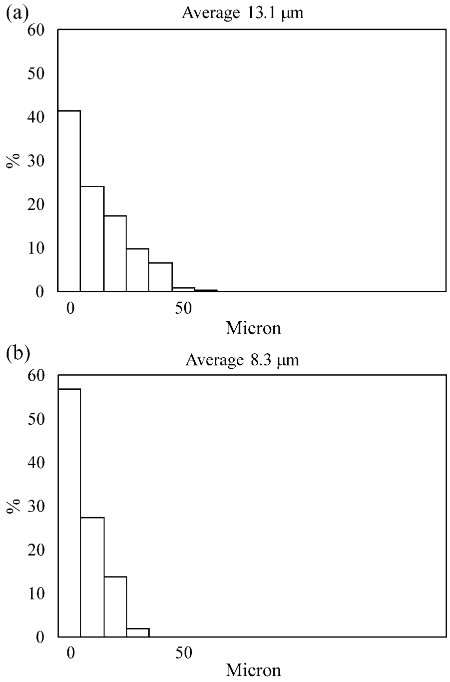


Fig. 3. The particle size distribution of (a) petroleum coke and (b) carbon active.

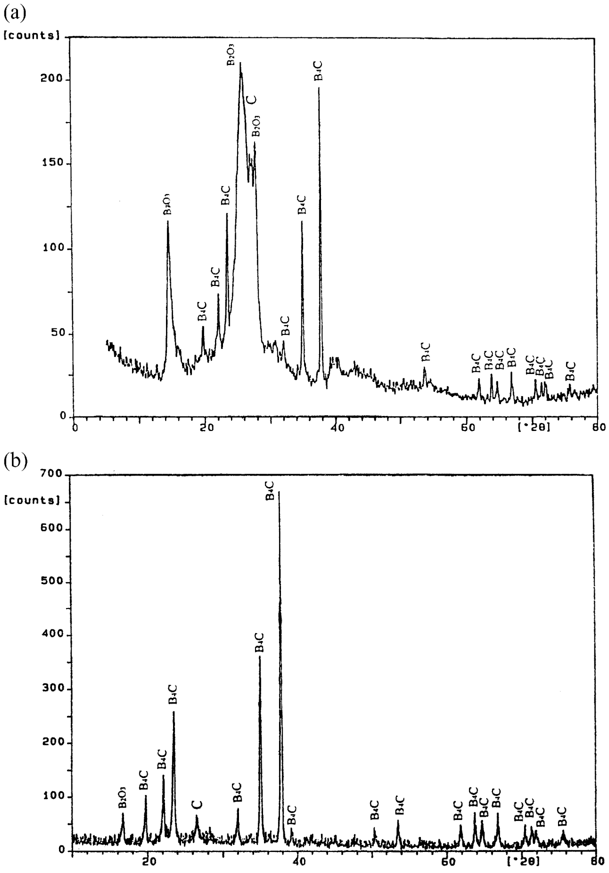


Fig. 4. XRD pattern of the powder containing boron carbide produced from the mixture of (a) H_3BO_3/petroleum coke = 3.5 (specimen No. 11) and (b) H_3BO_3/carbon active = 3.3 (specimen No. 5) at a temperature of 1470 °C for 1 h.

heating temperature and holding time were observed to have profound influence on the boron carbide formation. Increasing temperature and holding time resulted in an increase in boron and I_{B4C}/I_G ratio and a decrease in free carbon. This is due to obvious dependence of

