Copyright © 2009 Tech Science Press FDMP, vol.5, no.2, pp.123-136, 2009

Production of Carbon Nanotubes-Nickel Composites on Different Graphite Substrates

Munther Issa Kandah[1] **and Jean-Luc Meunier**[2]

Abstract: Multi walled carbon nanotubes (MWCNTs) were synthesized on different graphite types covered with thin layer of nickel catalyst by catalytic chemical vapour deposition using acetylene as hydrocarbon source. The produced carbon nanotubes were investigated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). The shape, quantity and diameter of the MWCNTs are shown to be affected by the type of the graphite substrate, the growth temperature and the hydrocarbon source flow rate. The diameters of the produced MWCNTs were ranged between 43 and 80 nm for pyrolytic (PYROID) and polycrystalline (AXF-5Q) graphite, respectively when the growth temperature was 800 °C and acetylene flow rate 570 cm^3/min. This graphite containing MWCNTs can be used as a cathode in the Physical vapour deposition (PVD) system to produce MWCNTs embedded in a Diamond-like Carbon (DLC) coating.

Keywords: Carbon nanotubes; Graphite; Chemical vapor deposition; Catalyst.

1 Introduction

The interest in carbon nanotubes (CNTs) started with the landmark paper on single-walled carbon nanotubes (SWCNTs) by Iijima (1991). Since then investigations on the physical properties of CNTs (Saito et al., 1998 and Tanaka et al., 1999) have opened new research areas and important potential applications in field emission and hydrogen storage (Dillon, 1997 and Choi et al. 1999). Their novel electronic properties have also led to the applications in nano-devices for example as diodes and nano-transistors (Tans and Devoret, 1997). The excellent mechanical properties of carbon nanotubes allowed researchers to investigate their use in composite coatings. Chen et al. (2002) for example prepared nickel-carbon nanotubes

---

[1] Corresponding author. Chemical Engineering Department, Jordan University of Science & Technology, P.O. Box 3030 – Irbid – 22110 – Jordan. Email: mkandah@just.edu.jo

[2] Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada. Email jean-luc.meunier@mcgill.ca

composite coatings on carbon steel substrates by means of an electro-deposition process. They prepared the nickel composites containing carbon nanotubes by co-depositing the CNTs suspended in an electrolyte with growing nickel during electro-deposition. They also found that the co-deposition of CNTs in a nickel electrolytic coating depends on parameters such as the length of CNTs, the cathodic current density, the agitation rate and the CNTs concentration in the bath.

Carbon nanotubes are currently being synthesized by three main methods: electric arc-discharge (Journet et al., 1997), pulsed laser-oven (Thess et al., 1996) and catalytic chemical vapour deposition (CCVD) methods (Dai et al., 1996). The catalysts used in the decomposition of carbon-based materials are transition metals, most particularly Fe, Co, Ni or their alloys, and these catalysts need to be of nanometric dimension (Derbyshire et al., 1975 and Baker, 1989). Single-walled carbon nanotubes (SWCNTs) have been produced by the decomposition of different carbon sources such as methane (Kong et al., 1998), ethylene (Kathyaini et al., 2004), acetylene (Satishkumar et al., 1998) and benzene (Cheng et al., 1998) in combinations with supported or floated fine metal catalysts. Maruyama et al. (2002) demonstrated a new catalytic chemical vapour deposition technique to synthesize high-purity SWCNTs at low temperature by using alcohol as the carbon source. Shimizu et al. (2005) prepared multi-walled carbon nanotubes (MWCNTs) on Hastelloy C276 by direct current (DC) plasma-assisted hot filament CVD in a CH_4/N_2 atmosphere. Yasuda et al. (2002) found a selective formation between CNTs and carbon nanoparticles (CNPs), in which polyyne-containing carbons were heated and irradiated by an electron beam in a transmission electron microscope. Smiljanic et al. (2001) produced multi-walled carbon nanotubes on the fiber of carbon paper supported Co-Ni or Fe catalyst by decomposing ethylene and heating only the metal catalytic sites of Co-Ni or Fe instead of heating the whole substrate.

According to our knowledge, the idea of producing MWCNTs embedded in diamond-like carbon films by coating the graphite substrate by MWCNTs then using it as cathode in the PVD system is not published yet. This paper reports on the growth of multi-walled carbon nanotubes on different graphite types. Multi-walled carbon nanotubes have been grown on five different graphite types based either on polycrystalline structures of varying porosity, or on an oriented graphitic plane structure. The graphite substrates contain different porosity, granulometry and electrical resistivity. The MWCNTs growth was achieved by catalytic chemical vapour deposition using acetylene as a hydrocarbon source with nitrogen at atmospheric pressure and a temperature of 800 °C.

