 FDMP, vol.4, no.4, pp.231-236, 2008

Production of Carbon Nanotubes on Different Monel Substrates

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Abstract: Multi-walled carbon nanotubes (MWCNTs) have been produced by chemical vapor deposition using acetylene as a hydrocarbon source at 700 °C. The Monel substrates coated with MWCNTs can be used later as cathodes in the Physical Vapor Deposition (PVD) systems to produce CNTs embedded in diamond-like carbon (DLC) film. This new method of generating MWCNTs on Monel substrates without using any catalyst is very simple and uses very little power compared to other CNTs generating techniques. Embedded CNTs in a crystalline carbon coat was observed on mirror-like polished Monel substrates at 700 °C but not on the rough Monel surfaces.

Keyword: Carbon Nanotubes, Monel, Chemical Vapor Deposition.

1 Introduction

Carbon nanotubes (CNTs), the new discovered member in the carbon structure family, attracted great researchers' interest due to their unique morphologies and various potential applications. The beginning of the nano-carbon materials appeared when Morinobu Endo (1975) was working on his PhD thesis, which was dealing with the synthesis of vapor grown carbon fibers by the decomposition of hydrocarbon at high temperatures in the presence of transition catalyst particles of less than 10 nm. He prepared the first carbon fiber of nanometer dimensions (∼7 nm). At this time they could not recognize the nanotubes presence within this fiber. Sumio Iijima (1991) used high-resolution transmission electron microscopy and observed carbon nanotubes for the first time. He used arc-discharge evaporation technique similar to that used for the fullerene synthesis and produced needle-like tubes. Each needle comprises coaxial tube of graphite sheets, ranging in number from 2 up to 50, in diameter from 4 to 30 nm and 1 μm in length. After that (in 1992), the Russian researchers reported the discovery of carbon nanotubes, but with much smaller length to diameter ratio (Kosakovskaya et al. 1992). The major breakthrough occurred in 1996 when Thess et al. (1996) reported their capability of producing bundles of aligned single-walled carbon nanotubes for the first time by laser vaporization of a target composed of Co-Ni/graphite at 1200 °C. The typical diameter of these single nanotubes was ranging between 1.4-1.7 nm.

Multi-walled carbon nanotubes contain several coaxial cylinders, each cylinder being a single wall carbon nanotube. The diameter of a nanotube is on the order of a few nanometers (∼ 50,000 times smaller than the width of a human hair), while its length can be up to several millimeters. Nanotubes are composed entirely of sp^2 bond, similar to those of graphite. This bonding structure, stronger than the sp^3 bond found in diamond, provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by Van der Waals forces. Under high pressure, nanotubes can merge together, trading some sp^2 bonds for sp^3 bonds, giving great possibility for producing strong, unlimited-length wire through, and high-pressure nanotube linking (Yildirim et al. 2001).

Carbon nanotubes can be synthesized by different methods described in (Yumura et al. 1999). Their high mechanical strength makes them good

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candidates for advanced composites (Schadler et al. 1998). They can be semi-conducting, semi-metallic, or metallic, depending on the tube helicity and diameter (Ebbesen et al. 1996), which open up a promising field in nanoscale electro-device applications. Their large specific area, hollow and layered structures indicate that they can be an ideal hydrogen storage material (Dillon et al. 1997) and adsorbent for heavy metal removal from water (Li et al. 1998).

Paradise and Goswami (2006) discussed carbon nanotubes from the time of their discovery to present day applications, specifically the production methods, properties and industrial applications of carbon nanotubes. Kouravelou et al. (2007) investigated the catalytic effects of the production of carbon nanotubes by chemical vapor deposition of ethanol. Harbec et al. (2007) produced carbon nanotubes (CNT) using a DC non-transferred plasma torch operated at a power of 30 kW in argon and producing a supersonic jet. They used Tetrachloroethylene (TCE) as the carbon raw material. Dasgupta et al. (2007) synthesized carbon nanotubes (CNTs) by catalytic chemical vapor deposition of acetylene diluted with nitrogen and using cobalt format supported on carbon black as the catalyst at 700°C in a quartz reactor for 30 min. Kadlečıková et al. (2007) produced bundles composed of multi-walled carbon nanotubes by catalytic hot filament chemical vapor deposition. Sun et al. (2007) synthesized single-walled carbon nanotubes (SWNTs) using dc arc discharge in H_2–Ar gas atmosphere with Fe_3O_4 as catalyst. Mora et al. (2007) produced single-walled carbon nanotubes (SWCNTs) using catalytic decomposition technique by injection of pre-prepared alumina supported catalyst powder into a modified vertical floating reactor. Kandah and Meunier (2007) produced multi-walled carbon nanotubes (MWCNTs) by chemical vapor decomposition using acetylene gas in the presence of Ferrocene catalyst at 800 °C, and then oxidized with concentrated nitric acid at 150 °C. They used both (oxidized and non-oxidized CNTs) as an adsorbents for Ni^{2+} removal from water.

