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Correlation between chemical vapor deposited diamond and carbon fibers substrates

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Abstract Diamond film formation has been studied on carbon felts (CF) substrates produced from polyacrylonitrile precursor, at different heat treatment temperatures (HTT). Scanning electron microscopy images have revealed a polycrystalline and preferential (111) diamond film covering the whole CF surface, even for deeper planes. The average grain size increased from 3.0 up to 6.0 μm for films grown on CF treated between 1000 and 2000 °C. This behavior may be attributed to different contributions associated to the facility to extract carbons atoms from CF substrate. For CF treated at lower HTT, higher carbon atoms amount will promote higher nucleation density on diamond films and consequently a smaller grain size. Raman spectroscopy indicated good quality diamond films and the lower amount of graphitic phase was observed for diamond grown on CF obtained at 2000 °C HTT. The microstructural properties of the CF were obtained by X-ray diffraction (XRD) and show a strong dependence with HTT.

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Introduction

Synthesis of diamond films on carbonaceous substrates is still unclear and has promoted new concepts of understanding the mechanism by which the diamond phase first nucleates. For chemical vapor deposition process graphitic carbon is the most stable carbon phase and diamond formation explanation is not easy. Some authors [1–5] have discussed that the diamond density increase is associated with quality film formation, when graphitic carbon is present on the growth surface. Angus et al. [3–5] have claimed that graphite as well unsatured aromatic (sp^2) compounds serve as sites of diamond nucleation and enhance the number of nucleation centers because of the diamond nuclei grow preferentially on prism planes of the graphite.

The deposition of diamond on carbon fibers (CF) substrate has already been studied for some authors [6–8]. However, there are not works in the literature that correlate the effects of CF structural properties, produced at different Heat Treated Temperatures (HTT), on diamond films grown on such substrates. During the deposition process, fiber etching and diamond nucleation occur simultaneously and compete kinetically. Ting and Lake [6] have investigated the formation of diamond on vapor grow carbon fiber (VGCF) and CF from polyacrylonitrile (PAN) using a microwave plasma enhanced chemical vapor depositon (MPECVD). Unfortunately, CF from PAN fibers were severely etched in microwave plasma, while diamond was successfully deposited on VGCF. Otherwise, diamond films were deposited on CF from PAN and pich fibers by MPECVD with success by Shah and Waite [7], using a pretreatment of the fibers in a bath containing methanol and diamond paste.

The diamond deposition on carbon fiber (VGFC) in different heat treated temperatures was investigated by Ting and Lake [8]. They observed that the heat treated temperatures of carbon fiber precursor affected both etching of fiber and nucleation of diamond.

The main purpose of this study is the growth and characterization of diamond films on CF treated at different HTT of 1000, 1500 and 2000 °C. In addition, CF structural parameters were analyzed by X-ray diffraction (XRD) and Raman spectroscopy. A strong correlation was observed between CF HTT and its structural properties and influences diamond film formation.

Experimental

Carbon fibers samples were produced from PAN precursor at different HTT by using temperature steps of 330 °C/h under inert atmosphere with nitrogen flow of 1 L h^{-1}, reaching the maximum temperature of 1000, 1500 and 2000 °C, standing at this maximum during 30 min until its cooling down to room temperature. The samples are denoted as CF-1000, CF-1500, and CF-2000 and consist of CF disks with 0.15 cm thickness and 1.8 cm diameter. Boron doped diamond films were grown by Hot Filament Chemical Vapour Deposition technique during 20 hours from 0.5% CH_4/H_2 gas mixture. The substrate temperature and total pressure were 730 °C and 6.5×10^3 Pa, respectively. The substrates were ultrasonically pre-treated in a mixture of 0.25 μm diamond powder and hexane. Boron source was obtained from H_2 line forced to pass through a bubbler containing B_2O_3 dissolved in methanol. This system permits the control of boron concentration in the films using a flow controller. The doping level used (5000 ppm B/C in methanol) corresponds to acceptor concentration of 1.5×10^{18} cm^{-3}, evaluated by Mott-Schottky Plot measurements in previous work [9] and correlated with Raman spectra [10].

Samples were kept in the vertical position inside the reactor between two pairs of parallel tungsten filaments that permitted the film growth on both sides, simultaneously. This procedure is important to guarantee the diamond growth covering all the carbon fibers including deeper plans. Images of diamond films were obtained by Scanning Electron Microscopy (SEM) from LEO 440. Micro-Raman spectra were recorded by a Renishaw microscope system 2000 in backscattering configuration at room temperature employing 514.5 nm argon-ion laser.

