

Production of boron carbide powder by carbothermal synthesis of gel material

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Abstract. Boron carbide (B_4C) powder has been produced by carbothermal reduction of boric acid–citric acid gel. Initially a gel of boric acid–citric acid is prepared in an oven at $100^\circ C$. This gel is pyrolyzed in a high temperature furnace over a temperature range of 1000 – $1800^\circ C$. The reaction initiation temperature range for B_4C formation is determined by thermal analysis. The optimal pyrolysis temperature of B_4C synthesis is investigated. During pyrolysis, the evaporation of boron-rich phases results in presence of free carbon in B_4C powder. The electron micrographs and particle size analyser reveal the generation of fine B_4C particles.

Keywords. B_4C ; carbothermal synthesis; gel material.

1. Introduction

Boron carbide is an advanced ceramic material. It occupies a significant place in the group of most important non-metallic hard materials. It is the third hardest material known and hardest material produced in tonnage quantities. In 1883, Joly reported the preparation of boron carbide and identified it as B_3C and then Moissan reported the production of B_6C . The stoichiometric formula of B_4C was identified in 1934. The boron carbide has a rhombohedral structure with 12-atom icosahedral clusters which are linked by direct covalent bonds and through three-atom intericosahedral chains. Boron carbide has single phase throughout the entire range (Thevenot 1990; Spohn 1993). Its high wear and impact resistance and low specific weight makes it suitable for application in ball mills, nozzle, wheel dressing tools, wire drawing dies, rocket propellant light weight armour plates etc (Alizadeh *et al* 2004). It can also be used as a reinforcing material for ceramic matrix composites. It is an excellent neutron absorption material in nuclear industry due to its high neutron absorption coefficient (Sinha *et al* 2002). Boron carbide can be prepared by reaction of elemental boron and carbon powder, carbothermal route, reduction of BCl_3 by CH_4 at $1500^\circ C$ by laser and low temperature synthesis from a CCl_4 , BBr_3 and Na mixture (Sinha *et al* 2002; Shi 2003). Recently, Khanra and Godkhindi (2005) prepared ultrafine B_4C powder by self-propagating high-temperature synthesis (SHS), whereas Carlsson *et al* (2002) prepared B_4C whisker by carbothermal vapour–liquid–solid growth mechanism. In

the present investigation, the B_4C powder has been prepared from the pyrolysis of boric acid–citric gel material and the pyrolysed product is characterized by different techniques.

2. Experimental

Boric acid (99.9% pure, Loba-Chemie, India) and citric acid (99.5% pure and particle size, 99.8% pure, S. D. Fine Chem, India) were used as precursor materials for boron and carbon, respectively. A mixture (10 g) of boric acid and citric acid (molar ratio 12 : 7) was dissolved in distilled water and then the solution was heated in an oven at $100^\circ C$ for 3 h. The solution became golden yellow gel, which was crushed into powder for pyrolysis. The differential thermal analysis and thermogravimetric analysis (DTA/TG) (Perkin Elmer, Pyris Diamond TG/DTA, Japan) of crushed powder was carried out from room temperature to $1400^\circ C$. The DTA/TG was done in XL grade argon atmosphere and the rate of heating was 10, $20^\circ C/min$. The crushed mass was next pyrolyzed over a temperature range of 1000 – $1800^\circ C$ in a graphite resistance-heating furnace (Thermal Technology Inc, USA) with a continuous flow of XL grade argon gas. The phase analysis of the pyrolyzed product was carried out by XRD technique (Philips PW 1840, The Netherlands). The black pyrolyzed powder was burnt at $600^\circ C$ for 2 h (air) for burning of unreacted carbon present in the product. The burnt product was also characterized by XRD. The morphology of the purified product was studied by a scanning electron microscope (SEM) (JEOL, JSM 840A, Japan). The particle size distribution of the product was determined by a particle size analyser (Malvern M7, UK) using the laser scattering

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technique. The transmission electron microscopic (TEM) studies on the leached and washed powder were carried out by putting the ultrasonically dispersed powders on a carbon coated copper grid using Philips electron microscope (CM 200, The Netherlands). The samples were analysed by 200 keV electron beam during TEM investigations.

