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## Synthesis and purification of Carbon nanotubes

### ABSTRACT

**A. Ali Moosa<sup>1,\*</sup>**  
**M. Ibrahim<sup>2</sup>**  
**R. F. Salloom<sup>3</sup>**

<sup>1</sup>Technical College –Baghdad,  
AlZaafurania, Baghdad, Iraq.

<sup>2</sup>Department of Chemical Eng.  
University of Technology  
Baghdad-Iraq.

<sup>3</sup>Department of Production  
Engineering and Metallurgy-  
University of Technology,  
Baghdad-Iraq.

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In this study, multi wall carbon nanotubes (MWCNTs) were synthesized by Chemical vapor deposition (CVD) method using two different catalysts (Fe nanoparticles) and (Ni nanoparticles) with two different substrates: Quartz and Alumina. Acetylene gas was used as a carbon source and Argon as a carrier gas at different temperatures and different times to study the effects of these parameters on CNTs yield. The produced MWCNTs were then purified by oxidation followed by chemical method involving treatment of MWCNTs with concentrated acids ( $H_2SO_4$  and  $HNO_3$ ) to remove impurities. The MWCNTs were then functionalized by acidic treatment. The functionalized MWCNTs were then coated with Nickel using electroless plating method. Metal matrix composites (MMCs) were prepared by powder metallurgy method using Al/uncoated MWCNTs and Al/coated MWCNTs. The results show that the diameter range of prepared MWCNTs was (30-50) nm. The yield of CNTs using Ni nanoparticles as catalyst is higher than that of using Fe nanoparticles as catalyst. The coated CNTs have diameters ranging from 65-85 nm. The hardness of Al/coated CNTs composites is higher than that of Al/uncoated MWCNTs composites.

**Keywords:** *Synthesis; Carbon nanotubes; Catalyst; Purification; Oxidation.*

### INTRODUCTION

Harry Kroto, Robert Curl, and Richard Smalley were awarded the Nobel prize in Chemistry for the discovery of a spherical molecule composed entirely of carbon atoms [1]. This nanometer-scale structure was named fullerene. An extensive research has been carried out on fullerene theory in the 1980s and 1990s and its synthesis. Before Iijima discovery in 1991 of CNTs by his transmission electron microscope observation, the CNTs were considered as filamentous carbon. This propelled the research related to one of the most actively investigated structures of the last century: nowadays called the carbon nanotubes (CNTs) [2]. After their discovery, carbon nanotubes have been of great interest, both from a fundamental point of view and for future applications.

\* Corresponding author:  
Prof.Dr.Ahmed Ali Moosa  
Technical College –Baghdad,  
AlZaafurania, Baghdad, Iraq.  
Tel +96 479 01793866  
Fax +96 479 01793866  
Email [ahmeda1752@yahoo.com](mailto:ahmeda1752@yahoo.com)

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The most eye-catching features of these structures are their electronic, mechanical, optical and chemical characteristics, which open the way to future applications [3]. Incorporation of a small amount of carbon nanotube into metals and ceramics leads to the formation of high performance and functional nanocomposites with enhanced mechanical and physical properties. Considerable attention has been applied to the development and synthesis of carbon nanotube-reinforced composites in the past decade [4].

The aim of this research is to prepare CNTs by using Chemical Vapor Deposition (CVD) method utilizing carbonaceous gas and two different catalysts and substrates. Also to study the parameters affecting MWCNTs production and to study the purification process of prepared MWCNTs.

## EXPERIMENTAL

### Catalysts preparation

Iron nanopowder with 50 nm particle size was used as catalyst to produce CNTs. The nanopowder was supplied by (MTI Company, purity 99.95 %, particle size 50 nm). A solution of 0.2 gm Fe nanopowder, 0.33 gm Novolac powder and 2.8 gm ethanol was prepared [5]. The solution was then sonicated for 2 hours to make good dispersion of nanopowder. The substrate was then dipped in this solution and then dried in a furnace for 1 hour at 80 °C and then heated in a furnace at 400 °C for 2 hours to oxidize the novolac. The

coated substrate was then used to prepare CNTs by CVD method.

The same procedures were used for Ni nanopowder. Ni nanopowder with 30 nm particle size was used as catalyst to produce CNTs. The nanopowder was supplied by (MTI Company, purity 99.9 %, particle size 30 nm).

