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Short communication

One step reduction of Boric Acid to boron carbide nanoparticles

Paviter Singh[a], Bikramjeet Singh[a], Manjeet Kumar[b], Akshay Kumar[a,*]

[a]Department of Nanotechnology, Sri Guru Granth Sahib World University, Fatehgarh Sahib 140406, Punjab, India
[b]Department of Materials Engineering, Defense Institute of Advanced Technology (DU), Pune 411025, India

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Abstract

Boron carbide (B_4C) nanoparticles have been successfully synthesized by carbo-thermic reduction of Boric Acid (H_3BO_3). This method is relatively low temperature synthesis route. It can be used for large scale production of B_4C. The synthesized nanoparticles have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and differential thermal analyzer (DTA) techniques. XRD analysis confirmed the formation of single phase B_4C. SEM and TEM analysis confirmed that the particles are spherical in shape with an average particle size of 12 nm. DTA analysis shows that the phase is stable upto 900 °C and the material can be used for high temperature applications.

Keywords: Boron carbide; Nanoparticles; Scanning electron microscopy

1. Introduction

Boron carbide (B_4C) is an extremely hard ceramic material used in tank armor, bulletproof vests, and numerous industrial applications [1]. Materials reduced to the nanoscale shows different properties as compared to its micro scale properties and this is also true for B_4C [2]. Metallurgists tried to reduce the size of B_4C for obtaining better properties. Nanostructured B_4C has the potential to become the new material for tools, dies and wear parts. Nanostructured B_4C materials have also shown promising results as a novel agent in T-cell guided boron neutron capture therapy (BNCT) for cancer treatment. In BNCT, high energy neutrons fall from a nuclear reactor. Boron atoms absorb these neutrons and release alpha particles which kills the tumor cells. Boron carbide nanoparticles are also used in biosensors [3]. These nanomaterials have superior properties and more homogeneous microstructures as compared to conventional boron carbide. Nano-grained boron carbide also allows optimization of specific properties without compromising others [4].

Earlier, B_4C has been synthesized by various routes such as ball milling [5], thermal plasma [6] and chemical process [7]. However, these techniques have many disadvantages. Ball milling compromises purity of product, consumes high energy and takes long time. In case of thermal plasma, high energy requirements are there and purity of the product is another issue. Most important route is the chemical route by which fine and uniform B_4C nanoparticles can be synthesized. Recently, thermo chemical technique was used to prepare B_4C using Boric Acid [8,9]. The chemical route can be used to get a higher yield having uniform particles of nanosize range. Furthermore, the processing parameters can be optimized to increase the yield with lower reaction time and temperatures. Proper design of the autoclave can make this process more suitable for the production and commercial exploitation of nanosized particles. Synthesis of nanostructured B_4C with recent process has demonstrated the utilization of this technique [10]. However, to achieve high purity B_4C nanoparticles processing parameters such as temperature and pressure plays an important role.

2. Experimental

Boric Acid (H_3BO_3), magnesium (activated) and acetone were used as initial ingredients. Acetone was used as a carbon

*Corresponding author.
E-mail address: akshaykumar.tiet@gmail.com (A. Kumar).

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source in the present study. The average particle size and purity of Boric Acid (H_3BO_3) powder were 20 μm and 99.9%, respectively. Magnesium (98%) was used as reducing agent. All the chemicals were used without further purification. For present investigations, a specially designed stainless steel (304) autoclave is used. The wall thickness of the autoclave is 20 mm. Traditional autoclaves cannot be used for these investigations. In typical experiments, Boric Acid (H_3BO_3), activated magnesium and acetone were put in an autoclave of 50 ml capacity in the ratio 4 (g):1.5 (g):40 (ml), respectively. The charged autoclave was heated at 700 °C (sample S1) and 800 °C (sample S2) for 20 h in two different experiments. After furnace cooling, the dark solid powders were taken out from the autoclave and treated with hydrochloric acid (1:3) to remove un-reacted Mg and other soluble phases from the product. The acid treated samples were washed with distilled water first followed by ethanol to eliminate the water absorbed in the powders. The powders were then dried at 50 °C for 5 h in a vacuum heating oven. The dried powders were characterized to investigate the formation of B_4C phase in the synthesized mass.

