# SYNTHESIS OF (B-C-N) NANOMATERIALS BY ARC DISCHARGE

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## ABSTRACT

The electric arc is one of the promising high temperature synthesis processes of carbon nanotubes. It offers the advantage to allow performing in-situ substitution of carbon atoms by hetero-elements in the graphene lattice. Our work aims to establish a correlation between the plasma properties, type and chemical composition of the obtained carbon nanotubes. This will allow getting a better understanding of the phenomena involved in the nanotube growth and substitution mechanisms.

## 1. INTRODUCTION

Single wall carbon Nanotubes (SWNTC-s) have metallic or semiconductor behaviour depending on their chirality and diameter [1,2]. Controlling the growth of these materials is until now a great challenge regarding the selectivity on their electronic properties.

It is possible to circumvent this problem by doping single wall carbon nanotubes with hetero-atoms, which can be incorporated in the honeycomb carbon lattice. It has been demonstrated that the insertion of Boron or Nitrogen [3], can greatly modify the electronic structure of carbon nanotubes (e.g. from semiconductor to metallic).

In this regard, Boron-Carbon-Nitrogen ($B_xC_yN_z$) nanotubes have potential applications such as photo-luminescent materials, electron emission, or high temperature transistors.

Such nanotubes can be synthesized by CVD, laser ablation or arc discharge using various (gaseous or solid) sources of B, C and N.

The electric arc process offers the advantage of performing in-situ substitution of carbon atoms. Unfortunately, it is noteworthy that very few results are available in the literature regarding the synthesis of $B_xC_yN_z$ nanotubes using this technique. It is then worth investigating further this route by using an original approach consisting in relating the synthesis conditions, the plasma parameters and the characteristics (type and chemical composition) of the obtained carbon nanoforms. This will allow getting a better understanding of the phenomena involved in the substituted nanotube growth.

## 2. EXPERIMENTAL

### 2-1.SYNTHESIS

The apparatus used consists in a cylindrical reactor of 25 liters, filled with helium or nitrogen and helium mixture at pressure of 60 kPa. The electrodes are placed in vertical configuration, as seen in Fig.1. So-called heterogeneous graphite anodes were prepared by drilling then filling a solid graphite anode with graphite powder (~1µm particle size), nickel (0.6 to 1.2 at %) and yttrium powders (0.6 to 1.2 at %) as catalysts, and a variable percentage of boron or boron nitride (1 to 4 at %).
The experiments were realized with an inter-electrode gap of 1mm and arc current ranging from 50 to 80 A. Each experiment was limited to

duration of less than two minutes to limit the pressure increase.

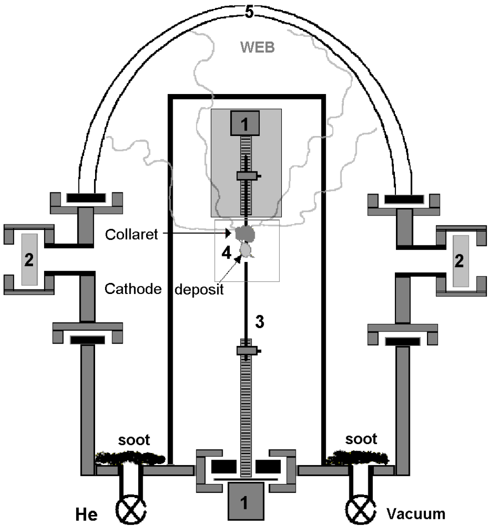


*Fig. 1 reactor of synthesis*

## 2-2.PLASMA DIAGNOSTIC

The optical setup used for the plasma spectroscopic study and the diagnostic theoretical background were presented in [4].
As the arc axis is vertical, a dove prism is used to obtain data along a radial profile of the arc in one single acquisition The electron temperature is determined from the Boltzmann diagram method using four neutral Ni I nickel atomic lines in the 350 nm spectral range.

## 2-3.CHARACTERISATION

After each experiment the carbon products obtained at various places in the reactor (indicated in Figure 1 as web, collaret and cathode deposit) are collected. The sample morphology was studied with a CM30 transmission electron microscope. Chemical composition and bounding environment was studied through Electron energy loss spectroscopy (EELS) operated at 80 kV (beam spot size 0.5 nm) to limit sample degradation.