### CVD furnace description

Two tube furnaces were used in CVD process with a maximum temperature of 1100°C. These two furnaces were designed especially for this work. Each furnace contains a quartz tube 60 cm long with 4.7 cm inside diameter and 5.2 cm outside diameter. Inside each furnace there is another quartz tube which is used as a reaction chamber with inside diameter of 2.8 cm and outside diameter of 3 cm. The schematic diagram of CVD furnace is shown in Figure 1. Throughout this work these chambers will be referred to as first and second reaction chambers.

One end of the first quartz tube reaction chambers has an inlet to permit passing of argon and acetylene gases to the chamber and the other end is open to permit the discharging of gasses. The first reaction chamber was used for preheating argon and acetylene gasses. The argon gas was charged to the first reaction chamber which is kept at a temperature of 350°C. The second reaction chamber contains the coated substrate on which CNTs will be deposited. The second reaction chamber was kept at a temperature of 750°C with the coated substrate inside it.

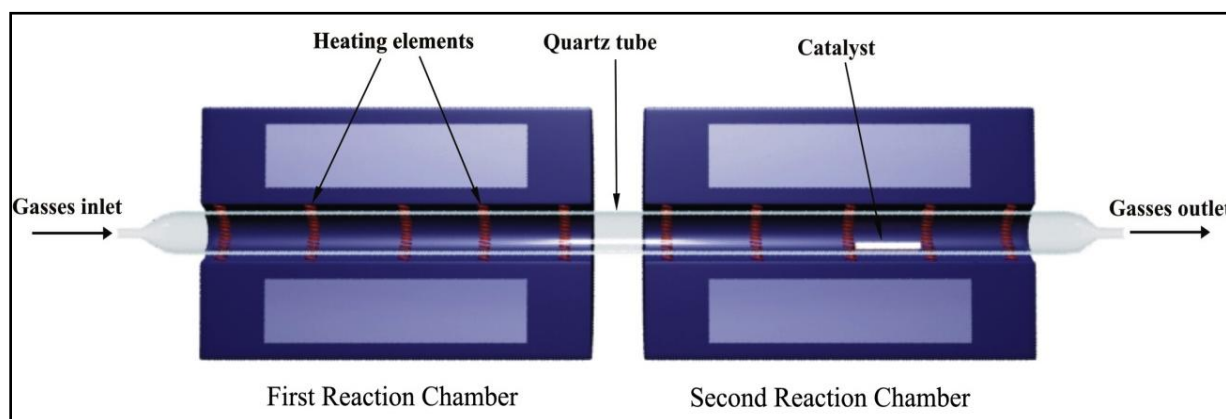


Fig. 1. Schematic diagram of CVD furnace

*Archive of SID***Carbon nanotubes preparation**

The argon gas was charged to the first reaction chamber which is kept at temperature 350°C. The second reaction chamber will be kept at temperature of 750°C with the coated substrate inside it. Argon gas is used as a carrier gas and also to prevent any oxidation of the substrate. When the temperature reached 750°C in the second reaction chamber, Acetylene gas was charged to the first reaction chamber spontaneously with Argon gas. The flow rates of the two gases were 0.4 SLPM for acetylene gas and 4 SLPM for argon gas. Different substrates (Quartz or Alumina) and different catalysts (Ni or Fe) were used at different times and different temperatures in order to study the parameters that affect the preparation of CNTs using CVD method.

**MWCNTs purification**

In order to purify the produced MWCNTs, and 0.5 gm of MWCNTs was put in a ceramic boat and then inserted inside the furnace at 450°C for two hours to oxidize the amorphous carbon. The MWCNTs were then dipped in 250 mL acidic solution (sulfuric acid and Nitric acid with a ratio (3:1)) [4], and stirred for 1 hour at 90°C. The MWCNTs was then removed from acidic solution using a centrifuge (Unimedica 800 centrifuge, China) at 3000 rpm for 10 minute). The remaining MWCNTs were washed with deionized water and then centrifuged for another 10 minute at 3000 rpm. This process was repeated 3-4 times until the pH of the solution becomes 7. The MWCNTs were then dried in an oven at 90°C for 2 hours.