3. Characterization

After acid leaching, the samples were characterized by X-ray (powder) diffraction technique. The pattern was recorded at room temperature by X-ray diffractrogram (Xpert pro PAN analytical) using monochromatic CuK_α radiation ($\lambda = 1.5418$ Å) at a scan speed of 5 °C/min. The range of the XRD pattern was $20^\circ \leq 2\theta \leq 80^\circ$. Differential thermal/thermal gravimetric analysis (DT/TGA) analysis of the powdered sample was done using STAR SW 1200 in nitrogen atmosphere. Platinum crucibles were used for sample analysis at 5 °C/min heating rate in a temperature range of 35–800 °C. The morphology, topography and composition study of crystalline phases of the sample was done by using a high-energy beam of electrons with the help of a scanning electron microscope (SEM) JSM-6510 LV (Jeol). Transmission electron microscopy (TEM) was done using the Hitachi H-7500 model.

4. Results and discussion

The X-ray diffractogram of S1 and S2 has been shown in Fig. 1 a and b, respectively. In sample S1 there is no peak of B_4C, only carbon (ICDD card no. 75-1621) along with unreacted Boric Acid (ICDD card no. 30-0620). In sample S2 the peaks are indexed with hexagonal boron carbide (ICDD card no. 75-0424). The presence of peaks of B_4C in the XRD pattern of this sample indicates the conversion of (H_3BO_3) to B_4C. The proposed reaction which may have occurred is

$$4H_3BO_3 + CH_4COCH_4 + Mg \rightarrow B_4C + 2CO_2 + H_2 + MgO + 8H_2O \quad (1)$$

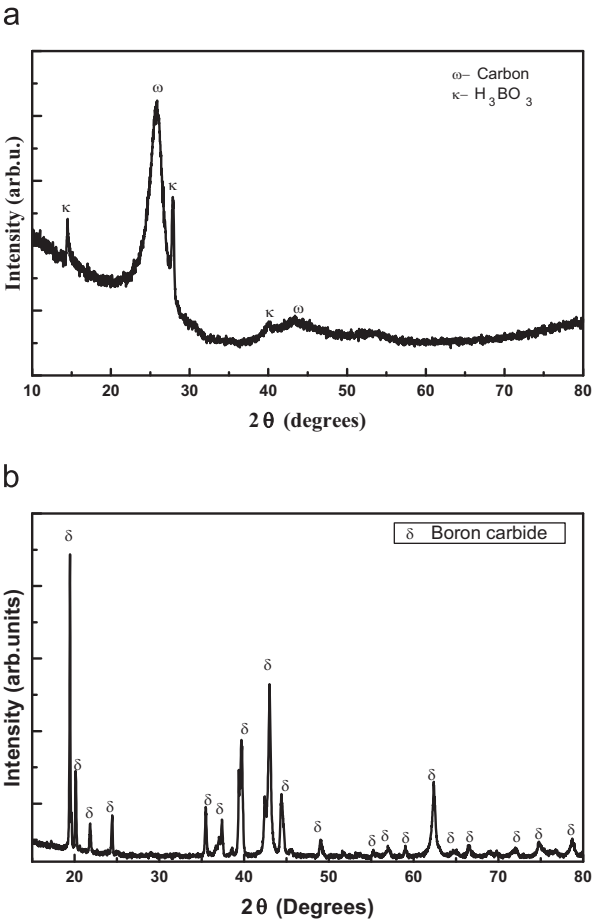

Fig. 1. (a) XRD of sample S1 and (b) XRD of sample S2.

In this case, hydrogen generated is helping in reduction of Boric Acid. Magnesium might have provided the active sites for the nucleation of B_4C. The access carbon has been consumed by the oxygen molecules released during the reaction. The particle size of the prepared sample was also calculated using the Hall Williamson formulae which comes out to be 18 nm [11–13].

Detailed thermal analysis was also done for sample S2 to check phase stability or any phase transition at elevated temperatures (Fig. 2). It has been observed that there is continuous weight loss till 620 °C. The graph may be analyzed by dividing it into two temperature zones: (i) 25–200 °C and (ii) above 200 °C. The weight loss in first zone is due to evaporation of water molecules [14,15]. The weight loss in next zone is because of burning of amorphous carbon; this weight loss is also supported by EDX analysis of the samples [16]. Above 620 °C, there is continuous weight gain in the sample which may be due to absorption of nitrogen gas [17]. Detailed SEM as well as EDX analysis of sample S2 was also done (Fig. 3). The SEM micrographs revealed that the particles are agglomerated but spherical in shape. EDX analysis is also shown in Fig. 3 which gives the percentage of various elements present in the phase. Fig. 4 shows TEM image of the sample S2. From micrograph, it has been observed that the particles are spherical in shape and the particle size varies from