Connecting Carbon Fibers by Means of Catalytically Grown Nanofilaments: Formation of Carbon−Carbon Composites

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The progressive formation of carbon/carbon (C/C) composites via a catalytic method by covering carbon fibers with a carbon matrix using C_2H_4/H_2 feedstock is investigated by SEM, TEM, and AFM microscopies and by XRD analysis. In the initial stages, intersecting nanofilaments of about 40−50 nm diameter are formed under relatively mild conditions at the surface of smooth carbon fibers with ∼6−8 μm diameter supporting Ni and Fe nanoparticles. A "porous nanotissue" which interconnects the original fibers is initially generated. At later stages a more compact C/C composite material is formed on a laboratory scale, which shows a high graphitization degree.

1. Introduction

Carbon fibers are the basic part of the lightweight composite for high-performance materials.[1] Depending on the application fields of the material, the filling of the composite can vary from polymeric to inorganic matrixes. Carbon/carbon (C/C) composites belong to the second group and consist of a fibrous carbon substrate embedded in a carbonaceous matrix. Even though the same element forms both of the phases or constituents, a C matrix of a C/C composite comes from two basic processes,[2−4] based on (i) the carbonization of an organic solid or liquid precursor and (ii) the infiltration and densification of gaseous hydrocarbons (CH_4, C_2H_4, C_2H_2, etc.) into textured carbon supports.

The main drawback of the first process is the very high temperature of the thermal treatment (2000−3000 °C) necessary to achieve a sufficient order of the C forms,[1,2,5] whereas the problem of the second process is related to the infiltration process, which may be more difficult in the internal part of the composite.[2−5] In both processes several cycles of impregnation and high thermal treatment or infiltration are required to obtain a good densification of the matrix composite.[2,5]

Metal catalysts are well-known to be active in forming C nanostructures[6−10] and to reduce the pyrolysis temperature.[10,11] The catalytic method requires a metal catalyst (usually Ni, Fe, or Co or alloys)[7,12−15] supported in the form of nanoparticles on the carbon fibers and a carbon feedstock (hydrocarbon, CO). The catalytic route to the synthesis of C/C composites allows quasicrystalline carbon to be deposited at moderate temperatures (600−1200 °C)[3,10,16] with a large carbon yield.[16] When hydrocarbons are used as feedstock, depending on the synthesis conditions and on the metal catalyst loading, the carbon matrixes may range from high surface area to dense materials, which suggests their potential employment as catalytic supports[7,17] or high-performance materials for mechanical applications.[1,2] It is commonly accepted that the reaction proceeds at the exposed surface of the metal and that the diameter of the carbon filaments produced catalytically is related to the diameter of the metal particles.[18,19] The growth of the filaments is governed by bulk diffusion and by carbon concentration gradients along the nanofilaments.[7,8,12,18,19] As often observed by many authors the metal particles can be located on the head of the carbon filaments.[18,19]

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Very small metal particles are more suitable for the synthesis of single-wall carbon nanotubes (SWCNTs), while larger particles favor the formation of multiwall carbon nanotubes (MWCNTs) or nanofibers.[12,18] For the synthesis of carbon matrixes, which is the aim of the present study, the control of the particle dimensions is not critical, because all particles are active in forming the carbon nanostructures and are useful for the formation of the filling phase. As the formation of porous (high surface area) or dense matrixes is governed by the synthesis conditions, in this work the step by step catalytic formation and growth of a carbon matrix on carbon fiber supports is followed by means of SEM, TEM, and AFM microscopies and XRD analysis. The aim is to partially contribute to the understanding of the factors affecting the matrix formation. It is shown that nanofilaments growing at the surface of the metal particles are the first products of the synthesis. By increasing the reaction time, a porous network of intercrossing filaments, which interconnect the original fibers, is generated. At later reaction stages a dense carbon matrix is progressively formed, embedding the carbon substrate with the formation of a dense composite. Evidence is presented on the role of the metal particles in the formation of the dense carbon matrix.

2. Experimental Section

The carbon substrate used in this work was constituted by unsized carbon fibers (TENAX 5001T 12K fibers, 6−8 μm in diameter). The fibers have been impregnated with a solution of $Ni(NO_3)_2 \cdot 6H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ salt in ethanol by an incipient wetness impregnation process followed by evaporation (120 °C) and calcinations in air (300 °C). The final metal content was in the 10−20 wt % range.

