UNIVERSITY OF BIRMINGHAM

School of Metallurgy and Materials

MRes in the Science and Engineering of Materials

Paul Murray

[redacted]

Low Temperature Synthesis of Boron Carbide Using a Polymer Precursor Powder Route

September 2010 – September 2011

This report is submitted in fulfilment of the requirements for the degree of MRes in the Science and Engineering of Materials.

Acknowledgements

The University of Birmingham

Dr. Isaac Chang

Dr. Lucian Falticeanu

Synopsis

Boron carbide has a leading role in high performance applications due to its extreme hardness, low density, high melting point, high Young's modulus, great resistance to chemical agents, excellent thermoelastic and thermoelectric properties and high corrosion and oxidation resistance. Due to its excellent properties it has many high performance applications including; body and vehicle armour, abrasive powder, nuclear applications and aerospace applications.

Currently, boron carbide is commercially produced by a carbothermal reduction process. This involves the carbon reduction of boric acid by heating in an electric heating furnace. However, the process has many associated problems, including:

- Considerable amount of free carbon residue in the final product.

- Difficulty and expensive to grind the product to fine particle size for densification.
- Requires a high temperature furnace operation.
- Control of temperature above 2027 °C is not possible.
- Non-uniform heating in an electric arc furnace resulting in some unreacted products.
- Contamination in the final product.

As a result of the problems with commercially produced boron carbide, an alternative method is required.

This work assesses the possibility of using a polymeric precursor, polyvinylalcohol (PVA) and boric acid (H_3BO_3) as the starting materials to synthesise boron carbide powder with a stoichometry of B_4C and a small amount of free carbon. The process steps involve:

- Mixing PVA and boric acid in a dehydration condensation reaction to synthesise polyvinylborate (PVBO).
- PVBO is pyrolysed to carbonise the PVA and remove water from the boric acid to leave carbon and boron oxide, the elements required to process boron carbide.
- Pyrolysed sample is heat treated to synthesise boron carbide.

A combination of FTIR, TGA, XRD, Raman Spectroscopy and SEM has been used to characterise the PVBO, pyrolysed product and final heat treated product as a function of starting raw materials and processing conditions.

The optimum processing conditions found were to use a composition of 3.7 g PVA and 1 g H_3BO_3, and to pyrolyse at 600 ^{o}C for 2 hours at a heating rate of 10 ^{o}C min^{-1} under Ar flow. The pyrolysed sample was subsequently heat treated at 1400 ^{o}C for 5 hours at a heating rate of 10 ^{o}C min^{-1} under Ar flow. This produced B_4C powder with the smallest amount of residual carbon. The results achieved therefore offer a potential low temperature and low cost alternative to the commercially produced B_4C.

Contents

1. Introduction and Literature Review

1.1. Introduction to Boron Carbide

Boron Carbide is a low-atomic non-metallic material.[1] It is the third hardest material known to man after diamond and cubic boron nitride, with the advantages of being relatively easy to be synthesized and stable up to very high temperatures.[2] It is also the hardest material produced in tonnage quantities.[3] Boron carbide compound was discovered in the mid-19th century as a by-product in the production of metal borides; however its chemical formula was unknown.[4] In 1883, Joy identified the compound B_3C and in 1894, Moissan identified the compound B_6C. The commercially produced boron carbide of today (with a stoichiometric formula of B_4C) was not discovered until 1934.[5] Boron carbide has a leading role in materials suitable for high performance applications due to its attractive combination of properties. These properties include high hardness, low density, high melting point, high Young's Modulus,[6] great resistance to chemical agents, high neutron absorption cross-section,[5] high corrosion and oxidation resistance[6] and excellent thermoelastic and thermoelectric properties.[1] The physical and chemical properties of boron carbide are given in Table 1. [1,6,]

Property	Value (units)
Hardness	29.1 GPa
Density	2.52 gm cm^{-3}
Melting Point	2450°C
Young’s Modulus	448 GPa
Shear Modulus	180 GPa
Fracture Toughness	2.9 – 3.7 MPa $m^{1/2}$
Neutron Absorption Cross-Section	600 Barns

Table 1. Properties of Boron Carbide

1.2. Structure of Boron Carbide

Boron carbide is a compositionally disordered material with a rhomboheadral phase which can exist in a wide range of compositions. This extends from $B_{10.4}C$ (8.8 atomic % C) to B_4C (18.8 atomic % C).[7]The homogeneity range is shown in the B-C phase diagram presented in Figure 1.

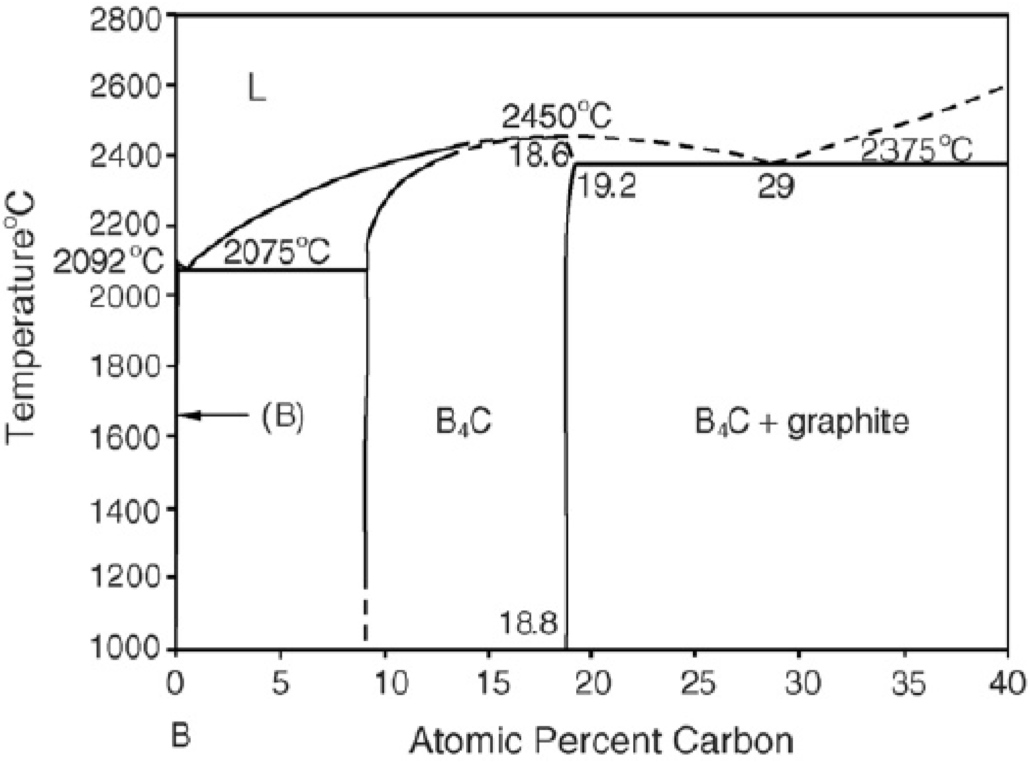


Figure 1. The Phase Diagram for the B-C System[7]

Boron carbide is established in the B-C system. Notations of boron carbide, such as B_4C, $B_{13}C_2$ and B_8 can be found. The stoichiometric B_4C is the most stable compound in B-C system and has superior properties, such as very high hardness and thermal conductivity. The reason for boron carbides excellent properties is due to its unique atomic structure. The most widely accepted structure of boron carbide consists of 12-atom icosahedra located at the corners of the unit cells.[7] This is shown in the schematic diagram in Figure 2.

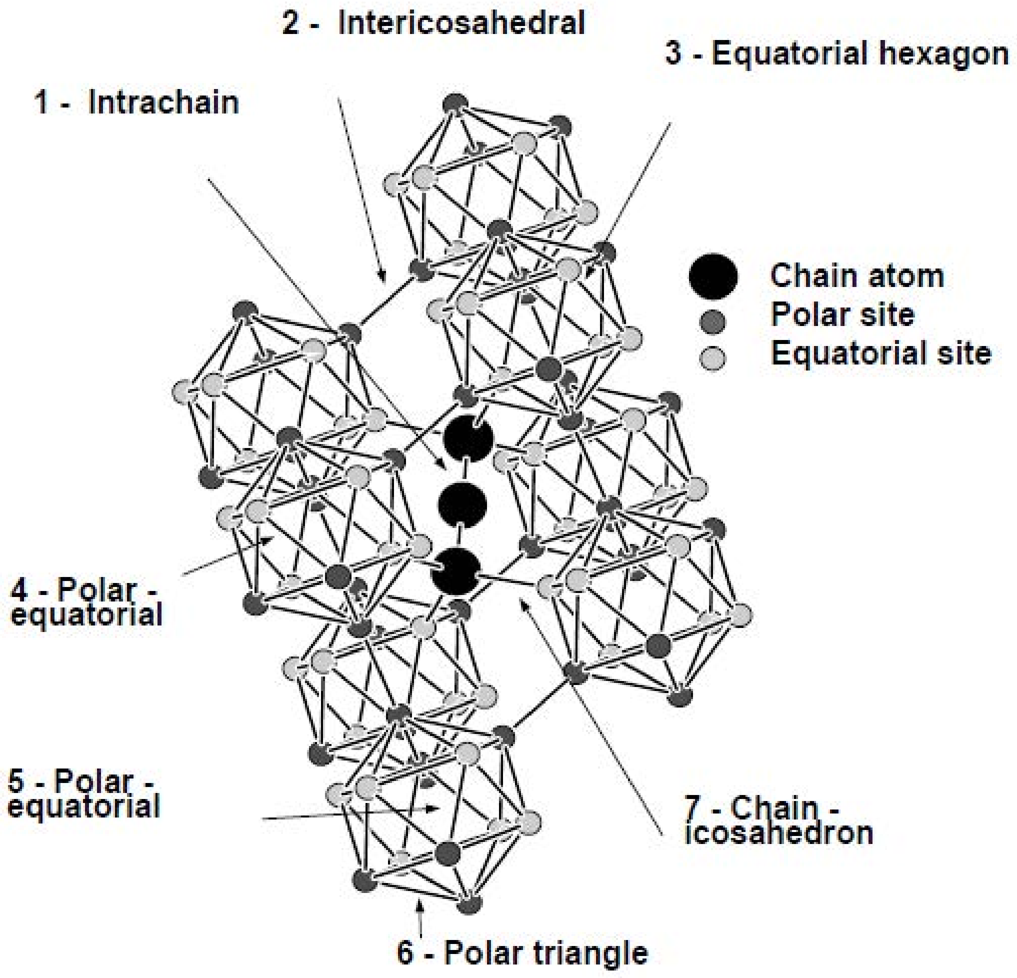


Figure 2. Schematic diagram of the structure of boron carbide Rhombohedral unit cell.[2]

The icosahedra generally consists of 11 boron atoms and 1 carbon atom ($B_{11}C$).[2] 6 atoms form the top and bottom triangular face of the icosahedra which sit at the polar sites and are directly linked to atoms in a neighbouring icosahedra via strong two-centre bonds along the cell edges.[7] The other six atoms form a hexagon in the plane perpendicular to the axis, known as the equatorial sites.[2] The atoms in the equatorial sites bond directly to other icosahedra by either three-centre bonds or to chain structures.[7] The majority of icosahedra have a $B_{11}C$ structure with the C atom placed in a polar site. However a few have a $B_{12}C$ structure or $B_{10}C_2$ structure with the two C atoms placed in two antipodal polar sites.[8]

The longest diagonal of the rhomohedral unit cell consists of a three-atom linear chain. Each end member of the chain is bonded covalently to an atom of three different icosahedra.[7] There is compositional disorder as carbon atoms replace boron atoms at a number of locations in the structure, including various icosahedral sites as well as within the three-atom intericosahedral chain.[9] There are three types of three-atom chains. These include: C-B-C, C-B-B and B-B-B. The most widely accepted and most stable structural model for Boron Carbide has $B_{11}C$ icosahedra that consist of C-B-C intericosahedral chains with 20 atomic % C.[10] The carbon-boron bonds in this three-atom chain are very strong.

Boron carbide structures can accommodate a large variation in carbon concentration without phase separation or interstitial occupancies.[11] However, if the carbon concentration is varied it will cause a change in the distribution of the atom chains.[10] A reduction in carbon concentration will cause C-B-C chains to progressively be replaced by C-B-B chains and form the composition $B_{13}C_2$. If the carbon concentration is lowered further the C-B-B chains are replaced by B-B-B chains and B_{12} icosahedra is formed.[10] This can also occur if the boron carbide becomes rich in boron. The carbon-boron bonds present in the three-atom chain are much stronger than boron-boron bonds in icosahedra.[12]

1.3. Application of Boron Carbide

Boron carbide is a suitable material for many high performance applications. Its outstanding hardness makes it a suitable abrasive powder. The particle sizes ranging from 1 µm to 10 mm means it can be used for polishing, lapping and grinding media for hard materials such as cemented carbides and technical ceramics.[5] In sintered form, boron carbide is also used as blasting nozzles, ceramic bearings and wire drawing dies due to its excellent wear resistance.[7]

Fully dense boron carbide is suitable for body and vehicle armour to protect against projectiles and ballistic threats. This can be used for helicopters or breast plates for a person's protection. This is due to its high hardness as well as its high impact resistance and low specific weight. [5] Fully dense boron carbide also has a high elastic limit which is referred to as the Hugoniot Elastic Limit (HEL). This is the maximum principle stress component under one-dimensional strain at a strain rate of approximately $10^5 s^{-1}$.[13]

Table 2 shows a comparison of physical properties between boron carbide and other ceramic materials that have been commercially produced and researched for use as armour applications.[13]

Material	Density (Kg/m^3)	Compressive Strength (GPa)	Hugoniot Elastic Limit (HEL) (GPa)	Young's Modulus (GPa)
Boron Carbide	2500	1.3	15	448
Silicon Carbide	3000 – 3200	3.9	8	380 – 430
Titanium Diboride	4500	3.75	8.6 – 13.1	520 – 550
Aluminium Nitride	3200	3 - 4	9.2	320
Silicon Nitride	3150	2 - 3	12	269
Aluminium Oxide (high purity)	3900	2 - 3	8.4	340 – 370

Table 2. Physical Properties of ceramics that have been produced for armour application

The values shown in Table 2 demonstrate that boron carbide has the best overall properties in terms of hardness and lightness and therefore is favoured for ceramic plates protecting against projectiles.

Boron carbide can also be used as a coating for various materials for different applications. For example, a coating can be applied to tools and then used for cutting various alloys such as stainless steel, titanium alloys and aluminium alloys.[5] It can also be used as a coating to provide protection for the application. For example, thin films can be applied to ultra-high density disk drives[14] or plasma-sprayed boron carbide can be coated on different types of stainless steel (0.3-2.00 mm) as a first-wall protection to protect against repeated thermal shocks from destruction loads.[15]

Boron carbide is used in many nuclear applications. It is used as a control rod, shielding materials and neutron detectors in nuclear reactors due to its ability to absorb neutrons. This is a result of its high B content, good chemical inertness and high refractoriness.[5] Furthermore; it is used in nuclear fusion reactors due to its thermal conductivity and thermal shock resistance.[7]

There are also several aerospace applications that currently use boron carbide for its properties. For example, B_4C can replace Be/Be alloys due to its low density, high stiffness and low thermal expansion.[7]

Boron carbide is also used as a strengthening medium because of its high modulus to density ratio (1.8×10^7 m). For example, it is used as a filamentary material for reinforcement of plastic matrixes.[16] Finally, boron carbide is used in electron devices that can be operated at high temperatures. For example, it can be used as a thermoelastic device by using it as a p-type semiconductor.[17]

1.4. Synthesis of Boron Carbide

There are several different methods for producing boron carbide. These include:

- Carbothermic Reduction
- Synthesis from elements
- Magnesiothermic reduction
- Chemical Vapour Decomposition

- Synthesis from polymer precursors.

1.4.1. Carbothermic Reduction

Commercially produced boron carbide is synthesised using a carbothermal reduction process. This involves carbon reduction of the inexpensive starting material boric acid (H_3BO_3) by heating in an electric heating furnace.

The overall carbon reaction can be presented as the following:[18]

$$4H_3BO_3 + 7C \longrightarrow B_4C + 6CO + 6H_2O$$

The reaction proceeds in three steps

$$4H_3BO_3 \longrightarrow 2B_2O_3 + 6H_2O \qquad (1)$$

$$B_2O_3 + 3CO \longrightarrow 2B + 3CO \qquad (2)$$

$$B + C \longrightarrow B_4C \qquad (3)$$

During heating the boric acid is converted to boron oxide by releasing water.[7] In step 2, the reduction of B_2O_3 with carbon monoxide occurs. Alizadeh et al.[19] suggests that this becomes thermodynamically feasible above 1400°C.[19] The temperature of the furnace is usually maintained at >2000°C to increase the rate of the overall reaction. This process is highly endothermic.[7]

The carbothermic reduction process of boric acid can occur in two types of electric heating furnaces. One furnace that can be used is an electric arc furnace. In this process, boric acid and petroleum coke is melted at very high temperatures. This is followed by crushing the resultant product and mixing it with a similar quantity of boric acid, which is then remelted. The reaction and cool down takes place over a long period of time due to the slow rate of heat conduction that controls the process.[20] The sintered mass of product which is produced then requires physical size reduction in order to achieve fine particle size suitable for densification. It is important to achieve a fine particle size with a high surface/volume ratio as this can enhance sintering compared to coarse particles. This can be done by crushing and grinding. However due to the extreme hardness of boron carbide, the size reduction step is extremely difficult and expensive and results in contamination of the product.[21]

The second type of furnace is the Acheson type furnace. This uses a graphite rod as the heating element. Partially reacted charge (boric acid and carbon) from a previous run is added around the graphite heating rod. On top of this, the new charge mixture of boric acid and carbon is added.[7] The furnace is then heated causing a reaction near the graphite rod and carbon dioxide to escape through the charge above. As the reaction continues, the charge is heated by conduction as well as by the heat of the escaping CO.[7] The process begins with boric acid (H_3BO_3) losing its water content and converting to boron oxide (B_2O_3). With further heating the B_2O_3 melts and forms a glassy film preventing CO escaping from the reduction zone.[7] The gases from the product form bubbles which increase in size as the pressure rises and consequently burst, causing some of the partially reacted charge to be ejected from the furnace and boron to escape in the form of boron oxide vapours into the atmosphere.[7] Following completion of the process, the top is broken open and the boron carbide surrounding the graphite rod is manually collected. The boron carbide is then crushed into a finer size, which is washed in water and leached in acid to remove contaminations.[7] In each run only a small amount of the charge is converted to carbide and the remainder is recycled in further runs.[7] Therefore, in this process conversion in each turn is low and the loss of boron is high. This process however is used for commercial production because of the cheap starting materials.

The electric arc furnace and the Acheson furnace processes have very similar reaction sequences. In these carbothermic reduction processes, petroleum coke or graphite can be used as reducing agents. Temperature and heat transfer are very important parameters in the formation of boron carbide. By influencing these parameters, the process can be improved by increasing the product quality and conversion efficiency. The formation of boron carbide is also highly dependent on phase changes of the reactant from solid to liquid to gaseous boron oxide as well as the heating rate and ultimate temperature.[21] A slow heating rate (< 100 K s^{-1}) results in the formation of boron carbide by nucleation and growth, showing a reaction through liquid boron oxide. An intermediate heating rate (10^3 – 10^5 K s^{-1}) results in formation of large and small crystallites, showing the reaction of carbon with liquid boron oxide and gaseous boron suboxides. A rapid heating rate ($>10^5$ K s^{-1}) results in smaller crystallite sizes, indicating a reaction through gaseous boron suboxides. Therefore to produce fine boron carbide powders which are required for dense articles, a fast heating rate is required.[7]

The carbothermic reduction process is used for commercial powder production due to the simple equipment and the cheap raw materials required which makes it economical. The powder prepared by this method has morphology and surface characteristics that are suitable for hot pressing and hot isostatic pressing.[19]

1.4.1.1. Problems with Commercially Produced Boron Carbide

There have been many different methods for producing boron carbide due to problems encountered in the production of commercially processed B_4C. Complete reaction of carbon is very difficult because the reaction by-product, such as carbon monoxide carries volatile boric species away from the reaction site, breaking the stoichiometry. This results in the final boron carbide containing a considerable amount of free carbon residue, hence deterioration of the final properties.[27] Due to boron carbides extreme hardness it is also difficult and expensive to grind the product into particle sizes fine enough for densification.[21] This factor as well as the high temperature furnace operations make it a very high energy intensive approach. This results in high cost of powder and low production capacity.[22] Approximately only 500t of boron carbide is produced every year. This is very small in comparison to steel, which yielded approximately 127 million metric tons (mmt) in April 2011 according to the World Steel Association[23]. Thus due to the limited availability of the materials there is a high demand for it and naturally the price for boron carbide is higher than other materials. For example, typical armour grade B_4C powder costs approximately \$50/lb compared to its cheaper alternative sintered aluminium oxide at approximately \$15/lb.[23] The high price and low production capacity of boron carbide have resulted in the readily available steel and aluminium alternatives being more commonly used materials for vehicle and body armour.

