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Electroless nickel–phosphorus and cobalt–phosphorus coatings on multi-walled carbon nanotubes

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Abstract

The multi-walled carbon nanotubes (MWCNTs) have drawn great attention due to their exceptional mechanical, physical, thermal and electrical properties. The MWCNTs as the reinforcements significantly improved the properties of materials. However, the major challenges in composites containing CNTs are the poor wettability and poor interfacial bonding between matrix and CNTs. In this study, the used MWCNTs have a diameter of 8–10 nm and 1.5 μm in length. MWCNTs are purified in HNO3:H2SO4, sensitized in Sn solution and activated in Pd solution at 90 °C, and coated with the Nickel and Cobalt elements using an electroless coating method. The holding time in the bath is 15, 30 and 60 min, and the bath concentration is also changed. The coatings are characterized by Scanning Electron Microscopy (SEM) equipped with electron dispersive spectrum (EDS), elemental mapping, x-ray diffraction (XRD), Raman spectroscopy, Transmission Electron Microscopy (TEM) and Fourier Transform Infrared (FTIR) spectrometer. The results showed that the Ni and Co coating layers are successfully formed on the surface of MWCNTs. The deposition rate is affected by the holding time and the bath concentration. The optimal results are obtained at the holding time of 60 min in the C concentration sample.

1. Introduction

The carbon nanotubes have attracted considerable interests, both from a fundamental point of view and for future applications in a wide range due to their unusually mechanical, structural and electrical characteristics such as high elastic modulus, high strength, lower density, superconductivity, thermal conductivity, flexibility, field emission behavior and ability to store hydrogen [1, 2]. Thus, carbon nanotubes are used as an ideal reinforcement material to advance the various properties of matrix materials. Young’s modulus of MWCNT is 1.7–2.4 TPa according to Ruoff et al the elastic modulus of multi-wall carbon nanotubes is between 600 and 1100 GPa, and the tensile strength is between 35 and 110 GP according to George et al and Singhal et al[3–5]. The wide industrial application ranges of CNTs mainly depend on the length and diameter of nanotubes. The nanotubes are an important reinforcement material in the design of metal matrix composite materials. CNTS have amphiphilic nature and display a non-reactive structure in a compound [6–9]. In the design of light-weight materials, employing reinforcements are still a big challenge and opportunity in exploring innovative composite structures. The composites reinforced by carbon nanotubes have some problems such as poor wetting, poor dispersion, agglomeration, voids and gaps dislocations that they may weaken or destroy the bond between reinforcement and the matrix [10]. The structural characteristic of composite materials depends on the bond at the interface. The wettability between reinforcement particles and molten metal is an important characteristic, managed by both the chemical and the geometrical structures of the contact surface, which can perform a key role in the performance of reinforcements. A chemical reaction occurs between the matrix and CNTs, which
encourages the formation of carbides like Al₄C₃ which reduces both mechanical and corrosion properties of composites. Mechanical properties of the composites mainly depend on a lot of potential factors such as the physical, chemical, mechanical properties and surface activity of reinforcement, proper and uniform distributions of reinforcement throughout the matrix, and the interfacial bond between the reinforcement and the matrix. The coating of reinforcement material improves the interfacial bonding and uniform distribution of reinforcement in the matrix and hinders the agglomeration. The influence of fabrication methods such as casting, mechanical alloying, mechanical/magnetic stirring and the physical properties of CNT also affect the interfacial bonding and the uniform dispersion of CNTs. To overcome these problems and improve the mechanical properties of composites, reinforcements are subjected to the surface-treated like coating methods.

One of the most important processes in the production of metal matrix composite is the coating of reinforcements to improve the wettability and the other properties of the composites. In the processes, the electroless coating technique has a lot of advantages such as uniform coating thickness, low cost, high corrosion and wear resistances. The electroless coating technique is a chemical deposition process that has been widely studied owing to its fascinating properties [11]. The coating technique is based on the conversion of ions with a reducing effect on the metal on the catalytic material surface. Depending on the type of the used reducer with the coating method, coatings containing the phosphorus (P) and boron (B) or pure metal coatings can be obtained. The electroless coating method can be easily coated even on uneven surfaces, anywhere and in contact with the solution. Electroless coatings are used in a wide range of applications, such as aerospace, automotive, machinery, chemistry, electronics, food and plastics, due to these superior properties it provides to the material [12]. The coating process affects the properties of the surface, wettability, corrosion resistance and adhesion. The surface functionalization of nanotubes increases the properties without changing the bulk properties and makes them attractive for different applications. The process variables of coatings such as ion type, pre-treatment, temperature, time and pH level affect the final properties of the coating. These parameters should be determined carefully. In this study, multi-walled CNTs are coated with Nickel and Cobalt using the electroless coating process. The effect of holding time and bath load on the Nickel and Cobalt coatings of CNTs is studied by SEM equipped with an EDS, elemental mapping, XRD, Raman spectroscopy, TEM and FTIR.
2. Material and method