## 3. RESULT AND DISCUSSION

### 3-1. Morphology of the products

Results show that for a low Boron content (~1%) SWCNT yield decreases when arc current increases (Fig-2.1). At low arc current the SWCNT yield is high but also the impurity content increases (i.e., carbon phases other than nanotubes). On the contrary high Boron content (~ 4%at B) SWCNT yield increases with increasing arc current or Yttrium quantities (Fig 2.2). We have noticed that in presence of boron, high content of nitrogen leads to strong reduction of SWCNTs yield.

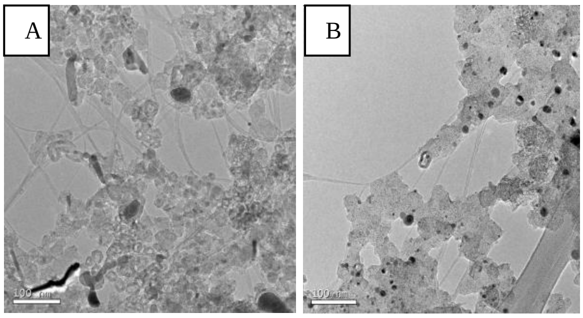


*Fig. 2.1 TEM image of web for 1%at B,0.6%at Ni and 0.6%at Y; (A) : current of 50A; (B): current of 80A.*

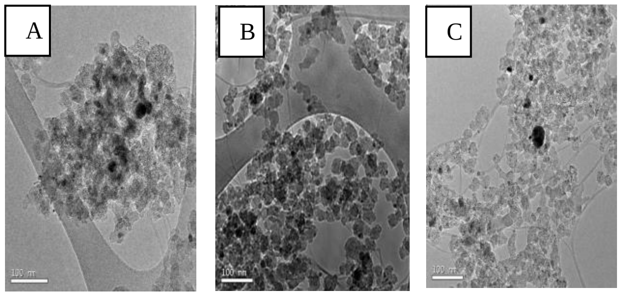


*Fig. 2.1 TEM image of web for 4%at B(A:I=50A-0,6%Ni 0,6%Y; B:I=800,6%at Ni 0,6at%Y; C: 0,6%Ni 1.2%Y*

The optimal conditions so far determined for obtaining a good SWCNT yield with a low impurity content are with using a 80 A arc current and an anode loaded with 4 at.% boron, 0.6 at.% nickel, and 1.2 at.% yttrium and a very low content of nitrogen gas. This was obtained by keeping the residual nitrogen after performing a primary vacuum (down to 1 kPa) before filling the chamber with helium. This can lead to effective and measurable substitution of the carbon by boron and nitrogen (yet not more than a few %) in SWCNTs.

## 3-2.PLASMA TEMPERATURE

For each set of conditions the plasma temperature was calculated from several measurements to assess the experiment reproducibility. Figure 3.1 shows the radial evolution of temperature with 1%at B for three arc current values.

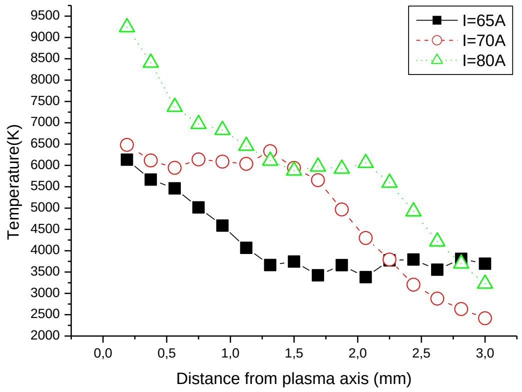


*Fig. 3.1 Radial temperature profile with 1% at B0.6%at Ni and0.6% Y*

One can see that the conditions corresponding to high purity (I = 80 A) is associated to higher electron temperature and stronger radial gradient, with axial temperature up to 9500 K.