Another major drawback of carbothermic reduction process is the control of temperature above 2027 °C is not possible. This leads to the vaporization of boron from the system affecting the B/C ratio. Therefore, more than 65 % of excess B_2O_3 is used to compensate for the loss of boron during the process.[24] Other issues which occur during the synthesis of commercially produced boron carbide powder include the non-uniform heating in the furnace. The central zone of the electric arc furnace reaches 2200 – 2500 °C and results in a B_4C composition. However the outer zones of the furnace are not as hot (1200 – 2200 °C) and results in unreacted products, which must be recycled.[5] The size reduction step also causes contamination with impurities.[21] As a result of these problems, several studies have investigated alternative methods for producing boron carbide powder.

Finally, the production of fully dense boron carbide needed for armour must undergo a hot pressing process. During this process hydrostatic pressure causes a decrease in stability of boron carbide, and segregated boron and graphite layers occur, which can accommodate between icosahedra.[25] Graphitic layers along intericosahedral voids correspond to slightly displaced B_{12} icosahedra.[25] B_{12} structure has B-C-C chains which are weaker chains than B-C-B chains resulting in a lower Hugoniot elastic limit (HEL). Therefore B-C-C chains are more likely to collapse under high impact, such as ballistic attack. It is required to minimise free carbon as it will reduce HEL and the chance of fracture through shear-induced amorphization.[25]

1.4.2. Synthesis from Elements

Boron carbide can be synthesised in many different methods. One method is to process it from elemental boron and carbon directly. This process begins by thoroughly mixing boron and carbon to form a uniform powder mixture. This is then pelletized and reacted at high temperature of >1500 °C in a vacuum or inert atmosphere.[7] The high temperature combined with a long holding time is required for complete conversion of the elements in B_4C. This is because the formation of a boron carbide layer causes further reaction to slow down due to slow diffusion of reacting species through this layer.[7] Boron carbide (B_4C) is then achieved by crushing and grinding the partially sintered pellet. In order to achieve high purity B_4C, high purity elemental boron is often used. This is produced by a fused salt electrolytic process.[26] This process has excellent control of purity and carbon content, and there is no loss of boron. However, due to the high cost of elemental boron this process is considered uneconomical. Consequently this process is only used for specialised applications such as, B^{10} enriched or very pure boron carbide. These compounds are used as neutron absorbers in the nuclear industry.

1.4.3. Magnesiothermic Reduction

Another alternative method for producing boron carbide is through reduction of boron oxide with magnesium metal.[21] This is known as a magnesiothermic reduction process.

This process can be presented as the following:[7]

$2B_2O_3 + 6Mg + C \longrightarrow B_4C + 6MgO$

The reaction proceeds in two steps

$$2B_2O_3 + 6Mg \longrightarrow 4B + 6MgO \qquad (1)$$

$$4B + C \longrightarrow B_4C \qquad (2)$$

Typically, the reactants (boron oxide, carbon and magnesium) are mixed and reacted by either heating to a sufficient temperature or through the use of electrical ignitors.[21] The thermite reaction is highly exothermic and self-propagating.[21] Due to the high vapour pressure of magnesium at the reaction temperature of >1000 °C, a cover gas such as argon is used.[7] This process can produce fine powders, however it is unsatisfactory for producing high purity powders because the powders are easily contaminated with residual magnesium .[21] The removal of these magnesium compounds is extremely difficult even after repeated digestions with hot acids.[27] This process will soon be obsolete for regular production of B_4C due to magnesium's high cost and impurities in the powder. [7]

1.4.4. Chemical Vapour Deposition

Due to the slow and non-uniform heating, chemical impurities, and subsequent processing complications of commercially produced boron carbide, there has been extensive research in producing high-purity, submicron size powders directly through vapour phase reactions. This process produces boron carbide by reacting carbon or hydrocarbons, using laser or plasma energy sources via chemical vapour deposition (CVD). The deposition is controlled by mass transfer and surface kinetics, which affects the stoichometry and the properties of the boron carbide phases grown.[7]

In laser CVD the energy of a laser beam is used to heat the surface of a substrate to the temperature needed for chemical vapour deposition. This results in deposits of boron carbide crystallites with high purity, high degree of crystallinity and good thermal stability. These attributes are a result of deposition occurring one atom at a time created by the focused laser spot.[7]

Plasma enhanced CVD provides a means for fabricating boron carbide thin films without the use of high temperatures (>1000 °C) and pressures (>50 Torr).[28] The process deposits thin films from a gas to a solid state on a substrate. This occurs after creation of plasma by radio frequency or dc discharge between two electrodes, the space between which is filled with reacting gases.[7] Different precursors such as BCl_3, BBr_3 and B_2H_6 have been used to grow boron carbides.[29]

Laser or plasma heating of reactant gases has several advantages. For example, the heating and cooling rates of the reactants are almost instantaneous, it has short and uniform reaction time (fractions of a second) with minimal exposure to high temperatures, and it produces submicron, uniform sized boron carbide.[21] However, while gas phase synthesised powders produce many of the desirable qualities, they are expensive to produce due to the high cost of processing equipment and gaseous raw materials (e.g. BCl_3). Care must also be taken when handling because the gases are hazardous. Using this process it is difficult to produce B_4C powder suitable for densification and large scale production.[7] Therefore, gas routes may not be practical for commercial use.[21]

1.4.5. Synthesis from Polymeric Precursors

A promising alternative to the high temperature reaction techniques for producing boron carbide powder is by using polymer precursors at lower temperatures. This process can be carried out in the temperature range 1000 to 1500 °C in a vacuum or inert atmosphere. Studies have researched several different types of polymer precursors because they have many advantages. For example, the use of polymer precursors will allow for precise control of ceramic composition, it can be formed into a desired shape and converted to a ceramic with possible retention of form, and it can undergo decomposition at lower temperatures allowing ceramic formation under milder conditions. These advantages all contribute to reducing costs.[30]

There have been several studies that have reported findings of producing boron carbide using polymeric precursors. Table 3 gives a comparison of these previous studies and their processing conditions and results.

Mirabelli et al.[31] reported a production route of B_4C using poly(vinylpentaborane) as a precursor. They found that 2 – ($H_2C = CH$) B_5H_8 will undergo thermal polymerization to vinylpentaborane oligomers, which can be converted to boron carbide when heated at 1000 °C for 8 hours in Ar flowing atmosphere. This produces B_4C with high ceramic yields under milder conditions than commercially produced boron carbide.[31] However, boranes are highly explosive and expensive starting materials making this process commercially unviable.[31]

Therefore researchers have studied the use of inexpensive, non-hazardous and readily available polymer precursors, which are used as a carbon source for the synthesis of boron carbide. In particular borate esters with B-O-C bonds of various polyols, such as glycerin[32] citric acid[6], cellulose[33], glucose[33] and polyvinylalcohol (PVA)[1] have recently been studied as promising precursors of B_4C powders.

Wada et al[1] reported boron carbide synthesis from boric acid and glycerin precursor by heating at a relatively low temperature of 1300°C for 4 hours. However, the product contained a large amount of residual carbon. This is a common disadvantage of boron carbide synthesis using organic precursors.[1] A study by Kakiage[31] overcame this problem by performing a pyrolysis process in air before the carbothermal reduction process. This study successfully synthesised crystalline B_4C powder without residual carbon by mixing equimolar amounts of boric acid and glycerine, which they then pyrolysed and heat treated at 1250 °C for 5 hours in an argon flow.[32]

Sinha et al[6] produced B_4C powder by a carbothermal process using boric acid and citric acid as raw materials. The starting materials form a stable gel under controlled pH condition when mixed. This gel was then pyrolysed under a vacuum at 700 °C, followed by heat treatment under vacuum at 1450 °C for 2 hours. A B_4C powder was produced comprising of equiaxial particles that show a narrow size distribution and a median particle size of 2.25 µm. However, this contained 11.1 wt% free carbon (graphite). This study also demonstrated that B_4C formation did not occur until heating the precursor powder to around 1050 °C.[6]

A study by Sudoh et al[32] reported B_4C microcrystals were synthesised from precursors composed of saccharides, such as glucose and cellulose, and boric acid at a relatively low temperature of 1500 – 1600 °C for 1 hour in an Ar flow. However, similarly to other studies using polymeric precursors there was a high amount of free carbon and residual boron oxide contained in the products.[33]

Finally, polyvinylalcohol (PVA) has been shown by Yanase et al.[1] to produce boron carbide when mixed with boric acid and prepared via carbothermic reduction process[1]. In this study, polyvinylborate (PVBO) was prepared by the condensation of PVA and boric acid, and used as a precursor for boron carbide. A PVA:H_3BO_3 molar ratio of 4.2:1 was used to prepare PVBO. PVA (2.47 g) was dissolved in 30 ml of distilled water by stirring and heating in a water bath at 80 °C. H_3BO_3 (0.795 g) was then dissolved in 30 ml of distilled water and added to the PVA solution under a hot condition with constant stirring. This formed a PVBO gel that was dried in an oven at 120 °C, followed by grinding into white PVBO powder. This powder was pyrolysed in air at 450 – 700 °C for 2 hours, and was then ground and heated at 1100 – 1300 °C for 5 hours at a heating rate of 10 °C/min in an Ar flow. The resulting product was characterised by powder x-ray diffraction (XRD). The results showed that pyrolysis at 600 °C for 2 hours resulted in the optimum C/B_2O_3 molar ratio of 3.3. Crystalline B_4C powder with minimal free carbon was then synthesized by heating the pyrolysed product at 1300 °C for 5 hours under Ar flow.[1]

Polymer Precursors	Study	Pyrolysis Temp (°C)	Heat Treatment Temp (°C)	Hold Time (hours)	Atmosphere	Final Product
Polvinylpentaborate	Mirabelli et al.	...	1000	8	Ar	Amorphous boron carbide
Boric acid and Glycerin	Wada et al.	...	1300	4	Ar	B_4C with large amount of residual carbon
Boric acid and Glycerin	Kakiage	550	1250	5	Ar	B_4C crystalline powder
Boric acid and Citric acid	Sinha et al.	700	1450	2	Vacuum	B_4C with 11.1 wt% free carbon
Boric acid and Glucose	Sudoh et al.	...	1500	1	Ar	B_4C with large amount of residual carbon and boron oxide
Boric acid and PVA	Yanase et al.	600	1300	5	Ar	B_4C with small amount of free carbon

Table 3. Comparison of boron carbide synthesis methods using polymer precursor

Limitations in commercially produced boron carbide has encouraged interest in the production of B_4C using a low cost, non-toxic and readily available polymer precursor through a pyrolysis and low temperature heat treatment route. Several studies have shown that crystalline boron carbide powder with a B_4C stoichometry can be produced in this process. However, a common problem found in these studies was a high amount of free carbon in the final product. Yanase et al[1] has shown the most promise in using polyvinylalcohol(PVA) and boric acid in producing B_4C at a low temperature with low free carbon.

An overview of the different processing routes of the production of boron carbide is shown in Table 4.

Production Method	Boron Source	Carbon Source	Advantages	Disadvantages
Carbothermic Reduction	• B_2O_3	• Petroleum coke • Graphite • Activated carbon	• Simple equipment • Cheap raw materials • Suitable for hot pressing	• High amount of free carbon • High loss of boron • Non-uniform heating • Requires subsequent grinding operations • Contamination during size reduction
Synthesis form Elements	• Boron	• Carbon	• No loss of boron • Good control of purity and carbon content	• Expensive starting materials
Magnesio-thermic Reduction	• B_2O_3	• Petroleum coke • Graphite • Activated carbon	• Produces fine powders	• Easily contaminated with residual magnesium • High cost of magnesium
Chemical Vapour Deposition	• BCl_3 • BB_{r3} • BI_3 • B_6H_6 • B_2O_3	• CH_4 • C_2H_4 • C_2H_6 • C_2H_2 • CCl_4	• High B_4C purity • High degree of crystallinity • Good thermal stability • Almost instantaneous heating and cooling rates • Short and uniform reaction time • Produces submicron uniform sized B_4C • Suitable for thin films, fibres, whiskers	• Expensive process • Not amenable for large scale production • Difficult to produce B_4C powder suitable for densification
Polymeric Precursors	• H_3BO_3 • B_2O_3 • Polyvinylpentaborane	• Glycerin • Citric acid • Cellulose • Glucose • PVA	• Precise control of ceramic composition • Low temperature process	• High amount of free carbon • Still in laboratory stage

Table 4. Comparison of boron carbide synthesis methods

1.5. Proposed Study

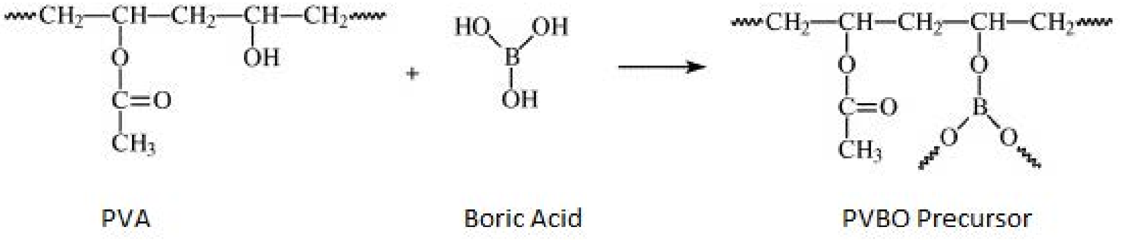
The aim of the proposed study is to achieve a low cost boron carbide powder with a stoichometry of B_4C with low free carbon. A study by Yanase et al.[1] achieved this by using polyvinylalcohol (PVA) and boric acid (H_3BO_3) as the starting materials. This is the only study to date that has achieved crystalline B_4C using PVA as a polymeric precursor and therefore this needs to be supported to increase the validity of the results.

There are several weaknesses of the study which need to be addressed and further investigated. This includes a lack of detail in the experimental method making it a difficult study to replicate. For example, the molecular weight of the starting materials is not provided, they do not provide an explanation as to why they used a PVA:H_3BO_3 molar ratio of 4.2:1, and no detail was given as to why the pyrolysis temperature range was 450 – 700 °C with a holding time of 2 hours. Similarly, details are not provided to why they used a temperature range of 1100 – 1300 °C with a holding time of 5 hours. The study focuses on the synthesis route of boron carbide powder and does not look at the structural changes occurring during pyrolysis. The relationship between the structural arrangement of the precursor and the lowering of the synthesis temperature of boron carbide powder has not yet been investigated.

Another weakness of the study is they do not replicate their findings. The results only show one XRD trace and therefore the findings lack validity. The XRD trace of their final product has a small carbon peak, which the study attributes to a small amount of residual carbon in the sample. To increase the validity of this result, the amount of free carbon needs to be measured.

The weaknesses of the Yanase et al.[1] study means that further investigation in the synthesis of boron carbide powder from PVA and boric acid is required. Therefore the proposed study will aim to replicate the Yanase el al.[1] study as well as increase the findings of PVA and boric acid synthesis route in creating boron carbide by investigating different variables in the synthesis route that have not been published before. This will include different molar ratios of PVA and boric acid, and how it affects the C/B_2O_3 ratio, and the structure of pyrolysed product. The study will also investigate the structural changes occurring during pyrolysis when heated at different temperatures and holding times. The relationship between the pyroslysis structure and the final boron carbide structure after heat treatment will be analysed. The temperature and holding time of the heat treatment process will also be varied to find the optimum conditions needed to achieve a crystalline boron carbide powder with a stoichometry of B_4C. If B_4C is achieved, the study will also measure the amount of free carbon in the final product with an aim of minimising it.

The proposed study will use polyvinylborate (PVBO) as the preceramic precursor. PVBO is formed in a condensation reaction from B-OH and PVA-OH units, from boric acid and PVA, respectively.[33] PVA is a water-soluble polymer with a hydroxyl group as a side chain and readily forms a B-O-C bond with $H_3BO_{3.}$[32] The reaction allows the introduction of boron atoms into an organic polymer, which acts as a means of crosslinking units. The synthesis reaction of PVBO and the idealised structure of PVBO is illustrated in Scheme 1.[33]



Scheme 1. Condensation reaction from PVA and boric acid forming PVBO[31]

A simple and cheap chemical route for the synthesis of PVBO is achieved by dissolving PVA and H_3BO_3 in hot water (above 80 °C), followed by blending the solution and drying until all water is evaporated.[1] FTIR analysis can be used to provide evidence of the formation of PVBO.

The PVBO will then be pyrolysed before the carbothermal reduction process. Pyrolysis is a thermochemical decomposition induced in organic materials through the absence of oxygen at elevated temperatures.[34] During the pyrolysis process previous studies[1, 6, 32] have shown that carbonization of PVA occurs while boric acid converts into B_2O_3. This results in a precursor consisting of carbon and B_2O_3, which are the elements needed to produce boron carbide. The pyrolysis process also removes residual carbon and any other unwanted components meaning that crystalline boron carbide can then be prepared with a small amount of free carbon at low temperatures.[33]

Following the pyrolysis of PVBO, synthesis of boron carbide is achieved in a carbothermal reduction process i.e. the reaction between carbon and B_2O_3.[34] The advantage of using B_2O_3 and carbon produced from pyrolysis of PVBO over the conventional method of mixing elemental boron and carbon is that it produces finer boron oxide which can be mixed intermittently with carbon. This results in the ability to produce a carbothermal reaction at lower temperatures. The overall carbothermic reduction reaction can be presented as the following:

$$2B_2O_3 + 7C = B_4C + 6CO$$[1]

This reaction shows that the optimum carbon to boron oxide (C/B_2O_3) molar ratio is 3.5. Therefore in order to determine the optimum amount of carbon in the pyrolysed PVBO precursor, the C/B_2O_3 can be calculated from weight of removed B_2O_3 and remaining carbon.[1] Boron oxide is soluble in hot water and therefore is easily removed by washing in hot water.[35]

Yanase et al.[1] showed that pyrolysed PVBO precursor with a C/B_2O_3 ratio of 3.3 can be heated at 1300 °C to form a boron carbide powder with a stoichiometry of B_4C, and a low amount of free carbon through a carbothermic reduction process.

1.6. Aim of Proposed Study

The aim of the study is to achieve a low cost boron carbide powder with a stoichiometry of B_4C and a small amount of free carbon. The low cost will come from using inexpensive polyvinylalcohol and boric acid as the starting materials. This study will also heat treat at lower temperatures compared to commercially produced boron carbide. To achieve B_4C powder, different molar ratios of PVA and boric acid will be pyrolysed at different temperatures and holding times. The C/B_2O_3 ratio will be calculated to find the optimum molar ratio. The pyrolsyed PVBO precursors will be heated to different temperatures at different holding times to achieve the optimum B_4C powder. Through varying the ratios of the starting materials and the environmental conditions by using previous studies as a starting reference, the aim is to achieve B_4C powder with little free carbon.

The study will investigate the structural changes occurring during pyrolysis when heated at different temperatures and times and the relationship between the pyrolysed structure and the final boron carbide structure after heat treatment.

2. Experimental Methods

2.1. Materials

Boric Acid (H_3BO_3) powder > 99.5 % hydrolysed and Poly(vinylalcohol) (PVA) powder 98% hydrolysed with typical Mw of 13,000 – 23,000 supplied by Sigma Aldrich was used in this study.

2.2. Materials Processing

2.2.1. Synthesis of Polyvinylborate (PVBO)

Poly(vinylborate) (PVBO) was prepared via a dehydration condensation reaction of PVA and H_3BO_3. PVA was dissolved in 30ml of distilled water by heating the water to 80°C using a hot plate and stirring continuously for 10 minutes. H_3BO_3 was also dissolved in 30ml of distilled water at 80 °C in the same process. The solutions were added together whilst continuously stirring to create a white PVBO gel. This gel was then dried in a box furnace at 100 °C until all water had been evaporated (approximately 1 hour). This was followed by grinding the white PVBO into powder using a pestle and mortar. Weight ratios of PVBO included:

- 3.1:1 (2.47 g PVA, 0.795 g H_3BO_3)[1]
- 1:1 (2 g PVA, 2 g H_3BO_3)
- 2:1 (4 g PVA, 2 g H_3BO_3)
- 3:1 (3 g PVA, 1 g H_3BO_3)
- 4:1 (4 g PVA, 1 g H_3BO_3).

The starting ratio of 3.1:1 was chosen based on previous literature[1.] The other ratios were chosen to gain a wide range of results after pyrolysis to see the effect it has on the structure of the precursor and find the optimum C/B_2O_3 molar ratio of 3.5. Following results found during the study, weight ratios of 3.3:1, 3.5:1 and 3.7:1 were pyrolysed and analysed to find the optimum C/B_2O_3.

