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Production of Nitrogenized carbon nanotubes (cnts) from Calcined petroleum coke (cpc) by ammonia-Cal argon arc plasma heating method

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ABSTRACT

In recent years nitrogenized carbon Nano tubes are finding increasing applications in semiconductor technology because of their superior electronic properties. In view of their better properties an attempt has been made in this investigation to produce nitrogenated multiwall carbon nano tubes (MWCNTs) by thermal arc plasma evaporation of calcined petroleum coke (CPC) powder in ammonia-Cal argon arc plasma in a vacuum controlled extended argon arc plasma reactor (EAAPR).

The morphology of the nitrogenized carbon nanotubes (CNTs) produced by heating the homogeneous mixture of CPC and 2.0 wt % boron in an ammonia-cal argon arc plasma was similar to the shape of a bamboo stick. The TEM studies on CNTs showed an average diameter of 50 to 60 nm and length of 4.5µm. The XRD spectrum showed peaks of graphitic phase and Raman spectral studies indicated Raman shift at 1350.29 cm^{-1} due to the presence of 'd' band reflection, shift at 1575 cm^{-1} due to the presence of 'g' band reflection and shift at 2685 cm^{-1} due to the presence of 'g' band reflections which confirm formation of CNT graphitic phase. The EDAX pattern showed presence of 27.58 at %, nitrogen in the CNT product.

Key words: *Extended argon arc plasma reactor (EAAPR), nitrogenized carbon Nano tubes (NCNT), Transmission electron microscopy (TEM), Raman spectra.*

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1. INTRODUCTION:

The discoveries on the occurrence of carbon fullerenes in the carbon soot by Kroto, Smalley and Curl[1] in 1985 and invention of carbon Nano tubes in 1991 by Iijima [2] have made enormous impact on the growth of modern technologies and made hitherto impossible tasks possible. In fact innovative technologies are being presently researched for the production of low cost high quality CNTs because there is an ever increasing demand of these materials for specialized applications[3] as mentioned in the literature. In short CNTs have revolutionized the modern technologies for the production of electronic components, advanced composites, fertilizers, and pharmaceuticals etc. Among the existing technologies for the production of high quality CNTs [4-10], the laser ablation, electric arc evaporation, thermal plasma arc evaporation have been found to be most suitable for bulk production of high quality CNTs.

Wang et al,[11] and Lin et al,[12] have

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synthesized carbon nitride Nano tubes (CN_x Nano tubes) by microwave plasma, chemical vapor deposition and these nitrogenized CNTs find applications in semiconductor industry and they are used in making biosensors, optical communication devices, gas storage media.

In the present research work an attempt has been made to produce nitrogenized MWCNTs by heating the homogeneous mixture of CPC and 2.0 wt % boron in an ammonia- cal argon arc plasma using a vacuum controlled (EAAPR) with a view to study the effect of mixing ammonia gas with argon plasma on the morphology and composition of the CNT product.

2. Materials and methods:

The CPC powder of 99.7 % purity, supplied by M/s. NALCO Ltd., Damanjodi, Bhubaneswar, India, was used as a base raw material. The argon gas of 99.9 % purity supplied by M/s Industrial Gas Co, Bhubaneswar, was used as a plasma forming gas. The NH_3 of 99.9 % purity, supplied by M/s Industrial Gas Co, Bhubaneswar, and amorphous boron of 99.0% purity, supplied by M/s. Merk (KGaA) Germany and VWR international Ltd ., UK BDH were used as the catalysts.

The CPC powder of -60 BSS mesh size was dry mixed with 2.0 wt % boron in a rotary ball mill for 0.5 h. A vacuum controlled EAAPR of 50.0 kW capacities was used for the heat treatment of the homogeneously mixed charge.

To begin with the hollow graphite cathode was lowered until its tip made perfect contact with the internal bottom surface of the cylindrical graphite crucible which was kept concentrically over the graphite anode. Then in a typical experiment, 200.0 g of homogeneous raw material powder mixture of CPC and 2.0 wt % boron was charged in to the toroidal space of the empty cylindrical graphite crucible. After charging the raw material a steady argon gas flow rate of 1.5 lpm was maintained through the hollow cathode and cooling water circulation to the hollow copper cathode holder was also maintained. There after a steady DC power supply of 50 V was supplied across the electrodes to generate a plasma arc over the charge and after establishment of the plasma arc the cathode was slowly with drawn to a height of 7- 8 cm above the anode tip in order to stabilize the plasma arc and maximize heat emission. Once the stability of the arc was established then ammonia gas was allowed to flow through cathode at a rate of 0.5 lpm with pre-existing flow of argon gas. The charge was evaporated in a hybrid plasma arc for 45 minutes.

