STRUCTURAL CHANGES VERSUS GRAPHITIZATION TEMPERATURE FOR STACKED-CUP CARBON NANOFIBERS

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Introduction

Filaments of carbon with a diametrer under 100 nm, generically referred to as carbon nanofilaments, can be produced in large quantities by catalytic chemical vapor deposition (c-CVD) from a carbon feedstock using a transition metal (Fe, Ni, Co and Cu) as catalyst. This process usually occurs in a hydrogen atmosphere at temperatures ranging from 500 to 1200ºC. There are several types of carbon nanofilaments depending on the arrangement of the graphene sheets. The so-called single or multi-wall carbon nanotubes (SWNT or MWNT) are comprised of graphene sheets, seamlessly rolled up in a cylindrical form, with the planes parallel to the fiber axis. When the graphene sheets are arranged in a different way the filaments are denoted as carbon nanofibers (CNF). There is a huge interest in the industrial applications of carbon nanofilaments. Many researchers are working in the improvement of the properties of carbon nanofilaments in order to get better results in some applications. Heat treatments at high temperatures can improve the properties of carbon nanofilaments by purifying them and by modifying their graphitic structure. Moreover, the change in the crystallographic structure of the carbon nanofilaments by heat treatment at high temperatures is useful to understand the graphitic structure and the mechanistic formation.

In this work we used commercial stacked-cup carbon nanofibers, produced by the floating catalyst method with natural gas as the carbon source and nickel as the catalyst (GANF1).The unique structure of GANF1, with no amorphous carbon coating at all, consists of a continuous graphite ribbon rolled up in a spiral form along the fiber axis, looking like a stacked cone structure. For its production, this type of carbon nanofiber needs the addition of a sulfur source in the production reaction. The sulfur forms nickel sulphide that is molten at the reaction temperature, forming a binary catalyst particle (Ni-NiS) which makes the spiral formation possible (Martin-Gullon, 2006). Other researchers working with nanofibers and nanotubes in a floating catalyst system with iron pointed out that a sulfur source was absolutely required in order to obtain a partially molten catalyst (Endo, 2003, Tibbetts, 1993, 1999; Balogh, 1999).

Graphitization of GANF1 was performed under helium at 1400, 1700, 2000, 2400 and 2800ºC. The graphitized samples have been characterized by X-Ray Fluorescence, XRD, Raman and TEM in order to study the evolution of the crystallographic structure versus graphitization temperature.

Experimental

GANF1 samples were heat-treated in a high temperature graphite furnace. Once the samples were loaded into furnace, this was vacuum-purged with He to remove residual air before heating at 50 ºC/min up to different final temperatures: 1400, 1700, 2000, 2400 and 2800ºC, with a 1 h dwell time under flowing He atmosphere.

The nickel and sulfur content in the graphitized and in the as-grown GANF1 was analyzed by X-Ray fluorescence (Philips Magix Pro) and by elemental analysis (Carlo Erba model CHNS-O EA1108).

Crystallographic changes during the graphitization process were characterized by an X-Ray difractometer (Seifert model JSO-DEBYEFLEX 2002 with a copper cathode). The interlayer spacing (002) distance, the graphitization index and the crystallite dimension L_c were determined following a

standard method (Iwashita, 2004). The difractograms were done between 2 and 90 2-theta degrees with a stepsize of 0.01 degrees.

The graphitized samples were also analyzed by Raman spectrometry. Raman spectra were obtained under ambient conditions from thin films of the samples deposited onto glass slides. A LabRam (Jobin-Ivon) with a charge couple device (CCD) was used. The excitation source was 514 nm Ar laser line.

Transmission electron microscopy (TEM) was performed with a JEOL JEM-2010 model provided with an EDS system OXFORD instruments INCA Energy TEM100. A special tilt holder was used in order to observe the cross section of the carbon nanofibers.

Results

The sublimation of the nickel particles present in the sample takes place during the graphitization process. Nickel content starts to diminish at 1400ºC, and above 2000ºC the nickel content is already negligible (figure 1). The sulfur content follows the same tendency as nickel. In fact, sulfur is present in the carbon nanofibers as nickel sulphide, and therefore, they are removed together.

