Continuous Mass Production of Carbon Nanotubes by 3-Phase AC Plasma Processing

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ABSTRACT

For the synthesis of carbon nanotubes (CNTs), the plasma process is an original new approach. Hereby, the carbon mass flow is no longer limited by a physical ablation rate (which is the limiting step in the production rate of the classical nanotube processes), but is freely adjustable. Moreover, the process is operated at atmospheric pressure and the NT rich soot is extracted continuously. The feasibility for producing a large variety of different nanostructures at high selectivity including Carbon MWNTs, SWNTs, nanofibers and necklaces nanostructures is well established. From the characteristics observed, it is concluded that the AC plasma technology shows a significant potential for the continuous production of bulk quantities of carbon-based nanotubes of controlled properties and novel nanostructures.
In this paper, the plasma process for continuous nanotube synthesis, typical process conditions prevailing and products are presented.

Keywords: Mass production, thermal plasma, carbon nanotubes, carbon nanostructures

1 INTRODUCTION

Since many years, nanotechnologies are considered as very promising, capable of revolutionising entire sectors of industry. However, a real breakthrough of nanotechnologies has not been achieved yet, most probably because of the failure to transfer these novel technologies to existing industries. The synthesis of pure nanotubes with selected properties is now achievable, but only in very small quantities. The unrestricted availability of nanotubes at a reasonable price will generate the growth of a range of technological areas.

The current state-of-the-art shows that constant progress is made towards the production of nanomaterials at low cost. These materials concern mainly the production of nanopowders of different species (e.g. ceramics and metals) and carbon nanotubes. CNTs have been identified to have many potential applications in a large field of different areas like biology, material and surface science, energy storage, gas storage, environmental technology, electronics, etc. However, their market is still limited because their methods of production are not yet efficient enough to produce them with controlled properties at a relatively low cost.

Present production methods for novel nanostructured materials applied in research or for commercial production can only provide very limited quantities of the order of few grams per hour. Accordingly, current market prices are prohibitive, which is, therefore, limiting research activity. Currently known processes for carbon nanotube synthesis use either of the following methods: Arc [1, 2, 3], laser [4], solar [5, 6], plasma [7, 8] or catalytic method [10, 11]. The first group, comprising the first four processes corresponds to the high temperature techniques in which CNTs formation process is based on the sublimation and recondensation of the carbon precursor. High temperature processes are used for the production of CNTs with a high degree of graphitisation (defect free), however, product yields necessitate a purification of the products to remove amorphous carbon. Within this group, arc, laser and solar processes are having many features in common, being all of them based on the ablation of a solid carbon target, working in batch mode at reduced pressure. These three processes having reached their limits in production rate. An original approach is taken with the plasma process. Hereby, the carbon mass flow is no longer limited by a physical ablation rate, but is freely adjustable. Moreover, the process is operated at atmospheric pressure and the NT rich soot is extracted continuously. Over the last ten years an industrial consortium composed of Timcal Belgium, Ecole Nationale Supérieure des Mines de Paris (ENSMP) and Centre National de la Recherche Scientifique (CNRS) has developed a new process based on a 3-phase AC plasma technology for the continuous mass production of carbon nanostructures.