This substrate was then contacted with a H_2/C_2H_4 gas mixture, following two distinct procedures (static or dynamic). In the former one, the Ni- or Fe-impregnated C fibers were placed in a high-vacuum system ($\sim 1.33 \times 10^{-6}$ mbar), heated to 400 °C, and reduced two times with 50 mbar of H_2 at 400 °C. The synthesis of the carbon nanofilaments was then performed by exposing, at 700 °C, the reduced metal catalysts to a H_2/C_2H_4 gas mixture (5:1 volumetric ratio, 500 mbar in total) for a total contact time of about 1 h. This procedure has been adopted because it allows the initial stages of the carbon matrix formation to be investigated. During this stage the yield in weight of the carbon matrix is very low (only a few percent).

The dynamic procedure has been carried out in a few steps by (i) exposing the impregnated C fibers (located in a cylindrical quartz furnace) to a 100 mL/min N_2 flow gas up to 400 °C at atmospheric pressure, (ii) replacing the inert atmosphere with a pure H_2 flow gas (100 mL/min) for 15 min at 400 °C, (iii) raising the temperature in H_2 to the desired value (550, 600, 650, or 700 °C), and then (iv) exposing the fibers to a flow of a H_2/C_2H_4 gas mixture (4:1 volumetric ratio) for the desired time (usually 60 min). By adopting this procedure, carbon yields up to 3500% have been quantified.

Carbon support and carbon composites obtained at the various steps of the synthesis have been characterized by SEM (Leica Cambridge Stereoscan 420 instrument, equipped with an energy-dispersive X-ray spectroscopy (EDS) instrument, by TEM (JEOL 2000EX instrument, 200 keV), and by AFM (Park Scientific Instrument Auto Probe LS). The crystallinities of the samples have been estimated by XRD analysis (X-ray diffractometer with Cu Kα radiation using a standard Bragg−Brentano geometry).

3. Results and Discussion

Although the metal particle diameter is not a critical parameter for the aim of this investigation, it has been evaluated by broadening of the metal lines of XRD patterns and by SEM and TEM analyses.

Figure 1 reports SEM and AFM images related to the sample synthesized following the static procedure in high-vacuum (HV) conditions. The SEM micrographs of the starting sample (Figure 1a,b) show that it is constituted by a collection of nearly parallel commercial fibers (TENAX 5001T 12K). The inset of Figure 1a shows the diffraction peaks of the carbonaceous material constituting the TENAX carbon fibers. Due to the quite high value of the full width at half-maximum (FWHM), the graphitization degree of the support is modest. In Figure 1b, the smooth character of the fiber surface is further evidenced by AFM (inset in the right part of the image). From these figures we can conclude that the starting material is constituted by fibers characterized by regular dimensions (∼6−8 μm in diameter) and by a uniform and smooth surface (at the adopted resolution). In the second inset of Figure 1b (upper part of the figure), an SEM image of a portion of a fiber containing Ni particles is also shown. From this image the presence of Ni particles apparently uniformly dispersed on the surface of the fibers can be observed, whereas from other images not reported for the sake of brevity, the predominant diameter of the Ni particles, coming from SEM observations, is about 50−60 nm. Particles of larger dimensions are also more rarely observed. Although the presence of particles characterized by smaller dimensions cannot be evidenced by SEM, their abundant presence is testified by TEM (vide infra) and by the XRD analysis. As a matter of fact, from the peak broadening and by using Scherrer's equation, $Lc = K\lambda/(\beta \cos \theta)$[20] (where λ is the X-ray wavelength, β is the FWHM of the diffraction line, θ is the diffraction angle, and K is a constant, which has been assumed to be $\cong 1$), scattering coherent domains, in the 26−29 nm interval, have been calculated. These figures are well below those obtained by SEM, which implies that smaller particles escaping the SEM observation are present. The presence of particles of smaller dimensions is supported even by the TEM observations (vide infra). In Figure 1c,d SEM micrographs of portions of the sample (similar to that shown in Figure 1b) after the growth of nanofilaments following the static procedure are shown. In particular, Figure 1c illustrates the situation of the nanofilaments grown in a narrow space between two adjacent fibers. The presence of a network of filaments interconnecting the fibers is well documented. This conclusion is further reinforced by the inset (right side on the bottom) illustrating SEM details of portions of the sample, where the existence of a complex reticulate of nanofilaments interconnecting two originally independent fibers clearly emerges. The presence of these interconnections clearly shows that a new porous carbon/carbon composite is gradually synthesized under the relatively mild conditions (550−700 °C) adopted in this experiment. Evidence of the formation of nanofilaments comes also from the AFM image (upper inset of Figure 1c),