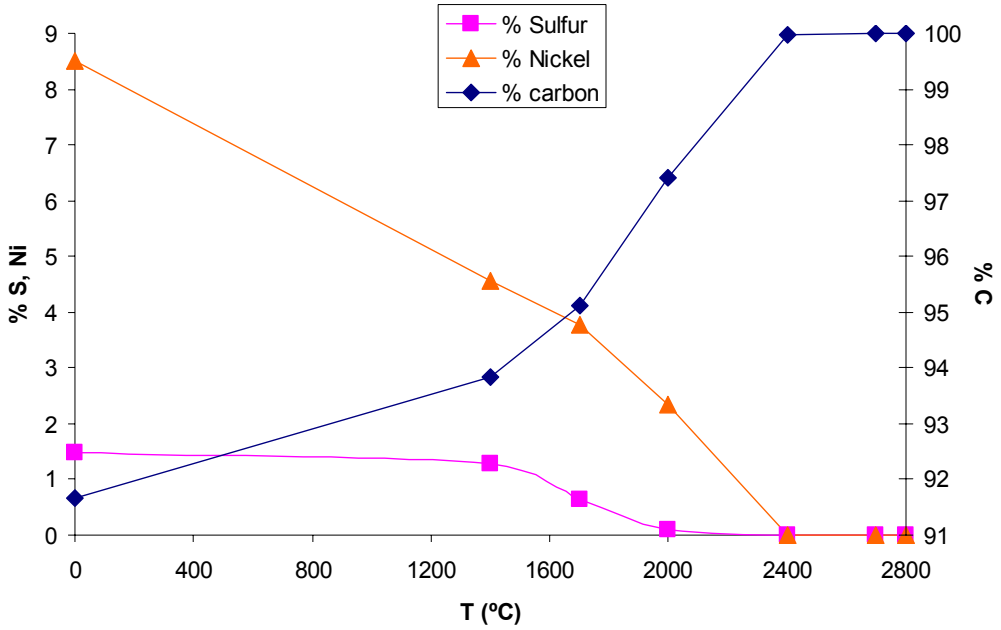

Figure 1. Evolution of the sulfur, nickel and carbon content with the graphitization temperature

Figure 2a shows the peak of (002) reflections obtained by XRD for the as-grown and graphitized samples. By increasing the graphitization temperature the (002) peak becomes sharper and shifts to higher angles. The interlayer spacing d(002) decreases slightly from 3.379 Å in the as-grown sample to 3.364 Å in the samples graphitized to 2400 and 2800ºC (see table 1). The crystallite dimension (L_c) also changes during the graphitization process; L_c value is 96 Å in the GANF as-grown sample, and increases greatly to 173 Å in the sample graphitized at 2800ºC. Figure 3 shows the variation of interlayer spacing (002) and L_c versus the graphitization temperature. There is an abrupt variation in the crystallographic structure between 1400ºC and 2400ºC, but there is no change between 2400 ºC and 2800ºC, indicating that there is no variation in the structure of the samples at higher temperatures.

Figure 2b shows the (112) peak for the samples as-grown and the graphitized at 2800ºC (2 theta = 83.6). The peak is sharply defined in the graphitized sample and poorly marked in the as-grown sample. Taking into account that the (112) peak is characteristic of an AB graphite stacking (Iwashita, 2004), it seems that during the graphitization process the graphitic structure of the carbon nanofibers is being arranged in an AB stacking structure.

