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REVIEW ON DIFFERENT SYNTHESIS METHODS OF BORON NITRIDE NANOTUBE (BNNT)

[1]Dr. R. Sarala, [2] R. Rajeeth Kumar, [3] S.V. Pradeep, [4]S. SanthoshKumar
[1]Associate Professor, Mechanical Department, Alagappa Chettiar Government College Of Engineering And Technology, Karaikudi, Tamil Nadu, India.,
[2]Student, Mechanical Department, Alagappa Chettiar Government College Of Engineering And Technology, Karaikudi, Tamil Nadu, India.,
[3]Student, Mechanical Department, Alagappa Chettiar Government College Of Engineering And Technology, Karaikudi, Tamil Nadu, India.,
[4]Student, Mechanical Department, Alagappa Chettiar Government College Of Engineering And Technology, Karaikudi, Tamil Nadu, India.

Abstract: Boron nitride nanotube has become the best reinforcement in any material composite due to its extensive thermal, chemical and optical properties. These nanotubes are hundred times stronger than steel and it has high oxidation resistance of 800°C than any other nanotubes. Since the CNT react with some matrix material, so BNNT is the best replacement where CNT fail due to its less reactive property. BNNT can retain its mechanical property even at higher temperature at very low density. The future of BNNT has a wide application. In this paper, the different synthesis method of developing BNNT is reviewed.

Keywords: Bnnt-Boron Nitride NanoTube, Cnt- Carbon NanoTube.

I. INTRODUCTION

Material development has started from the Stone Age, where humans used stone as a tool instead of wood. From there the development has not stopped yet. Materials like iron, steel, copper, cobalt, etc. gave way for development in material. Each material has its own specific properties, but there is a need that one material should behave well in all mechanical properties. This need made a way to develop composites. In composite, the reinforcement helps the matrix material to give extreme properties as we desire. There is increasing enthusiasm for two dimensional nanomaterials that have noval structure and unique properties of graphene. Boron nitride nanotubes (BNNT) are called white graphene, which have hybridized honeycomb structures of boron and nitride atoms.

Two dimensional porous boron nitrite nanotubes (BNNTs) have flexible features, high aspect ratios and high specific surface areas, thus can be used as a good inorganic additive to improve the adsorption capacity and stability of polymer matrix material. BNNTs will be promising as excellent inorganic nano filler to improve the hydrophobic, adsorption and flexibility of PVA foam. After adding BNNTs into PVA matrix, the formation of hydrogen bonds between BNNTs with abundant eOH functional groups and PVA can limit the movement of PVA chains, which is conducive to the increase of thermal stability and mechanical property of PVA foam.

Nano scale and sub-micron fibers show almost similar properties, thus fibers of micron size are considered as Nanotubes. Special properties of Nano tubes such as porous structure, large surface area to mass and tight pore size make them suitable to be used in a wide range of applications such as medical, filtration, barrier, wipes, personal care, composite, garments, insulation, drug delivery systems, energy storage, fuel cells, and information technology. Following their wide applications, studies have been focused in search of Boron Nitride structures of micro to nanotube such as hexagonal boron nitride nanotubes (BNNTs). BNNTs can also be used as reinforcement in composite materials which further improve its properties. The importance of BNNTs motivates the different research groups to develop their own techniques for its synthesis.

Hexagonal boron nitrate nanotubes will have a great impact in future research due to their thermal conductivity, electrical resistance, machinability, lubrication and thermal shock resistance. There are different synthesis methods for preparing BNNT such as polymer pyrolysis, carbon thermic reduction, high temperature metallurgical synthesis, chemical vapor deposition etc. this study explains the different methodology for preparing boron nitride nanotubes.

II. SYNTHESIS METHODS OF BORON NITRITE NANOTUBES (BNNTS)

High voltage electrospinning

Xia Li et al. has used the oxide and carbide form of Boron as an appropriate precursor for producing BNNTs. A common hypodermic plastic syringe with a needle of 0.36mm inner diameter was used to contain the appropriate precursor solution. During electrospinning, a high voltage power supply (DW-N503-4ACCD,- 50kV~0V) was used with its negative terminal connected with the syringe needle and a ground terminal connected with an aluminum foil. A graphite plate acting as the collector was placed on the aluminum foil. The distance between the syringe needle and the collecting graphite plate was set at 19cm. The electrospinning equipment was placed in a sealed box which was protected by nitrogen gas. The temperatures of box were from 80°C to 100°C. The voltages of the power supply were change from 8KV to 10KV. The fibers through electro spin that include a great lot of Carbon, Hydrogen and Chlorine are called green fibers. And this green fiber was heated up from room temperature to 140°C for 1h in a high temperature tube furnace with the protecting with ammonia gas. Further increasing temperature from 140°C to 1700°C for 1h by protecting with nitrogen gas. Foam like white boron nitrite nanotube is formed.

Chemical vapor deposition (CVD)

Zhengtang Luo et al. in his general growth mechanism for BNNT include the following process.

- Ammonia borane and borazine are chosen as precursors. Those are decomposed at high temperatures as boron that contains nitrogen.
- The boron with nitrogen is deposited onto the metal surface and combines into clusters.
- The clusters continuously grow into large boron nitride films.

Wellington M. da Silva et al. synthesized BNNTs using boron powder (B) and FeS/Fe2O3 catalyst powder (Catalyst/B = 0.02) was performed in a horizontal tubular reactor. The reactor consisted of an alumina tube with inner diameter of 40 mm and length of 1000 mm, inlet and outlet for the ammonia and nitrogen gas flow. Under an atmosphere of Nitrogen the synthesis was carried out with a heating rate of 10 ºC min-1 from room temperature up to 1150 ºC. Then, the Nitrogen gas flow was interrupted and NH3 reagent flow was added, with samples treated for three additional hours. After having completed these steps, the BNNTs cooled in a Nitrogen atmosphere down to room temperature.

