MASSIVE MULTI-WALL CARBON NANOTUBES PRODUCTION BY FLUIDIZED BED CATALYTIC CHEMICAL VAPOR DEPOSITION

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Multi-walled or single-walled carbon nanotubes (MWNT or SWNT, respectively) are today expected to bring significant breakthroughs in the fields of electronics and engineering materials [1]. However, the main bottleneck for NTs to find commercial applications is undoubtedly the development of processes able to reach large-scale productivities. Among the different techniques that have been applied for the synthesis of NTs [2], the catalytic chemical vapour deposition (CCVD) route appears to be the most promising due to the relative cheapness of NTs formed and its potential high yield productivity. We have successfully adapted a CCVD process to be used in a fluidised bed reactor.

The principles of the fluidised bed chemical vapour deposition (FBCVD) technology are quite simple. A catalytic powder is put in contact with a reactive gas in appropriate conditions of flow rate, pressure and temperature so as allow homogeneous and heterogeneous chemical reactions, leading to the catalytic formation of the desired product. The gas solid contact is regulated so as to fluidise each particle in the reactive gas, thus ensuring a vigorous mixing of powders by the gas. The control of the fluidisation quality is also of major importance to operate in isothermal conditions and to obtain uniform materials.

The objective of the present study is to optimise the operative conditions in order to prepare a change in the equipment scale towards industrial dimensions and productivities. The influence of the main operative conditions (temperature, inlet carbon source percentage, total gas flow, …) has then been evaluated. The analysed parameters are the carbon conversion into NTs, the NTs growth rate, the ratio between the weight to weight ratio between NTs and catalytic powder, the fluidisation characteristics, and the NT's morphology and structure deduced from FEG-SEM and TEM.

In the technology we have selected, a gas mixture of ethylene, hydrogen and nitrogen is used as the fluidising gas, and catalytic powders are mesoporous alumina particles, previously treated to deposit iron at various percentages. The experimental FBCVD reactor has an internal diameter of 5.3 cm and is 1 m height. The nominal temperature is around 650°C, the initial catalyst weight is 50 g, and the fluidization ratio is about 16.

One of the most meaningful results obtained for this process is the selectivity in MWNT, always close to 100 % (no soot neither encapsulated particles have ever been detected by TEM, see figure 1). The carbon conversion is always greater than 85%, and the productivity exceeds 25g/h of NT in this lab scale equipment.

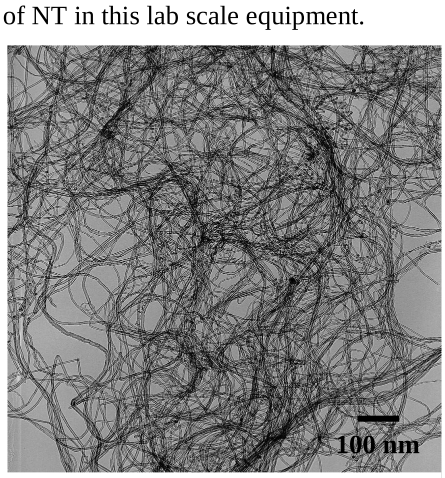

Fig 1 : General overview of the as produced

An interesting result concerns the evolution of the process features with time, as illustrated in figure 2.

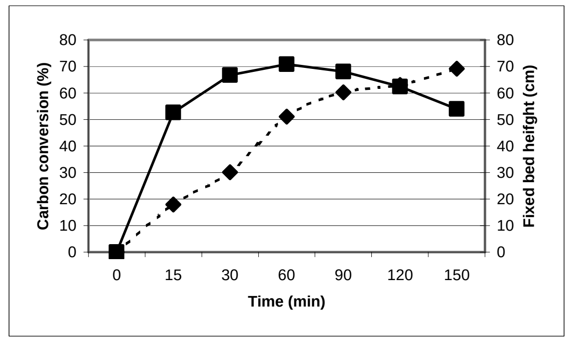

Fig. 2 Evolution with time of carbon conversion and fixed bed height.

It appears that the carbon conversion is maximal after 60 min of run, whereas a huge bed expansion is observed with time. This surprising behavior is due to the strong evolution of the powder morphology induced by NT growth. Indeed, NT form three-dimensional randomly oriented jumbles, in which the initial catalytic alumina powders are embedded. The apparent density of this very peculiar powder is very low, implying this high bed volume expansion.

Further works are currently in progress to finely tune the operative conditions for selective NT growth, to scale up the process and move a big step towards a low cost semi-industrial production.

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