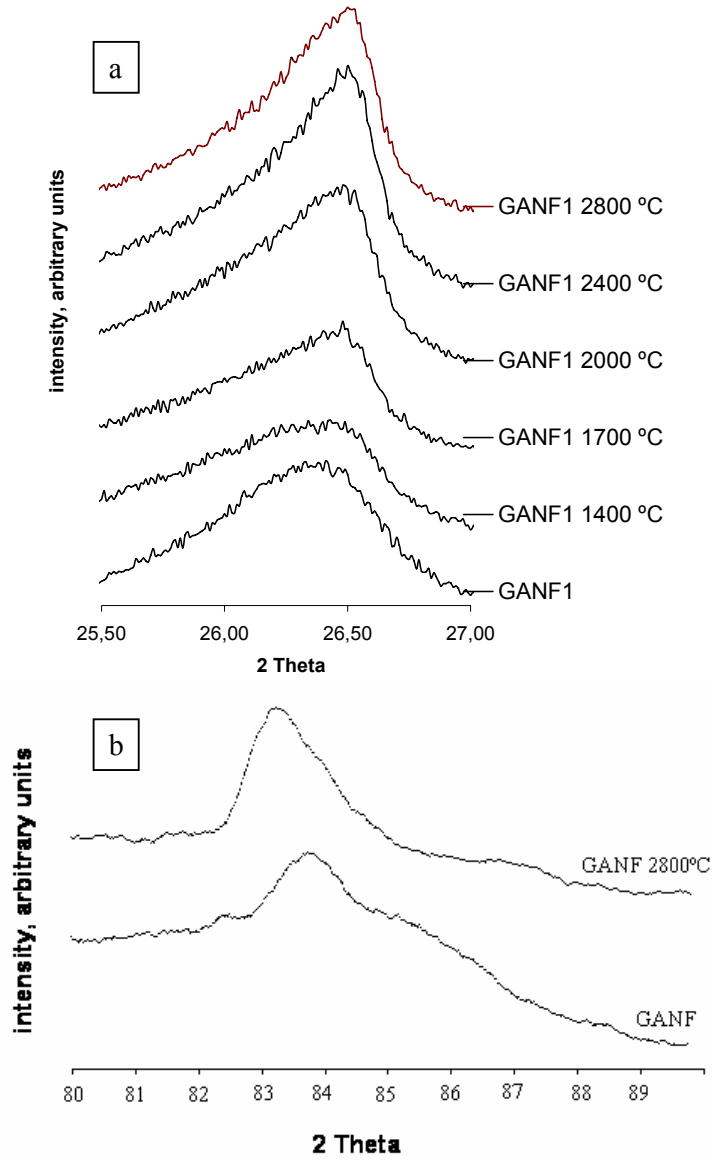

Figure 2. XRD profiles. The (002) and (112) peaks for the as grown and the graphitized samples

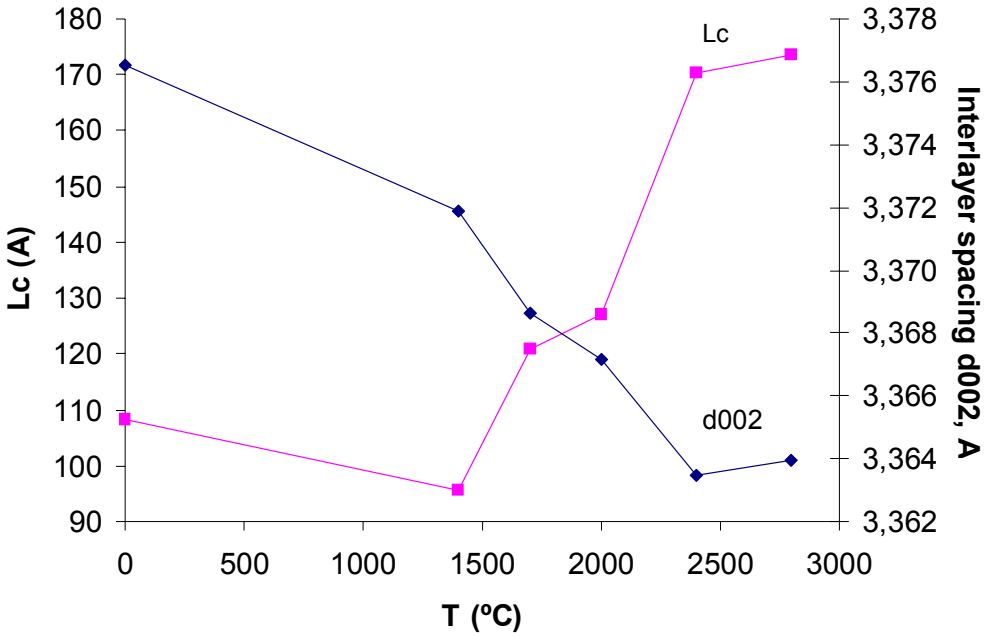

Figure 3. Crystallite dimensions and interlayer spacing d002 versus the graphitization temperature