**Functionalization of purified MWCNTs**

Functionalization of MWCNTs was carried out by treatment of purified MWCNTs with concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> with a ratio (3:1) [6]. The MWCNTs acidic solution was then sonicated for 20 minute at room temperature. Then, the acidic solution was removed using a centrifuge at 3000 rpm for 10 minute. The MWCNTs were then washed with deionized water and centrifuged for several times until the pH reaches 7.

**Electroless Coating of MWCNTs**

The surface of CNTs was considered a non-catalytic surface so that it was necessary to accomplish sensitization and activation processes

before electroless nickel plating process. These processes have been accomplished as follows:

**Sensitization:** This process was carried out by immersion of the functionalized MWCNTs in (0.1 M SnCl<sub>2</sub> and 0.1 M HCl) solution and sonicated for 20 minute.

**Activation:** The Sn<sup>+</sup> sensitized MWCNTs was stirred in activation solution of (0.0014 M palladium chloride, PdCl<sub>2</sub>, and 0.25 M HCl) [6, 7, 8, ] for 20 minute. The activated MWCNTs were then washed with deionized water and centrifuged to obtain activated MWCNTs.

**Coating of MWCNTs:** After sensitization and activation of MWCNTs, the MWCNTs were coated using Ni electroless plating bath for 15 minute and the MWCNTs were removed from plating solution by centrifugation and washed with deionized water to obtain nickel-coated MWCNTs.

**Al/MWCNTs Composites**

The composite materials were prepared by mixing the Al metal powder (particle size 50 μm, Metco company) with the MWCNTs. Two types of MWCNTs were used in composite materials, uncoated and Ni coated MWCNTs. The weight percent of the MWCNTs was (0.5, 1, 1.5, 2) wt% with the remaining weight percent of Al powder. Balls mill was used for mixing of Al powder together with MWCNTs for 9 hours to obtain good dispersion. The mixed powder of Al and MWCNTs was cold compacted in a die under pressure of 100 Mpa for 10 minutes by using uniaxial hydraulic press. The cold compacted sample has the dimensions (16 mm in diameter and 6 mm in height).

The Al/MWCNTs cold compacted composite was sintered in specially designed high strength steel mold. The mold was provided with high strength steel springs to lock the mold with the sample inside it to maintain the compaction pressure inside the mold and to avoid swelling of the sample during sintering process. The mold together with the sample inside it was put in a sealed steel cylindrical container which has an argon gas inlet and argon gas outlet. The sintering process was carried out at 450°C for 3 hours. [6].

## RESULTS AND DISCUSSION

### Effect of CVD process parameters on CNTs Yield

Figure 2 shows the CNTs yield vs. CVD process time using Fe and Ni nanopowders as catalysts on quartz and alumina as substrates. The CVD process temperature was fixed at 350 °C in the first reaction chamber and at 750 °C in the second reaction chamber. In general CNTs yield increases with increasing process time for most catalysts, and the variation in CNTs yield is due to the difference in catalyst activity between Ni and Fe. From Figure 2, the maximum yield was found for Ni nanocatalyst on quartz substrates.

Figure 3 shows the relationship between CNTs yield and CVD process temperature for 30 minutes processing time. It is clear that Ni catalysts produce more yield than Fe catalysts. This is due to difference in carbon absorption between Ni and Fe with temperature. By increasing temperature, carbon absorption by nanoparticles increase and carbon diffusion out of nanoparticles as CNT also increases and this is true for Ni catalysts. With Acetylene gas flow into furnace, the

gas will be super saturated. Then, the resulted carbon concentrations produced on Fe nanoparticles catalysts surface may exceed that needed for carbon diffusion. The accumulated carbon on the catalysts nanoparticles surface, thereby will reduce the effectiveness of the catalysts for the growth of CNTs (Qiuling *et al.*, 2007) [9]. In the CVD method, Ni nanoparticles catalyst will cause the growth of high yield CNTs.

For Fe catalyst nanoparticles the situation is different, whereas the carbon absorption by Fe particle increases rapidly with increasing temperature more than increasing in carbon diffusion out of surface as CNT, so the Fe catalyst nanoparticles is shield with absorption carbon layer that preclude the diffusion out of CNT at particle surface resulting in decreasing in yield with increasing in temperature. It was found that Ni is more active than Fe at high synthesis temperature [10]. On the other hand the particle size of Ni is less than Fe particles (30 nm for Ni and 50 nm for Fe) so the exposed surface area of Ni catalysts are more than Fe catalysts.