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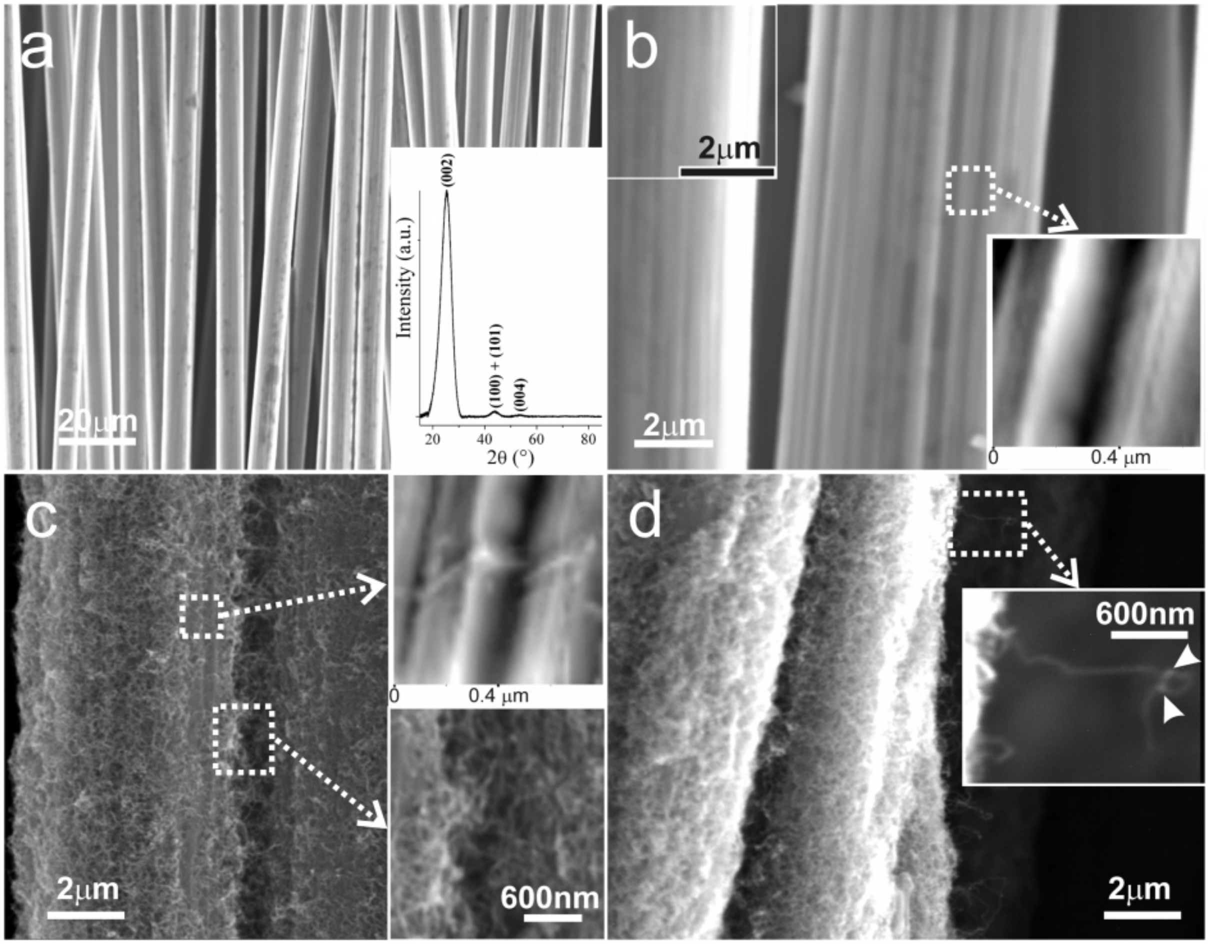

Figure 1. (a) SEM image of commercial carbon fiber substrates. In the inset the XRD peaks are reported. (b) SEM image of a couple of fibers (enlarged view). In the first inset (right side) the details of a fiber obtained by AFM are shown. In the second inset (left side) the details of a fiber covered by Ni particles are illustrated. (c) SEM image of two parallel carbon fibers, covered by a carbon matrix, grown following the static method at 700 °C. The first inset (right side on the bottom) shows the tissue of the interconnecting nanofilaments. In the second inset (right side on the top) an AFM image of a nanofilament, running across the substrate, is shown. This picture has been obtained on a region of the fibers where the grown carbon matrix is less dense. (d) SEM image of fibers covered by a carbon matrix like those shown in (c), but viewed in more external positions. In the inset an exploded view of a filament is shown. The presence of two Ni particles is evidenced by the small arrows on a small ring protruding far from the surface of the fiber.