Figure 4 shows the Raman spectra of the samples. All of them exhibit mainly two Raman bands at about 1335 and 1580 cm^{-1}. The first one corresponds to the D-band associated with the defects of the sample, and the second one (G-band) correspond to the graphitic band that is related to the order of the sample. Another band is present in the spectra; the D'-band appears as a shoulder of the G-band. This shoulder is indicative of defects in the graphitic structure (Rasheed, 2007). The D-band and the D' shoulder decrease as the graphitization temperature increase. The higher contribution of the D-band takes place in the GANF1 sample. The sample graphitized at 2800ºC has a low contribution of the D-band and of the D'shoulder. The annealing of the samples is effective. R value (I_D/I_G) is given in table 1; there is a gradual decrease in the R value with increasing the graphitization temperature.

Table 1. XRD and Raman analysis results

Graphitization temperature, ºC	Interlayer spacing d002, A	FWHM	Crystallite dimension Lc (A)	Graphitization index, %	R = I_D/I_G
-	3,377	0,189	108	74	0.97
1400	3,372	0,145	96	79	0,72
1700	3,369	0,119	121	83	0,69
2000	3,367	0,158	127	85	0,63
2400	3,364	0,151	170	89	0,50
2800	3,364	0,164	173	88	0.44

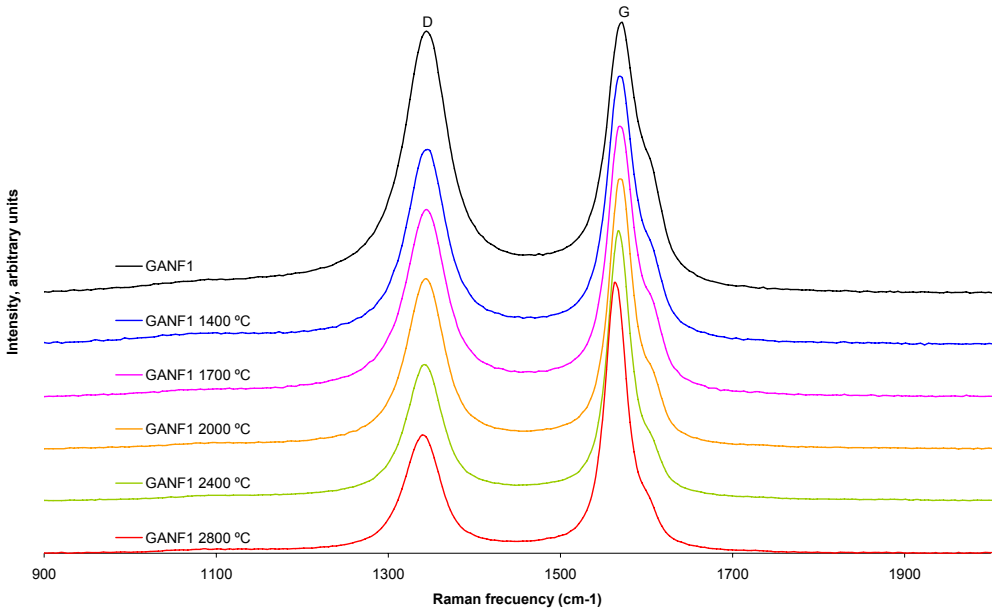

Figure 4. Raman spectra of the graphitized samples

The crystallographic changes in the carbon nanofibers can be directly observed by TEM. Figure 5a-b shows two micrographs of the GANF sample treated at 1400ºC. There are no structural changes with respect to the GANF as-grown sample: stacked-cup carbon nanofibers with a large hollow core with diameters ranging from 40 to 140 nm (Martin-Gullon, 2006).

The morphological changes start to become clearer at 2000ºC. Dehydrogenation of the internal and external edges of the graphite truncated cones takes place and therefore, two or more graphene sheets have to join together, forming 'loops', in order to stabilize the structure (Endo, 2003). These are observed in figure 5c.

