

Investigation of the Role of Boron Carbide during Carbothermic Formation of Hexagonal Boron Nitride

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ABSTRACT: In a study conducted in our department aiming at carbothermic production of hexagonal boron nitride from boron oxide; boron carbide formation was observed in the experiments conducted above 1300°C for 2 hours. It was seen that the amount of boron carbide in the reaction products decreased by increasing temperature or duration of the experiment. The objective of this study is to investigate the formation and utilization of boron carbide during boron nitride formation by carbothermic reduction of boron oxide in nitrogen atmosphere. For this purpose, experiments were conducted with activated carbon-boron oxide pellets under flowing nitrogen and argon at 1500°C for 30, 60 and 120 minutes with excess amounts of boron oxide than the stoichiometric ratio. Reaction products were analyzed by XRD and SEM. Amounts of formed boron carbide and unreacted boron oxide in the reaction products were determined by volumetric analyses of boron.

1. INTRODUCTION

Hexagonal boron nitride is a white, talc like powder which has graphite like sheet structure, thus it is often called white graphite. The layers, composed of boron-nitrogen hexagons, are stacked one over another; the boron atom in one hexagon being immediately above a nitrogen in the layer beneath. The chemical bond between B and N atoms in a hexagon is covalent, but the bond between layers is van der Waals type. The space between hexagons, which is higher with respect to B-N interatomic distance, allows hexagons easily slide over each other and provides the lubricating nature of hexagonal boron nitride (Saito, 1987).

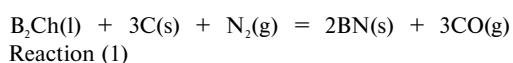
Boron nitride is stable in air up to 1000°C and up to 3000°C in nitrogen. Due to its lubricating property and high temperature stability, boron nitride is used in high temperature lubrication applications. It shows chemical inertness and corrosion resistance to molten metals combined with very good non-wettability against many metallic and silicate melts including Mg, Cu and their alloys as well as glass and slags. Thus, boron nitride is an ideal mold and

crucible material and also a mold release agent for many shaping processes. Because of excellent dielectric properties, BN is commonly used as an electrical insulator at both low and high frequencies. Adding boron nitride into plastics is a growing area. Boron nitride, when added into plastics, reduces friction, increases thermal conductivity, decreases thermal expansion and increases use temperatures, depending on the type of the plastic (Kempfer, 1990). Although h-BN powder is difficult to sinter, h-BN articles can be produced by hot pressing with additives. Hot pressed products can easily be machined with close tolerances at low costs by conventional shop tools (Haubner et. al., 2002).

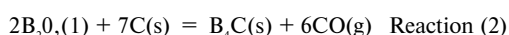
Due to these superior properties, a large amount of research has been conducted over the past few decades to produce boron nitride powders and shaped products. Principally, three methods are being used for producing h-BN on the industrial scale. One of these methods is the reaction of boric acid and ammonia in the presence of carrier substances (Popper, 1960). Another method is the reaction of boric acid with organic nitrogen

compounds such as melamine and urea (Parrish et. al., 1988; Babl et. al., 1969; Connor, 1966). These reactions take place at relatively low temperatures, about 1000°C; however produced BN needs to be heat treated under N₂ at 1500-2000°C for hexagonal boron nitride crystallization (Haubner, et. al., 2002).

Carbothermic formation of boron nitride, in which crystallized h-BN is produced, is the most commonly used industrial technique according to Roskill Information Services (Roskill, 2002). The carbothermic formation reaction of h-BN reaction takes place according to the following overall expression:

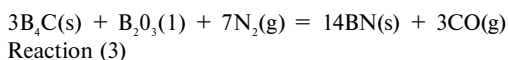


During carbothermic formation of h-BN, boron carbide formation, according to Reaction (2), is sometimes observed at temperatures over 1300°C; which is then consumed with increasing reaction temperature or duration (Aydoğdu, 2003).



Thermodynamic calculations show that boron carbide is not expected to be present in the system m flowing nitrogen (Aydoğdu, 2003). It was suggested that the formation of boron carbide takes place at points where nitrogen pressure is too low for boron nitride formation (Bartnitskaya et. al., 1990; Aydoğdu, 2003).

The reaction for the conversion of boron carbide into boron nitride proceeds according to the expression below:



The focus of this study is on the formation and utilization of boron carbide during carbothermic production of h-BN in flowing nitrogen. For this purpose, boron oxide-carbon compositions, with 100% and 150% excess boron oxide were reacted in nitrogen and argon atmospheres and reaction products were analyzed.