In this work, multi-walled carbon nanotubes have been produced by chemical vapor deposition on different Monel substrates to be used later as substrate in the PVD systems to obtain MWCNTs embedded in DLC or TiN films.

2 Experimental Procedure

Two Monel substrates (rough and mirror-like polished surfaces) were used in this study as substrates for carbon nanotubes (CNTs) growth (see Tab. 1). To grow carbon nanotubes (CNTs) on Monel surface, the substrate was placed in a horizontal quartz tubular reactor (50 mm inner diameter and 122 cm length) inside an electrical tubular furnace. The substrate was heated up gradually from room temperature to the required temperature (700 °C) within about 30 min under constant nitrogen gas flow rate of 43 cm^3/min and atmospheric pressure as shown in Fig. 1. The substrate was left in the reactor for half an hour at this temperature before injecting acetylene for typically twenty minutes. Nitrogen was kept flowing into the quartz tube for about 2 h after stopping the acetylene flow rate while the substrate is cooling down gradually to room temperature in order to prevent any oxidation of the produced CNTs. Multi-walled carbon nanotubes (MWCNTs) grown on the Monel substrates were directly observed by Scanning Electron Microscopy (SEM). Some of the samples were analyzed with Raman Spectroscopy, Oriented Image Microscopy (OIM), and X-ray Diffraction (XRD).

Table 1: Chemical composition limits of Nickel 400 alloy or Monel

Nickel	63%
Iron	2.5%
Copper	28-34%
Carbon	0.3%
Manganese	2%
Silicon	0.5%
Others	0.024%

3 Results and Discussion

The possibility of producing CNTs on rough and mirror-like polished metal substrate called Monel

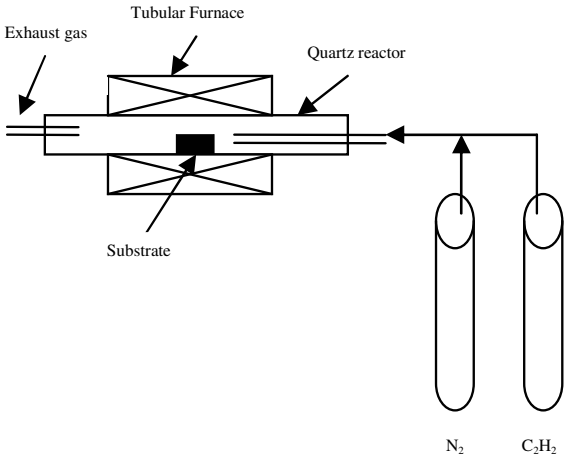


Figure 1: A schematic of the experimental set-up

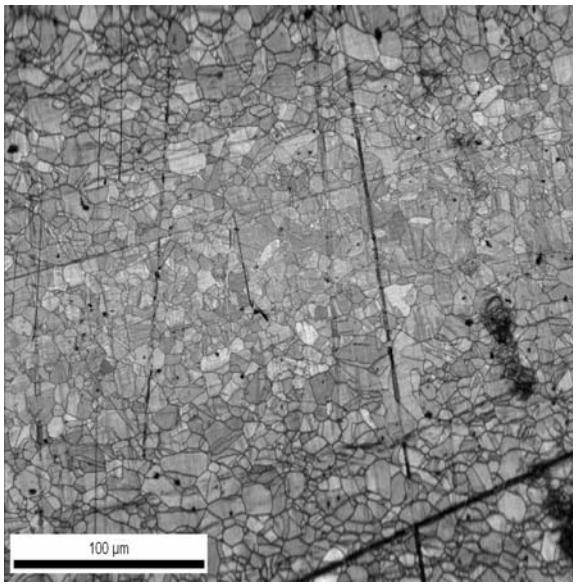


Figure 2: SEM image showing the orientation of the crystalline grain for mirror-like polished Monel substrate