3. Results and discussion

The synthesized powder is found to be black in colour. The DTA/TG plot of gel at different rates of heating is shown in figure 1. It shows two endothermic peaks at lower temperatures due to melting and dissociation (138°C and 169°C) of boric acid, respectively. But similar type of phenomenon is not observed for citric acid. This may be due to overlap or relatively a smaller magnitude of heat of melting and dissociation of citric acid precursors. The individual DTA/TG analysis reveals melting of citric acid at 157°C and then dissociation at 220°C. The dissociation reactions are given below



Figure 1 shows presence of a big hump in the range 1050–1100°C. This may be the indication of phase changes during pyrolysis. The XRD patterns of gel pyrolyzed at different temperatures are shown in figure 2. The pattern shows presence of B_2O_3 as a major phase with B_4C as a minor phase of gel pyrolyzed from 1000–1400°C range. The initial molar ratio (12 : 7) of boric acid and citric acid is equivalent

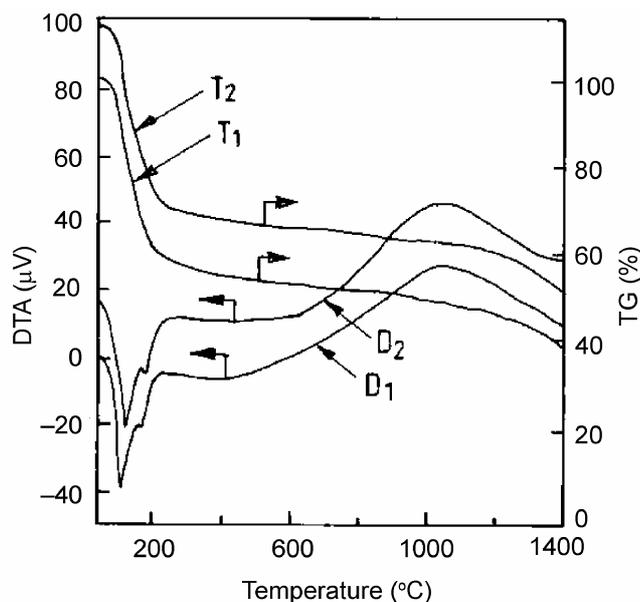


Figure 1. DTA/TG plot of gel material: D_1 , D_2 are DTA at 10, 20°C/min and T_1 , T_2 are TG at 10, 20°C/min.

to molar ratio of 2 : 7 of B_2O_3 and C. The overall pyrolysis reaction of gel can be written as



The TG plot shows sharp decrease of weight due to H_2O loss of the mixture (dissociation) and then uniform decrease of weight. A sharp decrease of weight is observed above 1000°C, which may be due to weight loss due to CO gas generation. The weight losses of the pyrolyzed samples are found to be ~77% and 80.2% at 1600°C and 1800°C, respectively. As per (3), the theoretical weight loss is calculated to be ~75%. The higher observed weight losses may be due to the evaporation of boron oxide and boron sub-oxide at higher temperatures. The reaction of carbon could have occurred with both liquid boron oxide and gaseous boron sub-oxide [$\text{B}_2\text{O}_{2(g)}$]. The rate of formation of gaseous boron sub-oxide increases with temperature (Alizadeh *et al* 2004). This indicates the B_4C formation to occur through the gaseous B_2O_2 . After 1500°C, the liquid B_2O_3 phase starts to form gaseous B_2O_3 . The kinetics of gaseous B_2O_3 phase formation is less than the rate of gaseous B_2O_2 formation (Alizadeh *et al* 2004). It is necessary to take some extra boric acid (reducing agent) in the reactant mixture to compensate the loss through the evaporation of B_2O_2 and B_2O_3 . The XRD patterns of the sample pyrolyzed at 1600 and 1800°C show presence of unreacted carbon and B_4C phase (figure 2). The intensity of carbon peak is found to increase at 1800°C as compared to 1600°C. The amount of free carbon of pyrolyzed product is found to be ~9.8 and 12.7% at 1600°C and 1800°C, respectively. The