The electroless coating method is the most common catalytic deposition process and can be applied to parts with complex geometries. The electron in the method is ensured by a reducing agent in default of electric current and this method is an autocatalytic process where the base is submerged in a solution to modify the surface. Figure 1 shows the SEM image of pure MWCNTs. The properties of MWCNT used (Nano-fine Nano Tech. Co. Ltd) are shown in table 1. The inside and outside diameters and length of MWCNTs are 5–8 nm and 8–10 nm, and 1.5 μm, respectively. The MWCNTs have a high specific surface area of 240 m² g⁻¹ and this may affect the various properties of composites like wettability, agglomeration, porosity and surface functionalization.

To perform the Nickel and Cobalt depositions on the surface of MWCNTs, the surfaces need to be sensitized and pre-activated which is called as pre-treatment. The surfaces of MWCNTs are subjected to the sufficient chemical activity and dispersion in electroless solution. Before the sensitization and activation treatments, the MWCNTs firstly are purified in HNO₃: H₂SO₄ = 1:3 for 15h to get rid of unwanted impurities. The chemical process will be increased the dispersion of MWCNTs and will be reduced the agglomeration of the particles.

Secondly, purified MWCNTs are sensitized and functionalized to obtain more nucleation sites in SnCl₂/HCI solutions at a temperature of 90 °C. Then particles are activated in a solution of 0.25 g l⁻¹ palladium chloride (PdCl₂) and 20.8 ml l⁻¹ HCl solutions at a temperature of 90 °C. After each step, MWCNTs have washed away with de-ionized water for maintaining a good quality of coating, followed by filtration and a drying process in the air. Finally, the electroless coating methods of Ni-P and Co-P are applied onto activated surfaces of MWCNTs. Tables 2 and 3 show the process parameters and compositions for the pre-treatment and coating bath.

The same process is repeated for both samples. Nickel sulfate (NiSO₄·6H₂O) and cobalt sulfate (CoSO₄·6H₂O) are used as sources of nickel Ni²⁺ and cobalt Co³⁺ ions, respectively. Ni and Co ions will be reduced and attach at these activated parts on the sidewall of nanotubes. The other electroless nickel and cobalt bath components are reducing agents, suitable complexing agents, stabilizers, and inhibitors. The electroless coating bath contains tri-sodium citrate (Na₃C₆H₅O₇·5H₂O) and sodium hypophosphite (NaH₂PO₂·H₂O) as a complexing agent and the reducing agent. A successful electroless deposition has been carried out in hypophosphite baths [13]. To maintain a fixed pH value (pH = 8.5) ammonia/ammonium chloride (NH₄Cl/NH₃·H₂O) is used as a buffer solution [14]. The processes mentioned above are carried out with continuous stirring at 300 rpm at 90 °C. In each step, the particles are rinsed with distilled water for 5 min. The holding period for the coating process is 15, 30 and 60 min and the coated samples are then placed on a drying oven at 100 °C for 2 h in the final step. The properties of coatings are researched by SEM equipped with an EDS, XRD, Raman spectroscopy, TEM, elemental mapping and fourier transform infrared spectrometer (FTIR).

3. Results

Surfaces and its morphologies of Ni-P and Co-P coated particles are examined by using field emission scanning electron microscope (FESEM) equipped with EDS, Raman spectroscopy and TEM. The structure of the coated samples is researched by the XRD method. Figures 2 and 3, display the images of SEM, elemental mapping and
Figure 2. (a), (i) SEM, (ii) Mapping and (iii) EDS images, map sum spectrum of Ni-Coated MWCNT samples at 15 min. (b), (i) SEM, (ii) Mapping and (iii) EDS images, map sum spectrum of Ni-Coated MWCNT samples at 30 min. (c), (i) SEM, (ii) Mapping and (iii) EDS images, map sum spectrum of Ni-Coated MWCNT samples at 60 min.
EDS with the different holding time. Also, the respective SEM images where the elemental mapping analyses of Nickel and Cobalt coatings are performed are included at the macroscopic level (500X–1000X) in these figures.