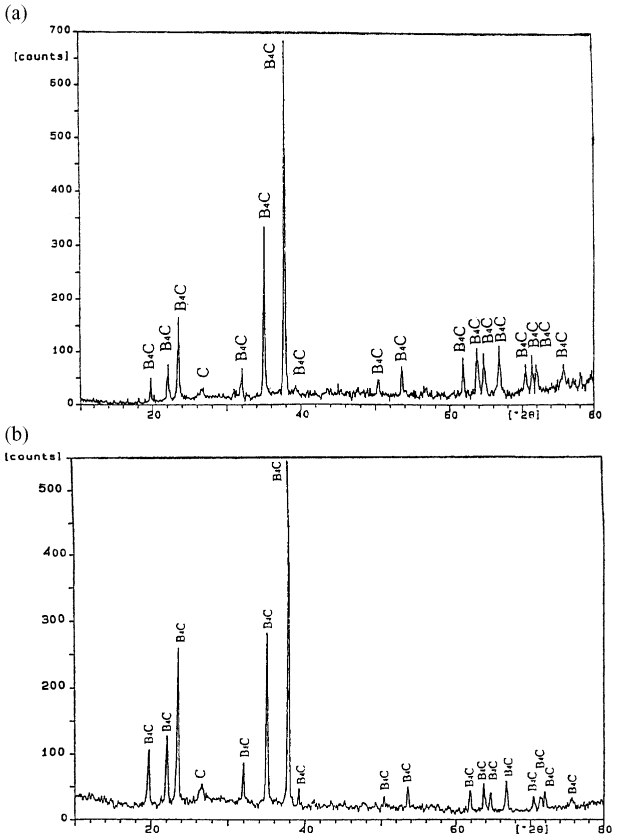


Fig. 5. XRD pattern of the boron carbide powder produced from the mixture of (a) H_3BO_3/carbon active = 3.3 (specimen No. 3) and (b) H_3BO_3/Petroleum coke = 3.5 (specimen No. 10) at a temperature of 1470 °C for 5 h.