2.2.2. Pyrolysing Poly(vinylborate) Powder Samples (PVBO)

The PVBO powders were placed in an alumina crucible and pyrolysed at 500, 600 and 700 °C for 1, 2 or 3 hours in an 'Elite Tube Furnace' (TSH16/2J/180) with a flowing argon atmosphere at a flow rate 4 LPM and a heating rate of 10 $°C\ min^{-1}$. This process was used to carbonize the PVA and remove water from boric acid. This left carbon and boron oxide, the elements required to process boron carbide. Pyrolysis also helped remove any residual carbon to minimise free carbon in the final product. The parameters were chosen based on previous literature[1] and on thermogravimetric analysis (TGA) of PVBO. The pyrolysis of PVBO left a black precursor that was ground into powder before heat treatment.

2.2.3. C/B_2O_3 ratio

Carbon to boron oxide (C/B_2O_3) molar ratio was calculated for each pyrolysed sample. To calculate the C/B_2O_3 ratio the mass of the sample was first weighed, followed by leaching out B_2O_3. Boron oxide is soluble in hot water and therefore was removed through submerging the pyrolysed sample in 80 °C distilled water that was heated by a hot plate. This was continuously stirred for 10 minutes to leave a solution containing carbon and dissolved B_2O_3 in water.

The solid carbon is separated from the dissolved B_2O_3 solution to find the carbon content produced after pyrolysis. The carbon was filtered out of the solution using a PTFE membrane filter paper with a pore size of 1 µm. The filter paper was left to dry and was then reweighed. This weight was subtracted from the original weight of the sample and filter paper to determine the remaining carbon. This was then subtracted from the original weight of the sample to give the amount of boron oxide.

From the mass of carbon and boron oxide in the PVBO precursor, the molar ratio was calculated. The calculation is shown in Appendix 1.

The optimum C/B_2O_3 ratio to produce boron carbide powder through heat treatment is 3.5[1].

2.2.4. Heat Treatment of Pyrolysed Samples

The pyrolysed PVBO samples were placed in an alumina crucible (8mm length) and heated at 1200-1500 °C for 1, 5 or 10 hours in an 'Elite Tube Furnace' (TSH16/2J/180) with a flowing argon atmosphere at a flow rate of 4 LPM and a heating rate of 10 °C min^{-1}. The parameter of 1300 °C for 5 hours was chosen based on previous literature[1] to increase the validity of their results. The time and temperature was varied to show the effect that these parameters had on the final boron carbide structure.

2.3. Materials Characterisation

2.3.1 Thermogravimetric Analysis (TGA)

The PVBO powders were analysed using a 'Netzsch Sta 449 C Cell' thermogravimetic analyser to measure the weight change of a sample as a function of temperature. The heating range was 50 - 800 °C with a flowing argon atmosphere and a heating rate of 10 °C min^{-1}. TGA analysis was used to help determine the pyrolysis temperature.

2.3.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was used in this study to identify the sample obtained by mixing PVA with H_3BO_3 via a condensation reaction. FTIR shows the infrared absorption spectrum which can be used to determine the chemical bonds in the composition. Powder samples are prepared through milling with potassium bromide (KBr) to form a very fine powder. The KBr was first dried in a box furnace at 100 °C. Approximately 2 % of the PVBO precursor was mixed with the KBr and ground into very fine powder using a pestle and mortar. This powder was then compressed in a hydraulic press to create a thin pellet which was analysed in a 'Nicolet 8700' FTIR.

2.3.3. X-Ray Diffraction (XRD)

The structure of the pyrolysed samples and heat treated samples were characterised using a powder x-ray diffractometer. The pyrolysed samples were scanned at a 2ϴ angle range of 0 – 80° with a scan rate of 0.044 °/s and the heat treated samples were scanned at a 2ϴ angle range of 20 - 80° with a scan rate of 0.33 °/s using CuKα radiation by a 'Bruker D8 Advance' X-Ray diffractometer. The XRD patterns were used to determine the crystal structure of B_4C and phase idenitifcation.

2.3.4. Scanning Electron Microscope

The morphology of the samples were studied using scanning electron microscopy with a 'Joel 6060' microscope. The images were taken using SEI.

2.3.5. Raman Spectroscopy

Raman spectra of boron carbides were characterised using a 'Renishaw inVia' Raman microscope by a series of Raman bands extending from 50 to 2000 cm^{-1} with 20 accumulations at a 10 % laser power. This was used to identify the amount of free carbon in the boron carbide powder as a function of processing conditions.

3. Results and Discussion

3.1. Polyvinyolborate (PVBO)

3.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

The product produced by mixing PVA and H_3BO_3 via a condensation reaction was analysed using FTIR. The results were compared to FTIR spectra of PVA and H_3BO_3. By comparing the absorption peaks of each material which corresponds to the frequencies of vibrations between the bonds of the atoms, it is possible to identify if polyvinylborate (PVBO) is synthesised.

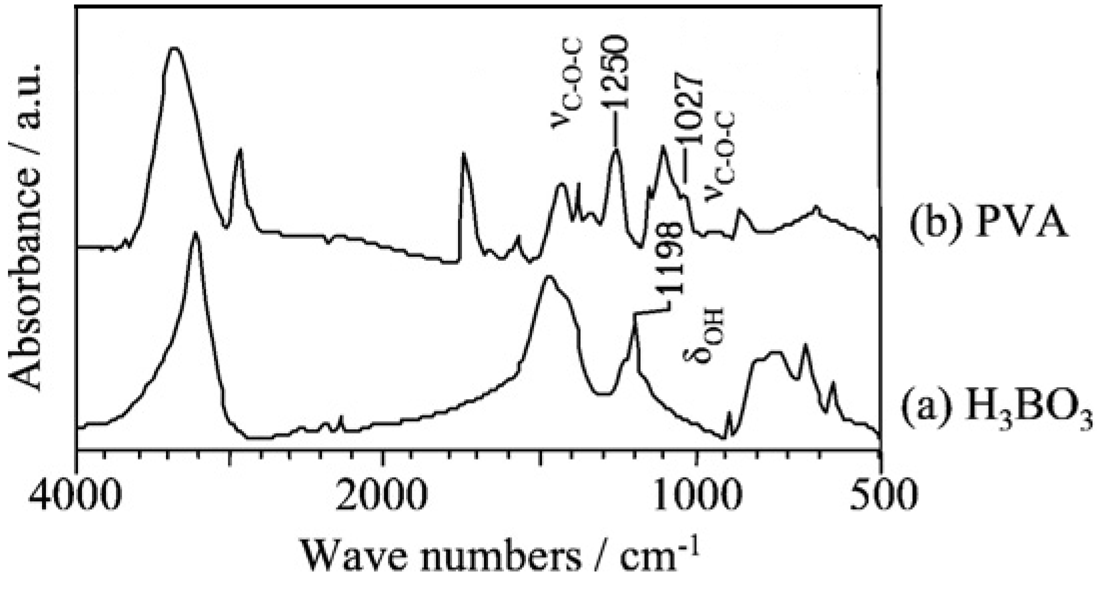


Figure 9. FTIR spectra of (a) Boric acid (H_3BO_3) and (b) Poly(vinylalcohol) (PVA)[1]

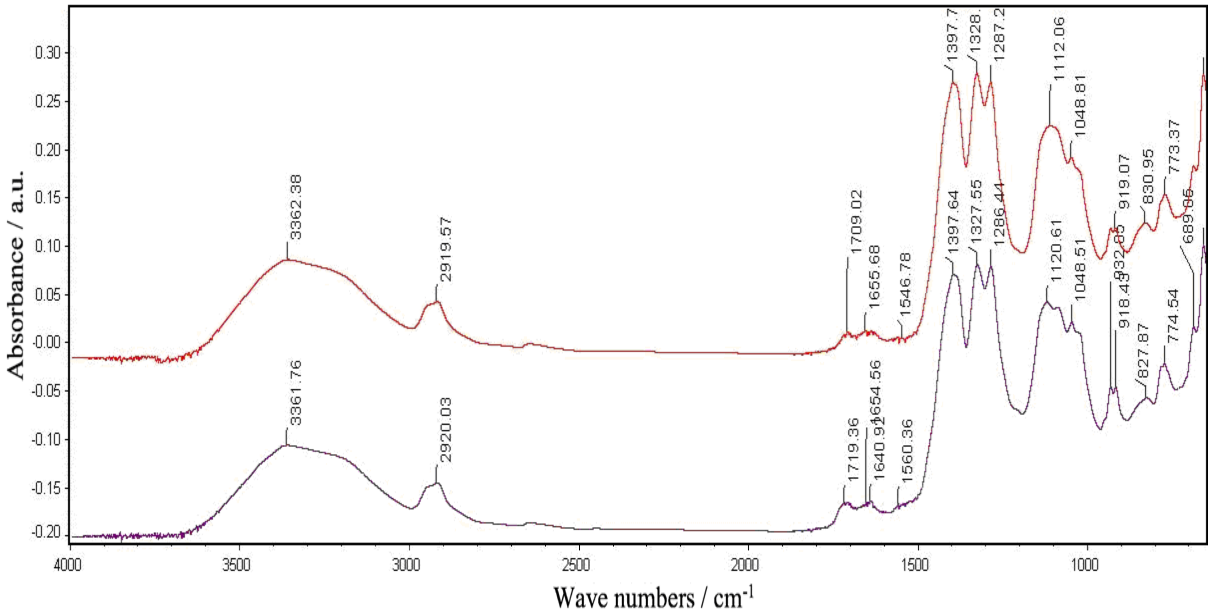


Figure 10. FTIR spectra of the Poly(vinylborate) (PVBO)(2.47 g PVA, 0.795 g H_3BO_3). The two lines show two different spectrums of the same sample to show the repeatability of the results.

Wavenumber (cm^{-1})	Assignment
3361	Stretching O-H
1287	Stretching B-O-C
1198	Deformation B-OH

Table 5. Main FTIR absorption of polyvinylborate (PVBO).

Figure 9 shows FTIR spectra of the starting materials, PVA and H_3BO_3 [1]. Figure 10 shows the FTIR spectra of poly(vinylborate) (PVBO); a precursor processed by mixing 2.47 g PVA and 0.795 g Boric Acid (3.1:1 PVA:H_3BO_3 weight ratio) in a condensation reaction. When comparing the results it demonstrates that PVBO was successfully formed. The main absorption bands and their assignments are displayed in Table 5. Figure 10 shows a broad absorption at 3361.76 cm^{-1} (line 1) and 3362.38 cm^{-1} (line 2). This is corresponded to the stretching band of O-H. However, this is less than that of PVA shown in Figure 9. This suggests that the consumption of the O-H group occurred by a reaction between alcohols and carboxylic acids to make an ester. Absorption observed at 1287.2 and 1286.44 cm^{-1} (Fig 9.) was attributed to stretching bands of B-O-C bonds, which confirm the occurrence of PVA chain cross-linking with H_3BO_3. Finally, the absorption band at 1198 cm^{-1} in H_3BO_3 spectrum (Fig. 9) is assigned to the deformation of B-OH which has disappeared in PVBO (Fig. 10). This confirms that a reaction has taken place and therefore caused the structure to change. The FTIR results show that borate ester (PVBO) was successfully formed when mixing PVA and Boric acid in a condensation reaction.

3.1.2. Thermogravimetric Analysis (TGA)

Following results showing polyvinylborate (PVBO) synthesis, the thermal behaviour was investigated via thermogravimetic analysis (TGA) to determine a suitable low-temperature for pyrolysis. The polymer was heated from 50 – 800 °C with a heating rate of 10 °C min^{-1} in a flowing argon atmosphere.

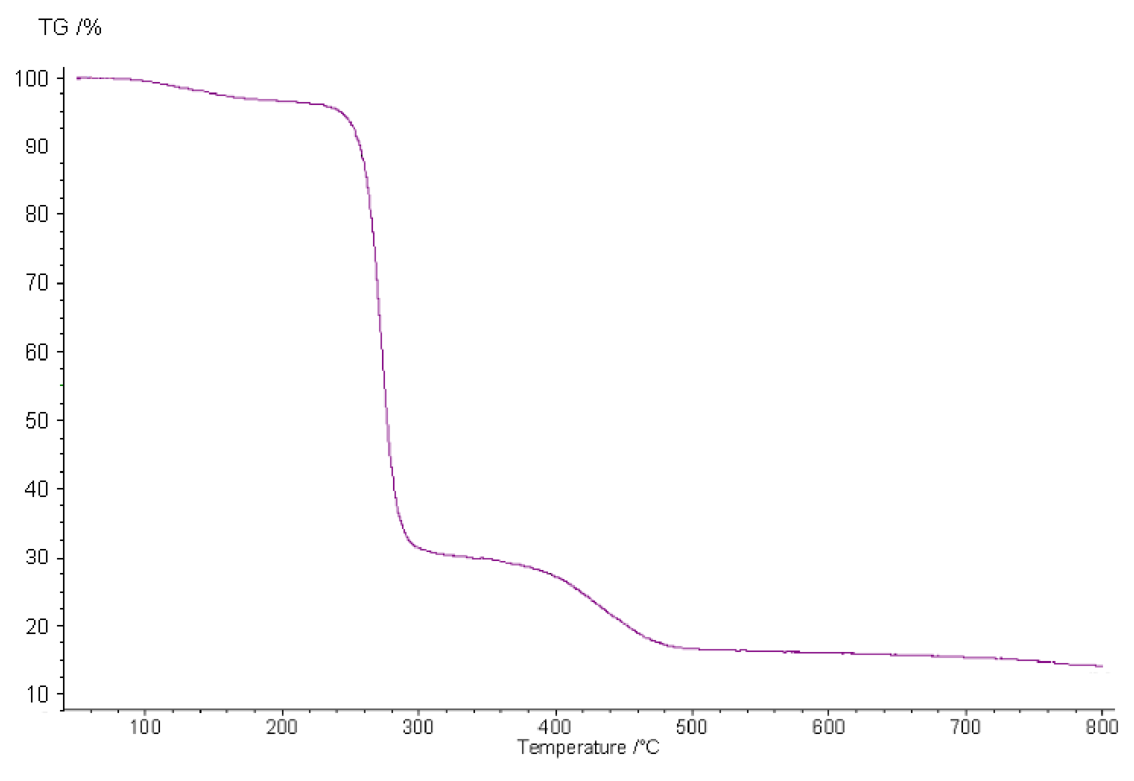


Figure 11. TG curve of PVA (98% Hydrolysed) at 10 °C/min (Ar flow)

Figure 11 shows the weight % as a function of temperature of the starting material, PVA. A first weight loss of PVA happened between 150 – 220 °C, followed by a dramatic second weight loss at 250 – 300 °C and a third weight loss at 400 – 500 °C. This left a residue of 10 wt% and a total weight loss of 86.6 wt%. The first weight loss is attributed to the elimination of polymer side groups and volatile products, such as water. Dehydration and elimination of side groups occurs due to the polymer melting. With the molten polymer, the mobility of the chains increases and hydrogen transfer occurs leading to depropagation and formation of alkyne end-groups[31]. The second weight loss is due to the partial breakdown of the polymer backbone because of an increase in temperature. The third weight loss is a result of the remaining polymer backbone elimination. This is consistent with previous studies by Weimer et al. (1992)[31]and Campbell et al. (2008)[32].

Figure 12 shows the thermal behaviour of PVBO with a weight ratio of 3.1 g PVA and 1 g H_3BO_3. This weight ratio was used based on the previous research by Yanase[1]. The TGA parameters used for PVA were repeated. The results show a first weight loss between 120 – 320 °C, a second weight loss between 340 – 390 °C and a third weight loss between 400 – 500 °C. This left a residue of 2 wt% with a total weight loss of 88.26 %.

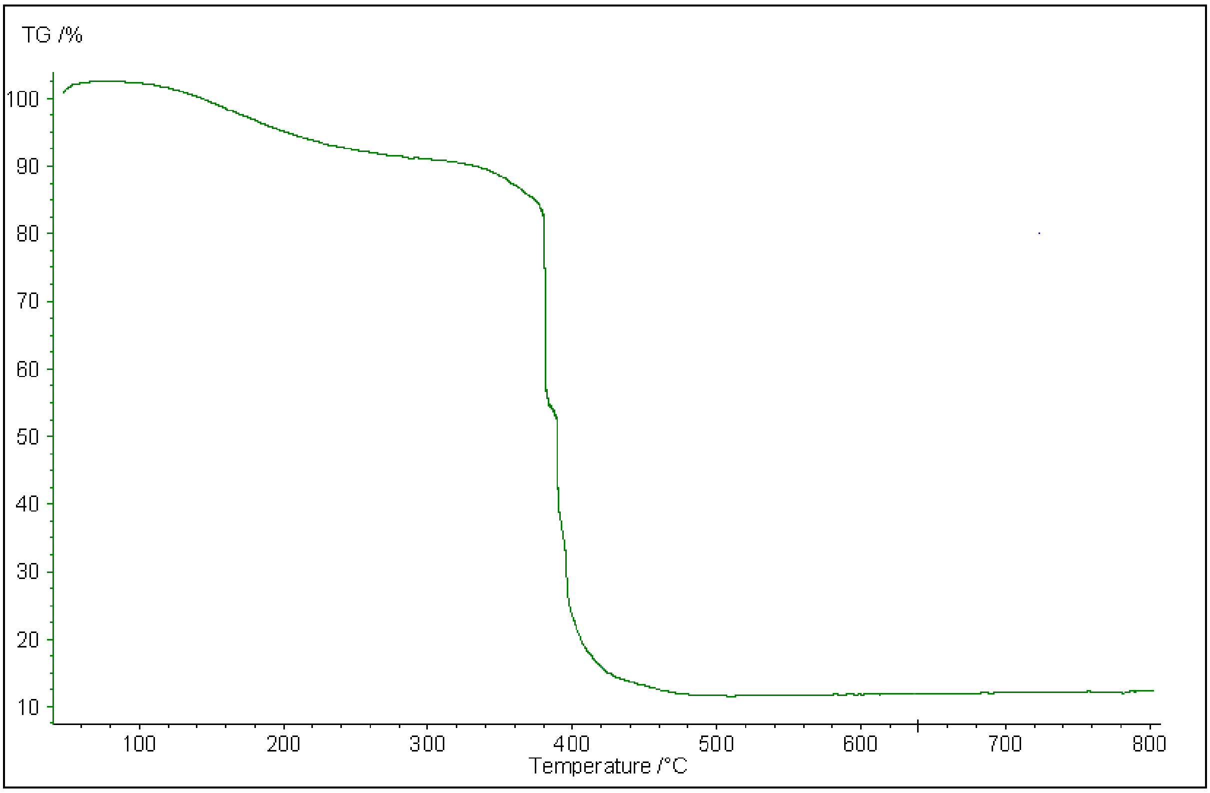


Figure 12. TG curve of PVBO polymer with a composition of 3.1 g PVA and 1 g H_3BO_3 at 10 °C/min (Ar flow)

Figure 13 shows the thermal behaviour of PVBO with a weight ratio of 3.7 g PVA and 1 g H_3BO_3. A first weight loss takes place between 120 – 300 °C, a second weight loss between 320 – 395 °C and a third weight loss between 400 – 500 °C. This left a residue of 20 wt% and a total weight loss of 76.85 %. The results were consistent with PVA with the elimination of side-groups at lower temperatures, followed by breakdown of the polymer backbone at higher temperatures.