2 Experimental Procedure

The five graphite types were given in Tab. 1 using the commercial names and data provided by the manufacturers. The graphites were manufactured in two different ways to obtain different microstructures (i.e., pyrolytic and polycrystalline). The polycrystalline graphites (PC, PS, PGCS-1, and AXF-5Q) were produced by Poco Graphite Inc., USA, while the pyrolytic graphite (i.e., PYROID) was produced by Specialty Minerals Inc., USA. The loading of the nickel catalyst on the graphite was achieved by dipping the graphite sample into a homogeneous solution formed from nickel chloride, sodium hypophosphate, sodium citrate and ammonia chloride for three minutes at solution temperature between 90 and 100 °C and pH value between 8.5 and 9 (Parthasaradhy 1989). Then, the graphite substrate was washed with deionized water, dried for 10 minutes at room temperature and stored in a dry place to be used for MWCNTs growth. For the MWCNTs growth process, the nickel coated substrate was placed in a horizontal quartz tubular reactor (50 mm inner diameter and 122 cm length) inside an electrical tubular furnace (Fig. 1). The substrate was heated gradually from room temperature to the required temperature between 700 °C and 1000 °C within about 30 min under a constant nitrogen gas flow rate of 43 cm^3/min. It was then left in the reactor for half an hour at this temperature before injecting the acetylene at flow rates between 570 cm^3/min and 800 cm^3/min for typically twenty minutes. Nitrogen was kept flowing into the quartz tube for about 2 h after stopping the acetylene flow while the substrate was cooling down gradually to room temperature in order to prevent any oxidation of the produced MWCNTs. Multi-walled carbon nanotubes grown on the graphite were directly observed by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and some of them were peeled off to be observed by Transmission Electron Microscopy (TEM).

3 Results and Discussion

Five graphite types were investigated in this work (see Tab. 1) to produce MWCNTs on their surfaces. The PYROID graphite was a highly oriented structure made using CVD techniques, the graphitic planes being oriented parallel to the growth surface of the material. This material essentially had no porosity, and had highly anisotropic transport properties showing high values in the direction parallel to the surface plane. The other four materials showed the typical polycrystallinity of graphitic materials, these being formed through a calcination process of the raw material, followed by powder generation with varying particle sizes, mixing with a binder and a sintering process. This led to different degrees of porosity and isotropic properties. The five graphite substrates were first inserted into the tubu-

Table 1: Properties of the five different graphite materials used in this paper

Graphite type	Grain size (μm)	Pore size (μm)	Electrical resistivity (μ.ohm.cm)
PYROID	Single crystal	0	250 (//)* 3×10^5 ($\perp$)
PC	5	n/a	11500
PS	5	1.2	2900
PGCS-1	15	3	1500
AXF-5Q	5	0.8	1400

* (//) parallel to the cathode surface
($\perp$) perpendicular to the cathode surface

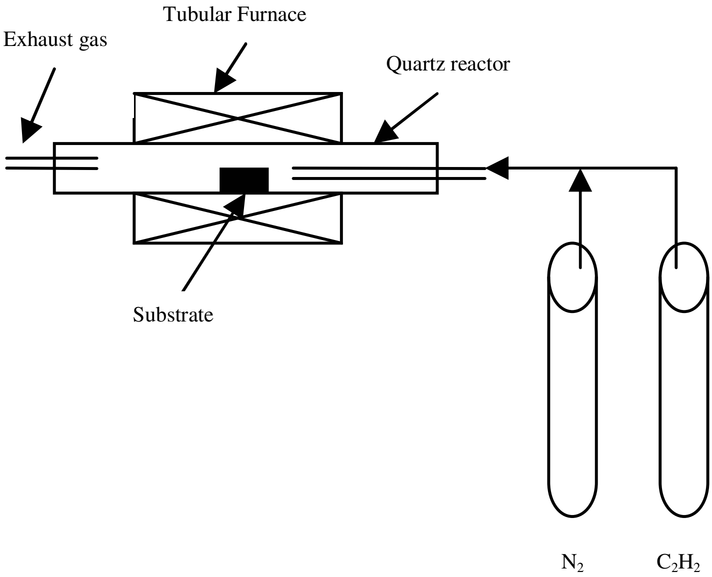


Figure 1: A schematic of the experimental set-up

lar quartz reactor without any catalyst precursor or pre-treatment, and heated to different temperatures from 700 °C to 1000 °C for half an hour under a nitrogen atmosphere. Acetylene gas was then injected for 20 min at different flow rates from 570 cm^3/min to 800 cm^3/min, followed by substrates cooling to room temperature. The samples were observed using field emission scanning electron microscopy (FE-SEM). No carbon nanotubes were formed on these graphite substrates except for