The dehydrogenation, and therefore the formation of loops, takes place to a large extent at 2400ºC. It can be seen in figure 1 that the sample treated at 2400ºC is composed of 99.9 % of carbon. Furthermore, a new change in the crystallographic structure occurs at 2400ºC as can be seen in figure 5d. The graphitic planes that form the cone stacking are formed by groups of 15-30 graphene layers. This fact may be related with the crystallite dimensions L_c, which increase with the graphitization temperature (figure 1). Figure 5e-f shows the carbon nanofiber sample treated at 2800ºC. There are no significant morphological differences between 2400ºC and 2800ºC samples.

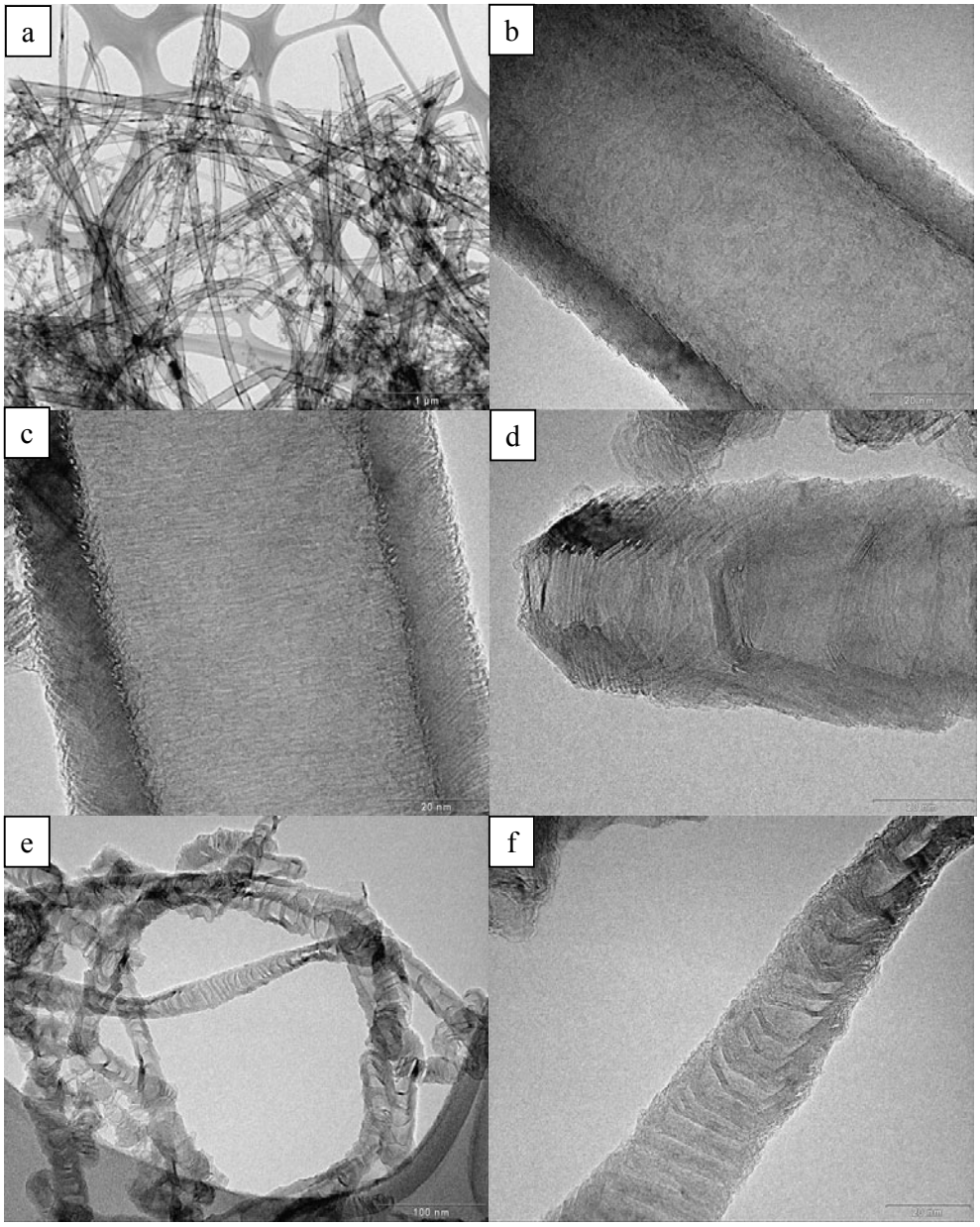

Figure 5. TEM images of GANF samples graphitized at different temperatures: (a-b) 1400ºC, (c) 2000ºC, (d) 2400ºC and (e-f) 2800ºC