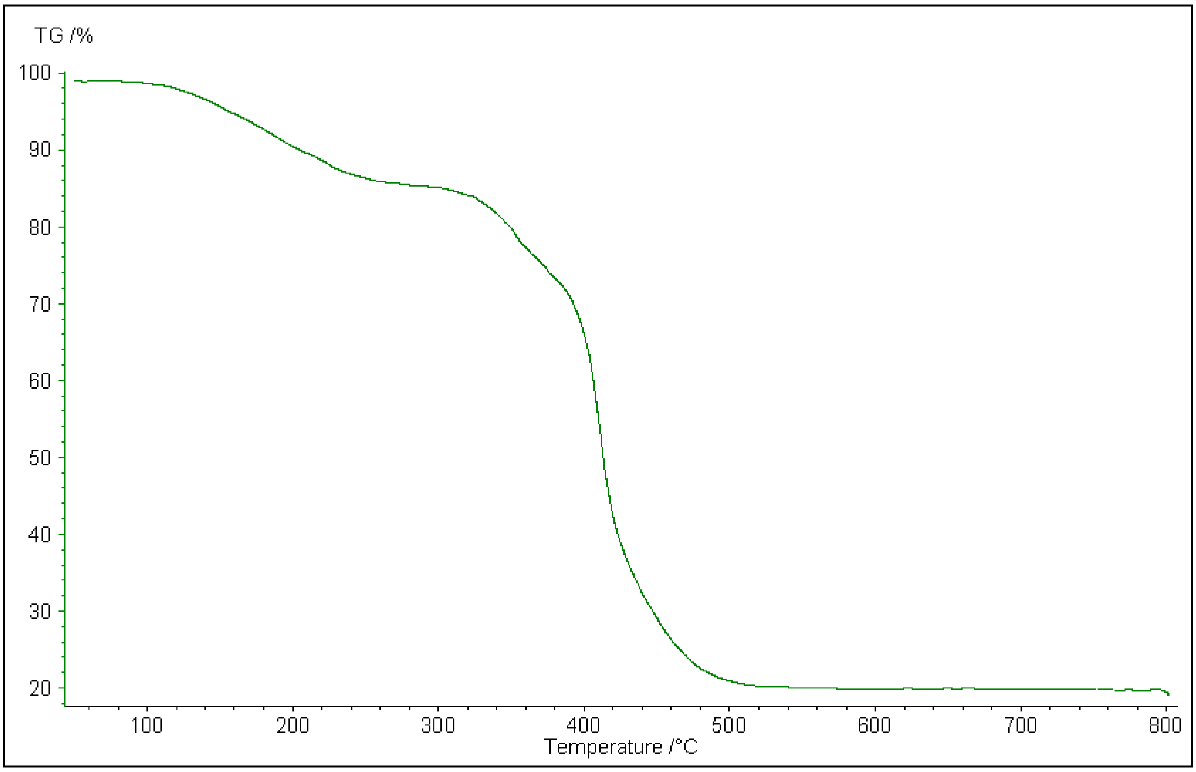


Figure 13. TG curve of PVBO polymer with a composition of 3.7 g PVA and 1 g H_3BO_3 at 10 °C/min (Ar flow)

Figure 14 shows a comparison of the thermal behaviours of PVA, PVBO with a composition of 3.1 g PVA and 1 g H_3BO_3 and PVBO with a composition of 3.7 g PVA and 1 g H_3BO_3.

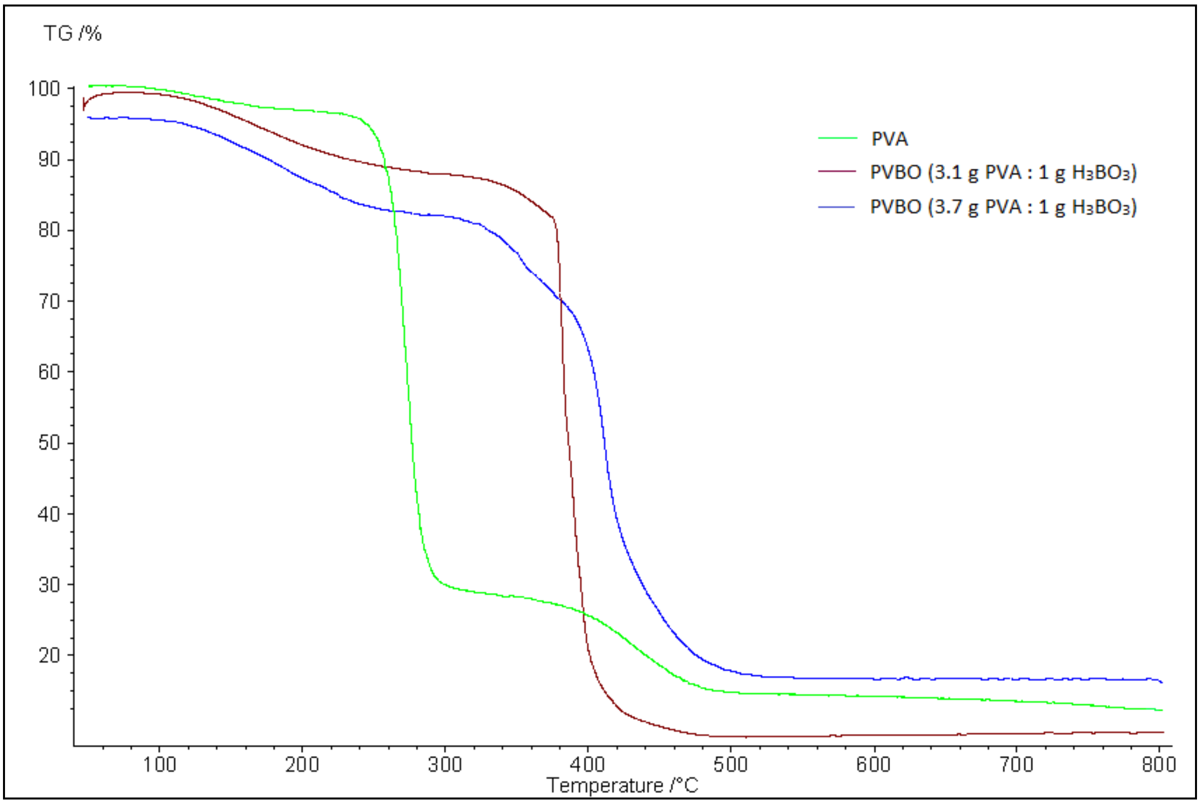


Figure 14. TG curves comparing PVA with PVBO (3.1 g PVA : 1 g H_3BO_3) and PVBO (3.7 g PVA : 1 g H_3BO_3) at 10 °C/min (Ar flow)

The results show that decomposition temperature of the PVBO sample was higher than that of pure PVA. This shows that PVBO has a better thermal stability than PVA. This improvement is due to the formation of B-O-C bonds during the condensation reaction. B-O-C bonds have a better thermal resistance than the C-O bonds of PVA. This is also confirmed by the FTIR measurement (Fig. 9 and 10). The residual substances remaining after heating

PVBO above 500 °C show carbonization was induced. Previous studies[1,6, 32] have shown that carbonization of PVA occurs and boric acid converts into B_2O_3 during pyrolysis. The results show that pyrolysis should take place at temperatures above 500 °C. This will result in a precursor consisting of carbon and boron oxide, which are the elements needed to produce boron carbide. The results also show that by increasing the proportion of PVA in the PVBO precursor causes an increase in residual substance after pyrolysis. This may be because an increase in the proportion of PVA will result in an increase in carbon. It is important to investigate different ratios and other parameters, such as temperature and time to find the optimum pyrolysis conditions that can then be heat treated to produce boron carbide with a stoichometry of B_4C and a small amount of free carbon.

3.1.3. XRD analysis of PVBO precursor

Figure 15 shows an XRD pattern of PVBO (3.7 g PVA : 1 g H_3BO_3) before pyrolysis. The hump indicates an amorphous polymer with crosslinking chains[33].

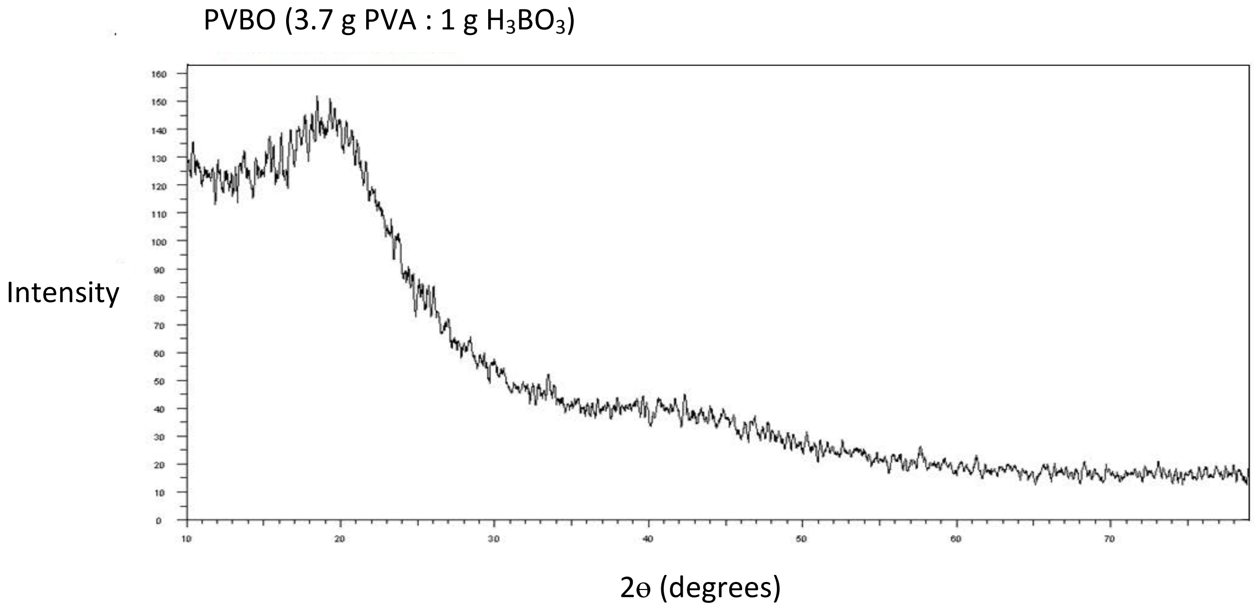


Figure 15. XRD pattern of PVBO (3.7 g PVA : 1 g H_3BO_3)

3.2. Pyrolysis

3.2.1. PVBO Compositions

Different compositions of PVBO were synthesised at temperatures 500, 600 and 700 °C for 2 hours. The temperature range is based on the TG results and previous literature[1]. The holding time of 2 hours is also based on previous research[1], however various holding times for pyrolysis will be investigated in this study. The PVBO compositions were synthesised from different weight ratios of PVA and H_3BO_3. These weight ratios are shown in Table 5.

Polyvinyl(alcohol) (PVA) (g)	**Boric Acid (H_3BO_3) (g)**	**PVA : H_3BO_3**
2	2	1 : 1
3	1	3 : 1
2.47	0.795	3.1 : 1
3.3	1	3.3 : 1
3.5	1	3.5 : 1
3.7	1	3.7 : 1
4	1	4 : 1

Table 5. Weight ratios (PVA and H_3BO_3) of PVBO precursors for pyrolysis.

3.2.2. Carbon to Boron Oxide (C/B_2O_3) ratio

The pyrolysis of PVBO led to the formation of a precursor consisting of carbon and boron oxide which are the elements required for the synthesis of boron carbide. Production of B_4C is achieved via a carbothermal reduction process. This can be presented as the following:

$$2B_2O_3 + 7C = B_4C + 6CO^1$$

The reaction shows that the optimum carbon to boron oxide (C/B_2O_3) molar ratio is 3.5. Therefore it is essential to obtain a C/B_2O_3 ratio as close to 3.5 as possible in order to produce boron carbide after further heat treatment with a stoichiometry of B_4C and with small amounts of free carbon. The C/B_2O_3 molar ratios of the various PVBO compositions after pyrolysis at 500, 600 or 700 °C for 2 hours in a flowing Ar atmosphere were calculated. The results are shown in Table 6 and Figure 16.

C/B_2O_3			
PVA : H_3BO_3	**Pyrolysis Temperature (°C)**		
	500	600	700
1 : 1	0.183	0.175	0.652
2 : 1	1.029	1.368	1.907
3 : 1	1.245	2.281	2.56
3.1 : 1	1.372	2.382	2.546
3.3 : 1	1.47	2.47	2.785
3.5 : 1	1.551	**3.23**	**3.16**
3.7 : 1	1.572	**3.42**	4.11
4 : 1	1.968	4.6	5.473

Table 6. C/B_2O_3 molar ratios of different ratios of PVA and H_3BO_3 after heating at 500, 600 or 700 °C for 2 hours in a flowing Ar atmosphere. Figures highlighted in red represent the best C/B_2O_3 ratio.

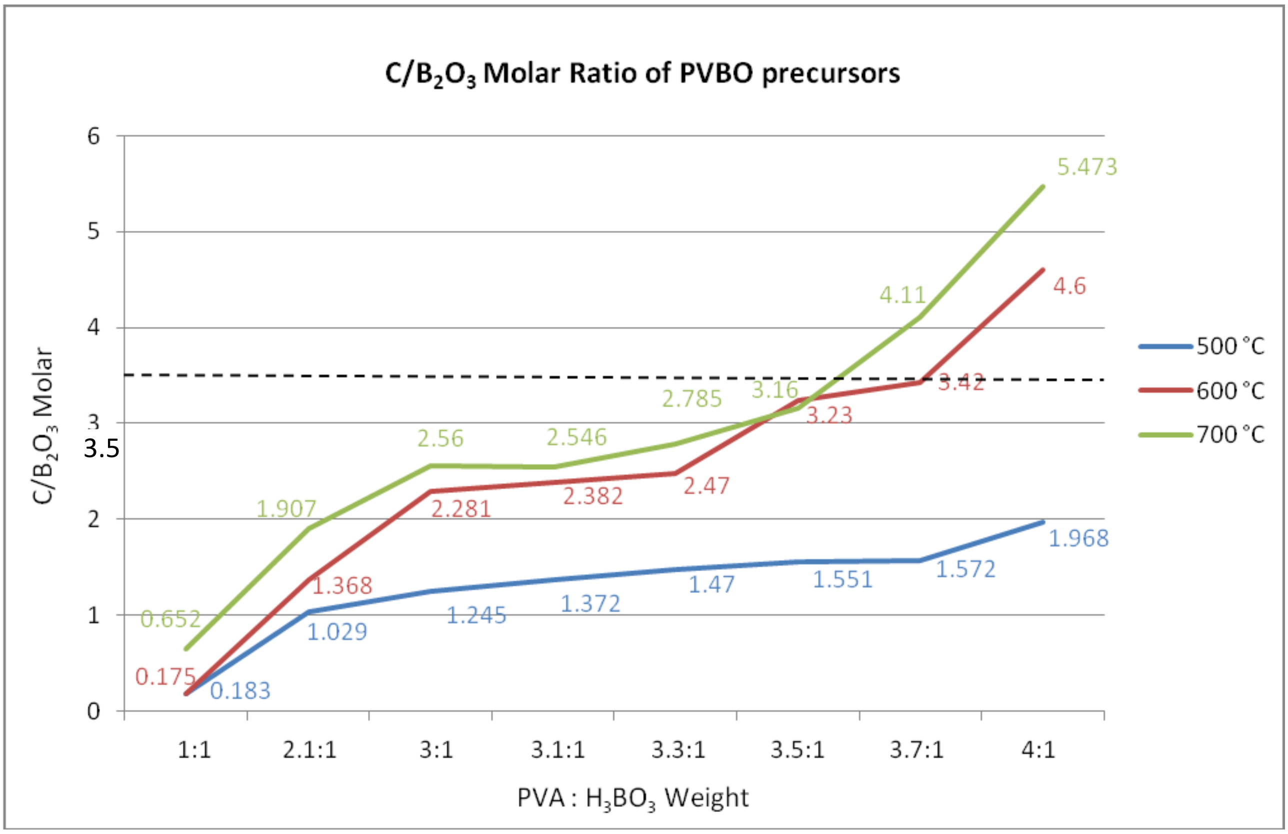


Figure 16. C/B_2O_3 molar ratio of different compositions of PVBO when pyrolysed at 500, 600 and 700 °C for 2 hours in a flowing Ar atmosphere. The dotted line indicates the optimum stoichiometric C/B_2O_3 molar ratio of 3.5.

Table 6 and Figure 16 shows that the C/B_2O_3 molar ratio closest to 3.5 is PVBO synthesised from a weight ratio of 3.7 g PVA and 1 g H_3BO_3 when pyrolysed at 600 °C for 2 hours. This gave an average value of 3.42. The results also show that PVBO synthesised from 3.5 g PVA and 1 g H_3BO_3 resulted in a C/B_2O_3 molar ratio of 3.23 when pyrolysed at 600 °C and a ratio of 3.16 when pyrolysed at 700 °C. These PVBO precursors are predicted to synthesise boron carbide with a stoichometry of B_4C and a low amount of free carbon because they are close to the optimum ratio of 3.5.

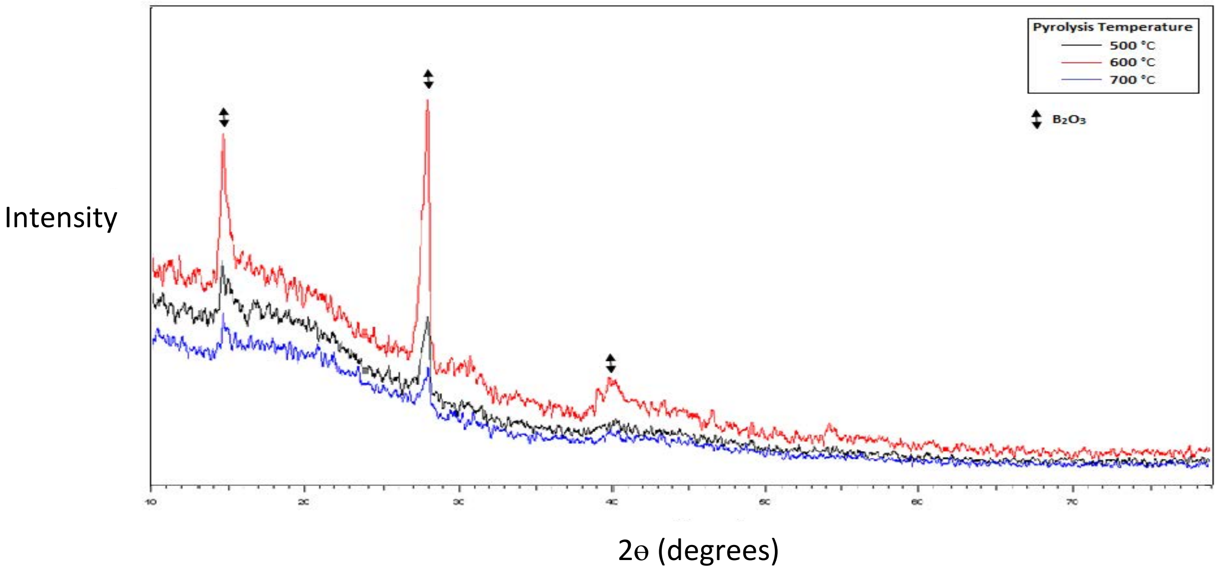
Figure 16 shows there is a general trend of an increase in C/B_2O_3 ratio when there in an increase in PVA. This is because an increase in PVA will result in a greater proportion of carbon in the PVBO precursor due to PVA carbonisation during pyrolysis. This therefore causes an increase in the C/B_2O_3 ratio.

The results also show that pyrolysis at 500 °C led to a low C/B_2O_3 ratio even with an increased PVA content. This may be because the polymer chains have not completely broken down at 500 °C, therefore complete carbonisation of PVA may not have occurred. This results in low carbon content and therefore a low C/B_2O_3 ratio. The increase in C/B_2O_3 molar ratio has resulted from an increase in temperature. It can be concluded that increasing the pyrolysis temperature promotes breakdown of the polymer chain and therefore an increases the carbonisation of PVA.[1]

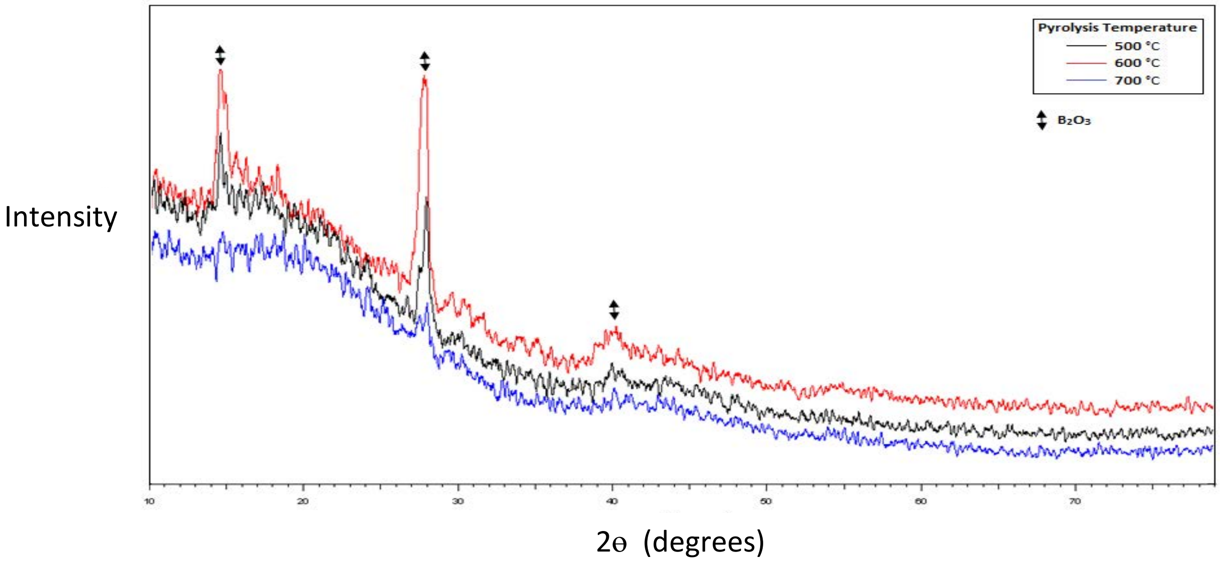
3.2.3. XRD analysis of pyrolysed PVBO precursors

Figure 17 shows XRD patterns of the PVBO precursors with different PVA and boric acid content when heated at 500, 600 and 700 °C for 2 hours under Ar flow.