After plasma heat treatment, the plasma arc was put off. The hot charge was cooled in argon gas stream up to 600 ºC and further furnace cooled to room temperature. The fine spongy mass deposited on the cathode tip and bottom portion of the lid were collected and stored in a sealed plastic bottle. The cooled spongy powder mass obtained after plasma heat treatment was annealed in air atmosphere in electrically resistance heated furnace at 600 °C for 1h to get rid of amorphous carbon dust present in it. The oxidized mass was leached in 5% v/v HCl for 30 minutes to remove metallic

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impurities which was subsequently rinsed with distilled water and dried at 110 °C for 2h. in an electrical oven. The purified powder was floatated in pure acetone. The heavy fraction was separated by decantation and suspension containing Nano carbon particles was filtered, rinsed and dried. The purified and annealed carbon Nano tubes were taken for characterization of morphology, crystal structure by Raman spectrometry. The chemical composition of CNNTs was determined by EDAX (TEM).

3. RESULTS AND DISCUSSION:

The chemical analyses of the CPC used in this work shows presence of Ni, Cu, Na, Ca, and K elements in the range of 0.21 to 0.86 ppm. While Fe, B element are present at 10 ppm level. The proximate analysis of the same shows presence of 1.7 wt % volatile matter, 0.2 wt % ash and fixed carbon content of 98.1 wt %.

The thermal plasma heat treatment of homogeneous powder mixture in a hybrid ammonia-cal argon plasma arc gives CNT yield of 15 wt %. The carbon suit produced has thread like structure.

Fig -1 shows Raman spectrum of CNTs produced in ammonia-Cal argon arc plasma. The Raman shifts are observed due to the presence of 'd' band at 1350.29 cm, $^{-1}$ 'g' band at 1575 cm^{-1}and third 'g$^{/'}$ band at 2685 cm, $^{-1}$ The 'd ' band shows presence of amorphous carbon while 'g' and 'g$^{/'}$ bands correspond to presence of graphitic phase and these specific shifts also correspond to nitrogenated CNT product.

Fig-2, (a, b and c) show TEM pictures of carbon Nano tubes whose morphology resembles to the shape of a hollow bamboo stick. The aspect ratio of CNT is around 70 and average diameter is 50 nm. The tubular morphology shows segregation of catalyst phase at the boundary walls of CNTs. Fig 4 (c), show high resolution TEM picture of CNTs depicting the multi wall layered structure. The inter layer distance is around 3.56 Å

Fig-3, shows EDAX of CNTs taken on an average surface, the spectrum shows presence of carbon as first major elements and N as second major element but Cu, O_2 are also present in small concentration. Since nitrogen is present in large quantity it goes to form substitutional solid solution in the graphene structure of the CNTs. The copper has entered in to the CNT matrix from cathode during TEM analysis. The overall chemical composition of the MWCNTs as depicted from EDAX can be represented as C→ 55.9 at%, N → 27.52 at %, O_2 → 4.3 at% and Cu → 15. 78 at %.

4. CONCLUSIONS:

1) The ammonia -cal argon arc plasma heating method gives product yield of over 15 % by weight of the initial carbon charge.
2) The shifts in the Raman spectrum depict the presence of CN phase and TEM observations show typical features of multi wall nitrogenized CNT product.
3) EDAX taken on an average surface of Nano tubes shows presence of 27 .52 at % Nitrogen in the nitrogen saturated CNT matrix.

