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Carbothermal route for preparation of boron carbide powder from boric acid–citric acid gel precursor

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Abstract

Boron carbide (B_4C) powder has been prepared by carbothermal process using boric acid and citric acid as raw materials. Aqueous solution of boric acid in presence of citric acid forms a stable gel under controlled pH condition. The gel on subsequent pyrolysis under vacuum yields a precursor powder consisting of boron oxide and carbon. The precursor is heated under vacuum at 50 °C/h up to 1450 °C and the product obtained has been characterized by X-ray diffraction (XRD), chemical analysis, particle size analysis and scanning electron microscopy. XRD pattern shows that the product consists of B_4C and carbon (graphite). Presence of free carbon (11.1 wt%) indicates boron loss in the carbothermal reaction. Boron loss has been calculated to be 11.3 wt%. Boron carbide powder obtained is composed of near equiaxial particles of narrow size distribution having a median size of 2.25 μm. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Boron carbide (B_4C) possesses a combination of properties, such as, high melting point (2447 °C), high hardness (28–35 GPa Knoop hardness), low density (2.52×10^3 kg/m^3), high Young's modulus (450–470 GPa), high corrosion and oxidation resistance etc., which give it a leading role among materials suitable for high performance applications [1,2]. Components made of dense boron carbide are widely used in wear resistance applications, e.g., as blast nozzles, wheel dressing tools, and light weight armor plates [2,3]. Boron carbide is also used in nuclear industry as neutron absorber and shielding material due to large neutron absorption cross-section of boron atoms [4]. Neutron absorption efficiency of boron carbide can be increased by isotopically enriching it with ^{10}B.

Boron carbide can be prepared by a variety of reactions including carbothermal reduction of boron–oxygen compounds such as boron oxide (B_2O_3), boric acid (H_3BO_3), borax ($Na_2B_4O_7$), boracite ($Mg_7Cl_2B_{16}O_{30}$) etc., as well as by the direct combination of the elements [2]. Commercially, B_4C is produced by carbothermal process using boric acid and carbon at a temperature near to the melting point of B_4C in a batch electric arc or resistance furnace [2,5]. Consistent with the process, the product obtained is in the chunk form and coarse grained. The product is subsequently crushed and intensively milled to produce powder. The milled powder is inherently associated with contamination resulting from the grinding media and hence requires an acid leaching for purification. Other routes for preparation of boron carbide powder include magnesiothermic reduction of B_2O_3 in the presence of carbon at 1000–1200 °C [2,6], reduction of BCl_3 by CH_4 at a temperature of 1500 °C by using laser [7].

Preparation of B_4C by carbothermal route has been reported to be associated with the loss of boron in the form of boron oxide/suboxide [8]. This is particularly important for production of enriched (^{10}B) boron carbide. Weimer et al. have reported the preparation of boron carbide by carbothermal process starting from homogeneous aqueous solution of boric acid and corn

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starch which yielded boron oxide and carbon respectively [8]. The process was carried out in a flow reactor using rapid heating mode under argon atmosphere in the temperature range of 1530–1850 °C. Though the process utilized excess boron oxide, the product contained 39.9% free carbon when the reaction was carried out at 1790 °C. Different form of carbon sources like dextrose, sucrose, starch, glycerol, polyvinyl alcohol etc. have been employed for the carbothermal reduction for the preparation of boron carbide powder [9]. However, boron loss has been observed in all cases.

Citric acid and other polyfunctional hydroxy-acids have been used extensively for complexing metal ions in a gel [10]. The gel on pyrolysis under vacuum or inert atmosphere yields a mixture of metal oxide and carbon in amorphous form. In the pyrolyzed product the mixing of oxide and carbon is expected to be more homogeneous than conventional mixing. In the present study, boric acid and citric acid have been used as source materials for boron and carbon respectively for the preparation of boron carbide powder by carbothermal process.