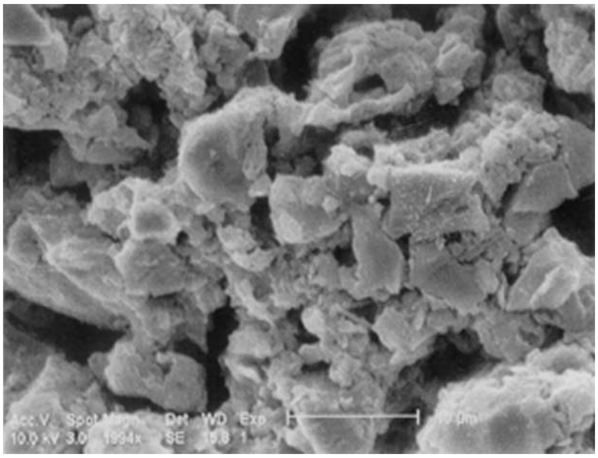


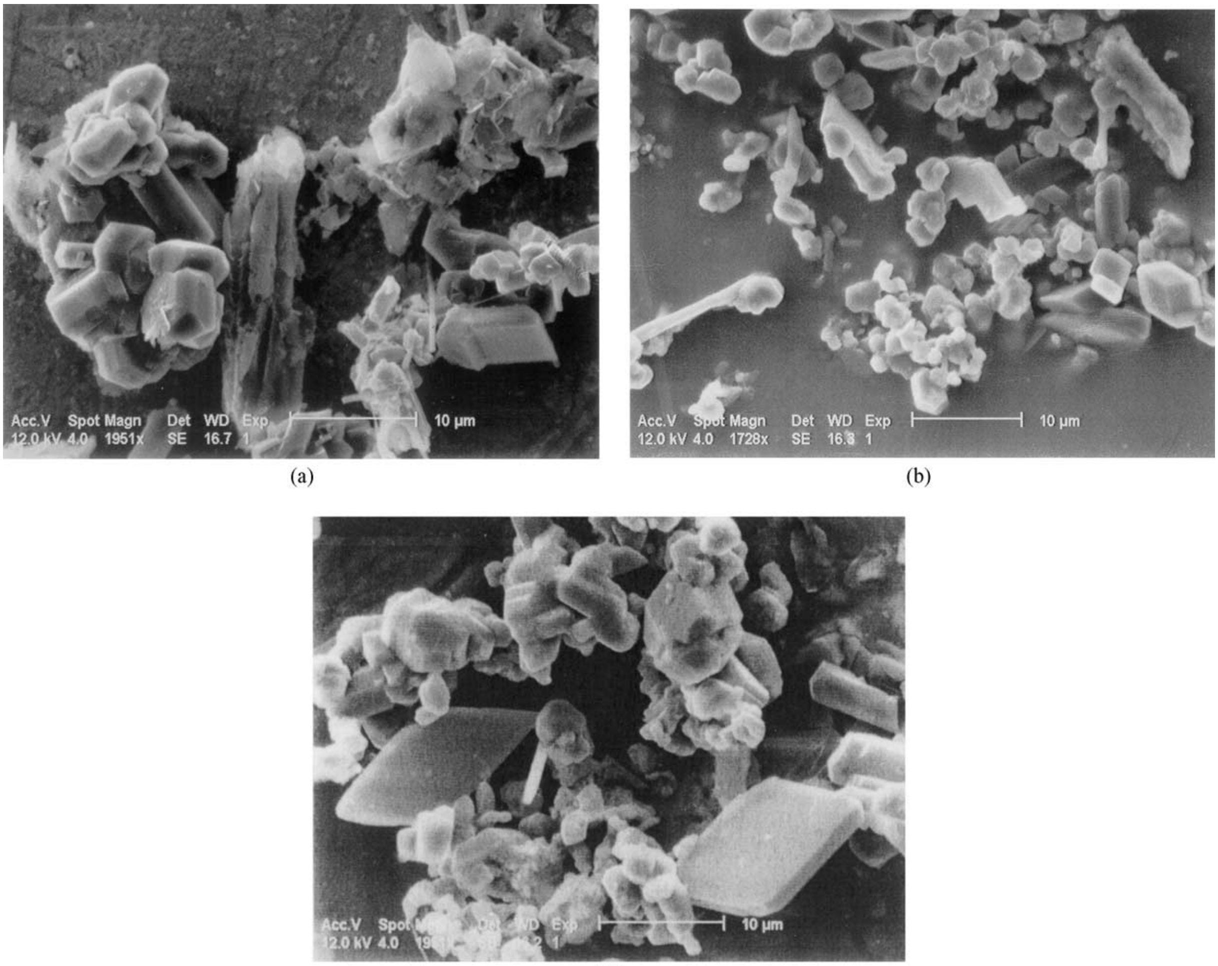
Fig. 6. Micrograph showing the morphology of the powder mixture of H_3BO_3/petroleum coke = 3.5 after a heat treatment in 1400 °C for 1 h (specimen No. 14). The boron carbide crystallites have not been formed.

reaction rate of boron carbide formation on both temperature and time. This result was also reported by Weimer et al.[10]

Fig. 4(a), (b) show XRD patterns of the powders containing boron carbide powder processed at a temperature of 1470 °C for 1 h from H_3BO_3/petroleum coke (specimen No. 11) and H_3BO_3/carbon active (specimen No. 5) mixtures, respectively. It can be seen that the powder processed from H_3BO_3/petroleum coke mixture contains more unreacted reactants compared to the powder processed from H_3BO_3/carbon active mixture. Furthermore, the I_{B4C}/I_G ratio and boron content were obtained 1.5 and 48.2 respectively for former mixture reactants, while these two contents were 12.9 and 73 respectively for the latter mixture reactants (see Table 2). This is maybe because carbon active has an amorphous structure and higher surface area than petroleum coke, namely it is highly reactive [see Fig. 3(a), (b)]. Therefore it may react with H_3BO_3 at lower temperature with a higher rate compared to petroleum coke to produce boron carbide. When holding time was increased to 5 h, the remaining un-reacted reactants mostly were disappeared in both cases (specimens No. 3 and No. 10) due to progressing the reaction [see Fig. 5(a), (b)]. This effect was also reported by Yoon et al.[11] who observed that the higher reactivity of carbon favoured the formation of boron carbide.

When processing temperature was decreased to 1400 °C no reaction took place among reactants to form boron carbide (see Table 2). This is also shown in Fig. 6 (specimen No. 14) in which no formed boron carbide crystallite is present.