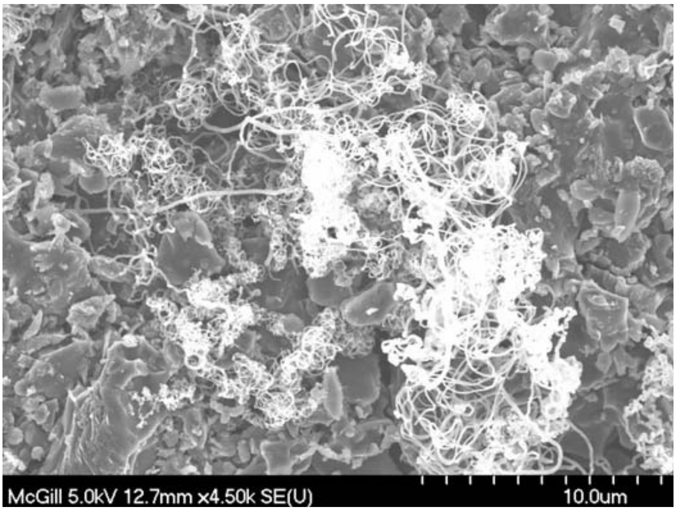


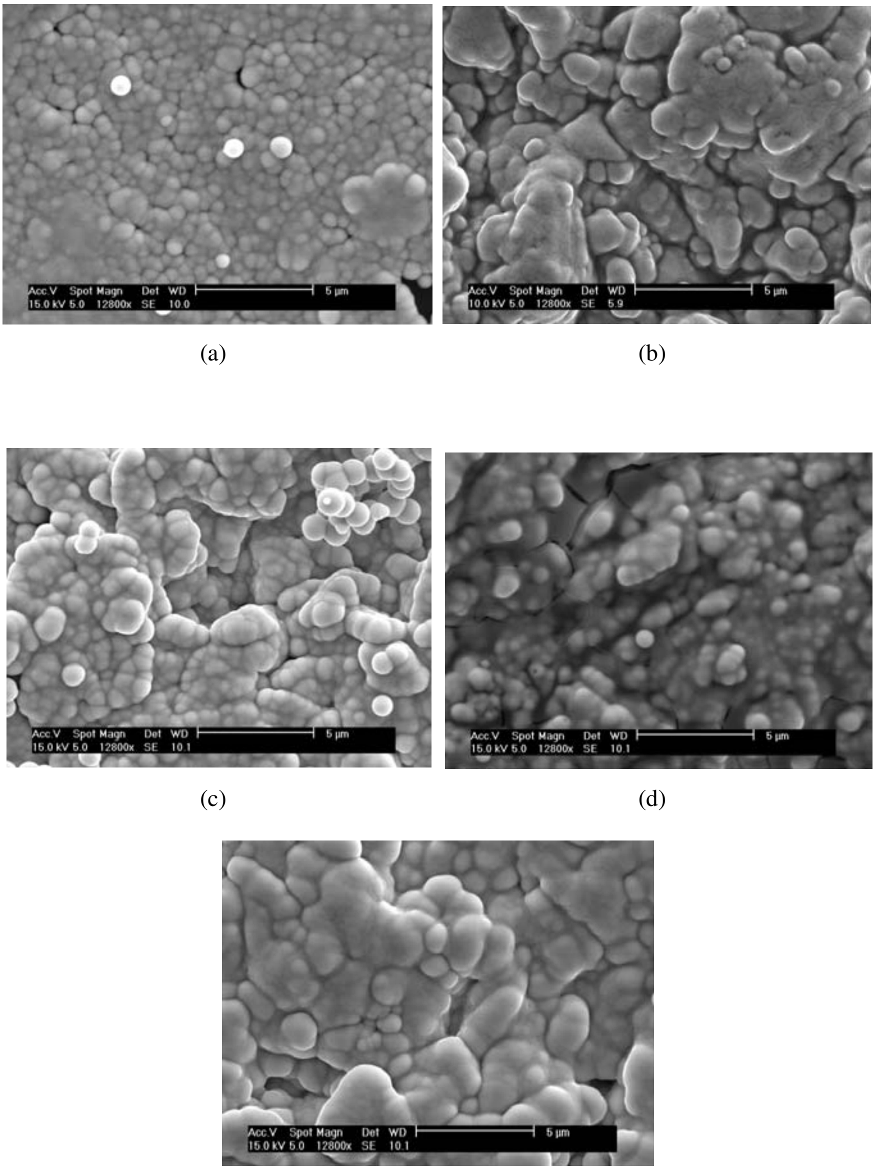
Figure 2: SEM image for CNTs on PC-graphite without the use of catalyst at 800 °C and 570 cm^3/min acetylene

some amount of CNTs observed together with a large fraction of amorphous carbon formed on the PC-graphite material at 800 °C and 570 cm^3/min acetylene as shown in Fig. 2.

To enhance the CNTs growth on the graphite substrates, a thin layer of nickel was plated on the different graphite types using an electroless plating technique. This step formed a fine and homogeneous layer of nickel on the surface of the graphite substrate. Figures 3a, b, c, d, and e show the morphology of graphite surfaces coated with nickel for the five graphite materials. PYROID graphite is quite distinctive in forming a very uniform coating consisting of spherical particles having around 500 nm in diameter with little size dispersion. The morphology of the nickel coat on the other polycrystalline graphite types showed less uniformity, with structures having typically 1 μm and larger size.