The influence of boron content for a current of 50 A is shown in Figure 3.2. It appears to a small amount of boron leads to no major axial temperature decrease, but with high boron content (about 4% at of Boron), the axial temperature drops by about 3000K. In our experiment we have observed that a high axial temperature is one of the conditions which give a highest yield.

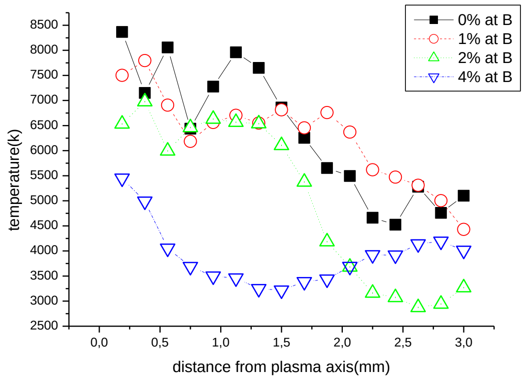


*Fig. 3.2 Radial temperature profile at I=50A with 0.6%at Ni, 0.6%at Y and 0 to 4% at B.*

In order to get high yield with high boron content the arc temperature needs to be increased: this was achieved by increasing arc current and using stronger yttrium content. Results of experiments with high boron content at 50 and 80 A with 0.6at% Y or 1.2at% Y are presented in Figure 3.3. For a current of 50 A when doubling the yttrium content the electron temperature slightly increases but the axial temperature remains unchanged with also no change in the nanotube yield. On the other hand, the conditions with 80 A and 1.2at% Y leads both to a strong increase of axial temperature (up to 8000 K) and radial gradient. This is associated with higher nanotube yield, and boron was detected in the studied nanotubes samples. In the case of experiments with low nitrogen content, carbon/boron/nitrogen structures were also detected. When further increasing the boron content (up to 8at%) the axial temperature drops again to the value obtained with low current and low yttrium content. This confirms that the cooling effect of boron can be compensated through increasing of current and yttrium content.

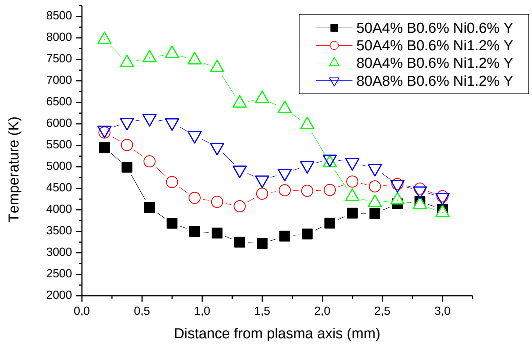


*Fig. 3.3 radial temperature profile with at I=50A*

The cooling effect of boron can be explained by its low ionization potential (8.29 eV), when compared to carbon (11.26 eV) or helium (24.58 eV). For temperature below 8000 K the resulting increase in the electrical conductivity will lead to a widening of the arc conducting channel and thus to a drop in its temperature.

## 3-3 CHEMICAL ENVIRONMENT:

When the materials are synthesized, it is primordial to know chemical composition and doping level, which is performed by the EELS method. Figure 3.4 shows the morphology of the

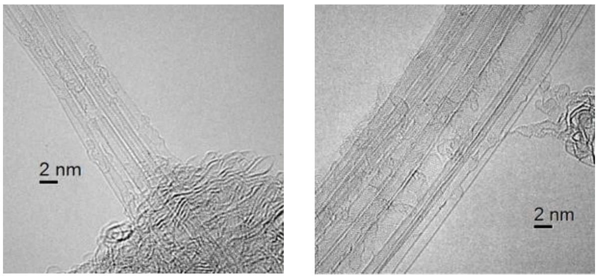


*Figure 3.4 Atomically resolved high resolution TEM confirms that carbon nanotubes are SWCNTs, with perfect structure, and associated with impurities lying on bundle surface.*

obtained SWNCTs under the optimal conditions indicated above. Fig. 3.5 displays the EEL spectra obtained for this sample.