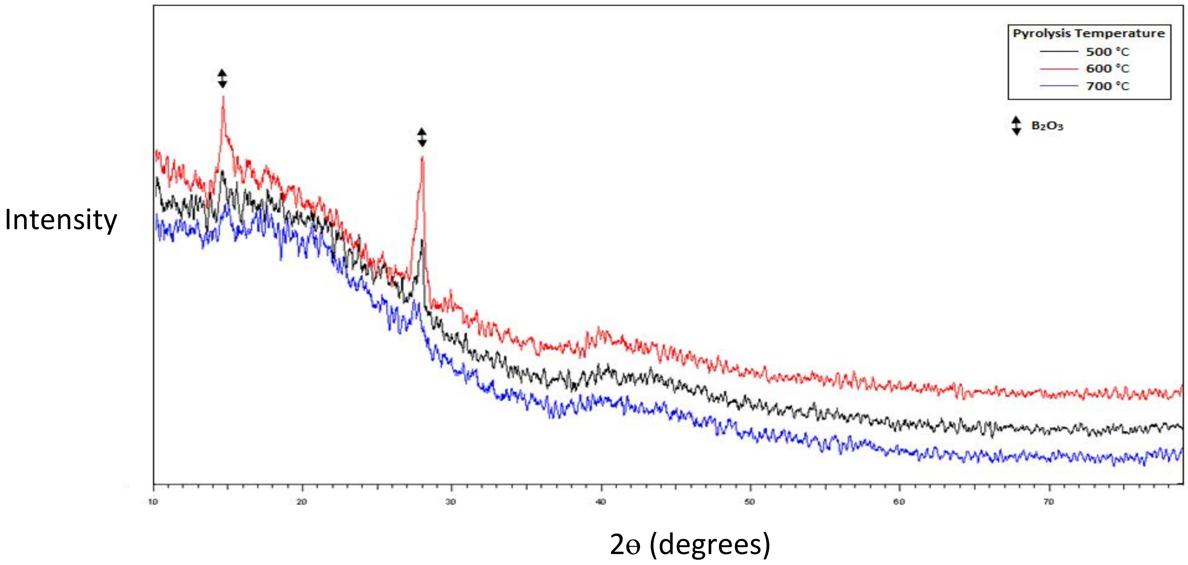
A - PVBO (2 g PVA : 1 g H_3BO_3)



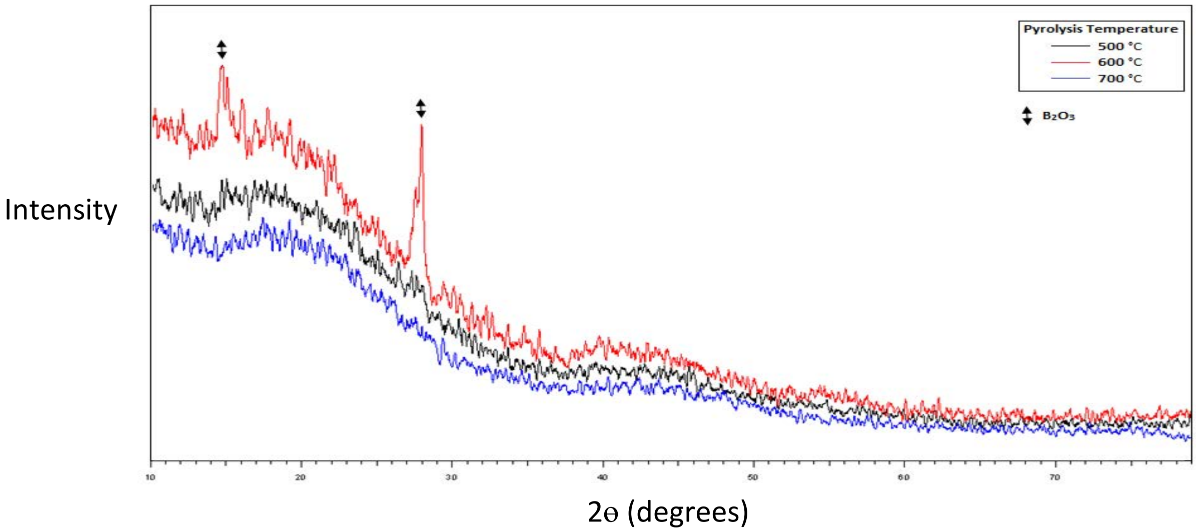
B - PVBO (3.1 g PVA : 1 g H_3BO_3)



C - PVBO (3.3 g PVA : 1 g H_3BO_3)



D - PVBO (3.5 g PVA : 1 g H_3BO_3)



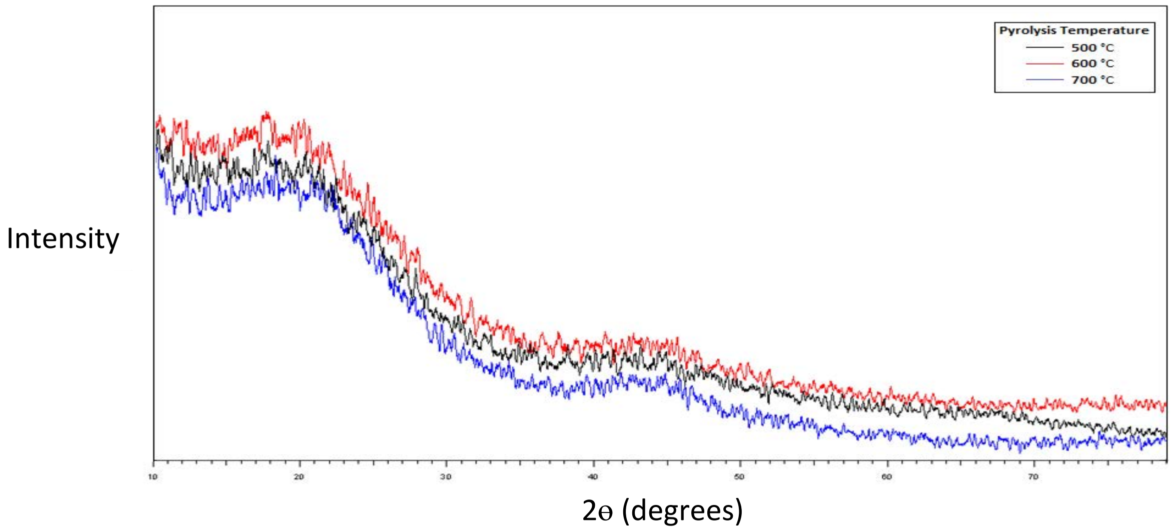

E - PVBO (3.7 g PVA : 1 g H_3BO_3)

Figure 17. XRD patterns of PVBO precursors produced from various weight ratios of PVA and boric acid after pyrolysis at temperatures 500, 600 and 700 °C for 2 hours under Ar flow.

In figure 17A, the peaks occur at angles 15, 18 and 40 degrees. These peaks correspond to the formation of B_2O_3. These peaks also occur in Figure 17B, 17C and 17D. In figure 17E there are no crystalline peaks and therefore the polymer is still amorphous.

The XRD patterns show that when PVBO is pyrolysed under the right conditions it results in crystalline boron oxide (B_2O_3). When the pyrolysed PVBO precursor is heat treated at elevated temperatures, as shown in Figure 20, it produces carbon containing phase, such as B_4C and free carbon. Therefore it can be concluded that the precursors contain amorphous carbon as it does not appear in the XRD pattern (Fig. 17) in addition to B_2O_3. The results show that by pyrolysing PVBO it results in the formation of boron oxide and carbon which are required to produce boron carbide.

XRD patterns A, B, C and D in Figure 17 all show that the intensity of B_2O_3 peaks is highest when pyrolysed at 600 °C compared to 500 and 700 °C. Therefore the temperature 600 °C was selected as the optimum temperature for the pyrolysis process.

The XRD patterns show that different PVBO compositions results in the same boron oxide phases. However, an increase in PVA results in a decrease in the intensity of the boron oxide peaks. This is because a lower amount of PVA will result in a lower amount of carbon after pyrolysis and therefore there will be a higher proportion of B_2O_3. This supports this study's C/B_2O_3 molar ratio results that show an increase in PVA results in an increase in carbon to boron oxide

Figure 17E shows that when the PVA content is too high compared to boron oxide content, the precursor remains amorphous after pyrolysis at 500, 600 and 700 °C for 2 hours. This is because the polymer chains of the PVBO precursor have not completely broken down even at the elevated temperature of 700 °C. This is due to the increase proportion of PVA. When comparing this to the XRD pattern of PVBO before pyrolysis (Fig. 15) the hump has broadened. This broadening is assigned to the formation of a graphitic carbon phase[33] and therefore shows that carbonisation of the polymer has begun. Despite the PVBO precursor remaining amorphous, the C/B_2O_3 ratio still remains high due to the increased amount of PVA and therefore an increased amount of carbon.

3.2.4. XRD analysis of leached PVBO after pyrolysis

Figure 18 shows an XRD pattern of a PVBO precursor after it has been stirred in hot water. The XRD pattern shows the disappearance of boron oxide peaks. It can therefore be concluded that the boron oxide has been leached out during this process. This provides support that the method of calculating the C/B_2O_3 molar ratios was accurate (Appendix 1).

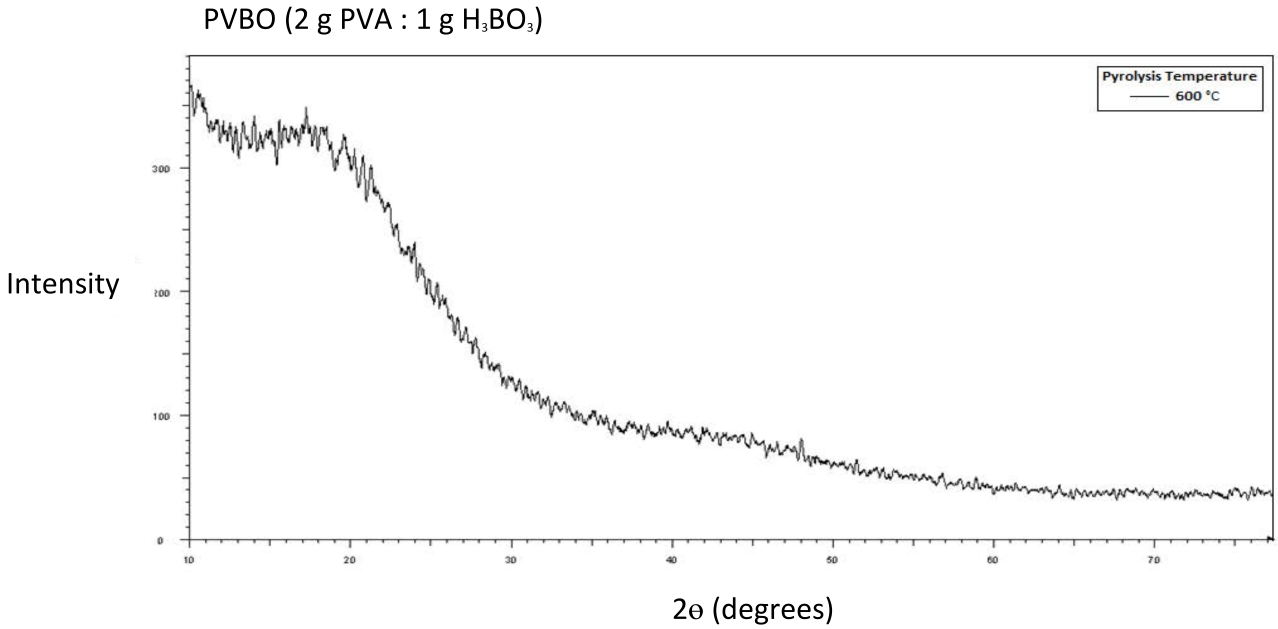


Figure 18. XRD pattern of PVBO (2 g PVA : 1 g H_3BO_3) that has been pyrolsyed at 600 °C for 2 hours in Ar flow after being placed in hot water (80 °C) and continuously stirred for 5 minutes.

3.2.5. Dwell time during pyrolysis

The holding time during pyrolysis of PVBO were also investigated in this study. Figure 19 compared XRD patterns of a PVBO precursor synthesised from 3.5 g PVA and 3.5 g H_3BO_3 after pyrolysis at 600 °C for 1 and 2 hours.

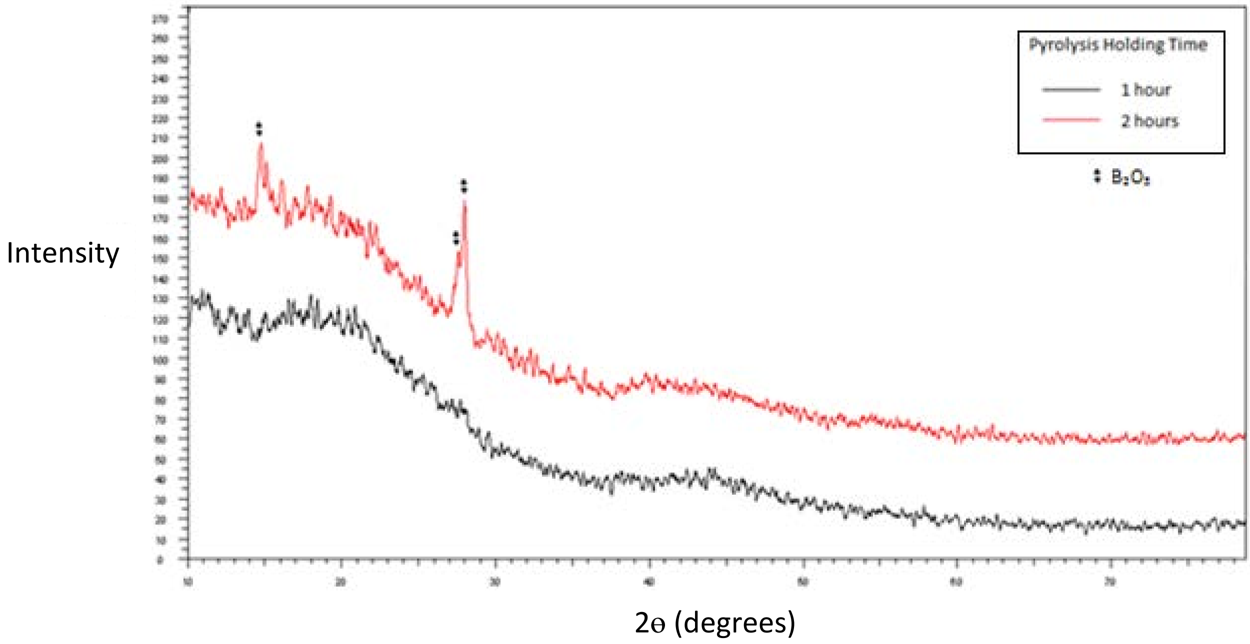


Figure 19. XRD pattern of PVBO (3.5 g PVA : 1 g H_3BO_3) pyrolsyed at 600 °C for 1 and 2 hours in a flowing Ar atmosphere.

Figure 19 shows that pyrolysing PVBO for 1 hour results in an amorphous precursor. This is because complete reaction has not taken place and there are still polymer chains present. The peaks shown following pyrolysis for 2 hours occurs at angles 15, 28, 29 degrees. These peaks correspond to the formation of B_4C. These results show that a 2 hour hold time is required.

3.2.6. Optimum pyrolysis parameters

Analysis of the C/B_2O_3 molar ratios and the XRD patterns of the pyrolysed PVBO precursors show that the optimum temperature is 600 °C and the optimum holding time is 2 hours. These results support the study by Yanase et al.[1] who found that B_4C with small amount of free carbon was achieved by pyrolysing a composition of 2.47 g PVA and 0.795 g H_3BO_3 (3.1:1) at 600 °C for 2 hours followed by heat treatment at 1300 °C for 5 hours. Therefore these pyrolysis conditions will be used before heat treating the different PVBO compositions to elevated temperatures to see if boron carbide is produced. The results however show different C/B_2O_3 ratio results than Yanase et al.[1]. They found that 2.47 g PVA and 0.795 g H_3BO_3 when heated at 600 °C resulted in a C/B_2O_3 ratio of 3.3. This study found that this gave a C/B_2O_3 ratio of 2.4. The ratio closest to 3.5 in this study was 3.4 which was achieved from 3.7 g PVA and 1 g H_3BO_3. A possible reason for the discrepancy between this study and Yanase et al.[1] could be due to a different molecular weight being used for the starting materials. Therefore it is important to investigate different PVBO compositions.

3.3. Heat Treatment

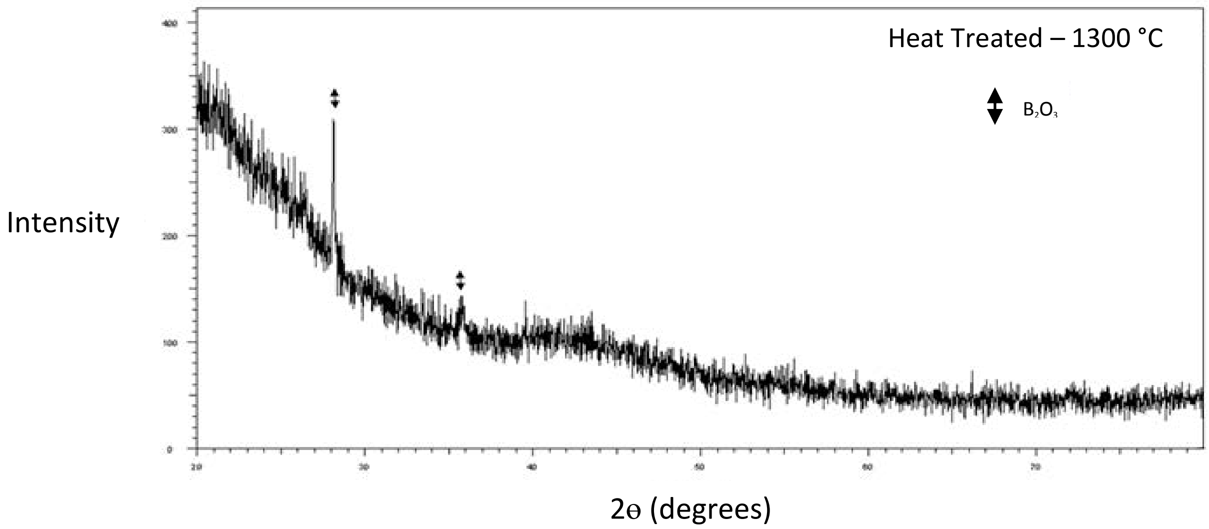
3.3.1. XRD analysis of heat treated samples with different PVBO compositions

The results so far have shown that by mixing PVA and H_3BO_3 in a condensation reaction and pyrolysing this sample under the right conditions has resulted in a powder precursor consisting of carbon and boron oxide. Previous studies[1, 6, 18, 31, 34] have shown that these elements can then be heat treated to achieve boron carbide via a carbothermal reduction method. The aim is to achieve a boron carbide powder with a stoichometry of B_4C and a low amount of free carbon using low temperatures. This has been achieved by Yanase et al.[1] but without any supporting evidence or repeated results. This study aims to support and improve these findings by investigating different parameters including; different PVA and H_3BO_3 ratios, different temperatures and different holding times.

Using the optimum pyrolysis conditions, different compositions of PVA and H_3BO_3 were then heat treated at 1300 and 1400 °C for 5 hours. The powders were analysed using XRD and the results are shown below.

Figure 20 shows a PVBO precursor of 2 g PVA and 1 g H_3BO_3 heated to 1300 and 1400 °C for 5 hours.

