SYNTHESIS OF BORON CARBIDE NANO PARTICLES USING POLYVINYL ALCOHOL AND BORIC ACID

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In this study boron carbide nano particles were synthesized using polyvinyl alcohol and boric acid. First, initial samples with molar ratio of PVA : H_3BO_3 = 2.7:2.2 were prepared. Next, samples were pyrolyzed at 600, 700 and 800°C followed by heat treatment at 1400, 1500 and 1600°C. FTIR analysis was implemented before and after pyrolysis in order to study the reaction pathway. XRD technique was used to study the composition of produced specimens of boron carbide. Moreover, SEM and PSA analysis were also carried out to study the particle size and morphology of synthesized boron carbide. Finally, according to implemented tests and analyses, carbon-free boron carbide nano particles with an average size of 81 nm and mainly spherical morphology were successfully produced via this method.

INTRODUCTION

Boron carbide, after diamond and boron nitride is known as the third hardest composition found in earth's crust. Boron carbide and ceramic based composites with boron carbide as matrix phase, due to their high hardness, low density, high chemical stability and many other physical and chemical properties, are used in different industries especially those exposed to severely erosive conditions [1]. Because of its mechanical properties, boron carbide is a used for grinding and cutting tools. for its chemical stability it's used to produce containers for keeping acids and highly corrosive chemicals and it's also used in thermocouples functioning at temperatures as high as 2200°C [2-4]. There are several methods for producing boron carbide which some of those them are: carbothermal method using boric acid, reduction of boron chloride with the presence of carbon using hydrogen and laser at 1500°C, the magnesiothermal synthesis, direct synthesis from boron and carbon and Chemical Vapor Deposition (CVD) [5-7].

Nowadays, there is great interest among researchers to develop methods for synthesis of boron carbide using polymer precursors. These are some of the reasons that make this method noticeable: 1. optimizing the properties of produced ceramic by changing the composition of initial polymer precursor. 2. The ability to have final production in processed forms (like films and fibers). 3. The possibility of synthesizing the ceramic at lower temperatures [8]. In this study, boron carbide nano particles were synthesized using polyvinyl alcohol and boric acid which are relatively cheap and available and effects of synthesis and heat treatment temperature were also investigated.

EXPERIMENTAL

The raw materials that were used in this research were polyvinyl alcohol with polymerization degree of 500 and boric acid (99.5%) both purchased from Merck Company.

27 gr polyvinyl alcohol and 22 gr boric acid were separately dissolved in 80°C distilled water using a mechanical mixer in 500 ml vessels for 30 min. Next, both precursors were mixed together in a 1liter vessel for another 60 min at 80°C and a white gel appeared as the product of this procedure. The produced white gel was heated and dried at 120°C for 6 hrs. Then the fragile product was crushed and ground to powder.

In this stage, the obtained powder was pyrolyzed. For this purpose, samples were put in alumina crucibles and heated in a furnace to 600, 700 and 800°C and were kept at these temperatures for 150 min; a heating rate of 160°C per hour was applied during the process. Sample pyrolyzed at 800°C, was analyzed by FTIR before and after the process. Heat treatment was done at 1400, 1500 and 1600°C, for 90 min with an Ar flow of 200 ml/min and a heating rate of 10 °C/min.

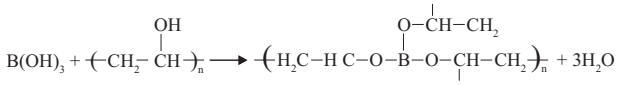
X-ray diffraction (XRD) analysis was applied in order to study the ultimate composition of produced boron carbide particles. Finally, for measuring the par-

ticle size and studying the morphology of produced articles, SEM (Philips: XL30, 20 kV) and PSA analyses were used.