2. EXPERIMENTAL WORK

Experiments were performed in a vertical tube furnace which had an 800 mm long mullite tube with 50 mm inner and 60 mm outer diameters. The furnace was heated with SiC heating elements. A Pt-Pt13%Rh thermocouple was inserted into the furnace tube from the bottom side of the furnace.

The thermocouple was connected to a programmable temperature controller, which kept the furnace at the desired constant temperature. Boron oxide-activated carbon mixtures were prepared with 100% and 150% excess amounts of B₂O₃ according to Reaction (1). Cylindrical pellets having 11 mm diameter, 19 mm height and 2 grams of weight were compacted in a uniaxial die.

Experiments were conducted by placing the pellets into the hot zone of the preheated furnace in a graphite crucible having 20 mm inner and 26 mm outer diameters, inside of which was lined with h-BN. The crucible was kept in the hot zone of the furnace by hanging to an alumina bar. After holding the sample at the desired temperature for a predetermined duration, the crucible was quickly removed from the furnace.

Boron nitride formation experiments were conducted in nitrogen atmosphere and boron carbide experiments were done in argon atmosphere. The gas was supplied from the bottom end of the furnace. The graphite crucible in which the pellet was contained had 2-4 mm diameter holes at the bottom and on the sides, in order to provide nitrogen or argon gas entrance into the crucible and to remove the formed carbon monoxide from the vicinity of the pellet.

While the sample was being placed into the furnace, the gas flow rate was kept at 200 cc/min. Time was taken as zero when the system reached steady state at the desired temperature. During the experiments, the gas flow rate was maintained at 20 cc/min.

The constituents of the products were examined by X-ray diffraction (XRD) analysis. Morphology of the produced powder grains was examined by scanning electron microscope (SEM). The amounts of unreacted boron oxide and formed boron carbide were determined by volumetric analyses of boron.

3. RESULTS AND DISCUSSION

In the previous study, which was conducted in a horizontal tube furnace, 50% excess boron oxide was used (Aydoğdu, 2003). In this study, 100% excess boron oxide was decided to be used, taking the loss of boron oxide by vaporization into account in the vertical tube furnace set-up.

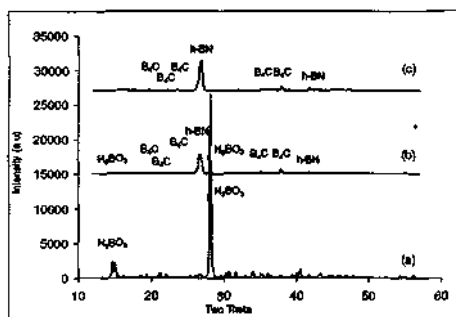


Figure 1. XRD patterns of the products of the experiments conducted for (a) 30, (b) 60 and (c) 120 minutes under nitrogen at 1500°C, in which 100% excess boron oxide was used.

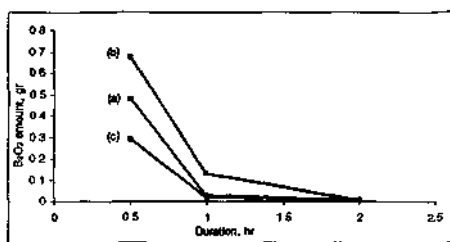


Figure 2. Variation of the amount of boron oxide with duration in the reaction products of the experiments conducted for 30, 60 120 minutes at 1500°C. (a) 100% excess B_2O_3 , reacted under nitrogen (b) 150% excess B_2O_3 , reacted under nitrogen, (c) 100% excess boron oxide, reacted under argon.

Formations of hexagonal boron nitride and boron carbide phases as well as consumption of boron oxide were followed by XRD analyses, which are given in Figure 1. It is seen from these XRD patterns that, the amount of boron oxide is decreasing with increasing duration and reaching zero in 2 hours; and the amount of hexagonal boron

nitride is increasing. Variation of the amount of boron oxide with duration in the reaction products, which was determined by volumetric methods, is given in Figure 2.