2. Theoretical considerations

The overall carbothermal reduction of boron oxide by carbon to produce B_4C powder can be written as

$$2B_2O_3(c) + 7C(c) \rightarrow B_4C(c) + 6CO(g). \tag{1}$$

Calculated equilibrium partial pressure values of CO (p_{CO}) of the reaction (1) at different temperatures have been given in Table 1. In the calculation the activities of solid species have been assumed to be unity. From the table, it is seen that under vacuum/inert atmosphere the reaction (1) is significant at temperatures above 1127 °C. Once the reaction product forms, the diffusion of reacting species is likely to become sluggish thus calling for higher temperature for reaction to proceed at a reasonable rate. However, at higher reaction temperature vaporization loss of boron in the form of its oxide/suboxides plays an important role. The loss of boron can be represented by the following equations:

$$B_2O_3(c,l) \rightarrow B_2O_3(g), \tag{2}$$

$$B_2O_3(c,l) + C(c) \rightarrow B_2O_2(g) + CO(g), \tag{3}$$

$$B_2O_3(c,l) + 2C(c) \rightarrow B_2O(g) + 2CO(g). \tag{4}$$

Vapor pressure of B_2O_3 and equilibrium partial pressures of the suboxides as per the reactions (3) and (4) at different temperatures are shown in Table 1. From this data significant loss of boron may be expected in the form of B_2O_3 and B_2O above 1127 °C. The loss of boron can be minimized if the reaction is carried out at lower temperature. Further, intimate mixing of B_2O_3 and C may improve the kinetics of the process.

3. Experimental

Boric acid (LR grade, H_3BO_3, S.D. Fine-Chem Ltd., Mumbai, India) and citric acid monohydrate (AR grade, $C(OH)(COOH)(CH_2COOH)_2 \cdot H_2O$, Fisher Inorganics & Aromatics Ltd., Chennai, India) were taken as starting materials for the preparation of boron carbide powder. The molar ratio of boric acid and citric acid was kept at 12/7 as it was found to give the necessary molar ratio of B_2O_3 and carbon in the subsequent step. Boric acid solution (2.5 M) was prepared by dissolving boric acid in distilled water at 85 °C. Citric acid was added to the boric acid solution and the solution was evaporated on a laboratory hot plate to remove excess water. During evaporation, temperature of the solution was constantly monitored with the help of a thermometer placed within the solution through a test tube. During evaporation the temperature of the solution increased up to 112 °C. The pH of the solution, during evaporation, was maintained within the range of 2–3 by adding concentrated AR-grade ammonia solution (25%). Under this pH condition, a transparent 'golden yellow colored' gel was formed and subsequently the gel was dried on hot plate. The dried gel was pyrolyzed under vacuum at 700 °C. The spongy black precursor mass obtained after pyrolysis of the gel was crushed to convert into powder form. The crushed precursor powder was compacted in a graphite die (25 mm diameter) at a pressure of 20 MPa using a uniaxial hydraulic press. The die was covered from top and bottom using two graphite plungers. The

Table 1
Equilibrium partial pressure/vapor pressure of carbon monoxide and boron oxides at different temperatures (pressures calculated from thermodynamic data) [11,12]

Temperature (°C)	$p_{B_2O_3}$ (Pa)	p_{BO} (Pa)	p_{B_2O} (Pa)	p_{CO} (Pa)
727	3.50×10^{-7}	1.64×10^{-7}	1.77×10^{-6}	1.99×10^{-2}
927	8.73×10^{-4}	3.90×10^{-4}	2.72×10^{-3}	6.23
1127	2.34×10^{-1}	9.59×10^{-2}	4.85×10^{-1}	3.61×10^{2}
1327	1.54×10^{1}	5.73	2.27×10^{1}	7.32×10^{3}
1527	4.01×10^{2}	1.35×10^{2}	4.40×10^{2}	7.40×10^{4}

top plunger contained a central hole of 6 mm diameter to ensure the release of gaseous products formed through reaction. The die was placed in a vacuum induction furnace and heated at a rate of 50 °C/h to 1000 and 1450 °C and holding at those temperatures for 2 h.

The intermediate precursor compound and the product were characterized by X-ray diffraction (XRD) and chemical analysis. XRD was carried out at a scan rate of 0.05°/s using CuK_α radiation by a Philips X-ray diffractometer (model no.: PW1830). The carbon analysis of the samples was carried out using ELTRA CS-800 carbon/sulphur determinator. Oxygen was determined by inert gas fusion method using LECO TC-136 oxygen/nitrogen determinator. For boron analysis, the samples were first fused with sodium carbonate followed by leaching with HCl solution. Boron was determined as boric acid by titration of mannitol–boric acid complex with standard sodium hydroxide solution (0.1 M) using phenolphthalein as indicator. The particle size of the final product was measured by using Horiba Laser particle size analyzer (model no.: LA-500). The morphology of the product was studied by scanning electron microscopy (SEM, model no.: JEOL JSM- T330A).