Results and discussion

For analyzing and discussing diamond morphology on CF substrates it is necessary to consider some important contributions, as the effects of HTT during the carbonization process for converting PAN precursor into carbon fibers associated with its influence on CF structural properties.

There are three basic successive stages in the conversion of PAN precursor into carbon fibers. The first stage is the oxidative stabilization where the PAN precursor is first stretched and simultaneously oxidized in a temperature range of 200–300 °C. This treatment converts thermoplastic PAN to a non-plastic cyclic or ladder compound [11]. Oxidative stabilization is a very important step in the fabrication of carbon fibers because improper stabilization may results in a blow-out of the core portion of the fiber during carbonization due to incomplete oxidation [11, 12] The second stage is the carbonization, after oxidation the fibers are carbonized at about 1000 °C without tension in inert atmosphere (usually nitrogen) for a few hours. During this process the noncarbon elements are removed as volatiles (i.e., H_2O, HCN, NH_3, CO, CO_2, N_2, etc [11]) to give carbon fibers with a yield of about 50% of the mass of original PAN. Most of the volatiles are evolved below 1000 °C; only carbon and some nitrogen (~6%) are left. The closing stage is the graphitization. The fibers are treated at temperatures between 1500–2000 °C and during this process may lose most of their noncarbon impurities and have a graphite-like structure. Further HTT, higher than 2000 °C does not cause any appreciable decrease in weight of the fiber, but improves the ordering and orientation of the crystallites in the direction of the fiber axis.

The Table 1 presents a set of CF experimental parameters for the three HTT studied during the

Table 1 PAN-CF parameters at different HTT obtained by four-probe method, SEM, XRD and first order Raman spectroscopy

HHT (°C)	CF diameter (μm)	ρ (Ω cm)	d_{002} (Å)	L_{002} (Å)	ω_D/ω_G	I_D/I_G
1000	10.4 ± 0.3	0.96 ± 0.39	4.34	11.6	2.76 ± 0.40	0.98 ± 0.02
1500	10.4 ± 0.14	0.11 ± 0.01	4.25	16.2	1.51 ± 0.38	0.79 ± 0.15
2000	10.07 ± 0.22	0.11 ± 0.006	4.16	23.1	0.92 ± 0.01	0.73 ± 0.05

carbonization process: resistivity (ρ), interlayer distance (d_{002}), pilling up width of layers (L_{002}) from XRD and FWHM ratio (ω_D/ω_G) and the relative intensity (I_D/I_G) between the D and G bands were obtained from Raman spectra. Resistivity values were evaluated from four-probe measurements and the average values of CF diameters were obtained directly from SEM images.

Table 1 shows that microstructural properties of the carbon fibers are strongly affected by HTT. The results from the first order Raman have presented that ω_D/ω_G and I_D/I_G decrease as HTT increases, which reveal that CF have more graphitization degree at 2000 °C. In addition, HTT influences the electrical properties due to the increase of preferential orientation of graphitic sheets in fiber axial direction at higher temperature and are in good agreement with the literature [13]. XRD results have shown that the interlayer distance calculated from (002) bands decreases with HTT increases while the pilling up width of layers (L_{002}) increases due to the large structural organization of carbon at higher HTT [14].

Considering the difficulty of growing diamond films on graphite due to sp^2 bond to be etched by atomic hydrogen present in the gas phase [15, 16], a suitable substrate pre-treatment was made to improve the diamond nucleation on CF keeping the sp^3 configuration dominant over sp^2 reconstruction. Figure 1 shows SEM morphology images of diamond film on CF-1000 (A), CF-1500 (B) and CF-2000 (C). The images demonstrate that CF surfaces were completely covered by a diamond polycrystalline film even for deeper planes. The grains are twined and faceted with symmetrical and smooth faces, confirming good diamond film. Besides, by inspection of the images A, B and C the grain size was estimated and present a variation in the range of 3.0 up to 6.0 μm between diamond/CF-1000 and diamond/CF-2000 samples. Cross section images (not shown) have presented a diamond coating thickness of around 3.0 μm for all samples analyzed that decreases for internal fibers, as expected, taking in to account the critical depth for diamond formation, mainly due to the atomic hydrogen diffusion mechanisms.

The quality of diamond films on CF substrates were studied by Raman spectroscopy. Figure 2 shows Raman spectra for diamond films on CF-1000 (A), CF-1500 (B) and CF-2000 (C), respectively. Raman spectra have evidenced the sharp 1332 cm^{-1} peak, indicating films constituted mainly by diamond crystals. In addition, a broad band centered at 1550 cm^{-1} appeared in (A) and (B) curves. This band is attributed to disordered graphitic phases and it is not observed in (C) curve.