It is clear from Figure 1 that boron carbide phase forms in the system during carbothermic production of hexagonal boron nitride. Chemical analysis of the products was performed in order to reveal the variation of the amount of formed boron carbide with duration. From the results of these analyses given in Figure 3, it is seen that the amount of boron carbide increased in the first hour and then decreased in the experiments conducted with 100% excess boron oxide. A possible explanation to this situation may be that while boron carbide formation occurs in the system according to reaction (2), at the same time consumption of boron carbide takes place by reaction (3). When carbon amount in the system becomes low, boron carbide formation slows down; and the amount of boron carbide begins to decrease by reaction (3), as long as there is available boron oxide in the system. However, when there is no boron oxide left, reaction (3) can not take place and formed boron carbide remains in the system with boron nitride.

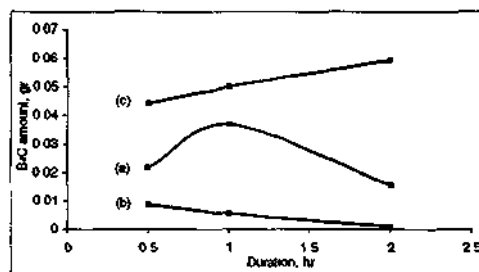


Figure 3. Variation of the amount of boron carbide with duration in the reaction products of the experiments conducted for 30, 60 120 minutes at 1500°C. (a) 100% excess B_2O_3 , reacted under nitrogen, (b) 150% excess B_2O_3 , reacted under nitrogen, (c) 100% excess boron oxide, reacted under argon.

SEM micrograph of a boron carbide rich region of the 100% excess boron oxide pellet reacted for 1 hour at 1500°C under nitrogen is given in Figure 4. It is seen that boron carbide particles have blocky and angular structure. Some grains have rhombohedral shape. Grain size is not uniform.

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There are grains in the range of 5-10 μ m; however, some grains are bigger than 10 μ m.

After seeing that boron carbide remained in the system when 100% excess boron oxide was used, 150% excess boron oxide was decided to be used. On the XRD patterns of the products of these experiments given in Figure 5, boron carbide peaks were hardly visible, the amount of which was determined by chemical analysis to be less than 1%. The amount of boron carbide in the products of the experiments conducted with 150% excess boron oxide was much less than the amount formed in the experiments with 100% excess boron oxide, as shown in Figure 3. These results indicate that the quantity of boron carbide in the reaction products decreases with increasing quantity of BaO₃ in the system. This may be taken as an indication that increasing B₂O₃ content in the system favors reactions (1) and (3) more than reaction (2).



Figure 4. SEM micrograph of a boron carbide rich part of product of the experiment conducted for 1 hour under nitrogen atmosphere at 1500°C, with 100% excess boron oxide.

When the experimental duration was 2 hours, h-BN grains seen in Figure 6 were obtained. XRD pattern of this sample is shown in Figure 5c indicates the presence of h-BN only. h-BN grains have plate like lamellar shape with grain size of about 1 μ m or less. The small grain size may be taken as an indication that 2 hours time is not enough at this temperature for the growth of h-BN grains.

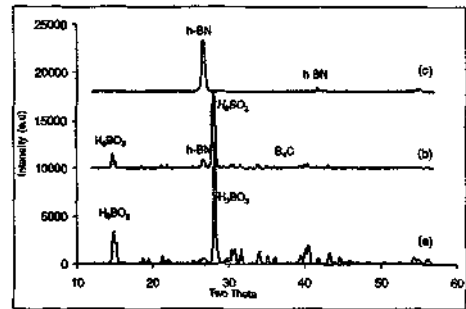


Figure 5. XRD patterns of the products of the experiments conducted for (a) 30, (b) 60 and (c) 120 minutes under nitrogen at 1500°C, in which 150% excess boron oxide was used.

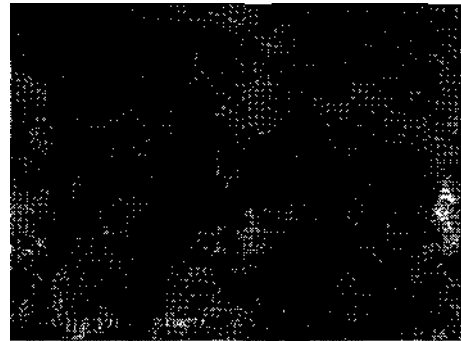


Figure 6. SEM micrograph of the product of the experiment conducted for 2 hour under nitrogen atmosphere at 1500°C, with 150% excess boron oxide.