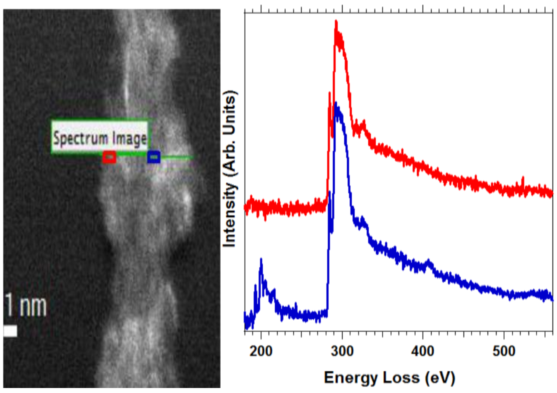


*Fig3.5 HAADF image and EEL spectra for a bundles nanotubes with a covering impurities indicate the presence of BN*

The spectra have distinct transition features corresponding to B-K, and N–K edges that appear at ~188 and 400 eV respectively. The C–K near-edge spectrum confirms the typical graphitic network with $sp^2$-hybridization where the $\pi^*$ band arises at 284.4 eV. Fig 3.6 - and also BN has been detected in these regions. Spectra on area showing pristine CNT (red comparing with those (blue) showing high content (~6%) of B & N.

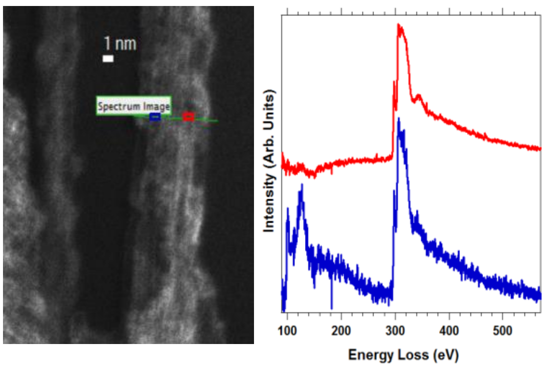


*Fig3.6 HAADF image and EEL spectra for a bundles nanotubes with a covering impurities indicate the presence of Silicon impurities*

It is very important to mention that other bundles which do not show any B content do not show any N content either. The Si-L edge at ~100 eV corresponds to silicon oxide ($SiO_x$) that could be present in the sheath covering the SWCTs bundles. Its presence can be due to contamination during the sample preparation or to impurities in the electrodes.

## 4. CONCLUSION

High content of B in the system is detrimental to the SWCNT yield. This is not necessary due to a direct effect on the tubes growth process since we have shown that it leads to strong cooling of the plasma. This will in turn affect the growth zone temperature and hinder tubes formation.
The detrimental effect of high B content can be somewhat compensated by increasing the plasma temperature, using higher current or higher content of Y.
Even with very low remaining presence of nitrogen, nanotubes bundles show high N content (3-6%) always combined with a high content in B (~6%).
It is proposed that tiny amounts of N in the system are needed to promote a high uptake of B (with N) in the graphene lattice. It is not clear yet whether B and N are dispersed among C in the lattice or is present as BN islands in the graphene lattice or even related to the amorphous sheath covering the NT.
Further works are planned to confirm our hypothesis.

## REFERENCES

[1] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus "Electronic structure of graphene tubules based on $C_{60}$", PHYSICAL REVIEW B, vol **46**- N° 3,1804-1811,1992

[2] N. Hamada, S. Sawada, A Oshiyama, "New One-Dimensional Conductors: Graphitic Microtubules", PHYSICAL REVIEW LETTERS, vol **68**, 1579-1582, 1992.

[3] R. Czerw, M. Terrones, J-C. Charlier, X. Blase, B. Foley, R. Kamalakaran, N. Grobert, H. Terrones, D. Tekleab, P. M. Ajayan, W. Blau M. Rühle, D. L. Carroll "Identification of Electron Donor States in N-Doped Carbon Nanotubes", NANO LETTERS, Vol.**1**, No.9, 457-460, 2001

[4] A.Mansour, M.Razafinimanana M.Monthioux, "Influence of the graphite filler material granulometry onto plasma features in the electric arc process applied to carbon nanotube synthesis». JOURNAL OF PHYSICS D: APPLIED PHYSICS , vol **42** , 1-11,2009