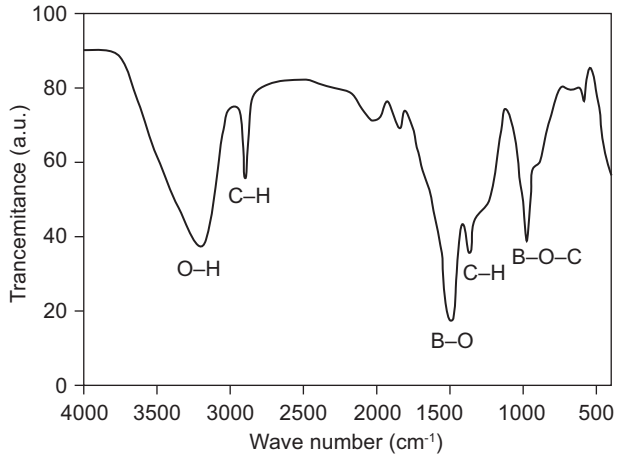
RESULTS AND DISCUSSION

Reaction pathway

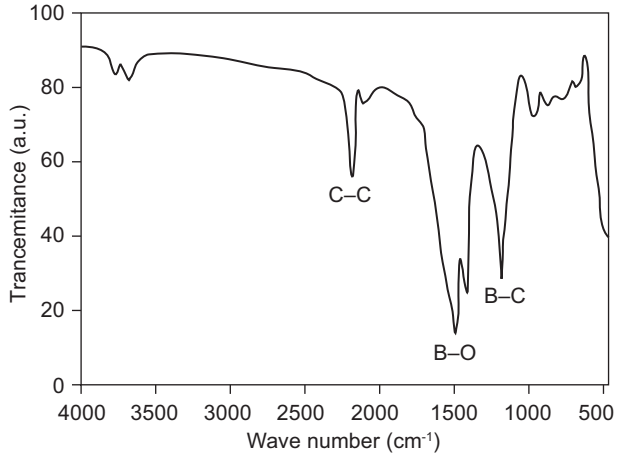
In order to study the reaction pathway, FTIR analysis of specimens was done before and after pyrolysis (at 800°C, for 150 min). According to previous studies [9], the expected reaction pathway is represented as following:



In Figure 1a,b FTIR analyses of the specimens before and after pyrolysis are shown. As it's illustrated in Figure 1-a, O–H, C–H, B–O, C–H and B–O–C bonds were detected in initial composition. The presence of B–O–C bonds indicates the occurrence of polyvinyl alcohol chain cross-linking with acid boric. Figure 1b shows that B–C, B–O and C–C bonds were formed after pyrolysis. Considering that boron carbide via conventional carbothermal method is synthesized at 1600°C and above [5], the presence of B–C bonds after pyrolysis at 800°C, indicates potential advantages of this methods for achieving final product at lower temperatures.



a) before pyrolysis

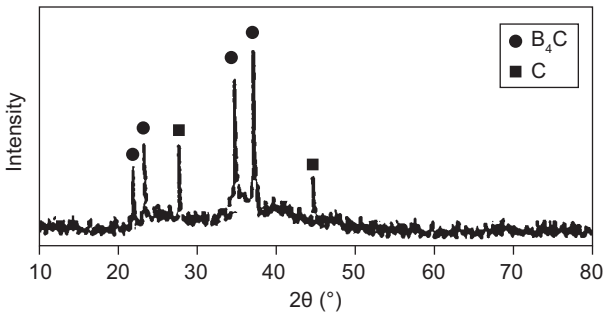


b) after pyrolysis

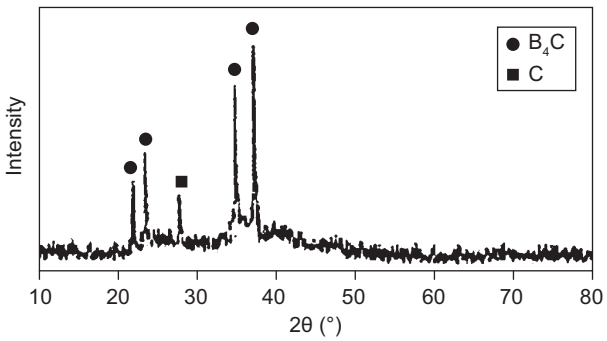
Figure 1. FTIR analysis of specimens at 800°C for 150 min (PVA : H_3BO_4 = 2.7 : 2.2)

The effect of pyrolysis temperature

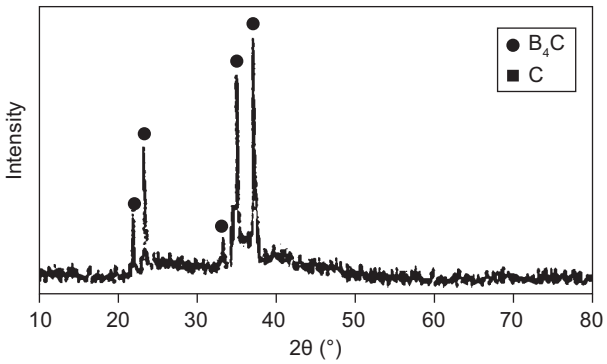
The result of powder X- ray diffraction analysis for specimens, which were pyrolyzed at 600, 700 and 800°C and then were exposed to heat treatment at 1600°C for 90 min are shown in Figure 2. As it can be seen in Figure 2, boron carbide could be successfully produced at all three



a) 600°C



b) 700°C



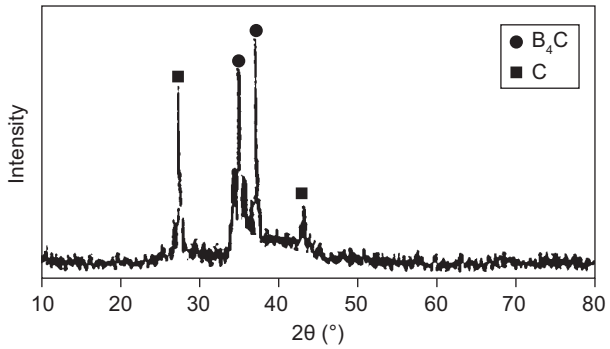
c) 800°C

Figure 2. XRD patterns of specimens pyrolyzed at 600, 700 and 800°C for 150 min and heat treated at 1600°C for 90 min (PVA : H_3BO_4 = 2.7 : 2.2)

