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# Growth of carbon nanofilaments on coal foams

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ABSTRACT

Nanofilamentous carbon was grown on a carbon foam by catalytic chemical vapour deposition (CVD) using the decomposition of ethylene/hydrogen mixtures over Ni. The carbon foam was obtained from a coal by a two-stage thermal process, with the first stage taking place at a temperature within the plastic region of the precursor coal. The extent of porosity and the pore size of the foam were mainly influenced by the pressure reached in the reactor during the first stage. In the CVD process, 700 °C was the optimum temperature for obtaining good yields of nanofilaments. A low ethylene/hydrogen ratio (1/4) in the reactive gas gave rise to almost only short and thin carbon nanostructures. A higher proportion of $C_2H_4$ (4/1, $C_2H_4/H_2$) gave better yields of nanofilaments, with good proportions of higher-length and higher-diameter (up to around 0.5 μm) structures. Among the carbon forms produced, transmission electron microscopy revealed the predominance of fishbone-type nanofibres, with some bamboo-like nanotubes being also observed.

## 1. Introduction

Carbon foams were first developed in the 1960s [1] as reticulated vitreous structures and in the following decades, many researchers explored various processing and precursor variations attempting to modify properties and reduce costs [2–6]. The use of coals as precursors for the manufacture of carbon foams (coal foams) through a controlled carbonisation process [7–10], represents an interesting cost-effective alternative to the carbonisation of polymers [3,11] or mesophase pitches [2,5,6,12].

Thermal isolation and heat dissipation are two of the main uses of these macroporous carbon materials [13], but low density and moderately high mechanical strength [14] combined with great versatility makes them candidates for great variety of applications beyond thermal management [2,12]. The pore dimensions of these materials are too large for some chemical applications, but there are many others, like electrodes for supercapacitors, in which ultralarge mesoporous carbons with well-interconnected pores of sizes ranging between 10 and 50 nm, combined with a microporous structure, are necessary [15,16]. On the other hand, the development of some surface area will be beneficial for other applications such as the use of the foams as adsorbents or catalyst supports [17].

In this work, the possibility of obtaining C/C composites by growing carbon nanofibres or nanotubes inside the pore structure of the carbon foam was investigated. As it has been reported for composite materials with matrices of different nature [18,19], the presence of nanofilaments could improve the mechanical strength and the electrical properties of the carbon foams, with potential interest for structural and electrochemical applications. The homogeneous distribution of the nanofilaments is essential for an improved material, while a specific step for creating links between them and the matrix is mandatory for a better mechanical performance [20], but not necessarily for an enhanced electrical conductivity [21,22].

The objective of the paper is to study the growth of nanofilaments in carbon foams by chemical vapour deposition (CVD) based on the decomposition of ethylene over Ni catalyst. The influence of the CVD conditions on the amount and morphology of the nanostructures produced in the confinement of the foam macroporous structure was investigated.

## 2. Experimental

A bituminous coal was used as the precursor of the carbon foams in this study. It was characterised by the Gieseler plasticity test (ASTM D2639-04), the crucible swelling test (ASTM D720-91) and proximate analysis (ASTM D3172). It was also studied by thermogravimetric analysis (TGA) (0.15–0.20 g, under $N_2$, heating at 2 °C min$^{-1}$ from ambient temperature to 1000 °C). Table 1 lists the characterisation data of the precursor coal. It possesses a plastic range of 84 °C (from 391 to 475 °C), with 437 °C being, simultaneously, the temperature of maximum plasticity and maximum weight loss.

Carbon foams were obtained from this bituminous coal by a two-stage procedure. The first stage was a pressurised carbonisation in a cylindrical stainless-steel reactor (5 cm internal diameter × 10 cm

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**Table 1**
Analytical data of the bituminous coal used as precursor for carbon foams

| | |
|---|---|
| *Gieseler plasticity test* | |
| Softening temperature (°C) | 391 |
| Solidification temperature (°C) | 475 |
| Plastic range (°C) | 84 |
| Maximum fluidity temperature (°C) | 437 |
| Fluidity (ddpm) | 6564 |
| *Crucible swelling test* | |
| Swelling index | 6 |
| *Proximate analysis* | |
| Volatile matter (% d.b.) | 34.7 |
| Ash (% d.b.) | 5.3 |
| *TGA* | |
| Initial weight loss temperature (°C) | 370 |
| Maximum weight loss temperature (°C) | 436 |
| Final weight loss temperature (°C) | 540 |

height) (Fig. 1). In a typical experiment, the precursor coal (ground to <212 μm) was moulded and pressed to produce a cylindrical piece (of almost the same dimensions as the reactor receptacle) that was subsequently wrapped in aluminium foil and loaded into the reactor under atmospheric pressure. The reactor, previously purged with argon, was then heated at 2 °C $min^{-1}$ up to the final temperature 450 °C by means of a fluidised bed sand bath and initially with the gas exit valve open. This prevented the presence of water during the reaction and the increase of pressure before reaching the plastic stage. The temperature was controlled using a Eurotherm 2116 controller, connected to a type K thermocouple located in the sand bath, outside the reactor but in contact with it. The good thermal conductivity of the stainless-steel prevents significant temperature gradients. When the initial weight loss temperature (Table 1) was reached, the gas exit valve was closed and, hence, pressure increased as volatiles kept being formed and maintained inside the reactor. After 2 h at the final temperature the reactor and its content were cooled down by switching off the oven (cooling time higher than 6 h).