The chemical composition of the thin layers covering the graphite substrates was determined using Energy Dispersive Spectroscopy (EDS). The spectrum in Fig. 4 showed clearly the presence of nickel, with other peaks which correspond to oxygen and phosphor. These oxygen and phosphor peaks result from the nickel deposition bath.

The five graphite substrates coated with nickel catalyst were used to grow carbon nanotubes by the decomposition of acetylene at a growth temperature of 700 °C and acetylene flow rate of 570 cm^3/min. Figures 5a-e show that very small amounts of



(a) (b)

(c) (d)

(e)

Figure 3: SEM images for (a) PYROID, (b) PC, (c) PS, (d) PGCS-1, (e) AXF-5Q graphite substrates coated with a nickel catalyst layer.

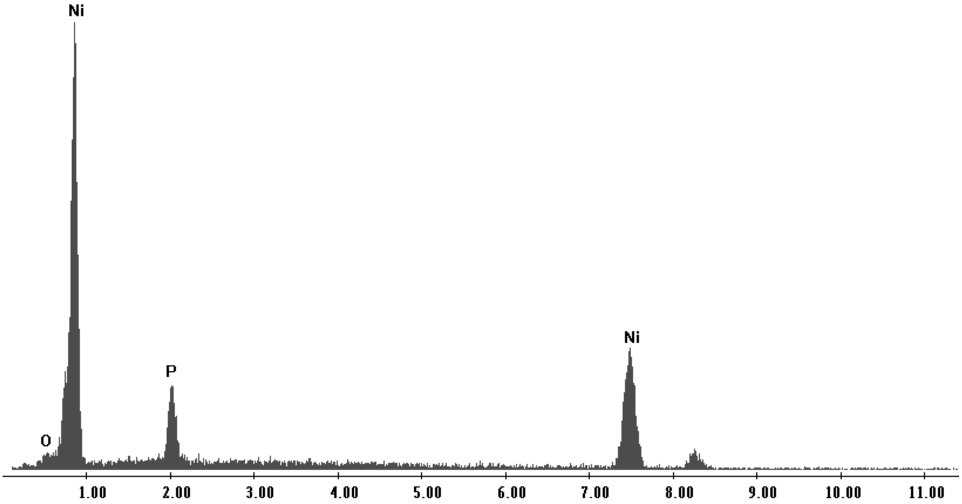
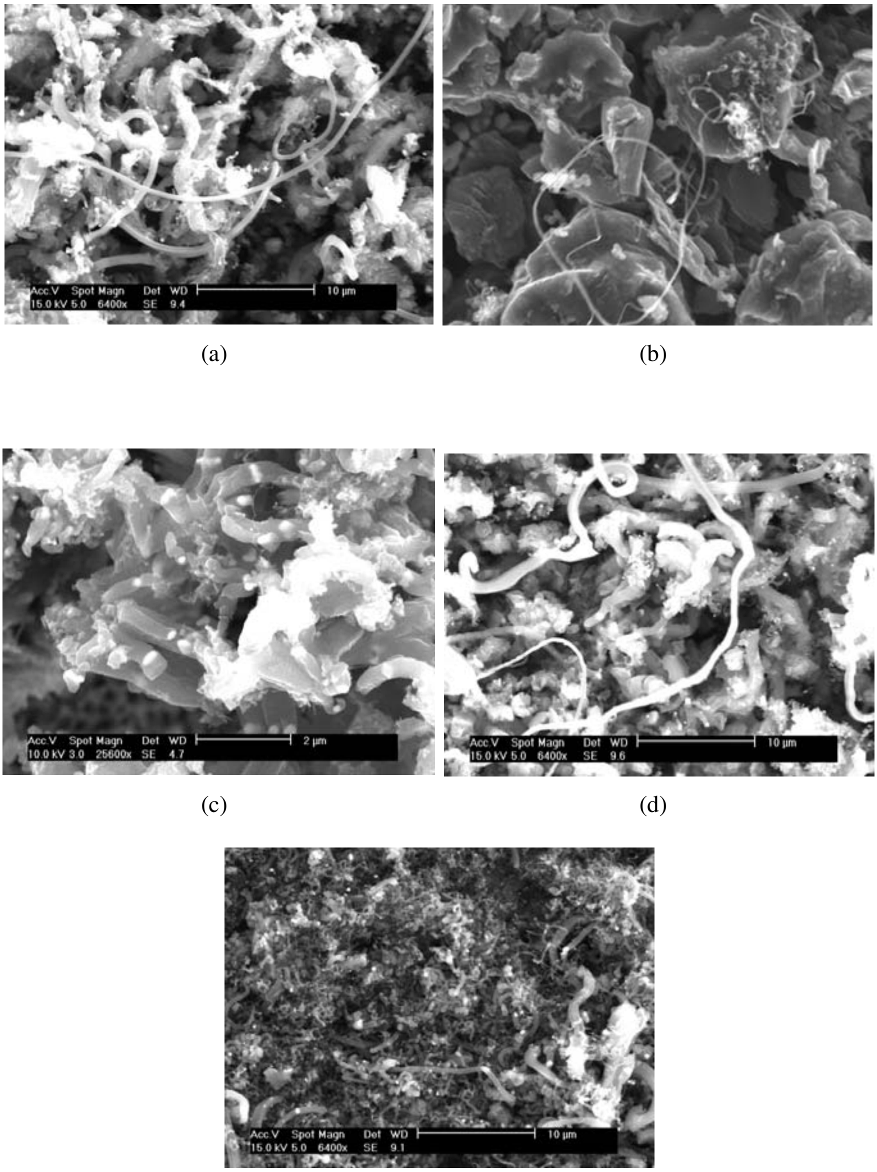