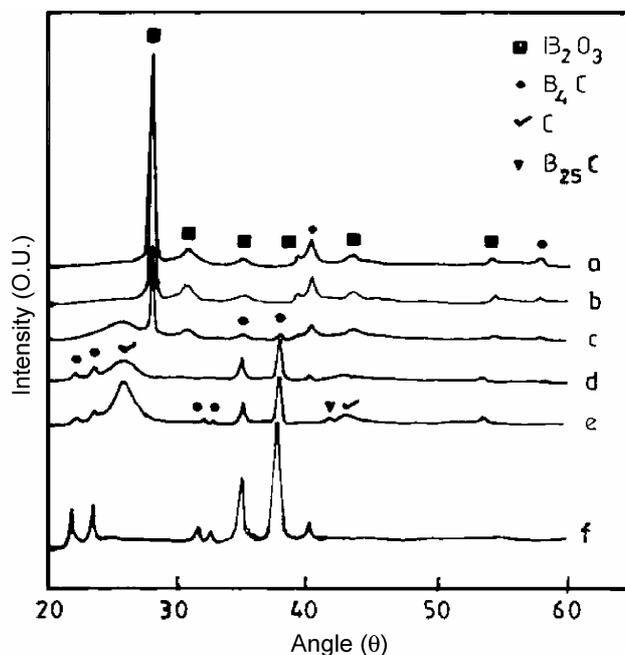


Figure 2. XRD patterns of gel pyrolyzed at different temperatures: a. 1000, b. 1200, c. 1400, d. 1600, e. 1800°C and f. after carbon removal (burning at 600°C).

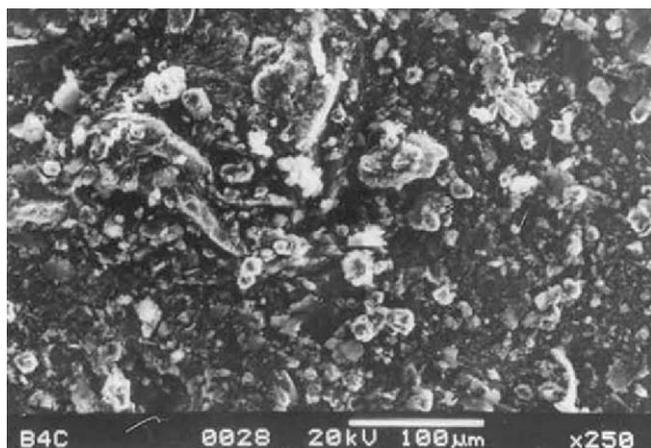


Figure 3. SEM image of purified powder pyrolyzed at 1600°C.

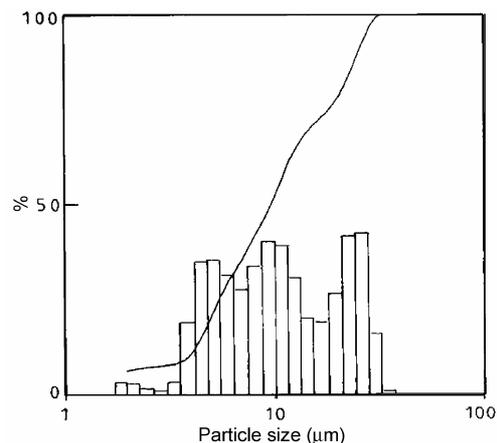


Figure 4. Particle size distribution of purified powder pyrolyzed at 1600°C.