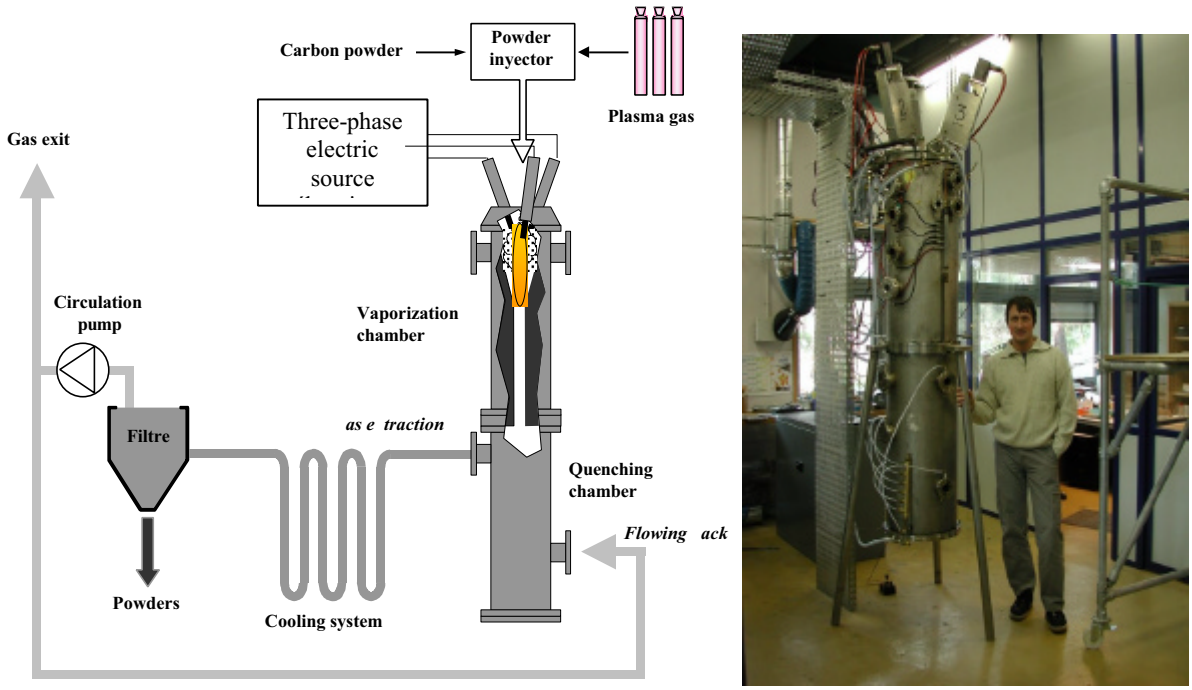

Figure 1: (Left) Scheme of the new configuration of plasma facility [9]. (Right) Plasma reactor in its present form.

This 3-phase AC plasma system; initially developed and optimised for the synthesis of novel grades of carbon black [12, 13] and later modified for the continuous synthesis of fullerenes [14, 15], has been adapted for the synthesis of carbon nanotubes and tube-like structures [7, 8, 9].

2 PLASMA PROCESS

These adaptations lead to the process scheme shown in Figure 1. The process can be briefly described as follows:

The plasma is generated by an arc discharge between three graphite electrodes placed in the upper part of the reactor. Simultaneously, an inert gas flows across the arc and the carbonaceous precursor and catalysts are injected into the high temperature region in or after the arc by a special powder injection system. Due to the high density of enthalpy obtained, the carbon and the metal catalysts are vaporised completely while passing through the graphite nozzle.

The quenching/sampling system collects the high temperature gas at a predetermined position in the reactor and cools it rapidly (quenching). The gas is filtered and a part of it is re-injected into the reactor. The fraction that corresponds to the flow rate initially entering the reactor as plasma gas is exhausted. This set-up (with recirculation) allows the extraction of a gas volume superior to the initial flow of plasma gas and therefore disconnects the dependency of these two parameters, which leads to an additional degree of freedom in relation to process operation.

Moreover, the reactor set-up is permanently being improved and industrial production of carbon nanotubes is envisaged.

3 RESULTS AND DISCUSSION

A large number of process parameters was investigated. A brief overview is given in Table 1.

Nature of precursor	Carbon Black + Ni, Co and Y at different concentrations. Ethylene + Ni
Nature of catalysts	Coating on carbon black Metal powder
Nature of plasma gas	Helium Nitrogen
Flow rates	Plasma gas Precursor
Quenching and cooling conditions	Location of product extraction

Table 1: Main process parameters investigated for nanotube production.