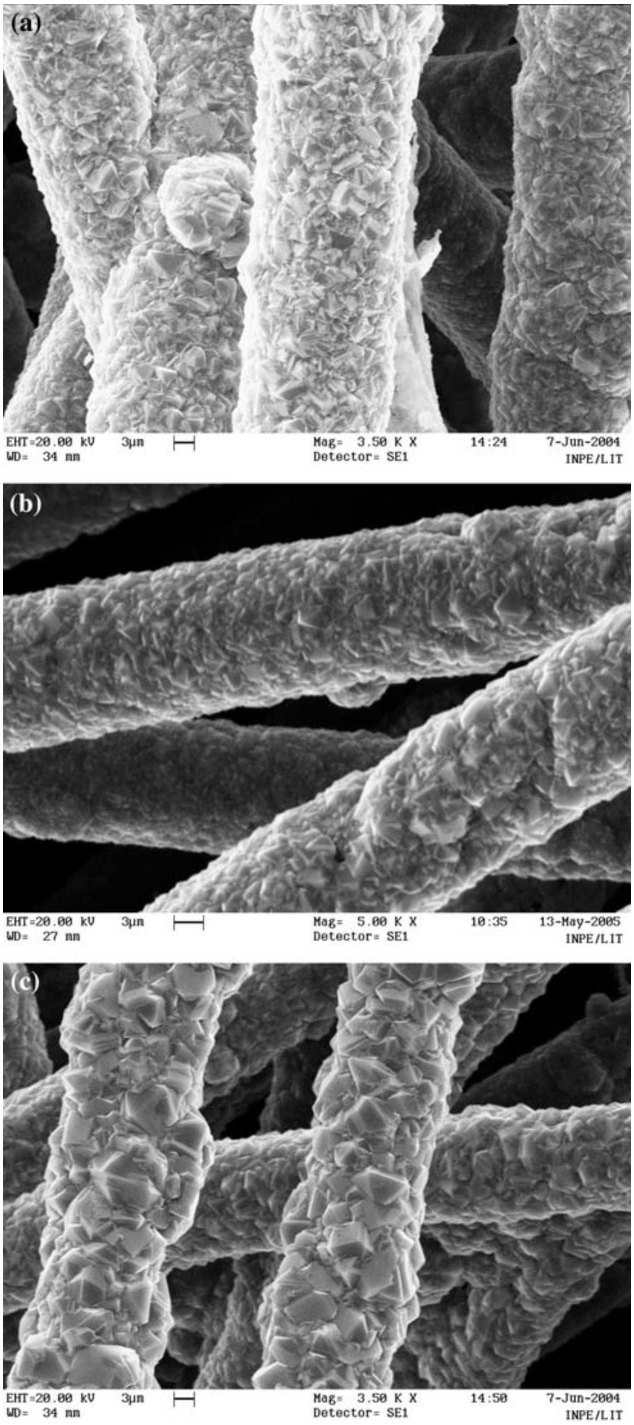

Fig. 1 SEM images for diamond film on carbon fibers substrates: (**A**) CF-1000, (**B**) CF-1500 and (**C**) CF-2000

The relative amount of diamond in the film, also called diamond purity, was obtained by a quantitative analysis of the Raman spectra of Fig. 2. The Fig. 3 shows separate contributions of diamond and disordered graphitic phases to the total Raman scattering, the whole Raman spectra were fitted with Lorentzian

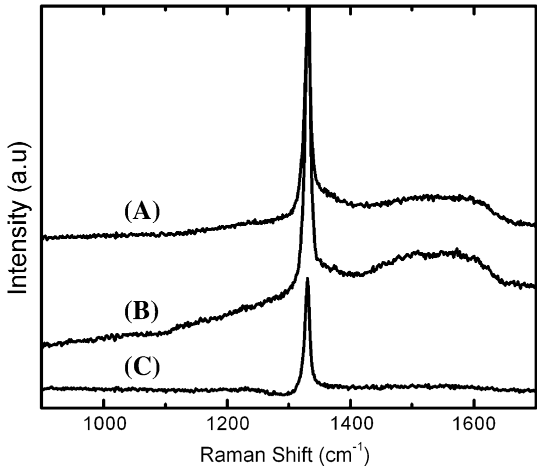

Fig. 2 Raman spectra of diamond films: (**A**) CF-1000, (**B**) CF-1500 and (**C**) CF-2000

lines for CF-1000 and the others follow the same procedure (no show). The broad band centered at 1550 cm^{-1}, was fitted considering three different contribution bands: the D and G peaks of polycrystalline graphite at around 1345 and 1560 cm^{-1}, and a low intensity band centered approximately at 1470 cm^{-1} attributed to a tetrahedrally bonded diamond precursor. The amount of diamond in the films was evaluated by the relation [17]:

$$C_d = 100A_d/\left(A_d + \frac{\sum A_i}{50}\right)$$

where A_d and A_i are the area of the fitted curves corresponding to the 1332 cm^{-1} diamond peak and the graphitic bands, respectively. This procedure was accomplished for all grown films, and Fig. 4 shows the result as a function of substrate HTT. The relative amount of diamond increases approximately from 88% in the CF-1000 sample to 99% in the CF-2000 sample.