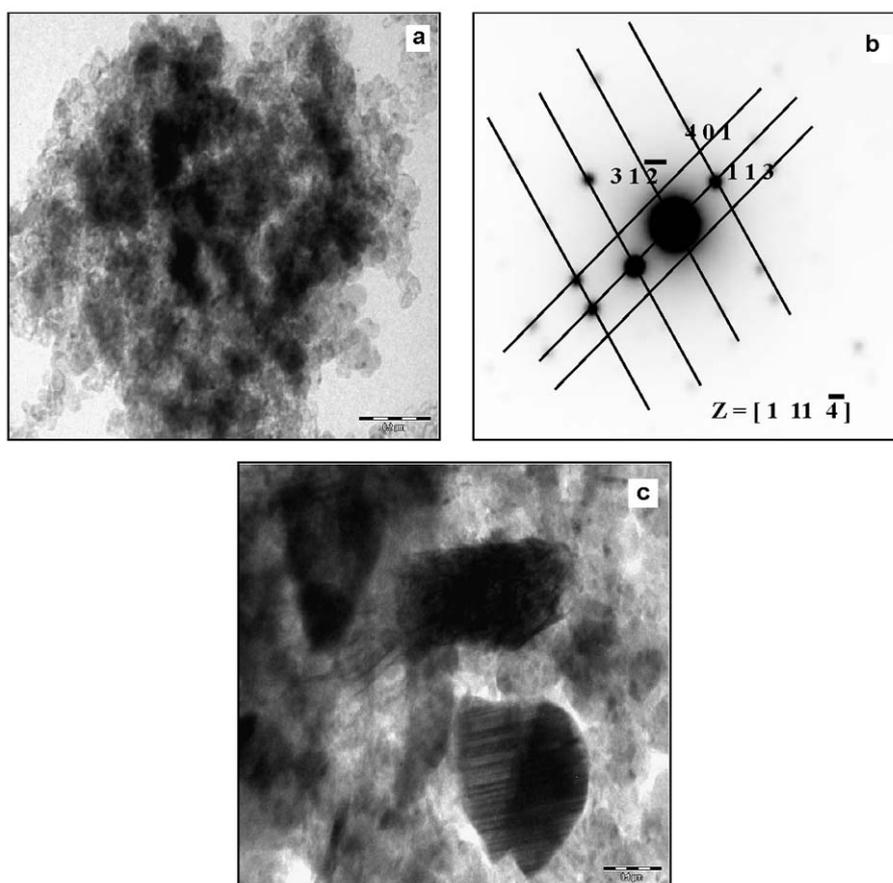


Figure 5. TEM images of purified powder pyrolyzed at 1600°C: a. B₄C powder, b. SAD pattern and c. twin formation in powder.

presence of free carbon in the pyrolyzed powder is possibly due to evaporation of more boron-rich phases from the mixture during pyrolysis. The pyrolysis at 1600°C may be the optimum temperature for production of B₄C powder with minimum impurity (free carbon) from the gel material.

The XRD pattern shows absence of free carbon after removal of carbon (burning at 600°C for 2 h) in case of gel pyrolyzed at 1600°C, which indicates removal of carbon at 600°C (figure 2f). It has also been seen that the amount of free carbon is much more when B₄C is prepared from

the mixture of B_2O_3 and amorphous carbon. It may be due to non-uniform mixture, which affects the kinetics of conversion of B_4C . The presence of small amount of fine carbon may help during densification of B_4C (Sinha *et al* 2002). The SEM shows mainly agglomeration of fine spherical particles (figure 3). The particle size analysis of the product pyrolyzed at $1600^\circ C$ shows bi-modal type of particle distribution (figure 4). The average particle size of B_4C powder is found to be $\sim 9.4 \mu m$. The TEM images of pyrolyzed powder are shown in figure 5. It shows agglomeration of fine particles and presence of defective structures like twins formation are also found. Such defects are generally formed in combustion synthesized powder due to high rate of cooling and shows higher sintered density than commercially available powder during pressureless sintering (Mishra *et al* 2004; Khanra *et al* 2005). The selected area diffraction (SAD) pattern shows presence of B_4C planes (figure 5b). Presence of defects like twins is often found in the synthesized powder (figure 5c). Such defects are generally formed in the combustion synthesized powder due to high rate of cooling and shows higher sintered density than commercially available powder during pressureless sintering (Mishra *et al* 2004; Khanra *et al* 2005). A detailed TEM study regarding presence of defect structures are under progress.

4. Conclusions

The B_4C powder can be produced by carbothermal reduction of gel material prepared from boric acid–citric acid mixture.

During pyrolysis, the B_4C formation starts over the temperature range of $1050\text{--}1100^\circ C$. The optimum pyrolysis temperature of B_4C is found to be at $1600^\circ C$. The generation of fine B_4C powder is confirmed from the SEM, particle size analysis and TEM study.

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