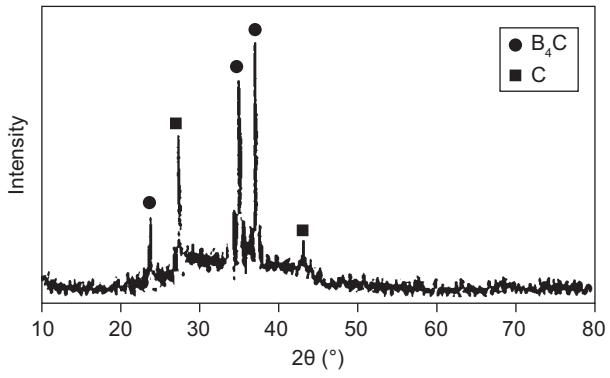
temperatures; however, the best results were achieved for samples pyrolyzed at 800°C. Some of the diffraction peaks in XRD pattern of specimens pyrolyzed at 600 and 700°C show the presence of carbon, but by increasing the pyrolysis temperature to 800°C, all peaks related to carbon were disappeared.

The effect of heat treatment temperature

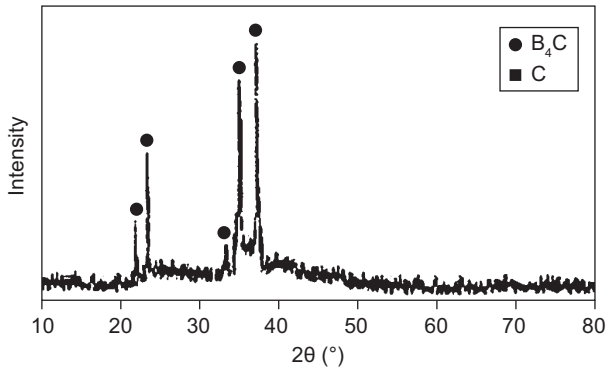
In Figure 3, XRD patterns of specimens which were first pyrolyzed at 800°C for 150 min and then heat treated at 1400, 1500 and 1600°C for 90 min, are shown. As it can be seen in Figure 3, traces of carbon were detected in specimens heat treated at 1400 and 1500°C, but by increasing the heat treatment temperature to 1600°C, only boron carbide picks are observed in XRD pattern.



a) 1400°C



b) 1500°C



c) 1600°C

Figure 3. XRD patterns of specimens pyrolyzed at 800°C for 150 min and heat treated at 1400, 1500 and 1600°C for 90 min (PVA : H_3BO_4 = 2.7 : 2.2)

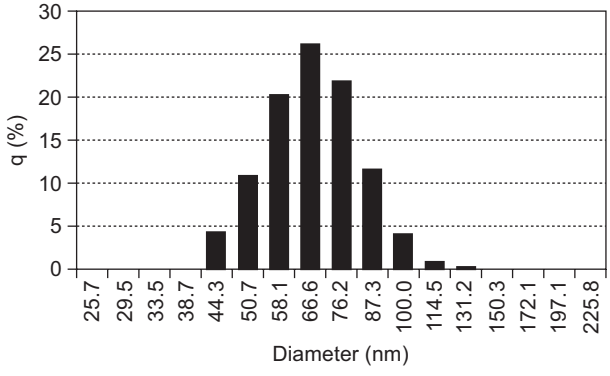
The industrial method for the production of boron carbide is carbon-thermal reduction of boric acid at a temperature over 2000°C [1]. In this study, carbon-free boron carbide could be achieved after heat treatment at 1600°C which is much lower and brings economical and technological advantages for this method. However, in a recent work, carbon-free boron carbide was produced after heat treatment at 1300°C for 5 hrs [10], but the process used in our study has two major advantages over that method run at 1300°C. Firstly, comparing the time of needed heat treatment, it is obvious that implemented method in current research is more economical. Secondly, the exposition to high temperature (1300°C) for 5 hrs, increases the ultimate particle size dramatically which is probably the reason that nano-sized boron carbide couldn't be achieved after 5 hrs of heat treatment while in this study nano-sized carbon-free boron carbide were successfully synthesized after 90 min of heat treatment at 1600°C.