Fig. 7(a) (specimen No 11) and 7(b) (specimen No. 10) show morphologies of powder products processed at 1470 °C from H_3BO_3/petroleum coke powder mixture for 1 and 5 h respectively. The morphology of this powder product is also shown in Fig 7(c) (specimen No. 15) when processing temperature is 1550 °C. It can be seen that the increasing both processing temperature and holding time resulted in decreasing the un-reacted raw materials and producing a powder product with a narrower particle size distribution. The latter result was



(a) (b)

(c)

Fig. 7. Micrograph showing the morphology of resulting powder containing boron carbide produced from the mixture of H_3BO_3/petroleum coke = 3.5 after a heat treatment in (a) 1470 °C for 1 h (specimen No. 11), b) 1470 °C for 5 h (specimen No. 10) and (c) 1550 °C for 1 h (specimen No 15). The formed boron carbide crystallites are shown in all figures.

also obtained when carbon active was used in the starting powder mixture instead of petroleum coke [see Fig. 8 for specimens No. 5, 3 and 8]. This effect was also reported by Weimer et al.[10] According to their explanation, reaction of carbon may occur with both liquid boron oxide and gaseous boron sub-oxide [$B_2O_{2\ (g)}$] to produce boron carbide. The rate of gaseous boron sub-oxide formation increases at higher temperature and with longer holding time. Thus the boron carbide formation reaction most likely occurs through gaseous boron sub-oxide. It means that at these conditions, reaction of gaseous boron sub-oxide may compete with direct reaction of liquid boron oxide with carbon.

Fig. 9(a) (specimen No. 3) and 9(b) (specimen No. 4) show XRD patterns of powder products processed at 1470 °C from H_3BO_3/carbon active powder mixture for 5 h without and with NaCl addition, respectively. The I_{B4C}/I_G ratio and free carbon (method I) were 25 and 0.59%, respectively, in the former specimen (No 3) whereas, these two contents were 29 and 0.47% in the latter specimen (No. 4). From these figs. and data presented in Table 2, it can be seen that the addition of NaCl into the powder reactants resulted in a decrease in un-reacted raw materials content and in an increase in formed boron carbide. It is believed that the NaCl acts as a catalyst and promotes the reaction by introducing micro-pores in the reactants powder mixture.[1] The same result was obtained when a mixture of H_3BO_3 and petroleum coke was used (see Table 2).

The stoichiometry of the processed boron carbide powders is highly variable (see Table 2). As previously disscused, it is influenced by the H_3BO_3/C ratio, surface area and reactivity of carbon bearing material and by processing temperature and holding time. Specimen No. 4 with 77.1 weight percent boron is the closest sample to the stoichiometric B_4C which contains 78.3 weight percent boron. This specimen has been made from a mixture of H_3BO_3 and carbon active powders with a ratio of 3.3 and 1.5 wt.% NaCl as a catalyst at a temperature of 1470 °C for 5 h.

Fig. 10(a) (specimen No. 8) and 10(b) (specimen No. 15) show particle size distributions of boron carbide powder processed at 1550 °C from the mixtures of H_3BO_3/carbon active and H_3BO_3/petroleum coke,