4. Results and discussion

Mixing citric acid in boric acid solution gives rise to a clear solution, which on evaporation yields a stable transparent gel if pH of the solution is controlled in the range of 2–3. The dried gel was pyrolyzed at 700 °C under vacuum in order to prevent the oxidation of carbon. Fig. 1(a) shows the XRD pattern of this precursor powder. The pattern exhibits only diffraction peaks corresponding to cubic B_2O_3. Carbon peaks do not appear in the XRD pattern of the pyrolyzed gel. However, when the pyrolyzed gel is heated at 1000 °C, graphite peak appears in the XRD pattern, as shown in Fig. 1(b). This indicates that the carbon present in the precursor powder pyrolyzed at 700 °C is amorphous. These XRD results suggest that on pyrolysis of the gel, boric acid converts into B_2O_3 while the citric acid yields only carbon.

The chemical composition of the pyrolyzed gel (700 °C) is shown in Table 2. The composition represents an atomic ratio of B:O:C of 4:5.85:6.86 which can be approximated to 4:6:7. This ratio corresponds to a molar ratio of 2:7 of B_2O_3 and C in the pyrolyzed gel. Further, the above B:C:O atomic ratio in the pyrolyzed gel precursor indicates that one mole of citric acid in the gel on pyrolysis yields three moles of carbon. The decomposition of citric acid under the present experimental conditions may be expressed as

$$C_6H_8O_7 \rightarrow 3C + 4H_2O + 3CO. \qquad (5)$$

The absence of any peak corresponding to B_4C in the XRD pattern of the precursor powder heated at 1000 °C suggests that the B_4C formation according to reaction (1) is not significant at this temperature. Under slow heating (50 °C/h) of the precursor powder, vacuum started falling at around 1050 °C indicating the start of the reaction; the vacuum improved to about 10^{-3} Pa

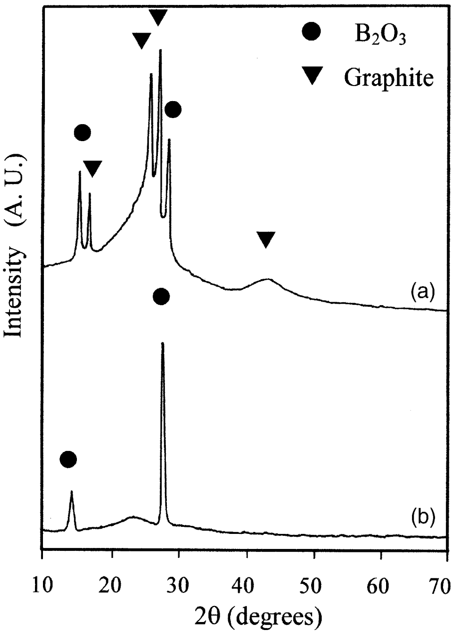

Fig. 1. XRD pattern of boric acid–citric acid gel pyrolyzed under vacuum at (a) 700 °C and (b) 1000 °C.

Table 2
Chemical analysis of precursor powder prepared by pyrolysing boric acid–citric acid gel at 700 °C for 2 h and the product obtained after heating the precursor up to 1450 °C

Element	Analytical method/instrument used	Boron carbide precursor (wt%)	Boron carbide product (wt%)
Boron	Titration	19.4	68.8
Carbon	ELTRA CS-800 carbon/sulphur determinator	36.9	30.0
Oxygen	LECO TC-136 oxygen/nitrogen determinator	42.0	1.0

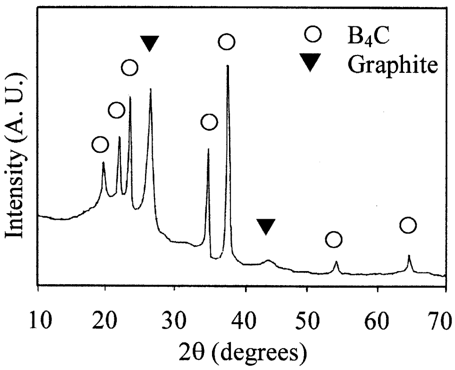

Fig. 2. XRD pattern of the product obtained by heating the pyrolyzed gel precursor powder up to 1450 °C.