Figure 4: EDS spectrum for PYROID graphite coated with a thin layer of nickel

micron size carbon tubes begin to grow on each graphite type and are accompanied by significant amounts of amorphous carbons. The presence of the thin layer of nickel catalyst has initiated and enhanced the growth of carbon nanotubes on all graphite materials at this lower temperature. To further enhance the CNTs growth and decrease the amount of amorphous carbon, acetylene decomposition was performed at different temperatures between 700 °C - 1000 °C using acetylene flow rate between 570 cm^3/min and 800 cm^3/min. The optimum temperature was found to be at 800 °C and acetylene flow rate at 570 cm^3/min.

Figures 6a-e showed these graphite surfaces that were covered with large amounts of MWCNTs. The transmission electron microscopy (TEM) image of Fig. 7 for the case of PYROID graphite confirmed the MWCNTs presence. It is clear that MWCNTs growth was enhanced significantly on all graphite materials when covered with a nickel catalyst layer, it is however interesting to note that different quantities and diameters of the MWCNTs were obtained. The tube diameters were in the range from around 43 to 80 nm, these being given in Tab. 2 for the various graphite types. The lengths of these MWCNTs were longer than 1 μm. The diameters observed increased steadily when going down the material list of Tab. 1.

Fig. 6a corresponding to PYROID showed the most uniform growth obtained, the smallest MWCNTs diameters and the smallest quantity of amorphous carbon impurities obtained. The polycrystalline graphite substrates showed smaller MWCNTs quantities, larger MWCNTs diameters, and associated with larger quantities of