The surface characteristics of materials like pure CNT, Ni-coated CNT and Co-coated samples can be studied with electron microscopies such as SEM and TEM. These analyses provide the detailed information about the morphology, crystal structure, uniformity, porosity occurrence and microstructures of materials. The elemental distribution, agglomeration and surface quality of the coating in this work are studied under SEM.

SEM and elemental mapping images of the coated MWCNTs show that the surface of MWCNTs is essentially covered by Nickel and Cobalt. The differences between figures 2 and 3 are mainly attributed to the numbers of Sn, Pd, Ni and Co particles. The process parameters and surface properties of MWCNTs may affect the thickness and surface quality of the coating. The Co-coated samples exhibit high agglomeration. It is reported that the surface roughness and wear properties of Ni-P-MWCNT coating increased [15, 16]. Some MWCNT particles are agglomerated and the fibers are tangled. They have appeared on the surface of the original nanotubes. The peaks of Pd indicated the less quantity of Pd particles that adsorbed onto particle surfaces. It is obvious that Ni and Co are uniformly dispersed on the MWCNTs according to the EDS results on the figures. EDS analysis calculates the percentage of elements in the coating, and the Ni and Co coatings are observed on figures and the percentage of elements are given in tables 4 and 5. Energy-dispersive X-ray Spectroscopy (EDS/EDAX) is done along with XRD to find the percentage of each element in the coating.

The activated MWCNTs are coated by Ni and Co for 15, 30 and 60 min. In tables 3 and 4, the list of map sum spectrum of Ni and Co coated MWCNTs are given, respectively. After sensitization and activation pretreatment, Pd and Sn are confirmed on top of the surface of MWCNT nanoparticles according to EDS results. The growth rate on Ni and Co coated regions looks significantly. The existence of Pd derived from the sensitization and activation pre-treatment is necessary for Ni-P and Co-P deposition. The Sn percentage in Co coating is lower than in Nickel coating. The Co rate advances linearly while the Sn rate reduces. The structures of the Ni and Co coating are determined by the x-ray diffractometer using Cu Kα radiation. XRD patterns of nanotubes processed with different bath times are shown in figure 4. The amorphous and crystalline natures and phase variations of coatings and can be revealed using the XRD method.

A single broad peak is seen around 26° of 2θ and indicative of the amorphous and microcrystalline structures of Carbon and the sharpness demonstrates that CNTs have a well-graphitized structure. In Ni and Co coated MWCNT samples, the intensity of the peak decreases significantly. The comparison of deposition bath time for
Figure 3. (a), (i) SEM, (ii) Mapping and (iii) EDS images, map sum spectrum of the Co-Coated MWCNT samples at 15 min (b). (i) SEM, (ii) Mapping and (iii) EDS images, map sum spectrum of the Co-Coated MWCNT samples at 30 min (c). (i) SEM, (ii) Mapping and (iii) EDS images, map sum spectrum of the Co-Coated MWCNT samples at 60 min.
60 min changed the nature of the deposition and lead to the same yet merely sharper peaks and increases in intensity that are seen in the diffraction samples owing to the crystallization process. XRD analysis shows peaks of Ni₃P, Co₉P, NiO, and CoO and these can be attributed to amorphous characteristics of the coating. The Raman spectra of Ni and Co coated MWCNTs are shown in Figure 5.

Raman spectroscopy is a sensitive, powerful and non-destructive technique, used for extensive characterization for understanding some properties of sp² carbons [17]. The spectroscopy is used to detect the graphite structure and the variation of graphitization with uncoated, Ni-coated and Cobalt-coated samples. The Raman spectrum of MWCNTs bundles contains two main typical bands of graphite. The first band in the spectroscopy is typical defect-free graphite and exhibits the characteristic G-band at 1580 cm⁻¹ corresponds to E2 graphite mode and indicating C–C stretching vibrations. The second band at 1342 cm⁻¹ demonstrates the

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Table 4. Map sum spectrum of the Ni coated MWCNT samples for different bath times of 15, 30 and 60 min, respectively (wt%).