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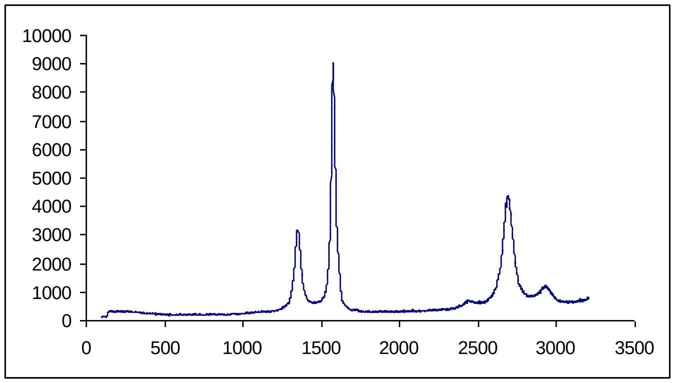
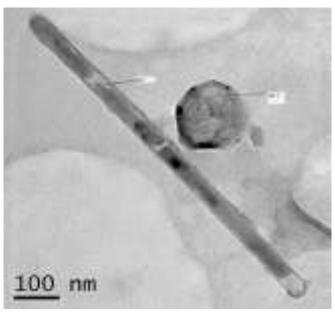
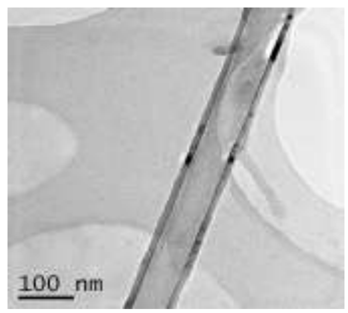


Fig – 1 Raman shifts of CNT produced in ammonia-cal argon plasma



a)



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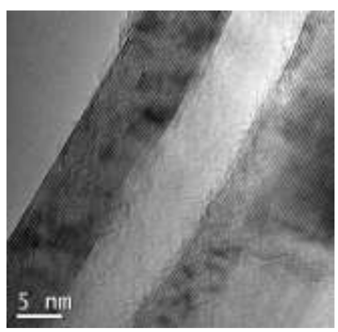

c)

Fig -2 TEM pictures of CNTs grown during heating of CPC charge in Ammonia-cal argon arc plasma

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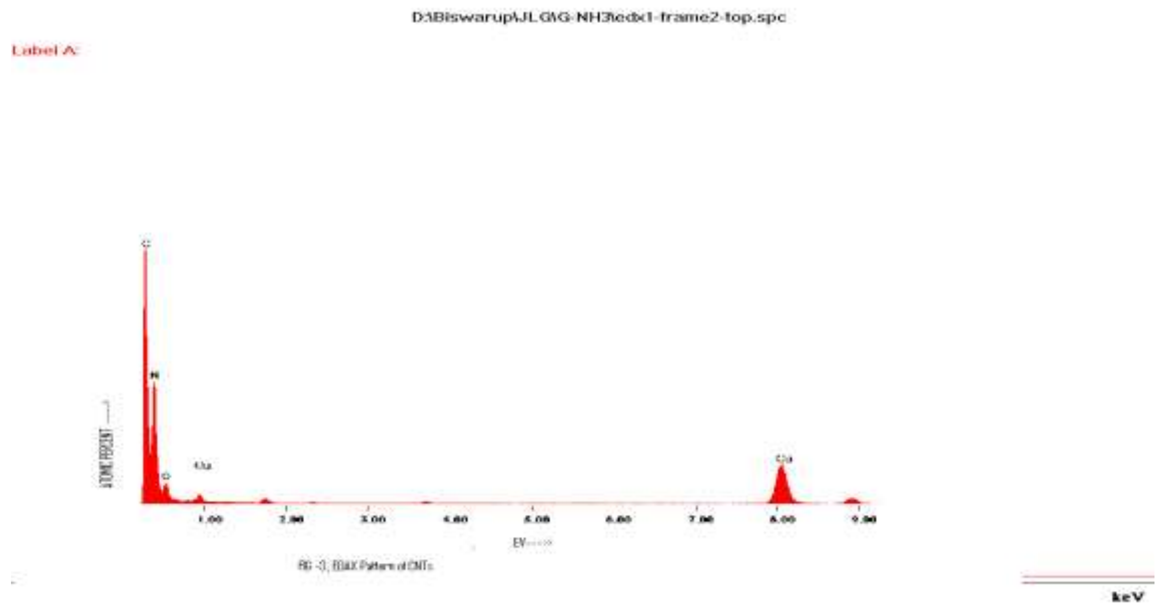

Fig- 3) EDAX pattern of CNT taken on an average surface

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