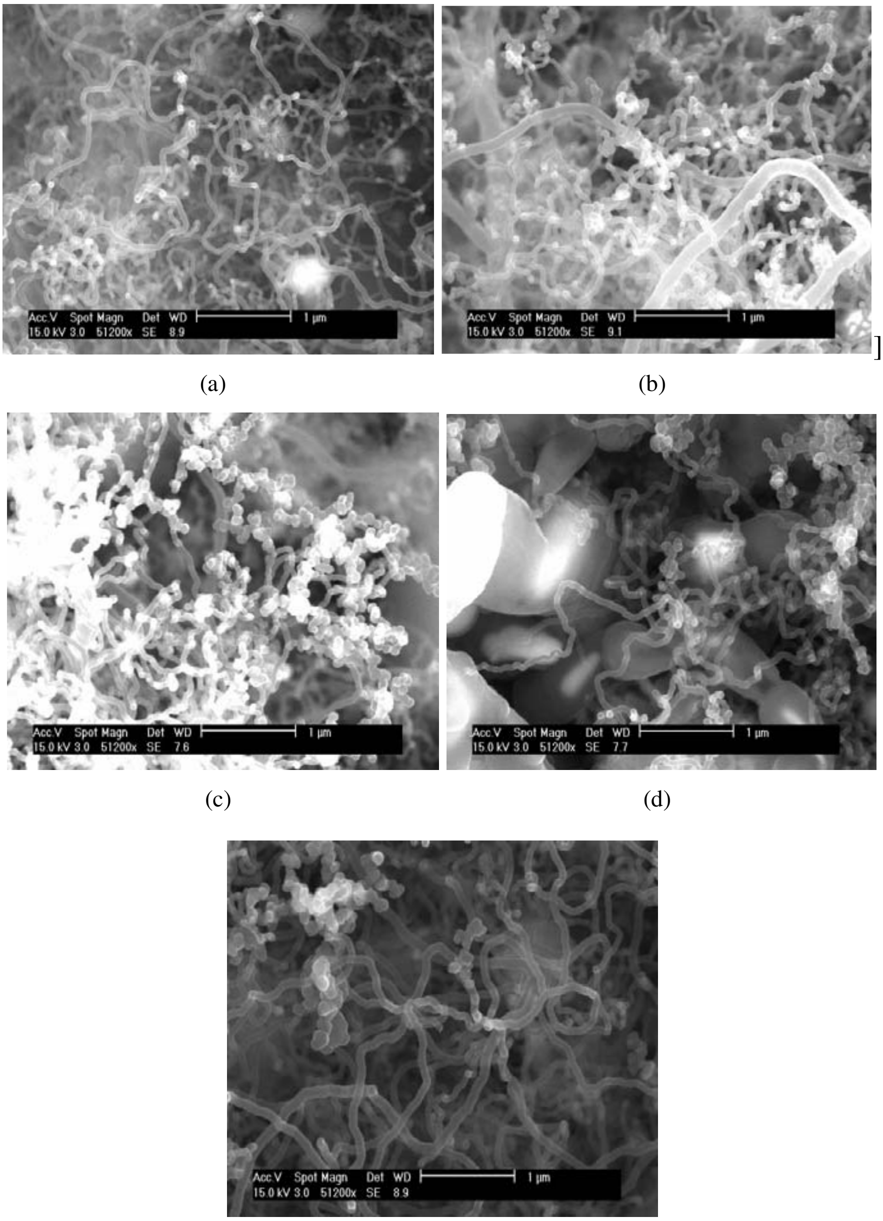


(a) (b)

(c) (d)

(e)

Figure 5: Carbon growth on five graphite materials coated with nickel catalyst at 700 °C and an acetylene flow rate of 570 cm^3/min. (a) PYROID, (b) PC, (c) PS, (d) PGCS-1, (e) AXF-5Q



(a) (b)

(c) (d)

(e)

Figure 6: SEM images of the surface of MWCNTs-Ni composites on different graphite substrates; a) PYROID; b) PC; c)PS; d) PGCS-1; e) AXF-5Q

Table 2: Diameters of the MWCNTs grown on the different graphite materials

Graphite type	MWCNTs average diameter (nm)
PYROID	43
PC	57
PS	60
PGCS-1	67
AXF-5Q	80

amorphous carbon. Fig. 6d showed the largest amorphous carbon impurity content, and this correlates with the material (PGCS-1) having larger grain size and porosity. These figures showed the possibility of forming MWCNTs on graphite materials in the presence of nickel catalyst, and illustrated that the quantities and diameters of MWCNTs were strong function of the various graphite surface properties. In order to encourage the formation of MWCNTs rather than amorphous carbon and other pyrolytic products, the hydrocarbon gas in these experiments was injected after a 30 minutes period of temperature stabilization under a nitrogen environment. Also, N_2 gas was kept flowing from the start of the substrate heating period until it was being cooled down to room temperature following the growth step. This procedure was necessary to prevent oxidation, which preferentially led to the formation of spherical-shaped carbon nanoparticles (CNPs). The TEM image of Fig. 7 seems to indicate a root growth mechanism was adopted here, as the vast majority of the MWCNTs observed have opened ends. The evolution of the MWCNTs structures observed on graphites with varying surface properties were believed to be the result of the Ni catalyst coating being affected by the various surface properties. Denser graphitic materials showed smaller surface structures of the Ni coating, with more uniformity over the graphitic surface.

The feeding method of acetylene was found to be important and affecting the shape, quantity and diameter of the MWCNTs formed. When the acetylene flow rate was increased to about 800 cm^3/min, it became more turbulence, and therefore inhomogeneous distribution of the carbon feed occurred. The diameters of the carbon nanotubes increased significantly under such conditions, forming in fact carbon nanofibers (CNFs) and decorated carbon shapes as shown in Fig. 8.

This is in agreement with the work of Kurt et al., (2001) who produced unusual carbon structures with multiple hollow cores when the gas-feed method was changed using an orthogonal copper tube in a floating catalyst method. Fig. 9 showed that there was some alignment of the CNFs perpendicular to the growth surface of the coating.

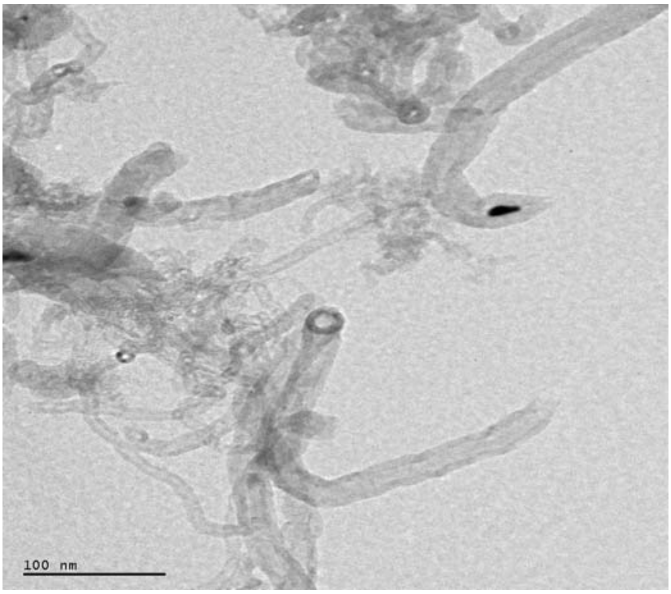


Figure 7: TEM image for the MWCNTs over PYROID graphite coated with a Ni catalyst layer