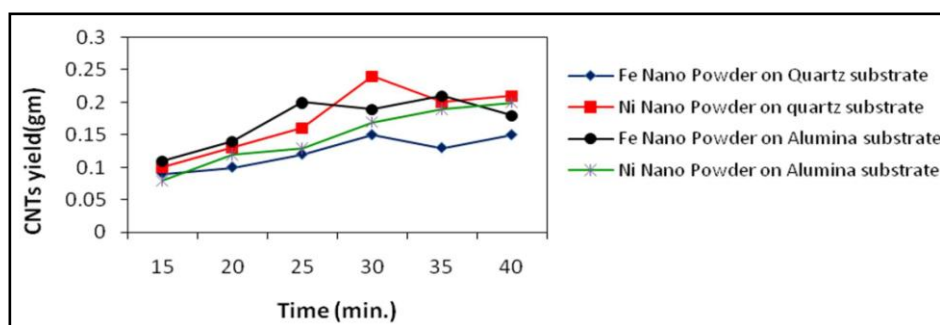


Fig. 2. Relationship between CNTs yield and CVD process time.

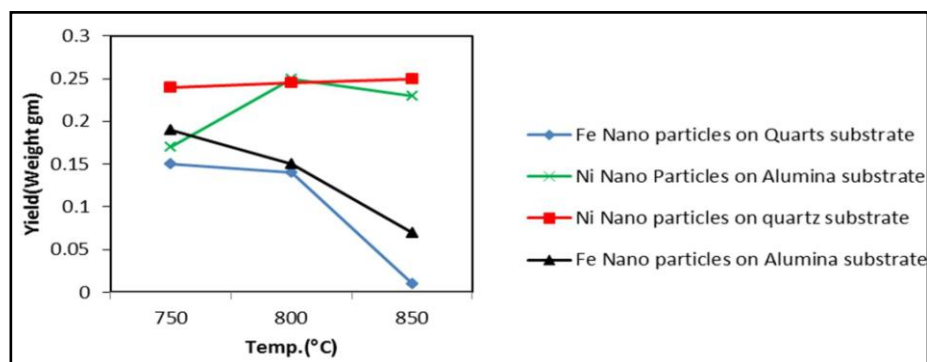


Fig. 3. Relation between CNTs yield and CVD process temperature

*Archive of SID***SEM Images of as Prepared CNTs**

Figure 4 show images of SEM for as prepared MWCNTs before purification. It is clear from these images that MWCNTs have different diameters ranging from 30 nm – 50 nm. The production of MWCNTs by CVD process using small nanoparticles catalyst diameter (50 nm for Fe, 30 nm Ni) resulted in small MWCNTs diameter.

In addition to MWCNTs these images show a lot of side products formed. The as-produced MWCNTs contain a lot of impurities. The main impurities in the soot are wrapped up graphite sheets (fullerenes), amorphous carbon, and metal catalyst [11]. These impurities will interfere with most of the desired properties of the CNTs.

**SEM Images of Purified CNTs**

Figure 5 show SEM images of MWCNTs after purification at different magnification. It is clear that amorphous carbon and metal catalyst particles have been removed successfully from MWCNTs after oxidation and acid treatment of MWCNTs.