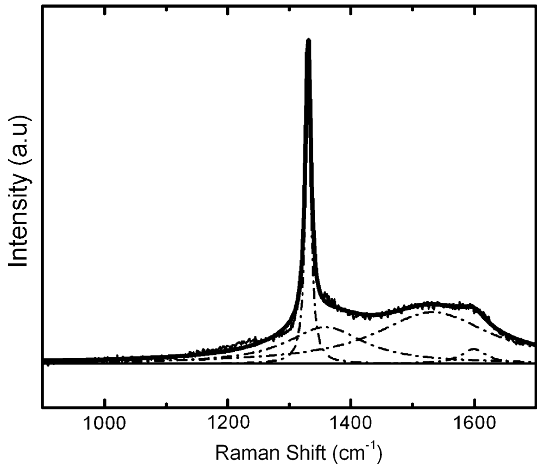

Fig. 3 Raman spectra with correspondent fitting for the diamond film on CF-1000 substrate

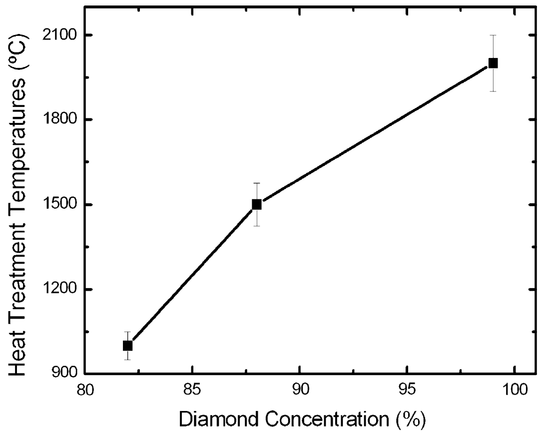

Fig. 4 The relative amount of diamond as a function of different HTT on carbon fibers substrates

The mechanism associated with the morphology and the diamond film purity on carbon fibers has a strong dependence with the carbon fibers structure acquired after the carbonization process. Diamond nucleation by hydrogenation of the graphitic edges precursor proposed by Angus et al. [3, 4], and confirmed with quantum chemical calculation by Mehandru et al. [5], is favored at prism planes rather than the basal planes, due to its dangling bonds. The hydrogen adsorption on the edges of graphite prim planes modifies the structure causing formation of a slight curvature. Also, according to Lambrecht et al. [3], this modification generates an energetically favorable situation for the formation of graphite/diamond interface. Carbon atoms in the graphite (0001) basal plane have a similar geometrical arrangement of those in the diamond (111) plane. This behavior is clearly observed in the presented preferential (111) diamond texture, Fig. 1C. Considering the crystallography of CF-2000 very similar to graphite structure, it is expected a similar mechanism for diamond formation. This mechanism can explain the highest grain size observed in this sample because the graphite organization may be favorable to diamond growth.

Conclusions

Diamond formation was studied on CF substrates produced from PAN organic polymer precursor at different HTT. CF structural properties knowledge and control have demonstrated to be very important for growing diamond films on such substrates. SEM morphology demonstrates that CF surfaces were completely covered by a diamond polycrystalline film even for deeper planes forming a three dimensional porous diamond sample. The grains are twined and faceted with symmetrical and smooth faces, confirming good polycrystalline diamond film as diamond/CF-2000 with predominant (111) crystallographic plane and largest grains, characteristic of a highest film growth rate. A variation of the average diamond grain size was also evaluated from SEM images and has achieved in range of 3.0 up to 6.0 μm for diamond/CF-1000 and diamond/CF-2000, respectively. Diamond coatings have presented a thickness of around 3.0 μm that decreases for internal fibers, as expected, taking in to account the critical depth for diamond formation, mainly due to the atomic hydrogen diffusion mechanisms. The quality of diamond films on CF substrates were studied by Raman spectroscopy and has shown that the relative amount of diamond increases approximately from 88% in the diamond/CF-1000 sample to 99% in the diamond/CF-2000 sample.

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