A - PVBO (2 g PVA : 1 g H_3BO_3)



B - PVBO (2 g PVA : 1 g H_3BO_3)

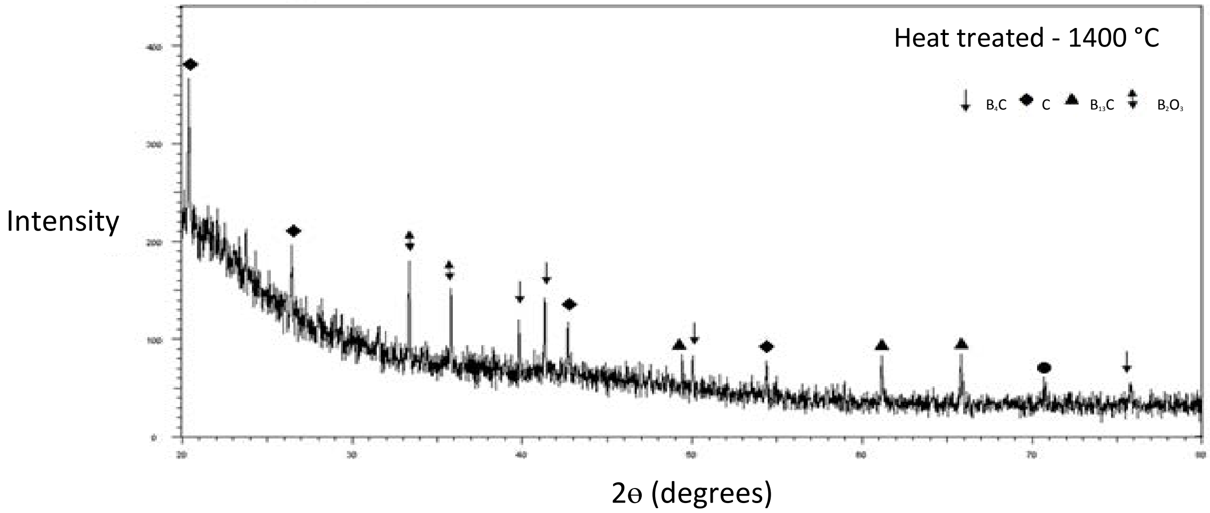
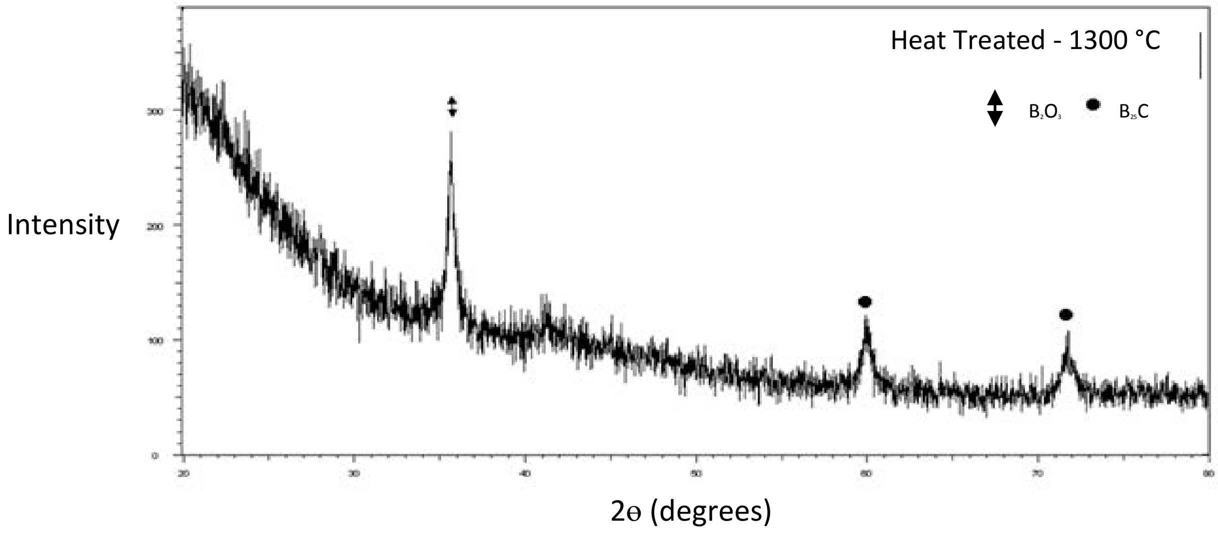


Figure 20. XRD patterns of PVBO with composition of 2 g PVA and 1 g H_3BO_3, pyrolysed at 600 °C for 2 hours and heat treated at 1300 °C (Fig. 20A) and 1400 °C (Fig. 20B) for 5 hours under Ar flow.

Figure 20A shows that no reaction has taken place when there is a low amount of PVA (2g) at 1300 °C. The XRD pattern shows there are still only boron oxide peaks. However, when this composition is heated to 1400 °C, as shown in figure 20B, some boron carbide begins to form. The XRD pattern shows that some boron carbide was produced with a stoichometry of $B_{13}C$ and B_4C in the sample. The $B_{13}C$ is a result of a low C/B_2O_3 ratio, meaning there will be a high proportion of boron oxide in the sample resulting in a boron rich boron carbide. The pattern also shows boron oxide is still present which means complete reaction has not occurred. By comparing the two XRD patterns it shows that an increase in temperature promoted the reaction and resulted in the formation of boron carbide even at a very low C/B_2O_3 ratio.

Figure 21 shows a PVBO precursor of 3.1 g PVA and 1 g H_3BO_3 heated to 1300 and 1400 °C for 5 hours.

A - PVBO (3.1 g PVA : 1 g H_3BO_3)



B - PVBO (3.1 g PVA : 1 g H_3BO_3)

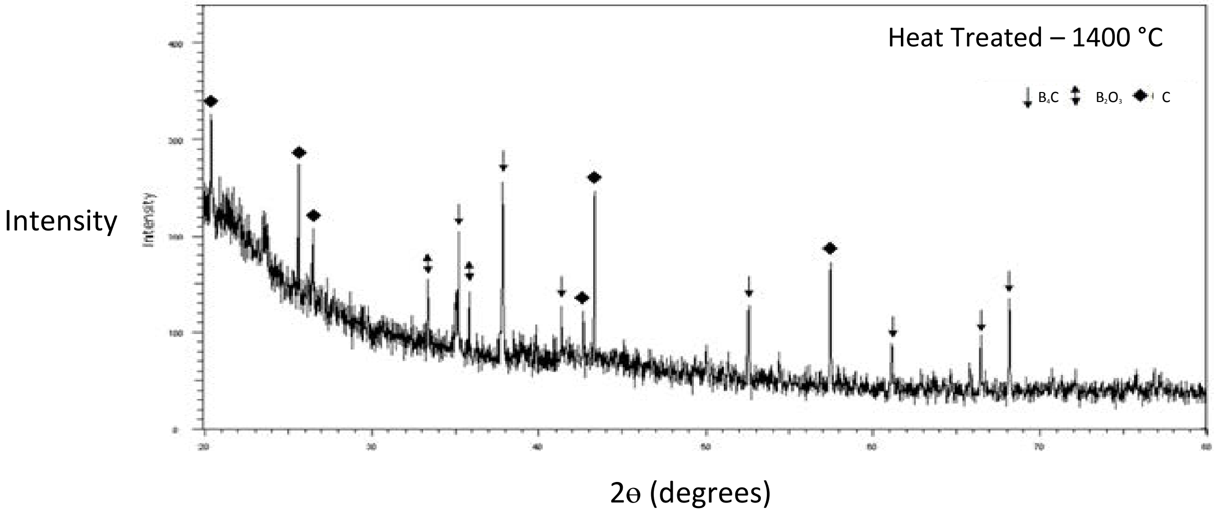
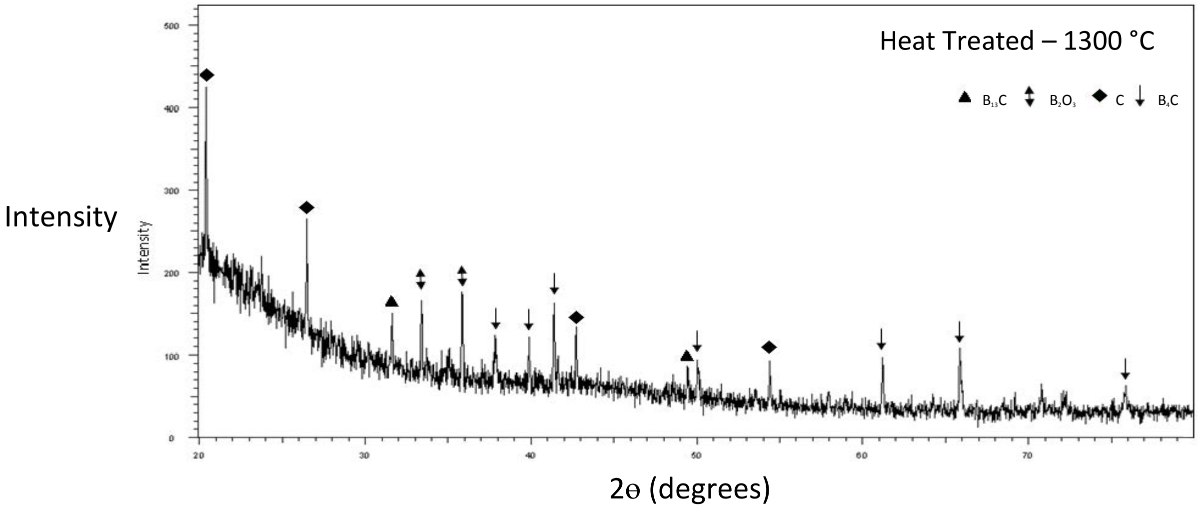


Figure 21. XRD patterns of PVBO with composition of 3.1 g PVA and 1 g H_3BO_3, pyrolysed at 600 °C for 2 hours and heat treated at 1300 °C (Fig. 21A) and 1400 °C (Fig. 21B) for 5 hours under Ar flow.

Figure 21A shows the XRD pattern for a PVBO composition of 3.1 g PVA and 1 g H_3BO_3 when heated at 1300 °C for 5 hours. These conditions replicate the study by Yanase et al.[1] who found that it resulted in the formation of B_4C with a low amount of free carbon. The results shown in figure 20B are very different to the findings of Yanase et al.[1]. This was expected due to the different C/B_2O_3 molar ratio. This study found that some reaction had taken place at 1300 °C when there is an increased proportion of PVA, however it resulted in the formation of boron carbon ($B_{25}C$). This is due to the low C/B_2O_3 ratio and therefore the high proportion of boron oxide. There was however still a large proportion of boron oxide in the sample. When the composition is heated to 1400 °C (Fig. 21B) it resulted in boron carbide (B_4C), carbon and a small amount of boron oxide. There is no indication of $B_{25}C$ present in the powder sample. The results show that increasing the proportion of PVA results in some reaction taking place at 1300 °C. When there is an increase in temperature there is an increase in the reaction but also a decrease in the amount of boron in the reacted boron carbide. This shows that increasing the temperature causes a greater loss of boron through vaporisation during the heat treatment process.

Figure 22 shows a PVBO precursor of 3.3 g PVA and 1 g H_3BO_3 heated to 1300 and 1400 °C for 5 hours.

A - PVBO (3.3 g PVA : 1 g H_3BO_3)



B - PVBO (3.3 g PVA : 1 g H_3BO_3)

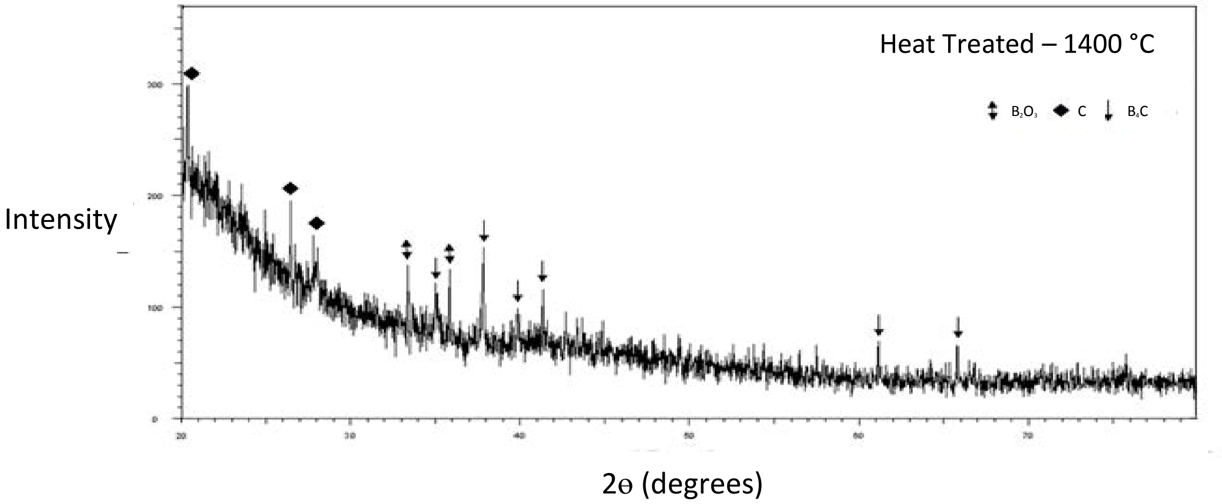


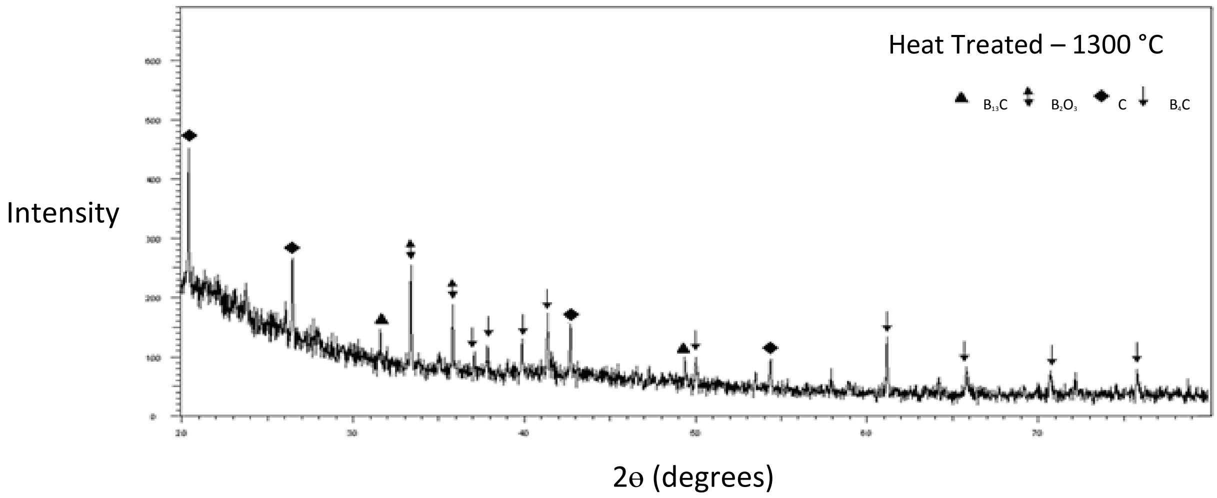
Figure 22. XRD patterns of PVBO with composition of 3.3 g PVA and 1 g H_3BO_3, pyrolysed at 600 °C for 2 hours and heat treated at 1300 °C (Fig. 22A) and 1400 °C (Fig. 22B) for 5 hours under Ar flow.

Figure 22A shows the XRD pattern of 3.3 g PVA and 1 g H_3BO_3 when heated to 1300 °C. The pattern shows the presence of boron carbide in the formation of $B_{13}C$ and B_4C, high amount of free carbon and small proportion of unreacted B_2O_3. When comparing this to figure 20A and 21A it further illustrates that an increase in PVA content results in an increase in reaction taking place. This is the first indication of B_4C forming under the lower temperature of 1300 °C. The patterns show that by obtaining a C/B_2O_3 ratio closer to the optimum ratio of 3.5 results in B_4C forming at lower temperatures.

When the temperature is increased to 1400 °C (Fig. 22B), boron carbide is synthesised only in the formation of B_4C. There is also a reduction in the amount of free carbon and a reduction in the proportion of boron oxide. This again shows the increase in temperature helps promote the reaction and increases the amount of boron lost through vaporisation. When comparing figure 22B with 21B it shows that by increasing C/B_2O_3 ratio results in a decrease in the amount of free carbon.

Figure 23 shows a PVBO precursor of 3.5 g PVA and 1 g H_3BO_3 heated to 1300 and 1400 °C for 5 hours.

A - PVBO (3.5 g PVA : 1 g H_3BO_3)



B - PVBO (3.5 g PVA : 1 g H_3BO_3)

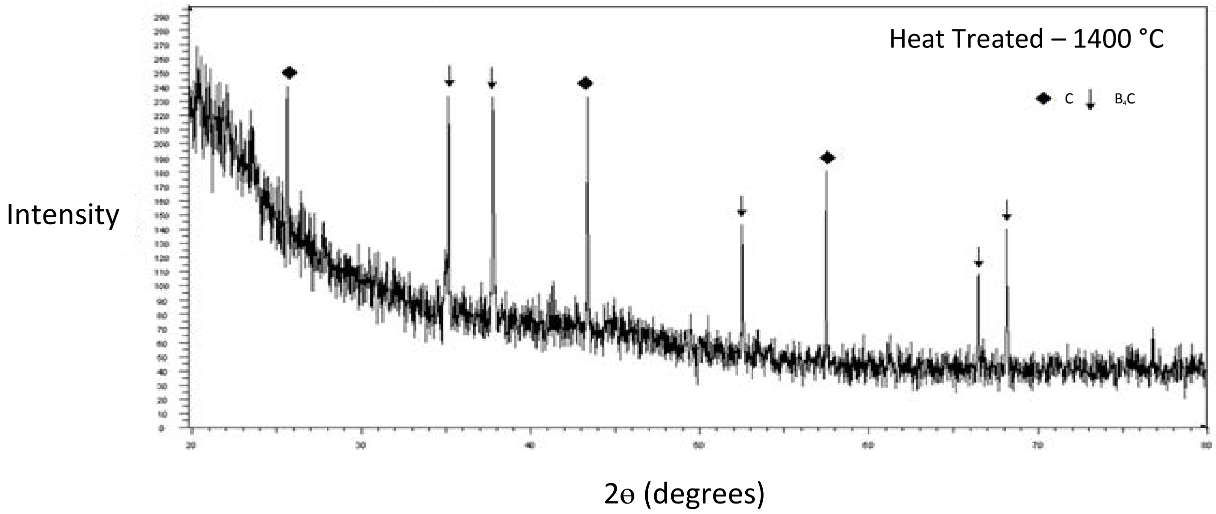
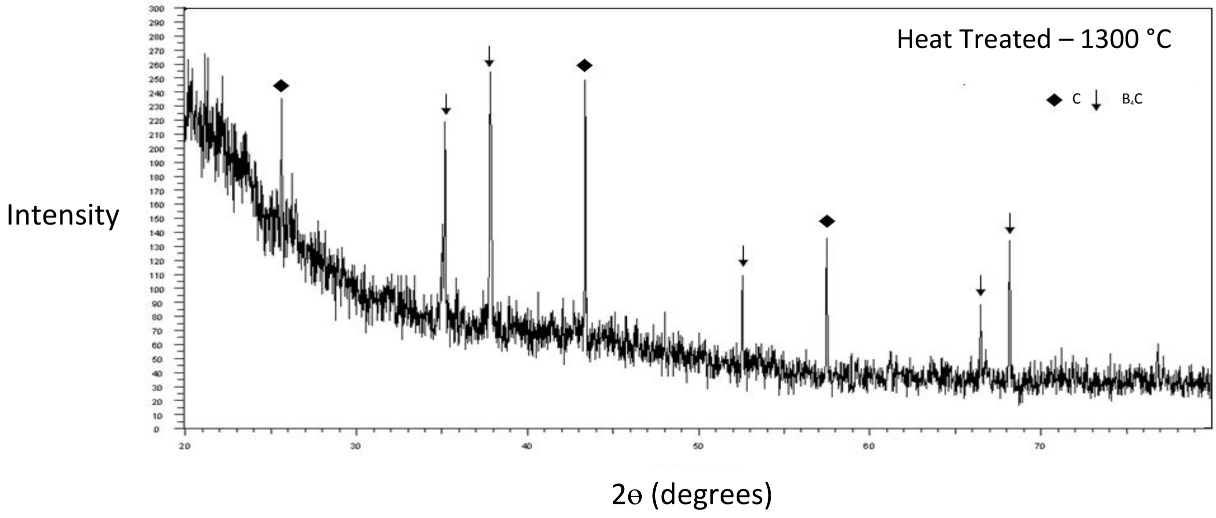


Figure 23. XRD patterns of PVBO with composition of 3.5 g PVA and 1 g H_3BO_3, pyrolysed at 600 °C for 2 hours and heat treated at 1300 °C (Fig. 23A) and 1400 °C (Fig. 23B) for 5 hours under Ar flow.

Figure 23A shows a similar XRD pattern to figure 22A. The small increase in the amount of PVA in the PVBO composition (3.5 g PVA : 1 g H_3BO_3) results in boron carbide (B_4C, $B_{13}C$), small amount of unreacted B_2O_3 and a decrease in free carbon when compared to figure 22A. When the temperature is increased to 1400 °C (Fig. 23B) it forms only B_4C and free carbon. This is the first time complete reaction has taken place. Therefore by increasing the C/B_2O_3 ratio and temperature helps facilitate a complete reaction.

Figure 24 shows a PVBO precursor of 3.7 g PVA and 1 g H_3BO_3 heated to 1300 and 1400 °C for 5 hours.