**AFM Images of Coated MWCNTs**

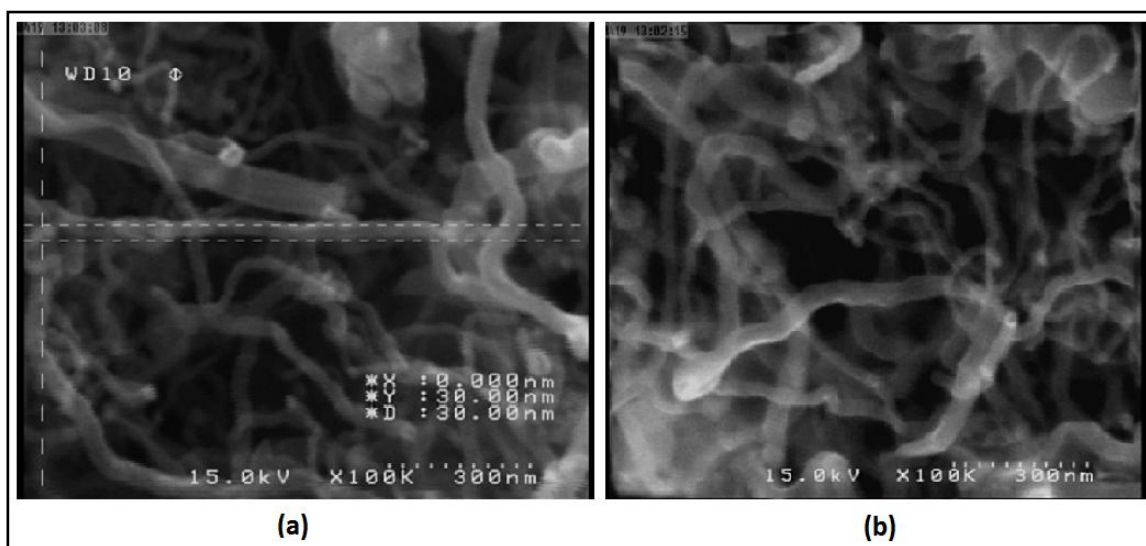
Figure 6a shows the SEM image of electroless Ni coated MWCNTs. The image shows clearly the deposited nickel layer. Before coating process the MWCNTs diameters were in the range 30-50 nm, after coating the diameters of MWCNTs

were in the range 65-85 nm. The three dimensional images of coated MWCNTs using AFM are shown in Figure 6b. As was mentioned before when nanotubes are deposited onto a surface, they overlap on each other. So there will be some deformation in the AFM image due to this overlapping between CNTs.

**Microstructures and Hardness of Al/CNTs Composites**

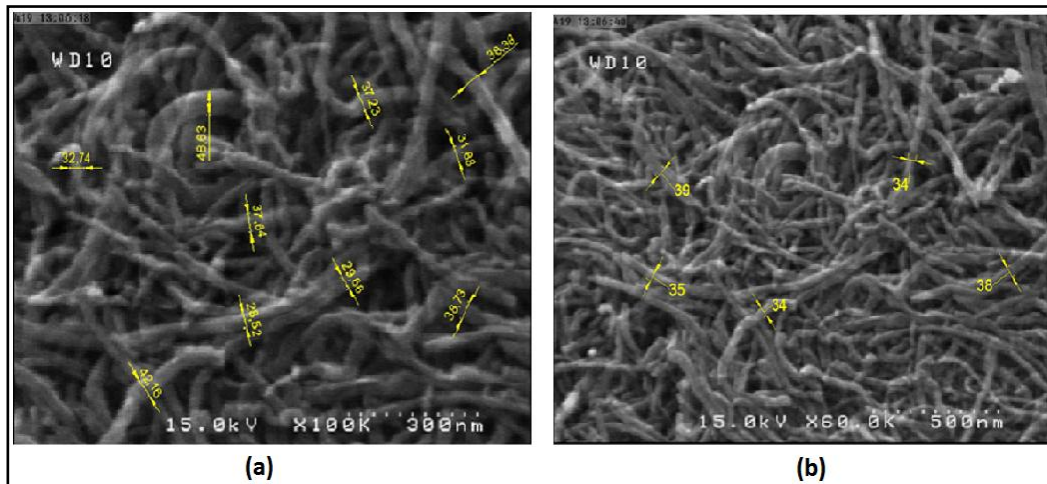
The microstructure of Al/uncoated MWCNTs composites reveals agglomeration and non-homogenous distribution of MWCNTs in Al matrix. The microstructure of Al/coated MWCNTs composites reveal good dispersion and homogenous distribution of coated MWCNTs in Al matrix. CNTs agglomeration increase with increasing the wt% of coated MWCNTs in Al matrix. Figure 7 shows the relationship between MWCNTs addition and the hardness of Al/MWCNTs composite. It is clear that the hardness of Al/uncoated MWCNTs composites increases with increasing the wt% of MWCNTs.

The hardness of Al/(coated) MWCNTs composites increases sharply for CNTs wt% between 0.5%-1%. Then, the hardness decreases for MWCNTs wt% between 1%-2wt%. This is due to enhancement in the wettability between Al matrix and coated MWCNTs.