Nevertheless, an interesting observation was noted using the tilt holder. Figure 6a shows the section of the GANF as-grown sample. As can be observed the cross section of the GANF as-grown sample is mostly rounded, like a pipe. Heat treatment at 2800ºC strongly rearranges the graphene sheets and the cross section of the carbon nanofibers becomes sharply polyhedral (hexagonal) (figure 6b).

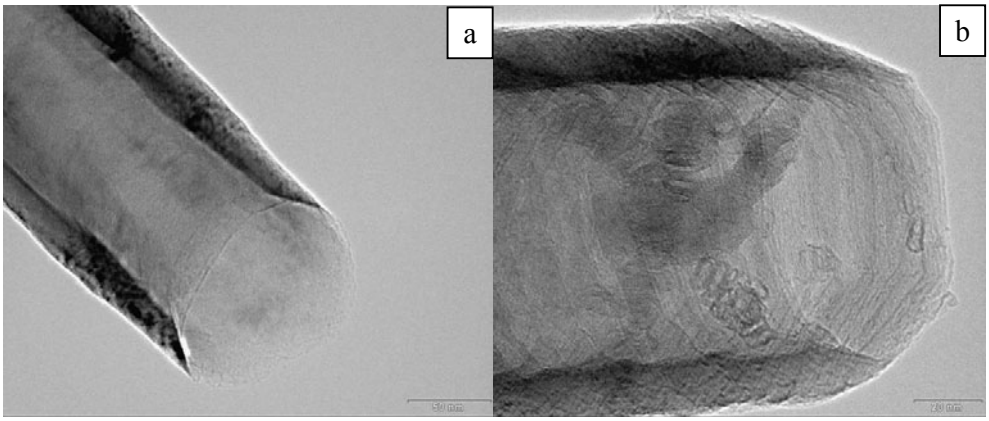

Figure 6. TEM images of the (left) as grown GANF sample and the (right) graphitized at 2800 ºC sample using a tilt holder

Discussion

It is surprising to compare the d(002) results obtained in the present work with others previously reported (figure 7). The d(002) value of the GANF as-grown sample (3.377 Å) is very low compared with other as-grown samples. MWNTs of a narrow diameters (Andrews, 2001) begin with d(002) of 3.4235 Å and after a graphitization process at 3000ºC reach a d(002) of only 3.3982 Å due to curvature impediment. Thicker MWNTs (Chen, 2007), with a slight p-CVD coating, present an interesting three stage behavior during their graphitization, with a final d(002) of 3.386 Å, which indicates a broad difference in the interlayer space before and after graphitization. Furthermore, a similar trend was found for stacked-cup carbon nanofibers (Endo, 2003) presenting a higher d(002) interlayer spacing (initial d(002) of 3.4238 Å and 3.3779 Å at 3000ºC). Pitch based carbon fibers with a diameter of 30 µm (Hamada, 1990) have less curvature impediment and can reach a d(002) value of 3.361 Å at 3300ºC. Another sample without impediments due to its configuration is the platelet carbon nanofibers (Yoon, 2004); in this case the interlayer spacing d(002) remains constant at 3.363 Å after a graphitization process at 2800ºC.