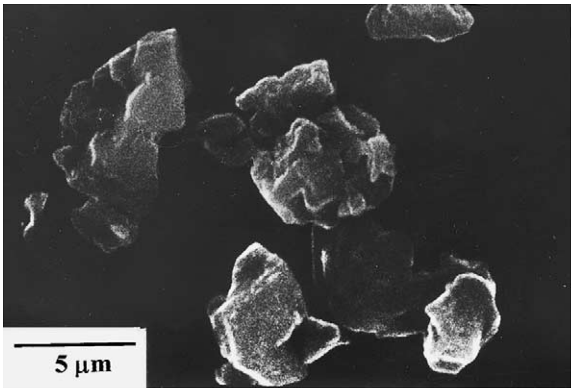

Fig. 4. SEM photomicrograph of the product after heating the pyrolyzed gel precursor up to 1450 °C.

after reaching 1450 °C. The XRD pattern of the product obtained after heating the precursor up to 1450 °C is shown in Fig. 2. The pattern shows peaks that can be assigned to B_4C and graphite. The chemical composition of the product is given in Table 2. Low oxygen content in the product indicates the completion of the reaction. On further heating of the product under vacuum at 1700 °C for 2 h, no significant weight loss was observed. The analysis of the chemical composition of the product shows that the product contains 88.9% B_4C and 11.1% free carbon by weight. The presence of free carbon in the product suggests that some boron has been lost during carbothermal reduction. In the precursor boron content was 19.4% and in the final product it is 68.8%. In the overall reaction from the pyrolyzed powder to final product 75% weight loss has been observed. From the mass balance, it has been calculated that the boron loss in the process is 11.3% of total boron content of the starting material.

The particle size distribution of the product obtained after heating the precursor powder up to 1450 °C is shown in Fig. 3. The powder is composed of particles with a narrow size distribution; the median size is 2.25 μm, whereas D_{90} is less than 4.7 μm. The fineness of the powder has also been confirmed by scanning electron microscopy. The particles are nearly equiaxial, as seen in the SEM photomicrograph (Fig. 4).

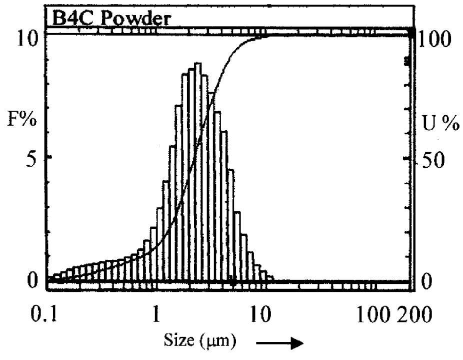

Fig. 3. Particle size distribution of the product obtained after heating the pyrolyzed gel precursor up to 1450 °C (F%—frequency distribution scale; U%—cumulative distribution scale).

Our results suggest that carbothermal process is inherently associated with loss of boron, which can therefore only be minimized. If excess boric acid is not used the product will be composed of B_4C and free carbon. The process described here yields B_4C powder at a relatively low temperature and is associated with lower boron loss than reported for carbothermal processes [8]. The free carbon in the product may have a beneficial effect on further processing of the powder. It has been reported in the literature that very fine graphite in B_4C powder can act as a sintering aid during consolidation of the powder into high-density particles [1,2,13,14]. Free carbon in B_4C is also reported to decrease the melting point at the B_4C–C interface to the eutectic point and thereby enhance material transport [15]. Moreover, free carbon migrates with grain boundaries during sintering and plays an important role in controlling grain-boundary mobility [14].

5. Conclusions

Boric acid and citric acid forms a stable gel in the pH range of 2–3, which on pyrolysis under vacuum yields a mixture of B_2O_3 and carbon. The carbothermal reaction takes place at a temperature below 1450 °C. The loss of boron, during the carbothermal reduction is significantly lower than reported in the literature. This may be of particular interest with respect to the preparation of enriched B_4C. The B_4C powder produced by this process is composed of equiaxial particles that show a narrow size distribution and a median particle size of 2.25 μm.

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