In a second stage, the carbonised products obtained were baked at 1100 °C for 2 h under argon, after a heating rate of 1 °C $min^{-1}$. Then, it was cooled down by switching off the oven.

The carbonised foams were subjected to a high temperature treatment by heating, under argon, up to 2200 °C, using a Pyrox VI 150/25 graphite furnace. Heating rates of 20 and 10 °C $min^{-1}$ were used in the temperature intervals of 0–2000 °C and 2000–2200 °C, respectively, with a residence time of 1 h at the final temperature.

The carbon foams were impregnated with a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (3, 15, 173 and 230 mmol $L^{-1}$) in $H_2O$/EtOH (1/1), by immersion of the foam in the solution and treatment for 1 h in an ultrasonic bath. Solvent was removed by evaporation under air at 100 °C, overnight. Fragments of the impregnated carbon foam with masses ranging from 0.1 to 0.5 g were placed in a tubular quartz reactor (50 cm height × 4 cm internal diameter) and treated with an $H_2$ flow of 100 $cm^3$ $min^{-1}$ at 500 °C during 1 h in order to reduce the $Ni^{2+}$ to $Ni^0$. Chemical vapour deposition experiments were carried out on the Ni-doped foams by treatment with an ethylene/hydrogen mixture (5/0, 4/1 or 1/4) during 0.5 h using the same quartz reactor at 700 °C.

The carbon foams were characterised by the determination of true and apparent densities by He and Hg displacement, respectively, mercury porosimetry and X-ray diffractometry (XRD). The impregnated foams and the carbon/carbon composites were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy.

X-ray diffractograms of the carbon foams were recorded in a Siemens model D5000 powder diffractometer that was equipped with a monochromatic Cu Kα X-ray source and an internal standard of silicon powder. Diffraction data were collected by step scanning with a step size of 0.015° $2\theta$ and a scan step time of 2 s. For each sample, five diffractograms were obtained, using a different representative batch of sample for each run. The interlayer spacing, $d_{002}$, was evaluated from the position of the (002) peak applying the Bragg equation. The crystallite sizes, $L_c$ and $L_a$, were calculated from the (002) and (110) peaks, respectively, using

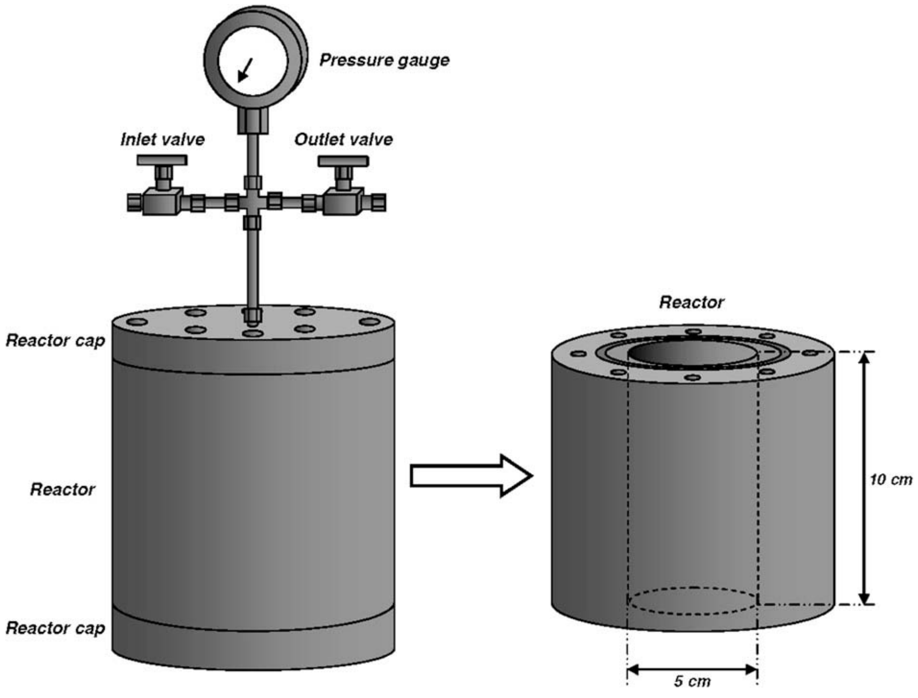

**Fig. 1.** Reactor used in the manufacture of carbon foams.