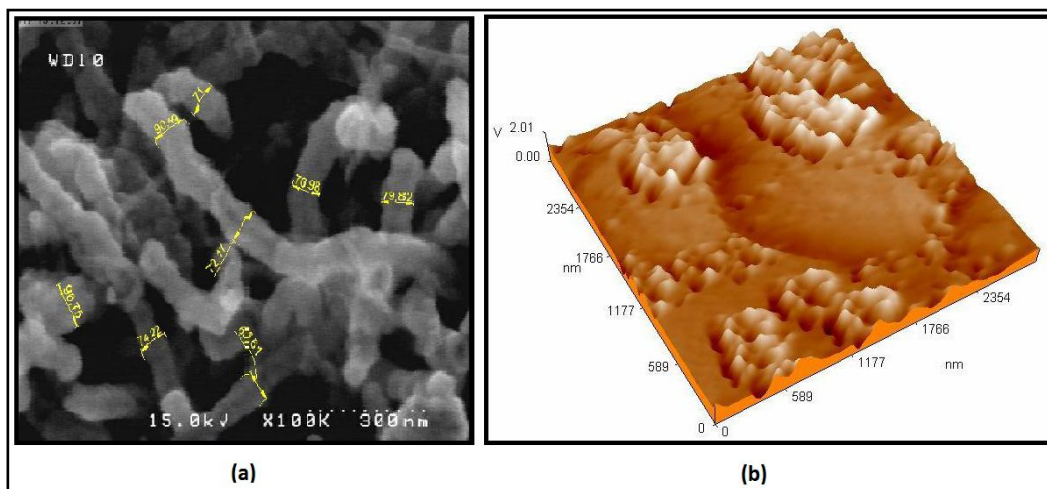


**Fig. 4.** SEM image of as prepared CNTs (a) using Ni nanopowder catalyst, (b) using Fe nanopowder catalyst.

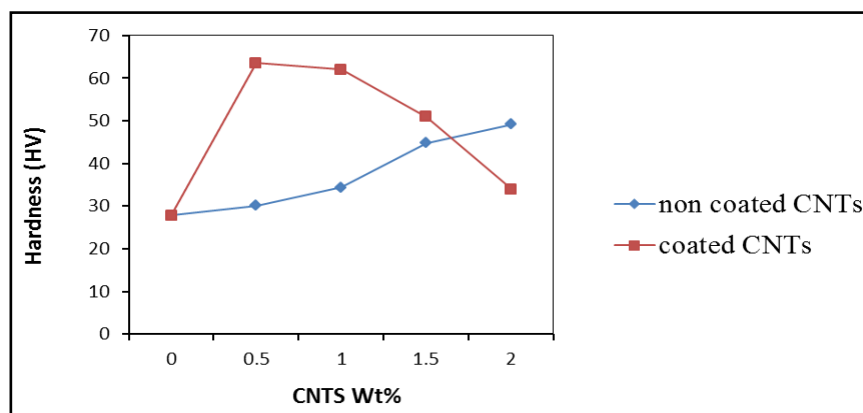




**Fig. 5.** SEM image of CNTs after purification, (a) using Ni nanopowder catalyst, (b) using Fe nanopowder catalyst.



**Fig. 6.** (a) SEM image of MWCNTs coated with electroless nickel, (b) 3D AFM image of nickel coated CNTs



**Fig. 7.** The relationship between MWCNTs addition and the hardness of Al/MWCNTs composite

## CONCLUSIONS

From this work, the following conclusions were obtained: CNTs synthesis process is affected by catalyst type, temperature and time parameters. Yield of CNTs is highly dependent on synthesis temperature. The maximum yield was obtained by using Ni nano particles catalyst at 800 °C synthesis temperatures and 30 minute process time using quartz substrate. At high temperature the yield of CNTs using Fe nanopowder is less than that of Ni nanopowder catalysts. The diameter range for prepared MWCNTs was (30 – 50) nm. Oxidation and acid treatment is an effective method for purifying of as prepared MWCNTs.

Nickel coating of MWCNTs has remarkably enhanced the wettability between MWCNTs and Al matrix. The hardness of Al/uncoated MWCNTs is lower than that of Al/coated MWCNTs due to the better wettability between coated MWCNTs and Al matrix.

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