First efforts trying to correlate operating conditions to obtained product, with the final aim of understanding carbon nanotube formation inside the plasma system, show very promising characteristics. High temperature measurements inside the reactor revealed that an initial cooling to a plateau temperature above metal catalyst

solidification and a following abrupt quenching are realized and can be freely adjusted and controlled, which presents one of the major advantages of the plasma process over conventional high temperature synthesis processes. Full details on these first correlations will be published by T. M. Gruenberger et al. [8].

All samples have been analysed using electron microscopy techniques (SEM/TEM/HRTEM) whereby multi-wall nanotubes (MWNT) have been found in many samples (Bamboo-like structures - Figure 2).

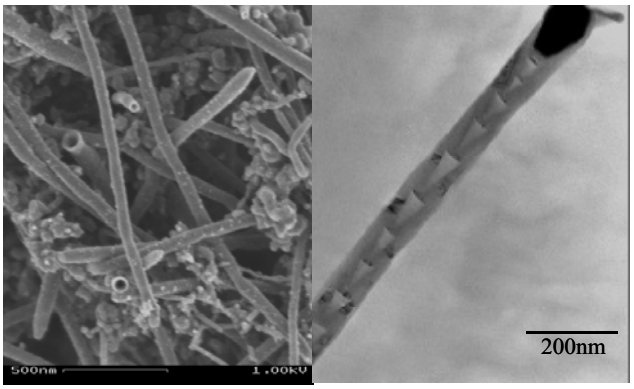

Figure 2: SEM image (left) and TEM analysis (right) of carbon bamboo-like structures (MWNT) [16]

The presence of single-wall nanotubes (SWNT) bundles and isolated SWNTs has been observed and has even been confirmed for samples collected from the product filter. Furthermore, the formation of carbon nanotubes in the gas phase by means of plasma processing seems to be confirmed also. The presence of bamboo-like, urchin-like, necklace, and others structures is frequently observed, which seems to be an indication that this process is capable of producing any kind of nanostructures. Finally, the reproducibility of the obtained products is confirmed, even for novel structures obtained under very special operating conditions.

The carbon samples originating from the internal wall of the reactor in the high temperature zone (wall sample) and from the bag filter (filter sample) have been analysed in detail. Electron microscopy analyses have allowed identifying three families of original carbon nanostructures, which can be associated to operating conditions.

3.1 Single Wall Nanotubes

SWNTs (Figure 3) have been produced for different operating conditions but the best results can be associated to a specific operating condition: Extraction of the product from the nozzle entrance zone. In this configuration, the process shows better general time-temperature characteristics required for nanotube formation than other configurations. The temperature just before the extraction zone is about 3000 – 3500 K. A very abrupt quenching is realised just after this zone (~10^6 K/s) and can be freely adjusted and controlled by the flow rate of the recirculation gas, which presents another major advantage of the plasma process over conventional high temperature synthesis processes.

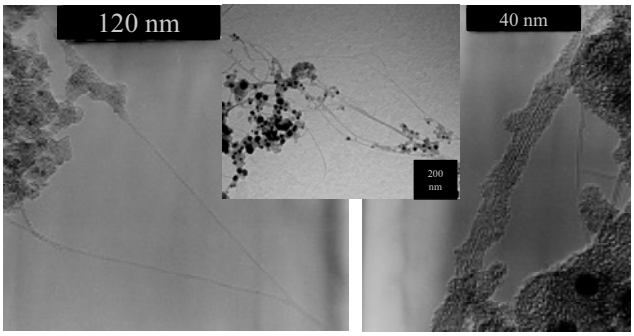

Figure 3: HRTEM Pictures of long SWNTs and SWNT bundles [16]

3.2 Carbon Fibres

The second family of nanostructures, are the carbon fibres (Figure 4). These nanostructures are produced with ethylene as carbon feedstock. The diameter of these carbon fibres is in the range of 20 – 50 nm with a length of few µm. The structure of these fibres is composed of an axial stacking of carbon layers with a low degree of organisation. The growth of these fibres is the result of the thermal decomposition of a hydrocarbon in presence of catalysts. This is a structure typically obtained at low temperature (< 1500 K) in presence of hydrogen.