A - PVBO 3.7 g PVA : 1 g H_3BO_3)

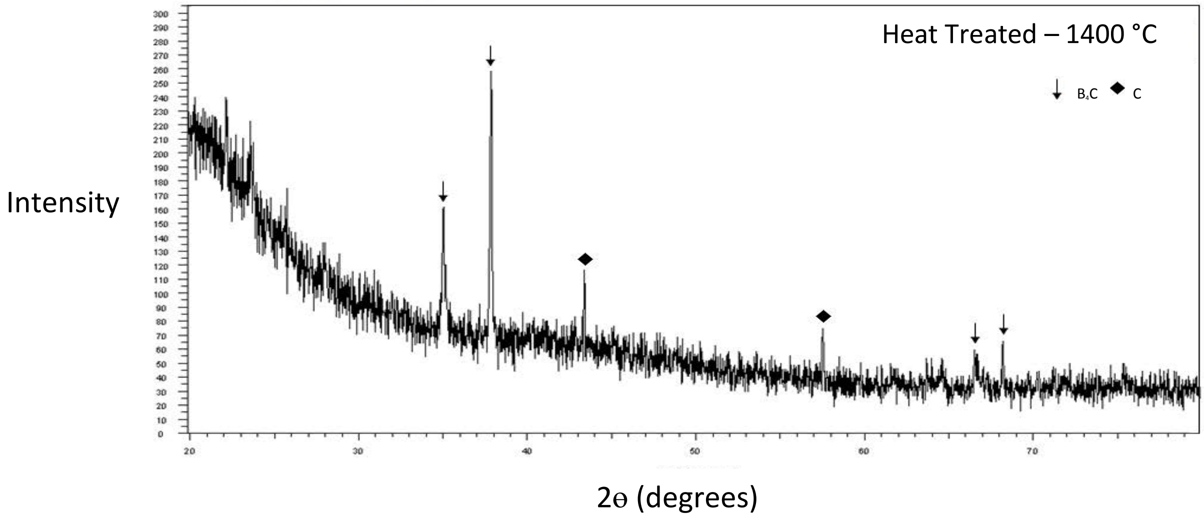

B - PVBO (3.7 g PVA : 1 g H_3BO_3)

Figure 24. XRD patterns of PVBO with composition of 3.7 g PVA and 1 g H_3BO_3, pyrolysed at 600 °C for 2 hours and heat treated at 1300 °C (Fig. 24A) and 1400 °C (Fig. 24B) for 5 hours under Ar flow

Figure 24A and figure 24B show a PVBO composition of 3.7 g PVA and 1 g H_3BO_3 after heat treatment at 1300 and 1400 °C respectively. Figure 24A shows a complete reaction has taken place and synthesised B_4C and free carbon at a lower temperature of 1300 °C. Figure 24B also shows a similar XRD pattern with B_4C but with a lower amount of free carbon.

To summarise, the results found by heating various PVBO compositions that have been pyrolysed at 600 °C for 2 hours and heat treated at 1300 and 1400 °C for 5 hours under Ar flow are as follows:

- 3.5 g PVA and 1 g H_3BO_3 at 1400 °C and 3.7 g PVA and 1 g H_3BO_3 at 1300 and 1400 °C resulted in complete reaction taking place and producing boron carbide with a B_4C

formation and free carbon. 3.7 g PVA and 1 g H_3BO_3 at 1400 °C for 5 hours resulted in the lowest amount of free carbon.

- An increase in temperature promotes reaction and therefore decreases the unreacted raw materials.
- An increase in temperature causes an increase in the loss of boron through vaporisation. Therefore by increasing the temperature, PVBO with low C/B_2O_3 molar ratio, still produces B_4C.
- An increase in C/B_2O_3 ratio nearer to the value of 3.5 results in B_4C forming at lower temperatures and a reduction of the amount of free carbon.

Following the results of different PVBO compositions, it is important to investigate other variables including heating temperature, holding time and pyrolysis temperature. As the PVBO composition of 3.7 g PVA and 1 g H_3BO_3 produced the best results when heated at 1400 °C for 5 hours, this condition was used for further investigation.

4.3.2. XRD analysis of heat treated samples after different pyrolysis temperatures

It is important to investigate the dwelling time of the heat treatment process and the effects it has on the production of B_4C and free carbon.

Figure 25 shows a comparison of PVBO precursors (3.7 g PVA and 1 g H_3BO_3) that have been pyrolysed at 500, 600 and 700 °C for 2 hours, followed by heat treatment at 1400 °C for 5 hours.

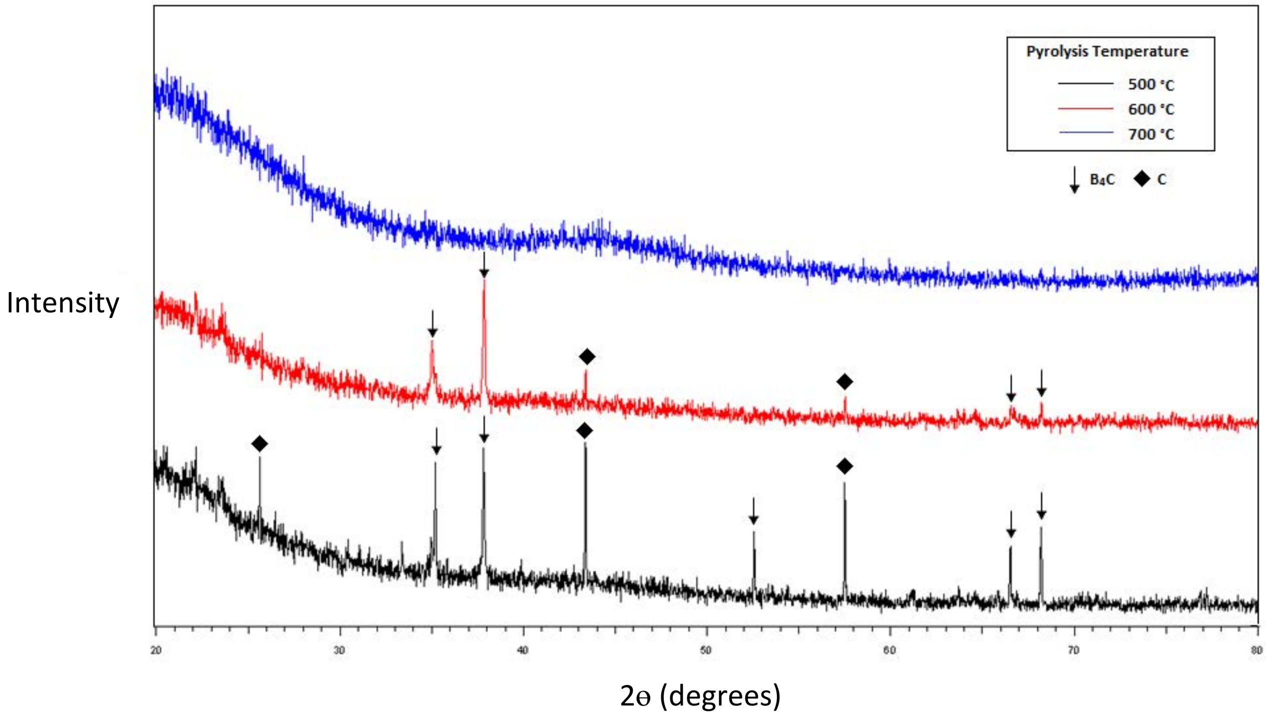


Figure 25. Comparative XRD patterns of PVBO (3.7 g PVA : 1 g H_3BO_3) pyrolysed at 500, 600 and 700 °C for 2 hours under Ar flow followed by heat treatment at 1400 °C for 5 hours under Ar flow.

Figure 25 shows the precursor pyrolysed at 500 °C exhibits B_4C and C peaks but also B_2O_3 peaks. This B_2O_3 is not present in the precursor pyrolysed at 600 °C. It can therefore be concluded that pyrolysis at 500 °C and heat treatment does not result in complete reaction taking place. This may be because complete breakdown of the polymer chains did not occur at 500 °C. When the sample is pyrolysed at 700 °C and heat treated it remains amorphous. This may be due to a high amount of boron being lost during pyrolysis because of the high temperature. This will result in a high proportion of amorphous carbon and therefore no reaction has occurred and boron carbide is not produced. The results show that the optimum pyrolysis temperature is 600 °C.

4.3.3. XRD analysis of different heat treatment temperatures

Figure 26 compares samples that have been heat treated at 1200, 1300, 1400 and 1500 °C for 5 hours under Ar flow.

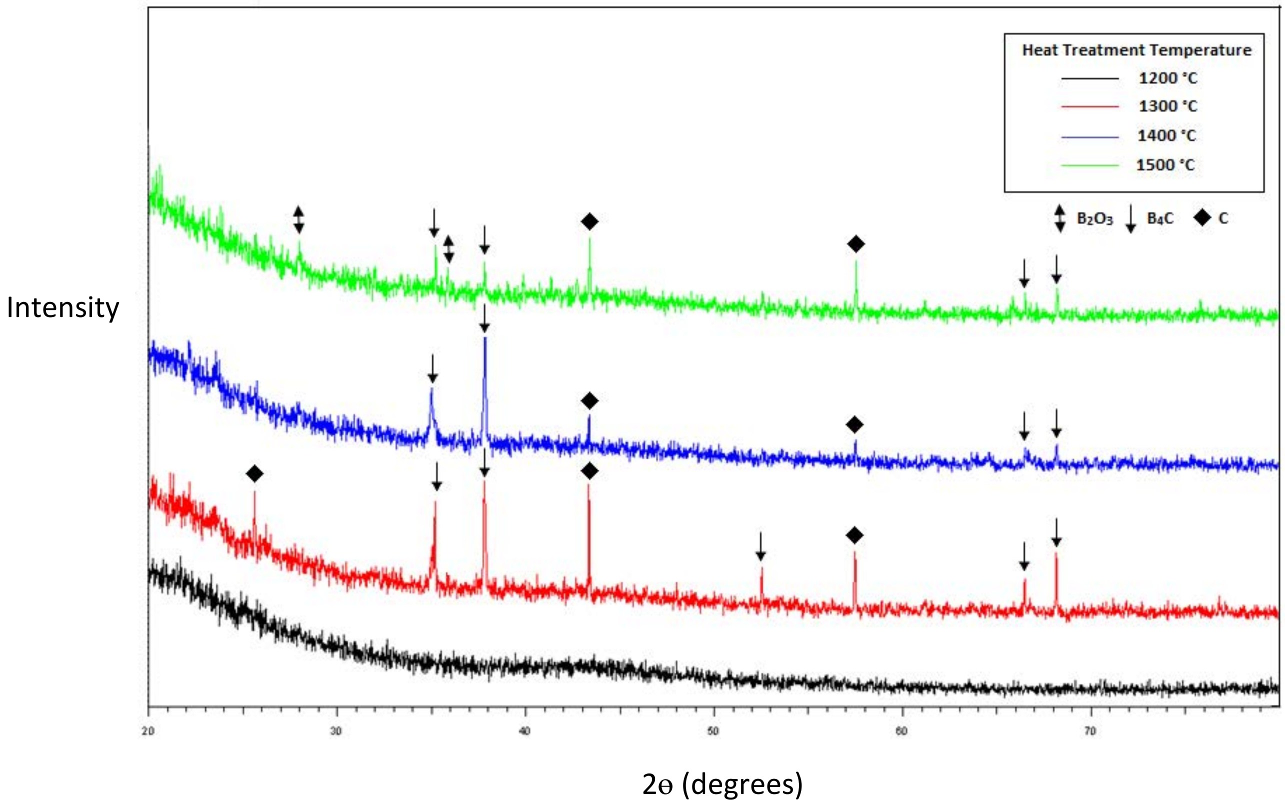


Figure 26. Comparative XRD patterns of PVBO (3.7 g PVA : 1 g H_3BO_3) pyrolysed at 600 for 2 hours followed by heat treatment at 1200, 1300, 1400 and 1500 °C for 5 hours under Ar flow.

The results show that at 1200 °C no reaction has taken place. The XRD pattern is the same as the XRD pattern of the pyrolysed precursor. At 1300 °C complete reaction has occurred and resulted in B_4C and carbon peaks. A similar pattern is shown when the sample is heated at 1400 °C, however there is a decrease in the amount of free carbon. This shows that increasing the temperature promotes reaction and results in a reduction in residual carbon. However if the temperature is increased too much it can cause oxidation to occur. This is shown by the XRD pattern of the sample after heat treatment at 1500 °C. The pattern exhibits B_4C, carbon and B_2O_3 peaks. This may be because the increase in temperature has promoted reaction and resulted in no remaining carbon to react with boron to produce boron carbide and therefore leaving boron oxide. If a higher temperature was used there would need to be an increase in PVA and therefore subsequently an increase in carbon. The aim of the study is to use low temperature synthesis to save on cost, therefore the results show that the optimum heat treatment temperature for this composition is 1400 °C.

3.3.4. XRD analysis of different heat treatment dwell times

Figure 27 compares PVBO precursors that have been heated to 1400 °C for 1, 5 and 10 hours.

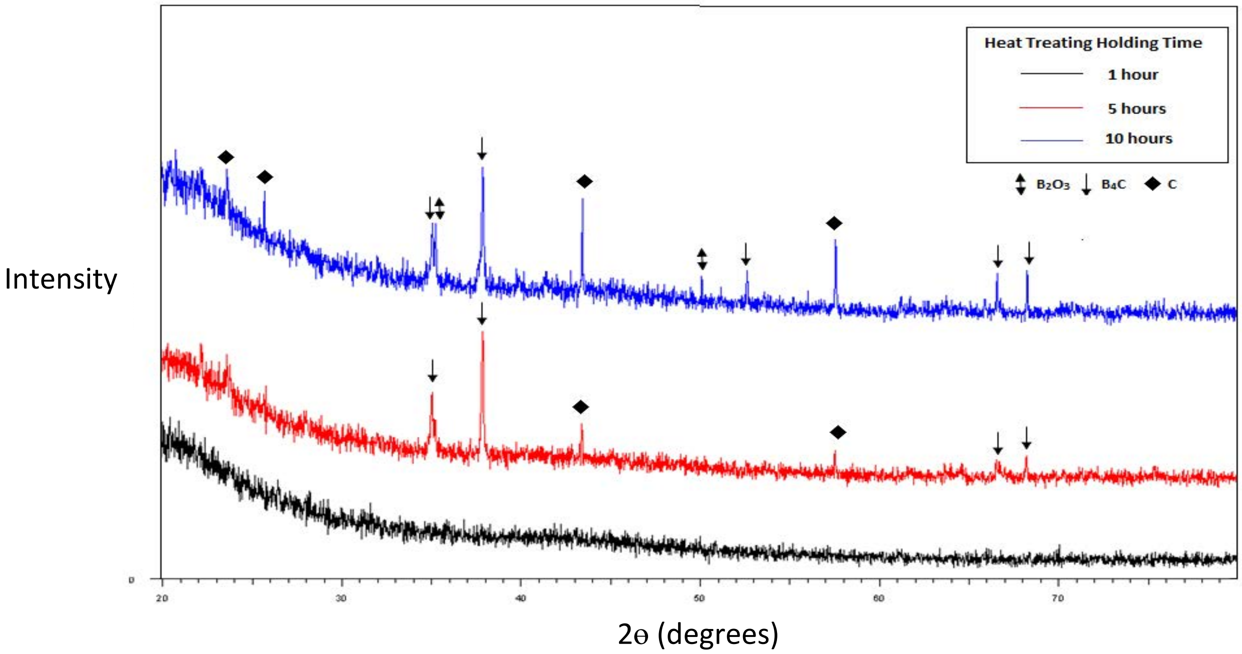


Figure 27. Comparative XRD patterns of PVBO (3.7 g PVA : 1 g H_3BO_3) pyrolysed at 600 °C for 2 hours followed by heat treatment at 1400 °C for 1, 5 and 10 hours.

The XRD pattern shows that after 1 hour no reaction has taken place. After 5 hours complete reaction has taken place. This shows that for boron carbide to form it requires heating for several hours to give enough time for the boron oxide to react with carbon. The XRD pattern shows that heating for 10 hours results in B_4C, an increased amount of free carbon and boron oxide begins to form. The increase in free carbon may be due to oxidisation occurring. The XRD pattern shows boron oxide peaks which results in remaining carbon and therefore an increased amount of residual carbon.

3.3.5. Optimum heat treatment parameters

The XRD results show that the optimum conditions for producing boron carbide powder with a stoichiometry of B_4C and a low amount of residual carbon was produced by mixing 3.7 g PVA with 1 g H_3BO_3 in a condensation reaction, pyrolysing the samples at 600 °C for 2 hours and heat treating at 1400 °C for 5 hours.

3.4. Microstructural Analysis

The powder produced using the optimum process conditions was analysed using Scanning Electron Microscopy. The micrographs are shown in figure 28 and 29.

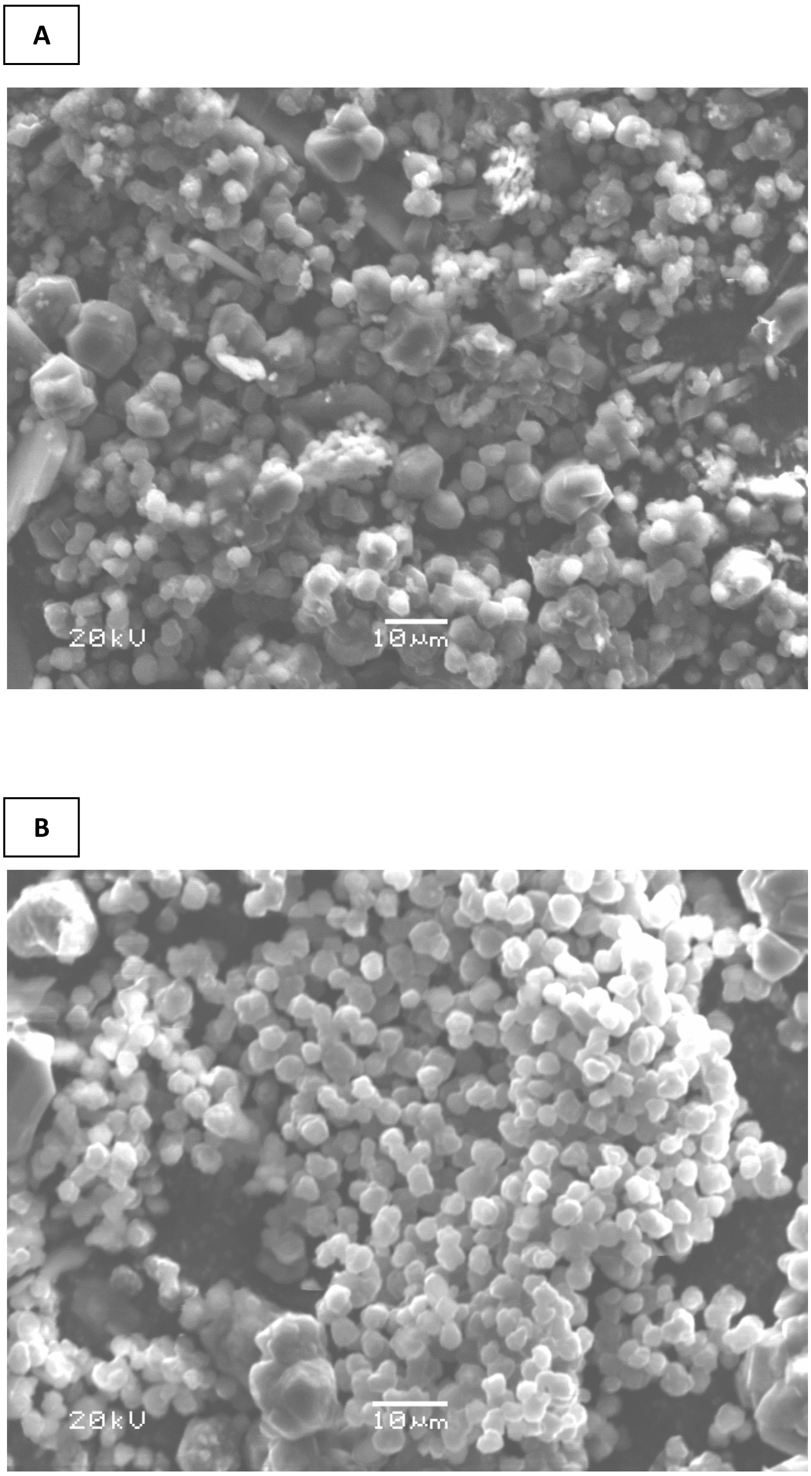


Figure 28. Micrographs (A and B) of boron carbide powder synthesised from 3.7 g PVA, 1 g H_3BO_3, pyrolysed at 600 °C for 2 hours and heat treated at 1400 °C for 5 hours.

Figure 28 provides support that boron carbide was produced. The micrographs show many equiaxial B_4C particles.