Particle size and morphology

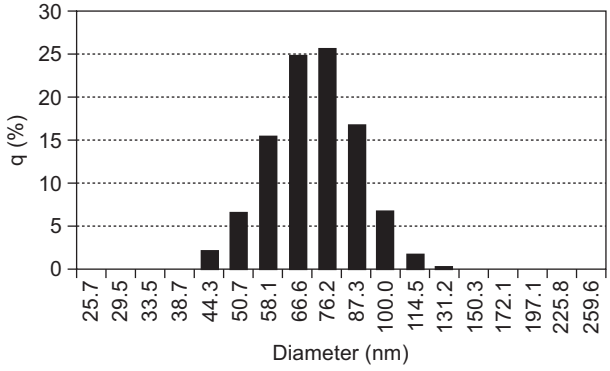
The heat treatment temperature is one of the factors that have a major effect on the ultimate particle size of produced boron carbide because all growth mechanisms that cause particle size increase, are activated and substantially dependent on temperature. However, achieving carbon-free boron carbide particles should be taken into account at the same time to choose the optimum temperature for the process.

In order to study the effect of heat treatment temperature on particle size, PSA analysis was carried out for samples of boron carbide which were heat treated at 1400, 1500 and 1600°C. The results of PSA analyses are illustrated in Figure 4. As it's shown in Figure 4, the average particle size of produced boron carbide constantly keeps growing by increasing the heat treatment temperature. It was measured 67 nm for samples heat treated at 1400°C, which increased to 71 and 81nm for samples heat treated at 1500 and 1600°C, respectively. Considering that carbon-free boron carbide was only achieved after heat treatment at 1600°C and the fact that 81nm as particle size is markedly fine, heat treatment at 1600°C is preferred for the optimum synthesis process.

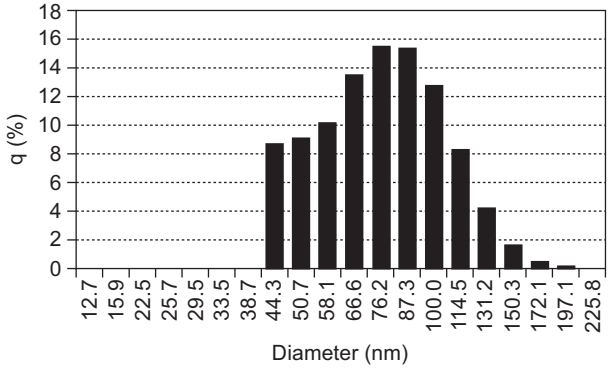
In Figure 5, SEM image of produced boron carbide nano particles which were synthesized after pyrolysis at 800°C for 150 min, followed by heat treatment at 1600°C for 90 min are shown. As it can be seen in images, produced boron carbide consists mainly of uniform ultrafine spherical particles, although rod-like particles are also rarely observed.



a) 1400°C



b) 1500°C



c) 1600°C

Figure 4. PSA graphs for boron carbide samples after heat treatment at 1400°C, 1500°C and 1600°C (PVA : H_3BO_4 = 2.7 : 2.2)

CONCLUSION

In this study, boron carbide nano particles were successfully synthesized using polyvinyl alcohol and boric acid. XRD analyses showed that boron carbide could be produced after pyrolysis at 600, 700 and 800°C for 150 min, followed by heat treatment at 1600°C for 90 min with Ar flow, but carbon- free boron carbide only could be achieved for samples pyrolyzed at 800°C. Studying XRD patterns of samples which were pyrolyzed at 800°C and heat treated at 1400, 1500 and 1600°C showed that production of carbon-free boron carbide in this method is achievable just by heat treatment at 1600°C and above. Finally, according to PSA and SEM tests carried out, produced carbon-free boron carbide after pyrolysis at 800°C for 150 min, followed by heat treatment at 1600°C for 90 min has the average size of 81 nm and the predominant morphology was spherical. However, rod-like particles were also rarely observed in SEM image.

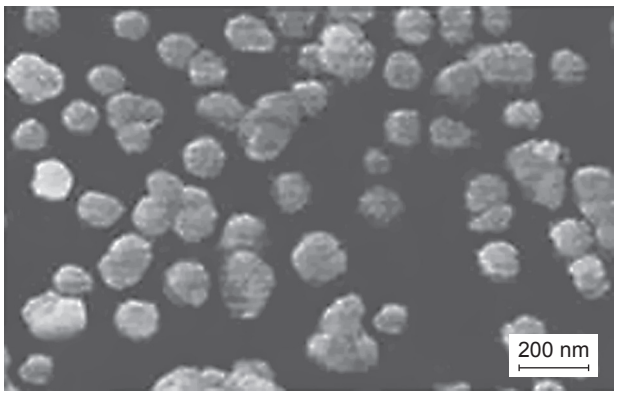


Figure 5. SEM image of synthesized boron carbide particles after pyrolysis at 800°C for 150 min, followed by heat treatment at 1600°C for 90 min.

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