Chemical Synthesis of Hexagonal Boron Nitride

Majid Mirzaee et al. used urea (ACS reagent, ≥99.0-100.5 %, SigmaAldrich), melamine (99. 0 %, Sigma-Aldrich), boric acid (ACS reagent, ≥99.5%, Sigma-Aldrich), and deionized water. Three methods were used to synthesize BNNT with different precursors:

- **Synthesis with urea and boric acid precursor:** First, boric acid and urea were dissolved in deionized water with a molar ratio of 1 to 48, and the temperature was increased to 65 °C to completely evaporate the deionized water. The resultant mixture was then transferred to a quartz boat and placed in a quartz reactor under nitrogen flux for 5 hours at 1050 °C to obtain a white powder.
- **Synthesis with melamine and boric acid:** 9.28 g of boric acid and 6.3 g of melamine were dissolved in 500 cm3 of deionized water. The mixture was placed at 85 °C for 12 h to evaporate the deionized water. The resultant mixture was transferred to a quartz tube furnace and subjected to nitrogen flux at 1050 °C for 4 h.
- **Synthesis with melamine-urea-boric acid:** Melamine was added to a mixture of urea and boric acid. The molar ratio of urea to boric acid was 1 to 5, while the proportion of melamine to boric acid was 0.9. These precursors were mixed and subjected to nitrogen flux for 3.5 hours at 1050 °C.

Dual zone quartz furnace method

Pervaiz Ahmad et al. synthesized BNNT from a mixture of Boron (B), Magnetite (γ-Fe2O3) and Magnesium oxide (MgO) powders at 1000 °C. A weight ratio of 2:1:1 (B: MgO:γ-Fe2O3) were taken in an alumina boat and mixed with the help of a conventional stirrer. The precursor's mixture was first annealed at 500 °C for two hour in the presence of the Argon atmosphere, and then allowed to cool down to room temperature in the same Argon atmosphere. The precursors were taken out from the boat and placed on the top of aluminum paper to view any apparent change of the precursors via naked eyes. After a while, the precursors were put back in an alumina boat and partially covered with a few Si-substrates. The experimental set up used in this work mainly consists of a dual zone quartz furnace and one end closed quartz test tube. The furnace is used as a heating system whereas the one end closed quartz test tube is used to prevent the wastage of the growth species and restrict the growth of the final product within a certain area. The partially covered boat with Si substrates was pushed inside the one end closed quartz tube placed below the heating filament in the quartz tube chamber of the furnace. The furnace was heated up to 800 °C in an Argon atmosphere. Afterward, the Argon gas flow was replaced by Ammonia gas flow at a flow rate of 300 sccm. The system was further heated up to 1000 °C with a heating rate of 10 °C/min, and kept for two hour in the presence of ammonia flow. At the end of two hour growth duration, ammonia flow is switched off and the system is slowly brought to room temperature in the Argon atmosphere. White species and spots are found at the top of precursors in the boat and Si substrate.

Modified O'Connor method

Erhan Budak et al. prepared boron nitride samples using the modified O Connor method . 2 g of boron oxide was mixed with 4 g of urea and 0.04 g of metal nitrates. The mixture was preheated to 200°C for 2h and then the obtained precursor was pulverized in a grinder. After that, the main heating process was performed in a stream of NH3 gas at different temperatures (1050, 1250, and

1450°C) for 2 h in a tube furnace. The obtained raw products were heated in 10% HCl solution, leached in 25 mL ethanol, and dried in an oven at 100°C. The remaining gray-white powder was pressed by 100bar at room temperature.

Freeze-drying and pyrolysis process

Xiangqian Gao et al. prepared BNNTs via a freeze-drying and pyrolysis process. Firstly, boric acid (H_3BO_3) and melamine ($C_3N_6H_6$) were dissolved in distilled water at 90 °C for 3 h to get a transparent solution. Then the mixed solution was kept at 80 °C for 6 h and naturally cooled down to room temperature. After filtration and drying, M·2B precursor was obtained. Subsequently, 1.2 g of M·2B precursor was dissolved in 200 mL of distilled water and kept at 90 °C for 3 h. Then the hot solution was frozen by liquid nitrogen and dried in the vacuum freezing dryer to obtain a white M·2B nano fiber precursor. The precursor was heated at 1050 °C for 4 h in a tube furnace. The reaction was carried out in a flow of N_2 (0.1 $Lmin^{-1}$). Finally, BNNTs were obtained.

III. CONCLUSION

Boron nitride nanotubes have attracted scientists for developing material research. The different synthesis process is discussed in detail in this paper. By analyzing the different processes of synthesis, chemically synthesized BNNT is the most favorable technique when compared with other processes. But it takes a long time for processing and there is a need for a catalyst to promote the process. Quartz furnace method is also a feasible method but it needs to be more accurate and stable. Synthesis of continuous boron nanotubes (BNNTs) have the merit of high strength, low density, corrosion resistance and strong performance through the wave characteristics. They can be used in piezoelectric, pyro electric, photo-galvanic and optical applications, as well as in humidity and chemical sensors. They can also form composites with polymers, glass and ceramics. And ceramic matrix composites (CMCs) based on BNNFs show excellent electrical transmissivity at critical components of aerospace vehicles. We believe this report helps the researchers to find different ways to synthesize BNNTs.

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