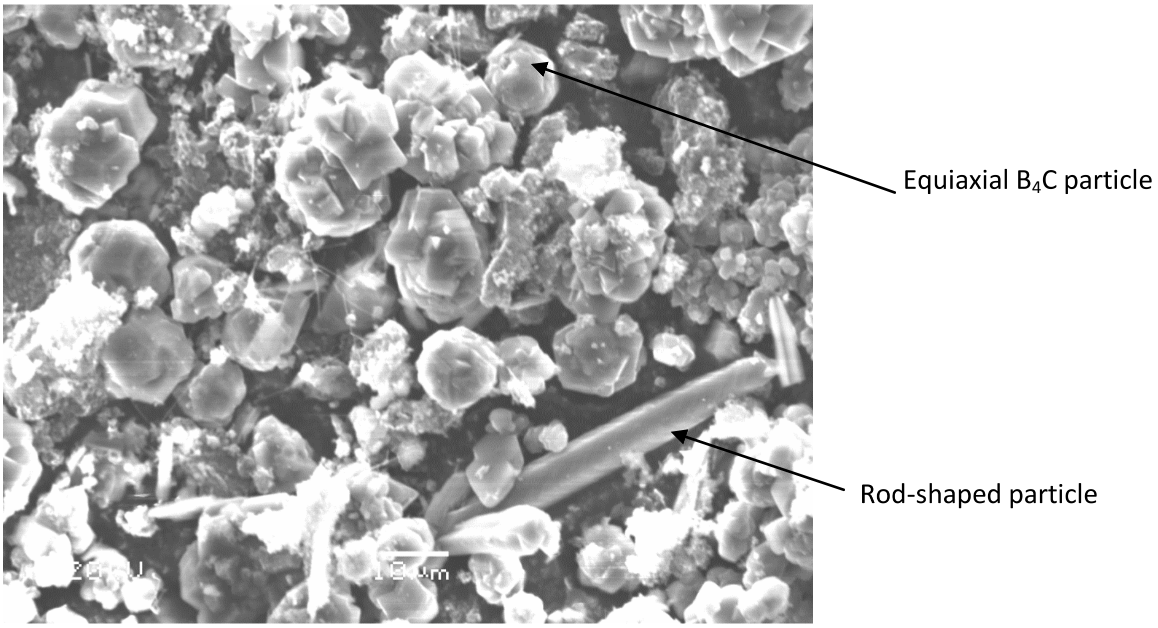


Figure 29. Micrographs of boron carbide powder synthesised from 3.7 g PVA, 1 g H_3BO_3, pyrolysed at 600 °C for 2 hours and heat treated at 1400 °C for 5 hours.

Figure 29 again shows B_4C icosahedral particles. There is also evidence of a rod shaped particle, which are commonly produced during carbothermic reduction B_2O_3[36]

3.5. Raman Spectroscopy

Raman spectroscopy was carried out on the boron carbide processed by the optimum conditions to observe the amount of free carbon. A typical experimental Raman spectrum of residual carbon is shown in Figure 30.

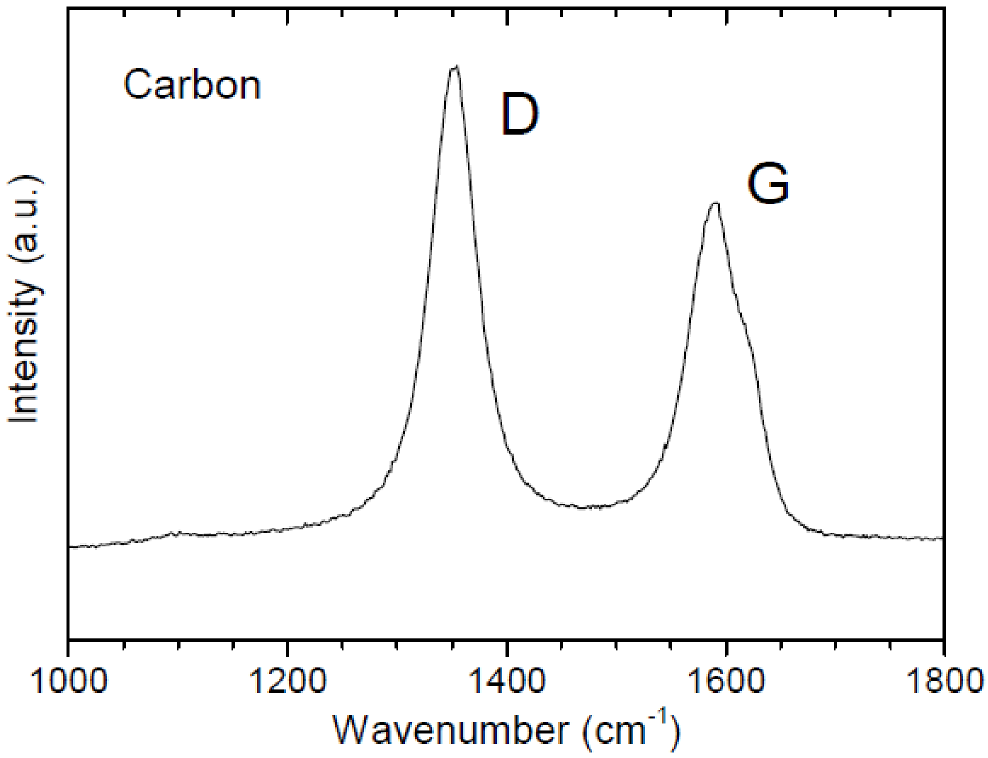


Figure 30. A typical Raman spectrum of carbon showing characteristics D and G bands[37]

In Figure 30, the D band (1300 – 1360 cm^{-1}) is observed in carbons containing vacancies, impurities or other symmetry-breaking defects. The G band (1589 cm^{-1}) derives from the in-plane stretching vibration of the double C=C bonds[38].

The B_4C powder synthesised using the optimum processing conditions found in this study were examined using Raman spectroscopy. The results are shown in figure 31.

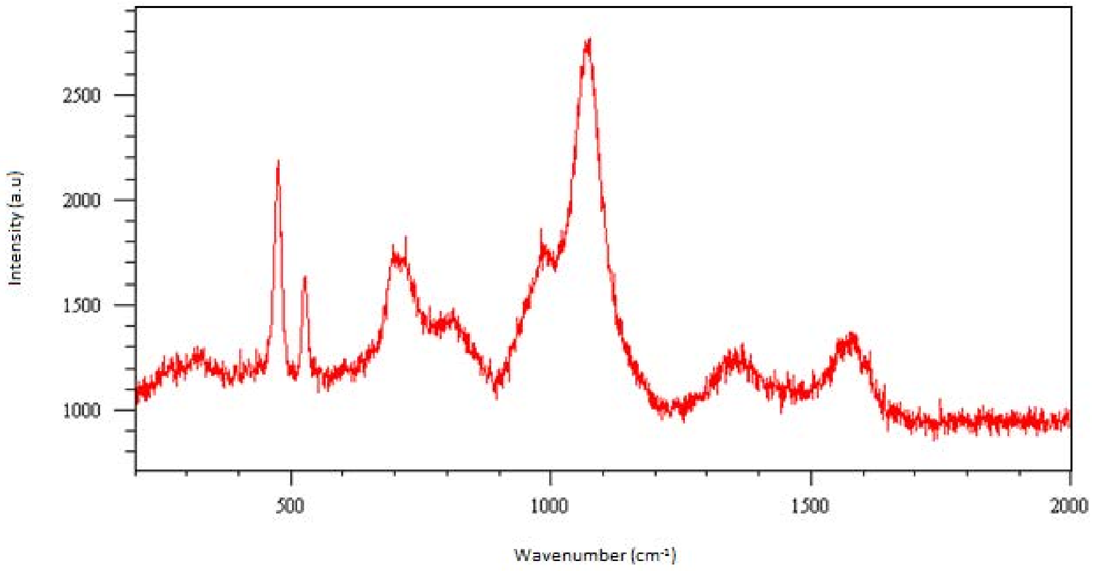


Figure 31. Raman spectrum of B_4C synthesised from 3.7 g PVA, 1 g H_3BO_3, pryolysed at 600 °C for 2 hours and heat treated at 1400 °C for 5 hours.

Figure 31 shows intensity peaks at 1350 cm^{-1} and ^{1}1589 cm^{-1}. This shows the presence of free carbon in the boron carbide powder. This supports the findings found in the XRD analysis.

4. Conclusion

Due to the slow and non-uniform heating, chemical impurities and subsequent processing complications of commercially produced boron carbide, this study investigated the production of B_4C from a polymer precursor at low temperatures. The aim of the study was to produce a low cost boron carbide powder with a stoichometry of B_4C and a small amount of free carbon. This was achieved through mixing polyvinylalcohol (PVA) with boric acid (H_3BO_3), which was subsequently pyrolysed and then heat treated. Several parameters were investigated, including:

- PVA and H_3BO_3 composition
- Pyrolysis temperature
- Pyrolysis dwell time
- Heat treatment temperature
- Heat treatment dwell time

The following conclusions can be drawn from the results and discussion section:

4.1. Optimum conditions

- The optimum conditions for the synthesis of B_4C with low amount of free carbon was achieved by the following:
    - 3.7 g PVA and 1 g H_3BO_3 was mixed together in a dehydration condensation reaction to form polyvinylborate (PVBO).
    - The PVBO was pyrolysed at 600 ^oC for 2 hours at a heating rate of 10 ^oC min^{-1} under Ar flow. This resulted in the elements boron oxide and carbon.
    - The pyrolysed sample was heated at 1400 ^oC for 5 hours at a heating rate of 10 ^oC min^{-1} under Ar flow.
    - The resulting product was B_4C powder with a relatively low amount of free carbon.

4.2. Pyrolysis

- During pyrolysis the PVBO breaks down in three stages:
    - Stage 1 – Elimination of polymer side groups and volatile products.
    - Stage 2 – Partial breakdown o f polymer backbone.
    - Stage 3 – Remaining polymer backbone breakdown.

- Pyrolysis should take place at temperatures above 500 °C and with a minimum dwell time of 2 hours. This will result in a precursor consisting of carbon and boron oxide.
- Increasing the temperature promotes breakdown of the polymer chain.
- A long enough dwell time is required for complete breakdown to occur.

4.3. Heat Treatment

- Increasing the temperature promotes reaction.
- A C/B_2O_3 molar ratio near to 3.5 is required to achieve complete reaction and result in B_4C.
- A minimum temperature of 1300 °C and a minimum dwell time of 5 hours were required for complete reaction to occur.

The study shows it is possible to produce boron carbide powder from a polymeric precursor. The advantages of this method Is the low temperature operation and low material costs. It also results in B_4C powder and therefore does not require subsequent grinding operations. However, a major drawback of this approach was that although residual carbon was minimised it was not removed. Further investigation of this method is required before it can be considered as a possible replacement to the commercially produced boron carbide.

5. Recommendations for Further Work

5.1 Use of alternative polymeric precursors

Several different polymer precursors have been investigated as a carbon source for the synthesis of boron carbide. However, it is a relatively new area of research with very few studies conducted. Therefore, further investigation of alternative polymers (e.g. citric acid, glucose, glycerine) could be conducted to validate existing results and to increase these findings by exploring different variables.

5.2. Removal of residual carbon

A potential method to remove the remaining residual carbon in the final B_4C product was shown by Takano et al.[39] This study showed that carbon could be removed successfully by applying hydrogen. Therefore, potential further work of this study could be to heat treat the pyrolysed sample in a flowing hydrogen atmosphere rather than an argon atmosphere.

5.3. Densification of powder

In order to compare the B_4C powder produced in this study with commercially produced B_4C, the properties need to be compared. Therefore, the author suggests that the powder is densified by application of external pressure, for example, hot pressing or hot isostatic pressing with the possible addition of a sintering aid. The small amount of residual carbon could be seen as beneficial during densification because it acts as a sintering aid. It has been shown that carbon can reduce the oxide layer of the boron carbide powder and therefore promote sintering and hinder grain growth[36]. Other sintering aids that could be investigated include carbide or boride additives. These have been found to increase the flexural strength and fracture toughness of B_4C by grain refinement.[36]

5.4. Pyrolysis and Heat treatment in a single operation

The process used in this study could be improved by pyrolysing and heat treating the sample in a single operation. This will reduce a process step and therefore reduce the overall cost. The author suggests that an investigation is carried out to heat the PVBO sample to 600 °C for 2 hours and then heat to 1400 °C for 5 hours to see if the same results are achieved.

Acknowledgement

The author would like to thank Dr Isaac Chang and Dr Lucian Falticeanu for there support provided during this project. The author would also like to thank Professor Paul Bowen and the University of Birmingham for funding this project.

6. References

---

[1] Yanase, I., Ogawara, R., & Kobayashi, H. (2009). Sythesis of boron carbide powder from polyvinyl borate precursor. *Materials Letters* , 91-93.

[2] Lazzari, R., Vast, N., Besson, J. M., Baroni, S., & Dal Corso, A. (1999). Atomic Structure and Vibrational Properties of Icosahedral B4C Boron Carbide. *Physical Review Letters* , 3230-3234.

[3] Khanra, A. K. (2007). Production of boron carbide powder by carbothermal synthesis of gel material. *Bul. Mater. Sci.* , 93-96.

[4] Gao, F., & klug, D. D. (2007). Theoretical study of new superhard materials: B4C3. *Journal Of Applied Physics* , 1-5.

[5] Thevenot, F. (1990). Boron Carbide - A Comprehensive Review. *Journal of the European Ceramic Society* , 205-225.

[6] Sinha, A., Mahata, T., & Sharma, B. P. (2001). Carbothermal route for preparation of boron carbide powder from boric acid-citric acid gel precursor. *Journal of Nuclear Materials* , 165-169.

[7] Suri, A. K., Subramanian, C., Sonber, J. K., & Murthy, T. S. (2010). Synthesis and consolidation of boron carbide: a review. *Institute of Materials, Minerals and Mining* , 4-39.

[8] Mauri, F., Vast, N., & Pickard, C. J. (2001). Atomic Structure of Icosahedra B4C Boron Carbide from a First Pinciples Analysis of NMR Spectra. *Physical Review Letters* , 1-4.

[9] Emin, D. (2006). Unusual properties of icosahedral boron-rich solids. *Journal of Solid State Chemistry* , 2791-2798.

[10] Bidgeloo, J. A., & Hadain, A. M. (2009). Synthesis of High Purity Micron Size Boron Carbide Powder from B2O3/C Precursor. *International Journal of Recent trends in Engineering* , 176-180.

[11] Balakrishnarajan, M. M., Pancharatna, P. D., & Hoffman, R. (2007). Structure and bonding in boron carbide: The invincibility of imperfections. *New Journal of chemistry* , 473-485.

[12] Tallant, D. R., Aselage, T. L., Campbell, A. N., & Emin, D. (1989). Boron carbide structure by Raman spectroscopy. *Physical Review B* , 5649-5656.

[13] Holmquist, T. J., Rajendran, A. M., Templeton, D. W., & Bishnoi, K. D. (1999). A Ceramic Armor Material Database. *The Nation's Laboratory for Advanced Automotive Technology* , 1-240.

[14] Chen, Y., Chung, Y., & Li, S. (2006). Boron carbide and boron carbonitride thin films as protective coatings in ultra-high density hard disk drives. *Surface & Coatings Technology* , 4072-4077.

[15] Van der Laan, J. G., Schnedecker, G., Van Osch, E. V., Duwe, R., & Linke, J. (1994). Plasma-sprayed boron carbide coatings for first-wall protection. *Journal of Nuclear Materials* , 135-140.

[16] Gatti, A., Cree, R., Higgins, J. B., & Feingold, E. (1965). Boron Carbide Continuous Filaments. *Technical Report* , 65.

---

[17] Sasaki, S., Takeda, M., Yokoyama, K., Miura, T., Suzuki, T., Suematsu, H., et al. (2005). Thermoelectric properties of boron-carbide thin film and thin film based thermoelectric device fabriacted by intense-pulsed ion beam evaporation. *Science and Technology of Advanced Materials* , 181-184.

[18] Alizadeh, A., Taheri-Nassaj, E., & Ehsani, N. (2004). Synthesis of boron carbide powder b a carbothermic reduction method. *Journal of the European Ceramic Society* , 3227-3234.

[19] Goller, G., Toy, C., A, T., & Gupta, C. K. (1996). The production of boron carbide by carbothermic reduction. *High Temperature Materials and Processes* , 117-122.

[20] Weimer, A. W., Roach, R. P., Haney, C. N., Moore, W. G., & Refaniello, W. (1991). Rapid Carbothermal Reduction of Boron Oxide in a graphite Transport Reactor. *AlChE Journal* , 759-768.

[21] Weimer, A. W., Moore, W. G., Roach, R. P., Hitt, J. E., Dixit, R. S., & Pratsinis, S. E. (1992). Kinetics of carbothermal reduction synthesis of boron carbide. *Journal of the American Ceramic Society* , 2509-2514.

[22] Campbell, J., Klusewitz, M., LaSalvia, J., & Chin, E. (2008). Novel Processing of Boron Carbide (B4C): Plasma Synthesized Nano Powders and Pressureless Sintering Formaing of Complex Shapes. 1-5.

[23] *April Crude Steel Production 2011*. (2011, May 20). Retrieved May 20, 2011, from World Steel Association: http://www.worldsteel.org/?action=newsdetail&id=329

[24] Rao, M. (2003). Physical and mathematical modeling of boron carbide manufacturing process. *Indian Institue of Science* , 1255-1265.

[25] Fanchini, G., McCauley, J. W., & Chhowalla, M. (2006). Behavior of Disordered boron Carbide under Stress. *Physical Review Letters* , 1-4.

[26] Jain, A., Anthonysamy, S., Ananthasivan, K., Ranganathan, R., Mittal, V., Narasimham, S. V., et al. (2008). Characterization of electrodeposited elemental boron. *Materials Characterization* , 890-900.

[27] Jung, C., Lee, M., & Kim, C. (2004). Preparation of carbon-free B4C powder from B2O3 oxide by carbothermal reduction process. *Materials Letters 58* , 609-614.

[28] Lee, S., Mazurowski, J., Ramseyer, G., & Dowben, P. A. (1992). Characterization of boron carbide thin films fabricated by plasma enhanced chemical vapor deposition from boranes. *Journal of Applied Physics* , 4925-4933.

[29] Sezer, A. O., & Brand, J. I. (2001). Chemical vapor deposition of boron carbide. *Materials Science and Engineering* , 191-202.

[30] Mirabelli, M. G., Lynch, A. T., & Sneddon, L. G. (1989). Molecular and Polymeric Precursors to Boron-Based Ceramics. *Sold State Ionics* , 655-660.

[31] Kakiage, M., Tahara, N., Yanase, I., & Kobayashi, H. (2011). Low-temperature synthesis of boron carbide powder from condensed boric acid-glycerin product. *Materials Letters* , 1839-1841.

[32] Kakiage, M., Tahara, N., Yanagidani, S., Yanase, I., & Kobayashi, H. (2011). Effect of boron oxide/ carbon arrangement of precursor derived from condensed polymer-boric acid product on low-temperature sythesis of boron carbide powder. *Journal of the Ceramic Society of Japan* , 422-425.

[33] Barros, P. M., Valeria, I., Yoshida, P., & Schiavon, M. A. (2006). Boron-containing poly(vinyl alcohol) as a ceramic precursor. *Journal of Non-Crystallie Solids* , 3444-3450.

---

[34] Gheorghe, C., Marculescu, C., Badea, A., Dinca, C., & Apostol, T. (2009). Effect of Pyrolysis Conditions on Bio-Char Production from Biomass. *Proceedings of the 3rd WSEAS Int. Conf. on RENEWABLE ENERGY SOURCES* , 239-241.

[35] Chakrabarti, A., Xu, T., Paulson, L. K., Krise, K. J., Maguire, J. A., & Hosmane, N. S. (2010). Synthesis of Boron Nanorods by Smelting Non-Toxic Boron Oxide in Liquid Lithium. *Journal of Nanomaterials* , 1-5.

[36] He, J. L., Shen, Z. Q., Liu, Z. Y., He, L. L., Yu, D. L., Guo, L. C., et al. (2007). Carbon-rich boron carbide in the eutectic product synthesized by resistance heating of B2CN in graphite. *Journal of Alloys and Compounds 437* , 238-246.

[37] Li, X. (2010). *Use of Boron Carbide Nanowires Result in Lightweight Fabric.* Available: http://www.azonano.com/news.aspx?newsID=16845. Last accessed 16th Feb 2012.

[38] Reynaud, S. (2010). Fabrication and characterization of carbon and boron carbide nanostructured materials. *University of New Jersey* , 38-64.

[38] Takano, M., Itoh, A., Akabori, M., & Ogawa, T. (2001). Oxygen Solubility in Dysprosium Mononitride Prepared by Carbothermic Synthesis. *Journal of Alloys and Compounds* , 235-239.

7. Appendix

Appendix 1

Equation to calculate C/B_2O_3 molar ratio:

Number of moles = mass (g) / molar mass for each constituents.

C / B_2O_3 = Ratio number of carbon moles / Number of B_2O_3 moles.