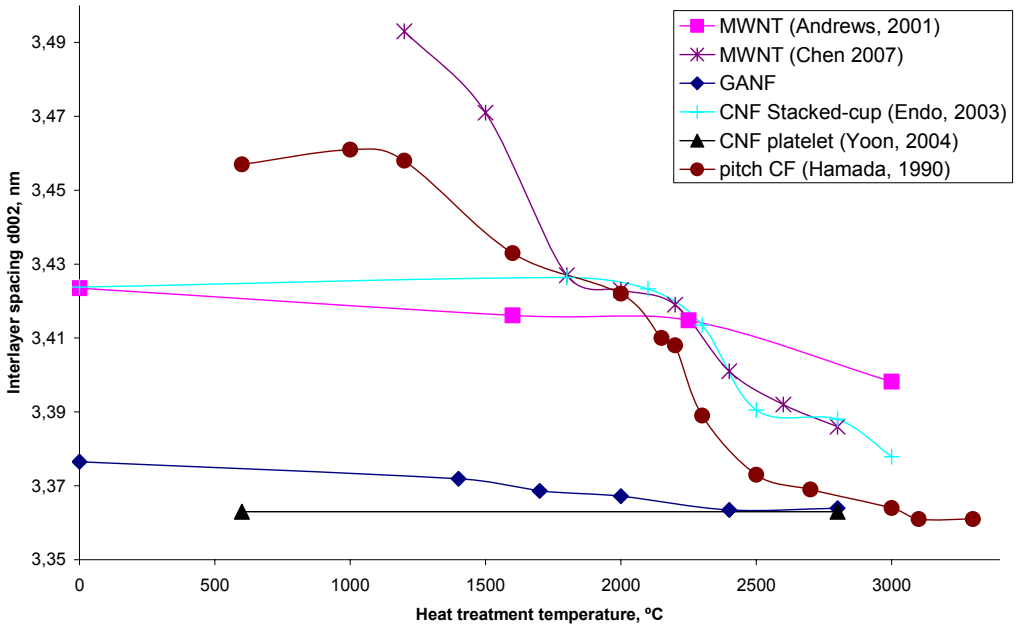

Figure 7. Interlayer spacing versus graphitization temperature of (Andrews, 2001) MWNT (15-30 nm), (Chen, 2007) MWNT (50 nm aprox.), stacked-cup nanofibers GANF1 (80 nm average), (Endo, 2003) stacked-cup nanofibers (50-150 nm), (Yoon, 2004) platelet nanofibers (80-300 nm) and (Hamada, 1990) pitch CF (30 µm)

The total absence of pyrolytic carbon in the surface of the GANF as-grown carbon nanofibers (Vera-Agullo, 2007) makes them highly graphitic, even for the as-grown materials. Interlayer d002 changes with graphitization are small for GANF1 in comparison to other nanofilaments, although crystallographic and structural changes are widely marked above 2000ºC: the sample undergoes a great rearrangement; its cross section turns faceted polygonal and the graphitic planes grouped have an AB stacking according to the appearance of the (112) peak in the XRD (figure 8).

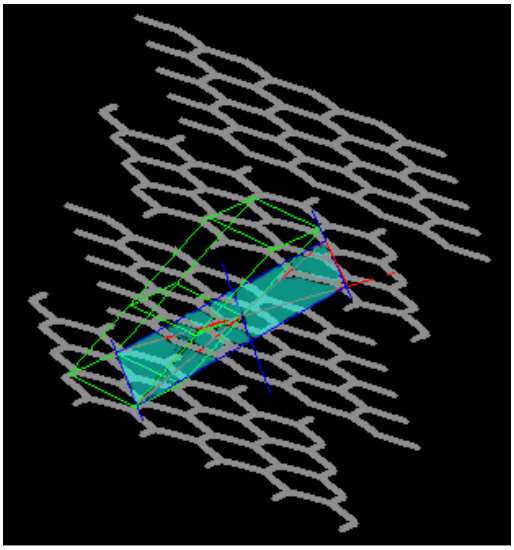

Figure 8. 112 plane into the graphite unit cell

Conclusions

GANF stacked-cup carbon nanofibers have been graphitized and characterized. XRD, Raman and TEM analysis have shown that there are severe morphological changes when they are subjected to thermal annealing.

The samples graphitized above 2400ºC are free of inorganic impurities, hydrogen and functionalities and are composed only of carbon. Moreover, severe crystallographic modification takes place in the GANF carbon nanofibers; the graphene layers are forming groups of 15 or 30 planes in an AB graphite stacking and the cross section becomes clearly polygonal instead of rounded.

These morphological changes are very interesting from the point of view of the mechanistic understanding and from the point of view of possible improvement of the behaviour of the graphitized carbon nanofibers in some applications as fuel-cells or composites (Tibbetts, 2004).

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