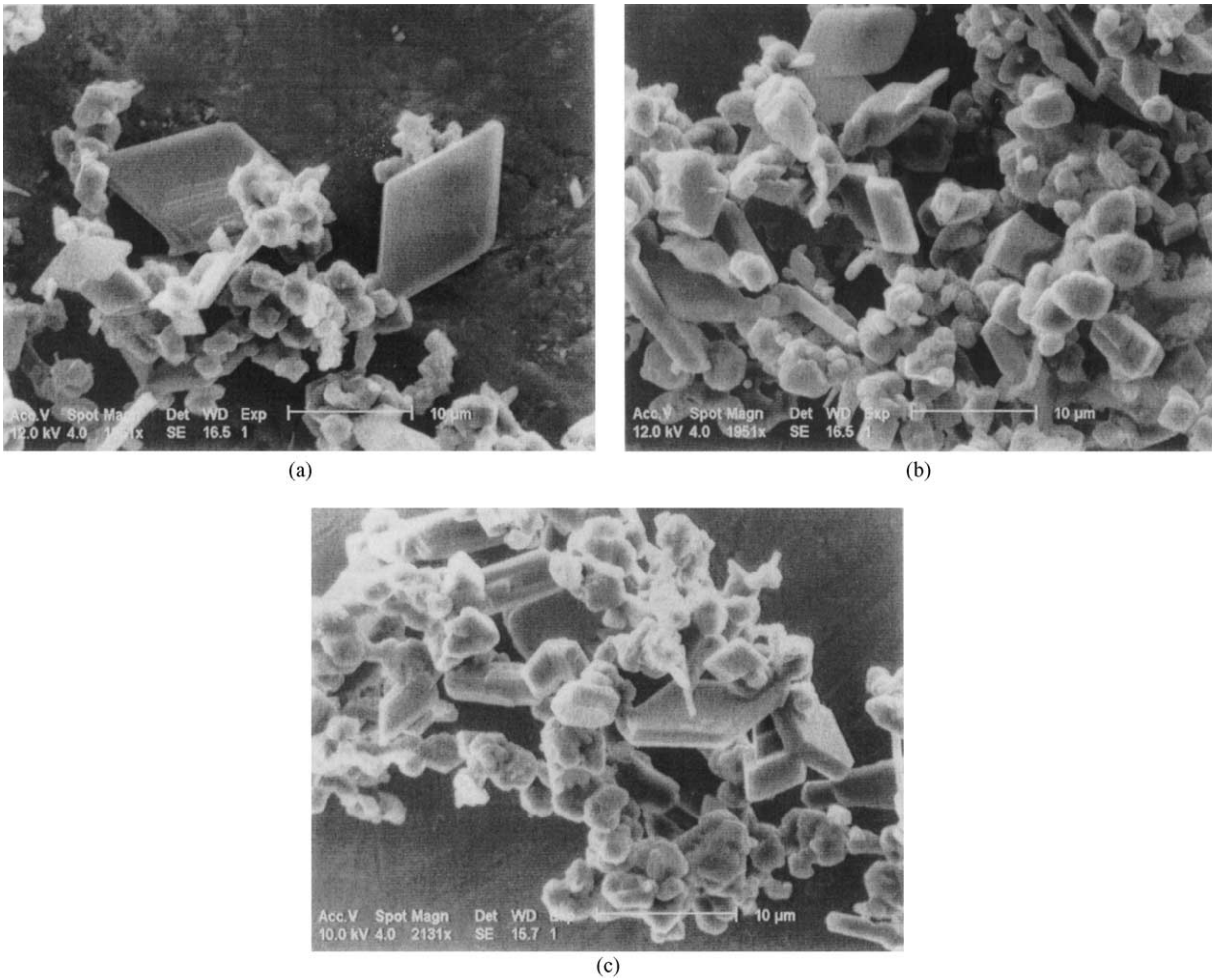


Fig. 8. Micrograph showing the morphology of boron carbide powder produced from the mixture of H_3BO_3/carbon active = 3.3 after a heat treatment in (a) 1470 °C for 1 h (specimen No. 5), (b) 1470 °C for 5 h (specimen No. 3) and (c) 1550 °C for 1 h (specimen No. 8).