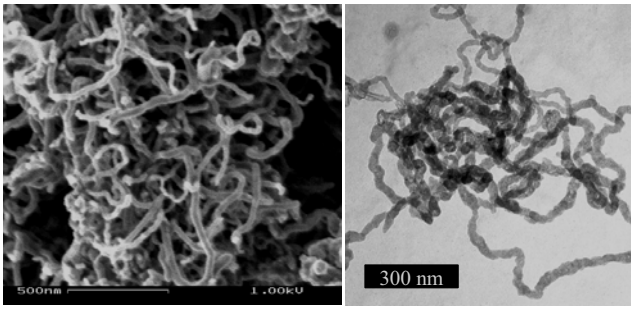

Figure 4: SEM image (left) and TEM analysis (right) of carbon nanofibers [16].

3.3 Carbon Necklaces

The third and most original group of nanostructures, are the carbon necklaces (Figure 5). These nanostructures are produced with Nitrogen as plasma gas. Carbon nano-necklaces usually curve smoothly and entangle together. The bamboo-like appearance of successfully joined segments is clearly seen. The segments in the carbon nano-necklaces are actually short variable-diameter compartments with one end sealed and the other one open. Some of these segments are completely filled with the Ni-Co catalyst used during the synthesis.

TEM and HRTEM pictures show a high degree of graphitic organisation in the thickness of the segments. The

best well-organised structures have been identified on the wall samples. High temperature measurements inside the reactor revealed that with Nitrogen plasma gas, the axial and radial temperature distributions in the plasma reactor are much higher than with Helium (temperature along the graphite wall can reach 2500 K) and seems to be a fundamental parameter in the production of carbon necklaces [16].

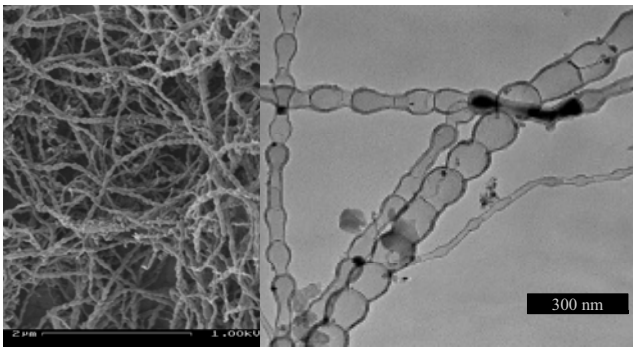

Figure 5: SEM image (left) and TEM analysis (right) of the carbon necklace nanostructures [16].

4 CONCLUSIONS AND PERSPECTIVES

The feasibility for producing a large variety of different nanostructures at high selectivity including carbon MWNTs, SWNTs, nanofibers and necklace nanostructures is well established. From the characteristics observed, it is concluded that the 3-phase AC plasma technology shows a significant potential for the continuous production of bulk quantities of carbon-based nanotubes of controlled properties and novel nanostructures.

As microscopic analyses give only qualitative information on the sample composition and do not allow the quantification of the nanotube content, purification (oxidation and acidic attack) of the most promising samples will be carried out to quantify the NT yield. However, rough estimations derived from the micrographs let assume that yield for CNTs is in the range of 10 to 50 % in as-produced soot with a production rate of 250 g/h.

Although, quantitative evaluations of the products can not be correlated to operating conditions yet, but due to its flexibility and controllability in terms of residence times and quenching rates, the plasma process shows a great potential for further development. First efforts trying to correlate operating conditions to obtained products, with the final aim of understanding CNT formation inside the plasma system, show very promising characteristics and seem to be an indication that this process is capable of producing any kind of nanostructures. Future efforts will need to focus on the product selectivity of the production process.

The plasma process is addressing products currently obtained by the so-called arc method and novel products. The other high temperature processes having reached their limits in production rate, the 3-phase AC plasma process can be considered as an improved highly flexible version of the same family with an enormous potential for further up-scaling to an industrial size at commercially viable cost.

ACKNOWLEDGEMENT

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