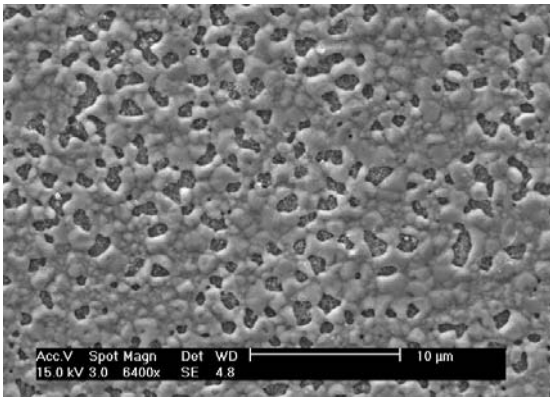
or nickel 400 alloy without any catalyst was investigated in this study. Fig. 2 shows the crystal grains and orientations for a mirror-like polished Monel substrate, in which the grain size was about 2 μm in diameter, while Figures (3a, 3b and 3c) show SEM micrographs for carbon nanotubes embedded in a crystalline carbon film on mirror-like polished surface. The lower magnification image shown in Fig. 3a confirms that the high-uniformity image in Fig. 3c is not a specially selected view of the sample.

The strong peaks corresponding to Ni were clearly revealed in the XRD spectrum (Fig. 4) for this film, while the MWCNTs were observed from Raman spectrum (Fig. 5). The presence of nickel in the Monel substrate allows the MWCNTs to be formed without using any catalyst since nickel acts as a catalyst.

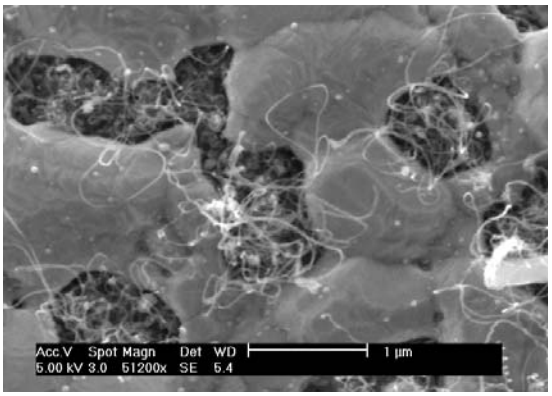
Raman spectroscopy is a powerful and sensitive technique for studying the structure of carbonaceous materials. The Raman spectra in Fig. 5 exhibited two lines about 1350 cm^{-1} and 1590 cm^{-1} corresponding to the D (defect) and G (graphitic) lines of polycrystalline graphite which refer to the presence of multi-walled carbon nanotubes. The D band structure relates to the amounts of amorphous carbon introduced during growth. The G mode (graphitic) at 1590 cm^{-1} relates to the graphitized carbon arranges in hexagonal rings (MWCNTs, nano-onions, carbon nanoparticles). The presence of the RBM mode "between 100-350 cm^{-1}" which indicates some single walled carbon nanotubes (SWCNTs) is not shown in this spectrum. The intensity ratio of the 1350 cm^{-1} line to the 1590 cm^{-1} line is used to estimate the extents of graphitization of the carbon nanotubes. As shown in Fig. 5, the intensity of about 1590 cm^{-1} is much stronger than that at 1350 cm^{-1} which indicates that the MWCNTs have a good extent of graphitization. According to Salvetat et al. (1998), the mechanical properties of CNTs are dependent upon the degree of order within the tube wall, i.e., the more graphitized the CNTs, the better its mechanical properties.

The same experiments were repeated under the same conditions but now on rough Monel surface. It is clear from Fig. 6 that the quantity of the produced CNTs and the amount of amorphous carbon were more than those produced on the mirror-like polished Monel substrate. It is also noticed that the crystalline carbon film disappeared on the rough Monel surface. This is another evidence to support that the CNTs growth depends on substrates morphology and structure.