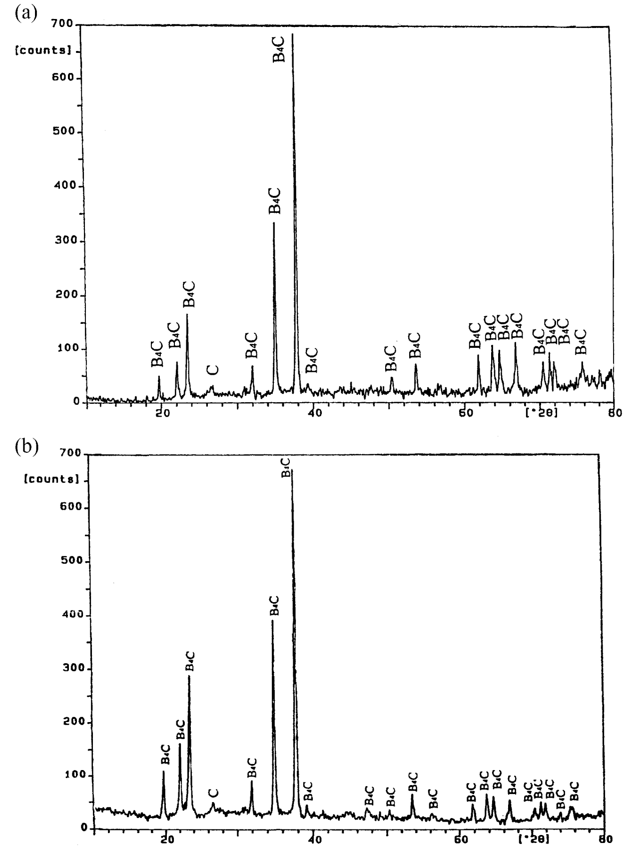


Fig. 9. XRD pattern of the boron carbide powder produced from the mixture of H_3BO_3/carbon active = 3.3 after a heat treatment in 1470 °C for 5h (a) without additive (specimen No. 3) and (b) with an additive of 1.5 weight percent NaCl (specimen No. 4).

respectively. As can be seen there are finer particles (<20 μm) in the latter specimen than in the former one. In addition, the particle size of carbon active powder was smaller than that of petroleum coke (Fig. 3). This finding is in agreement with Weimer et al.'s[10] result. It may be explained in terms of a reaction occuring between carbon active and boron oxide at a lower temperature than that between petroleum coke and boron oxide due to the higher surface area and reactivity of carbon active than those of petroleum coke. According to Weimer's explanation, limited nucleation of boron carbide occurs due to a reaction between carbon active and boron oxide at a lower temperature. The subsequent growth of those limited nuclei will result in the formation of large crystallites. Nevertheless, the effect of temperature on the size of crystallites is not yet fully understood.

4. Conclusions

A carbothermic method has been used to produce boron carbide powder from boric acid and carbon active or petroleum coke. The boron carbide powder was not formed from the mixture of reactants, when the processing temperature was as low as 1400 °C. Boric acid to carbon active ratio of 3.3 and boric acid to petroleum coke ratio of 3.5 were found to be the optimum ratios to yield boron carbide without free carbon. Increased temperature and holding time resulted in a narrower crystallite size distribution of formed boron carbide. The addition of NaCl (1.5 wt.%) into the mixture reactants promoted the reaction and resulted in an increase in the boron carbide content.

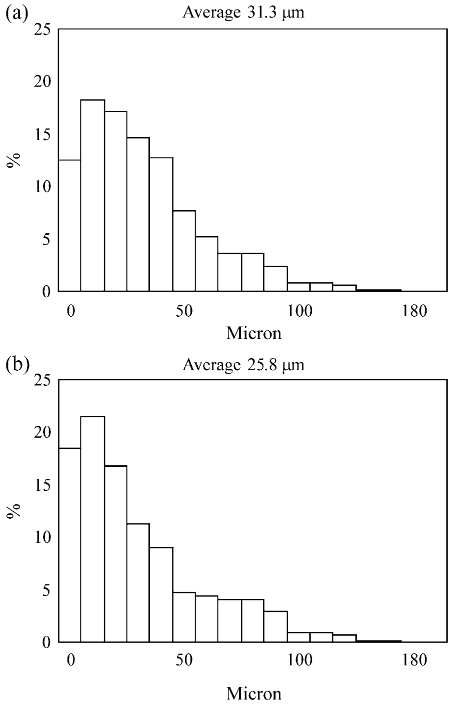


Fig. 10. The particle size distribution of boron carbide powder produced from the mixture of (a) H_3BO_3/carbon active = 3.3 (specimen No. 8) and (b) H_3BO_3/petroleum coke = 3.5 (specimen No. 15) after a heat treatment in 1550 °C for 1 h.

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