where a single nanofiber running perpendicular along two adjacent carbon fibers is observed. In Figure 1d the view of the profile of a fiber located in a more external position (i.e., without a second one in a vicinal position) is illustrated. In this picture (and in the inset as well), it is possible to appreciate more clearly the growth of protruding 2 μm long filaments, whose approximate diameter is about 40−50 nm. Notice the presence, along a partially closed ring, of two metal particles with an approximate 50−60 nm diameter. This result confirms that the filaments grow catalytically at the surface of individual particles.[17] From this observation it is inferred that, during the carbon matrix formation, part of the metal particles leave the surface of the fibers and act as fluctuating and independent catalytic centers. These centers, transported into the bulk of the growing carbon matrix, play a critical role in favoring the progressive formation of the porous phase. In conclusion, this experiment suggests that the formation of a "porous nanotissue" occurrs when these filaments meet the other ones coming from adjacent fibers.

The results obtained for a sample treated under dynamic conditions are illustrated in Figure 2. The image in Figure 2a shows that the original fibers (indicated by the broken line) are nearly completely buried by the carbon matrix, and consequently, their profile is hardly distinguishable. Notice that the thickness and the density of the layer of filaments are definitely larger than those obtained with the static procedure because the dynamic method is more efficient. The details reported in Figure 2b,c show clearly the individual filaments originating in the dense nanotissue, whose diameter is substantially similar to that of the static experiment. In Figure 2b the presence of metal particles located at the end of the filaments is more clearly evidenced. This result definitely confirms that during the growth of the carbon matrix a fraction of the metal particles leave the fiber surface, where they are initially located, and then they are transferred into the carbon matrix, where they act as independent centers. In the inset of Figure 2b, a TEM image of a portion of the porous nanotissue scratched from the fibers is shown. From this figure we can see that, besides the largest filaments, already evidenced by SEM, other smaller nanofibers are abundantly present, which escaped the SEM observation. These nanofibers have a diameter in the 10−20 nm range and are formed at the surface of "free"