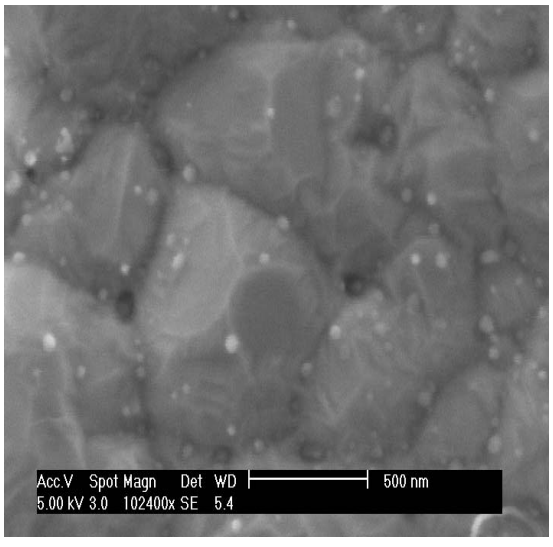
Finally, it is of interest to know how strongly the tubes are bound to the Monel surface. It



(a)



(b)



(c)

Figure 3: a: SEM micrograph showing the crystalline carbon film at low magnification on mirror-like polished surface; b and c: SEM micrographs (at higher magnifications) for figure 3a showing the carbon nanotubes embedded in a crystalline carbon

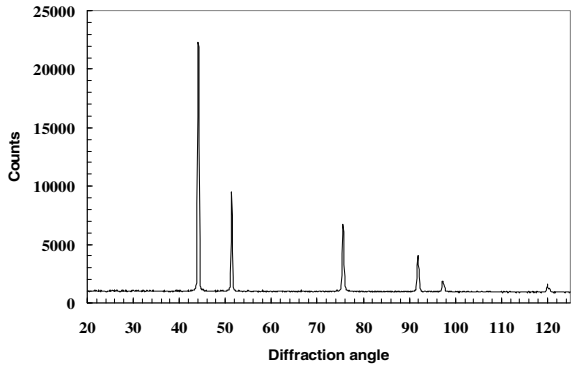


Figure 4: XRD (Teta 2 teta) spectrum for Fig. 3

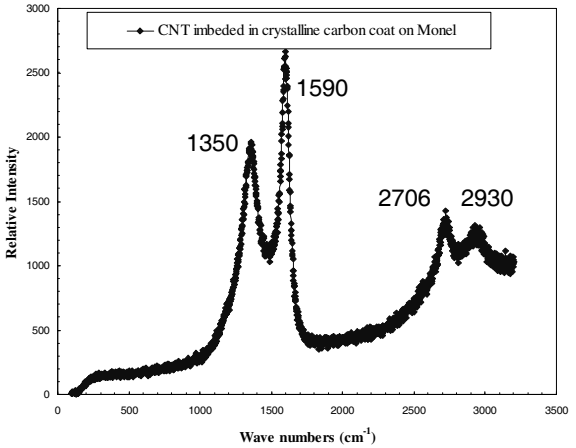


Figure 5: Raman spectrum for CNTs embedded in a crystalline graphitic film

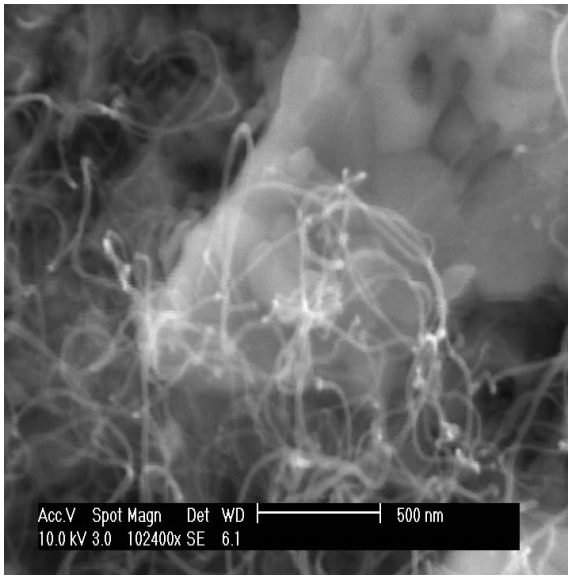


Figure 6: SEM micrograph showing the carbon nanotubes on rough Monel substrate

was found that it is not possible to remove the tubes from the substrate by blowing with strong air pressure.

4 Conclusions

In this work, it was demonstrated that it is possible to obtain MWCNTs, firmly attached to different Monel substrates. Chemical vapor deposition using acetylene as a hydrocarbon source at 700 °C was used for the MWCNTs production.

It is also found that the properties of the substrate surface such as its roughness or smoothness strongly affecting the morphology of the carbon nanotubes grown over the surface of the substrate.

Acknowledgement: The authors wish to acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds québécois 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.

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