To obtain additional information on the formation of boron carbide, experiments similar to those conducted under nitrogen were performed under argon atmosphere. Activated carbon-boron oxide pellets, identical to the ones used in the h-BN production experiments were prepared with 100% excess boron oxide and subjected to argon atmosphere at 1500°C for 30, 60, 120 minutes. Variation of the amounts of boron oxide and formed boron carbide in these experiments are presented in Figures 2 and 3, respectively. It can be seen that the amount of boron carbide formed under argon was not much higher than the amount formed in nitrogen atmosphere. This result may be taken as

an indication that boron carbide might be an intermediate product in the carbothermic production of h-BN, forming at regions where nitrogen pressure is too low for boron nitride formation. However, it can not be deduced from these data whether boron carbide is a necessary intermediate product for h-BN formation or not.

Formation of boron carbide was followed by XRD analysis, which is given in Figure 7. It is seen from the figure that the amount of boron carbide increases with increasing duration. h-BN peak observed in this figure is most probably due to h-BN contamination of the pellet from the h-BN lining of the graphite crucible, in which the experiment was performed. Fe_2O_3 contamination may have taken place during calcination of boric acid.

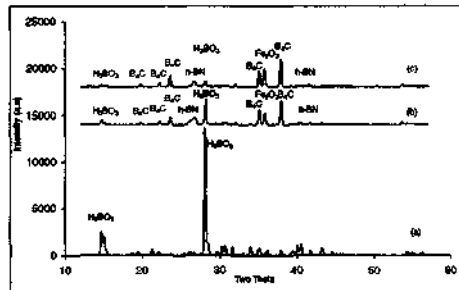


Figure 7. XRD patterns of the products of the experiments conducted for (a) 30, (b) 60 and (c) 120 minutes under argon at 1500°C, in which 100% excess boron oxide was used.

From the SEM micrograph in Figures 8, blocky and angular morphology of boron carbide grains formed under argon is observed. Some grains are in the range of 5-10 μ m while there are others larger than 10 μ m. Average grain size of boron carbide particles formed under argon atmosphere was similar to those formed under nitrogen during the production of h-BN.

To check the rate of transformation of boron carbide into h-BN according to reaction (3), a boron carbide-boron oxide pellet was prepared with 150% excess boron oxide according to reaction (3) and subjected to nitrogen atmosphere for 2 hours at 1500°C. Boron carbide used in this experiment was a commercial boron carbide powder, grain size of

which was <10 μ m, as indicated by the supplier. During the SEM analyses of the product of this experiment, small h-BN grains formed on B₄C grains were identified by energy dispersive analysis by X-ray (EDAX). However, it was observed in the SEM analyses that the amount of these h-BN particles was very little. This may be taken as an indication that conversion of B₄C into h-BN by reaction (3) is very slow as compared to reaction (1), which is in accord with the findings of Aydogdu (Aydogdu, 2003).



Figure 8. SEM micrograph of the product of the experiment conducted for 2 hours under argon atmosphere at 1500°C, with 100% excess boron oxide.

4. CONCLUSIONS

Formation of boron carbide during carbothermic production of h-BN was investigated within the scope of this study. Activated carbon-boron oxide mixture pellets with 100% and 150% excess boron oxide were subjected to nitrogen gas at 1500°C for 30, 60 and 120 minutes. It was observed in the reaction products of the experiments in which 100% excess boron oxide was used that boron carbide existed with h-BN and formed boron carbide was not completely converted into h-BN with increasing duration, since there was no boron oxide left in the system. However, increasing the amount of boron oxide in the starting mixture to 150% excess caused a decrease in the amount of boron carbide in the reaction products. This may be taken as an indication that increasing B₂O₃ content in the system favors reactions (1) and (3) more than reaction (2).

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From the results of the experiments conducted with 100% excess boron oxide under argon atmosphere, it was seen that the amount of boron carbide formed under argon was not much higher than the amount formed in nitrogen atmosphere. This result may be taken as an indication that boron carbide might be an intermediate product in the carbothermic production of h-BN, forming at regions where nitrogen pressure is too low for boron nitride formation. However, it is not clear whether boron carbide forming in the system is a necessary intermediate product for h-BN formation or not.

It was inferred from the results of the experiments conducted at 1500°C under nitrogen with boron carbide-boron oxide mixture pellet that conversion of B₄C into h-BN by reaction (3) is very slow as compared to reaction (1). Therefore, B₄C formation during carbothermic production of h-BN should be avoided in order to complete the h-BN formation reaction in shorter duration.

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