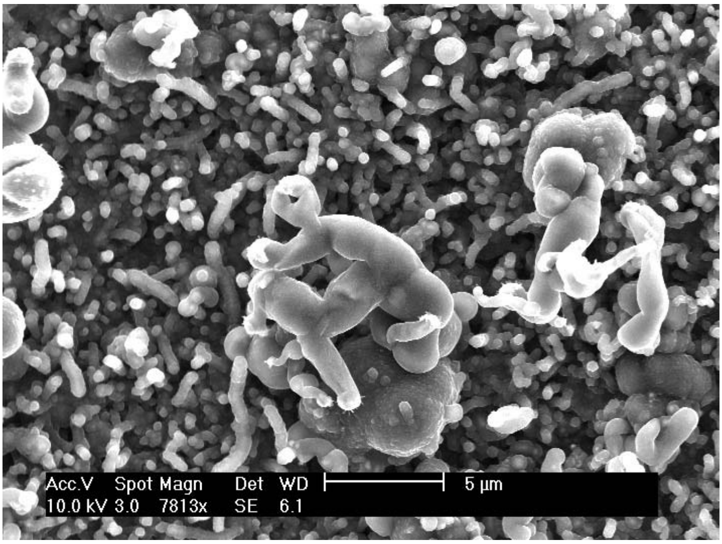


Figure 8: SEM image for the CNTs growth on PC-graphite covered with a nickel catalyst layer at 800 °C, and 80 cm^3/min of acetylene

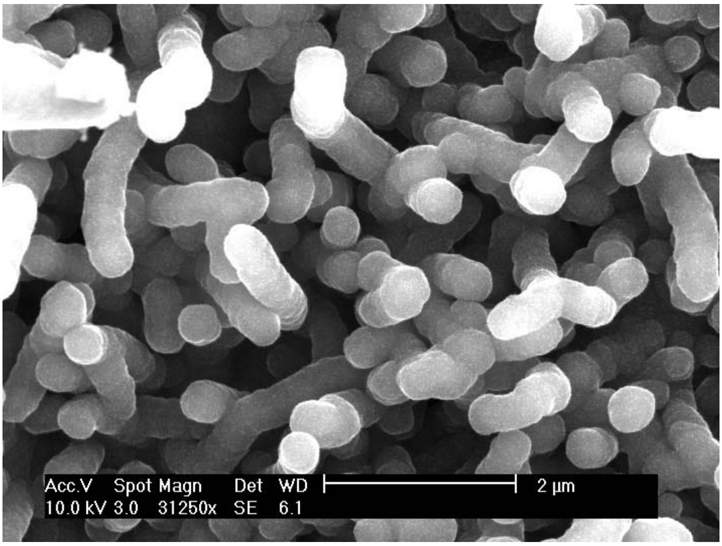


Figure 9: SEM image showing the formation of CNFs on PC-graphite coated with nickel catalyst

4 Conclusions

It was demonstrated in this paper that MWCNTs can be grown on different graphite types having different surface properties coated with a thin layer of nickel. Catalytic chemical vapour deposition using acetylene as a hydrocarbon source at 800 °C was used for the MWCNTs production. The diameters of the MWCNTs, the uniformity of the growth process and the amount of carbon impurities (non-CNTs) were showed to vary with graphite types, decomposition temperature and hydrogen flow rates. Dense and more uniform carbon surfaces seem to improve the quality of the growth process, leading to multi-walled carbon nanotubes having smaller diameters and better surface homogeneity of the deposits. This was attributed to the nickel catalyst layer showing finer structures on dense graphitic materials. The decomposition of acetylene (C_2H_2) at 800 °C over the surface of graphite substrates coated with a thin layer of nickel catalyst may also generate decorated carbon nanotubes when the hydrocarbon feed becomes inhomogeneous. Much smaller amounts of CNTs deposits were obtained directly on specific graphitic surfaces without any catalyst being added. These MWCNTs can be transferred and embedded into a diamond-like coating by using this graphite containing the MWCNTs as a cathode in the Physical Vapor Deposition (PVD) system.

Acknowledgement: The authors wish to acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds quèbècois de la recherche sur la nature et les technologies (FQRNT), McGill University, and Jordan University of Science & Technology for the financial support during the sabbatical leave for Dr. Kandah at McGill.
The authors also highly acknowledge the efforts of Eng. Marwan Azi for the SEM analysis, Dr. Gui-Ping Dai for the TEM analysis and Eng. Naveen K. Reddy for his help in the electroless coating experiments.

References

Baker, R.T.K. (1989): Catalytic growth of carbon filaments. *Carbon.* vol. 27, no. 3, pp. 315-323.

Chen, X.H.; Cheng, F.Q.; Li, S.L.; Zhou, L.P.; Li, D.Y. (2002): Electrodeposited nickel composites containing carbon nanotubes. *Surf Coat Technol.* vol. 155, pp. 274-278.