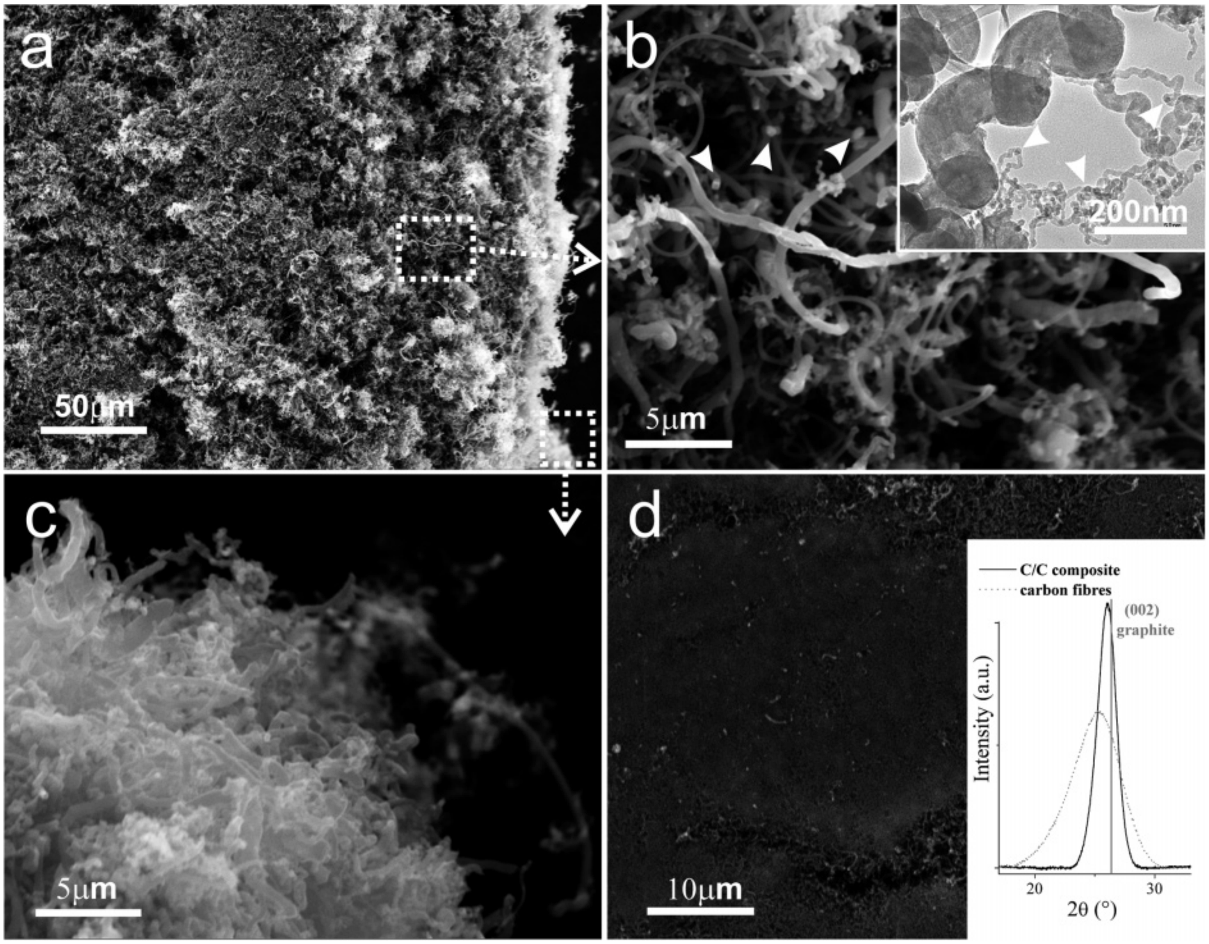

Figure 2. (a) SEM image of C/C composites obtained under dynamic conditions at 650 °C on Ni-supported carbon fiber catalysts. The dotted lines evidence the positions of the underlying fibers. (b) SEM enlarged image of a selected area in (a): low-density region. In the inset, a TEM image of a portion of the carbon matrix is shown. Besides the nanofilaments having an average diameter of 50−60 nm, the position of metal Ni particles is evidenced by the small arrows. (c) SEM enlarged image of a selected area in (a): profile view of a high-density region. (d) SEM image of the details of a dense C matrix generated at a longer reaction time. In the inset, the XRD peaks of the C/C composite and of the original carbon fibers are reported in comparison with the position of the (002) graphite peak, shown by the vertical line.

metal particles with a diameter in the same interval (arrows in the inset). This result confirms the XRD data because it firmly demonstrates that the metal particle diameter spreads in a very large 10−60 nm interval. We think that the smallest particles play a fundamental role in the builddup of a compact carbon matrix under flow conditions because they are likely the most versatile and mobile centers for filling the smallest voids within a carbon matrix. When the reaction time under dynamic conditions is increased to 1.5−2 h, the carbon matrix structure changes from that characteristic of a nanoporous material to that of a compact and dense material. This is shown by an image of the C/C composite originated under dynamic conditions after 2 h of contact time (Figure 2d). From this image we can notice that the original fibers are completely buried and that large parts of the samples are now constituted by a compact and uniform carbon matrix. The XRD pattern of this carbon matrix is characterized by a (002) diffraction peak, showing a small value of the FWHM, typical of a high graphitization degree of the C/C matrix. The graphitization degree is definitely higher than that of carbon fibers used as the initial support.

On the basis of this figure, from the (002) peak the value of the d_{002} interlayer spacing (3.430 Å) and the apparent crystallite size along the c axis, L_c (4.1 nm), were obtained, in agreement with literature data.[21,22] It must be pointed out that this carbon matrix shows in the diffractogram a broad and complex band instead of separated (100) and (101) peaks, which overlap the (010), (002), and (011) Ni diffraction peaks (data not reported for the sake of brevity). This means that the apparent crystallite size along basal planes, L_a, cannot be easily obtained. In addition, other peaks at higher θ values relevant for obtaining L_a cannot be easily detected. However, it is expected that interlayer distances and crystallite sizes could be hardly modified by further graphitization processes.

Similar experiments have been performed on Fe-supported carbon fiber catalysts following an equivalent procedure and identical reaction times. The obtained results are essentially similar to those obtained on Ni-supported catalysts as far as the morphology of the obtained carbon matrix is concerned. For equivalent reaction times the weight increase is however smaller than that of the Ni-based systems. On this basis, it is inferred that the Fe-based catalyst is less efficient than the Ni-based one. Due to the similarities between the results obtained on Ni-based and Fe-based systems, a detailed

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description of the results obtained on the Fe catalyst is omitted for brevity.

4. Conclusions

The obtained results demonstrate that the catalytic method affords an effective and low-temperature way to synthesize carbon/carbon composites ranging from microporous to more compact materials. Static conditions favor the formation of a porous network constituted by intercrossing nanofilaments. Otherwise dynamic conditions promote the formation of a compact carbon matrix characterized by a high graphitization degree. The role of the smallest metal particles in promoting the formation of a dense carbon matrix is highlighted.

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