Cheng, H.M.; Li, F.; Sun, X.; Brown, S.D.M.; Pimenta, M.A.; Marucci, A.; Dresselhaus, G.; Dresselhaus, M.S. (1998): Bulk morphology and diameter distribution of single-walled carbon nanotubes synthesized by catalytic decomposition of hydrocarbons. *Chem Phys Let.*; vol. 289, pp. 602-610.

Choi, W.B.; Chung, D.S.; Kang, J.E.; Kim, H.Y.; Jin, Y.W.; Han, I.T.; Lee, Y.H.; Jung, J.E.; Lee, N.S.; Park, G.S.; Kim, J.M. (1999): Fully sealed, high-brightness carbon-nanotube field- emission display. *Appl Phys Lett*; vol. 75, no. 20, pp. 3129-3131.

Dai, H.; Rinzler, A.G.; Nikolaev, P.; Thess, A.; Colbert, D.T.; Smalley, R.E. (1996): Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide. *Chem Phys Lett*; vol. 260, pp. 471-475.

Derbyshire, F.J.; Presland, A.E.B.; Trimm, D.L. (1975): Graphite formation by the dissolution- precipitation of carbon in cobalt, nickel and iron. *Carbon.* vol. 13, no. 2, pp. 111-113.

Dillon, A.C.; Jones, K.M.; Bekkedahl, T.A.; Kiang, C.H.; Bethune, D.S.; Heben, M.I. (1997): Storage of hydrogen in single-walled carbon nanotubes. *Nature.* vol. 386, pp. 377-379.

Iijima, S. (1991): Helical microtubules of graphic carbon. *Nature.* vol. 354, pp. 56-58.

Journet, C.; Maser, W.K.; Bernier, P.; Loiseau, A.; Chapelle, M.L.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J.E. (1997): Large- scale production of single-walled carbon nanotubes by the electric-arc technique. *Nature.* vol. 388, pp. 756-

758.

Kathyaini, K.; Nagaraju, N.; Fonseca, A.; Nagy, J.B. (2004): Catalytic activity of Fe, Co and Fe/Co supported on Ca and Mg oxides, hydroxides and carbonates in the synthesis of carbon nanotubes. *J Mol Catal A Chem.* vol. 223, pp. 129-136.

Kong, J.; Cassell, A.M.; Dai, H. (1998): Synthesis of individual single-walled carbon nanotubes on patterned silicon wafers. *Nature.* vol. 395, pp. 878-881.

Kurt, R.; Karimi, A.; Hoffmann, V. (2001): Growth of decorated carbon nanotubes, Chem *Phys Lett.* vol. 335, pp. 545-552.

Maruyama, S.; Kojima, R.; Miyauchi, Y.; Chiashi, S.; Kohno, M. (2002): Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol. *Chem Phys Lett.* vol. 360, pp. 229-234.

Parthasaradhy, N.V. (1989): *Practical electroplating handbook.* Prentice Hall, Englewood Cliffs, New Jersey, pp. 353-354.

Saito, R.; Dresselhaus, G.; Dresselhaus, M.S. (1998): *Physical properties of carbon nanotubes*. Imperial College Press, London.

Satishkumar, B.C.; Govindaraj, A.; Sen, R.; Rao, C.N.R. (1998): Single-walled nanotubes by the pyrolysis of acetylene-organometallic mixture. *Chem Phys Lett.* vol. 293, pp. 47-52.

Shimizu, Y.; Sasaki, T.; Kodaira, T.; Kawaguchi, K.; Terashima, K.; Koshizaki, N. (2005): Effect of plasma conditions on fabrication of multi-walled carbon nanotubes grown perpendicularly on Hastelloy C276. *Dia Relat Mat.* vol. 14, no. 1, pp. 11-15.

Smiljanic, O.; Dellero, T.; Serventi, A.; Lebrun, G.; Stansfield, B.L.; Dodelet, J.P.; Trudeau, M.; Désilets, S. (2001): Growth of carbon nanotubes on Ohmically heated carbon paper. *Chem Phys Lett.* vol. 342, pp. 503-509.

Tanaka, K.; Yamabe, T.; Fukui, K. (1999): *The science and technology of carbon nanotubes*. Elsevier, Amsterdam.

Tans, S.J.; Devoret, M.H. (1997): Individual single-wall carbon nanotubes as quantum wires. *Nature.* vol. 386, pp. 474-477.

Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y.H.; Kim, S.G.; Rinzler, A.G.; Colbert, D.T.; Scuseria, G.E.; Tomanek, D.; Fischer, J.E.; Smalley, R.E. (1996): Crystalline ropes of metallic carbon nanotubes. *Science*; 273: 483-487.

Yasuda, A.; Mizutani, W.; Shimizu, T.; Tokumoto, H. (2002): Carbon-nanotube formation mechanism reduced from the in situ observations: selective growth of nanotubes and nanoparticles, *Physica B.* vol. 323, pp. 269-271.