| Time | C   | Sn  | O   | Na  | Al  | P   | Ni  | Cl  | S   | Fe  | Co  | Si  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 15   | 41.4| **30.8** | 16.9 | 4.5 | 1.9 | 1.8 | 1.6 | 0.5 | 0.3 | 0.1 | 0.1 | 0.1 |
| 30   | 60.1| 14.1 | 18.3 | 2.8 | 2.2 | 2   | **0.6** | 0.5 | 0.1 | 0.1 | 0.1 | 0.1 |
| 60   | 49.1| **24.3** | 19.7 | 2.6 | 1.7 | 1.3 | **0.9** | 0.2 | 0.1 | —   | —   | 0.1 |

Table 5. Map sum spectrum of the Co coated MWCNT samples for different bath times of 15, 30 and 60 min, respectively (wt%).

| Time | C   | Sn  | O   | Na  | Al  | P   | Cl  | S   | Fe  | Co  | Ca  | Pd  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 15   | 44.1| 5.1 | 22.6 | 12.3 | 2.3 | **1.8** | 1.8 | 0.4 | 2.4 | 0.2 | **7.2** | 1   | 0.2 |
| 30   | 45.1| **3.5** | 25.3 | 11.6 | 3.4 | **2.5** | 2.5 | 0.2 | 1.1 | 0.4 | **6.9** | —   | —   |
| 60   | 33.1| **1.7** | 29.5 | 16.5 | 1.8 | **3.3** | 3.3 | 0.1 | 2   | 0.2 | **11.8** | —   | —   |
Figure 4. X-ray diffraction pattern of (a) pure MWCNTs, (b) nickel and (c) cobalt coated MWCNT samples for 15 and 60 min.

Figure 5. Raman spectra of MWCNT samples (a) with Ni-coated and (b) Co-coated samples.
Figure 6. TEM images of Nickel-coated (a) 15 min (b) 60 min and Cobalt-coated samples (c) 15 min (d) 60 min.

Figure 7. FESEM and elemental mapping images of samples (a) A concentration (b) B concentration (c) C concentration.
characteristic D-band that is enabled by the irregularity in carbon systems \[18, 19\]. The morphology and quality of uncoated, Ni and Co coated MWCNTs are photographed by TEM analysis in figure 6. The TEM analysis is used to reveal the distribution and density of Nickel and Cobalt elements in the coated particles. It is observed that the surfaces of MWCNTs are clean as shown in TEM images. The outer surfaces contain Ni and Co layers and the outer diameter of the MWCNTs depends on the thickness of these layers. In certain regions, nanoparticles covered by thick graphite layers are observed in a bath time of 60 min.

In order to detect the influence of bathing compositions on Nickel coating of MWCNT, the sensitization, activation and coating baths are concentrated in different rates showed in table 6. Thus, the bathing load is changed. The multi-walled carbon nanotubes \(0.5 \text{ g}\) are exposed to the sensitization, activation and coating procedures for 60 min at 90 °C temperature \[20\]. The pH measurements of the electroless coating bath are carried out with a pH meter and the weighing process is carried out with a precision scale of 0.0001 g. The baths are stirred with a magnetic stirrer. The surface characteristics of electroless Nickel and Cobalt coated particles are investigated by FESEM, electron dispersive spectrum (EDS) and mapping.

FESEM and elemental mapping images, and EDS spectrum of Nickel coated samples with different concentrations are illustrated in figure 7 and table 7. The FESEM images of the declared samples display that the samples are coated with nickel. The assumption is proved by the EDS results of samples A, B and C in table 7.

In the spectrums and element analysis, the presence of nickel is clearly observed. Nickel contents of samples for A, B and C concentrations are 17.34%, 30.96 and 33.25%, respectively. From concentration A to C, Nickel content increases linearly. It is not observed the Carbon element for C concentration. According to elemental mapping images, it can be concluded that nickel shows the homogeneous distribution in the samples. The FTIR spectra of pure MWCNTs, Ni-coated and Co-coated particles are showed in figure 8. The CNTs display very weak peaks of C-C owing to its nature. The most prominent peak for pure CNT is observed at the wavenumber of around 1600 cm\(^{-1}\). There are different peaks between the wavenumber of 1000 and 1500 cm\(^{-1}\) and at the wavenumber of around 3000 cm\(^{-1}\).

After the coating process with Nickel and Cobalt, a strong peak appears between wavenumber of 2000–2500 cm\(^{-1}\). The peaks between the wavenumber of 1000 and 1500 cm\(^{-1}\) sharpened after coating.

4. Discussion

The surface morphology, compositional analysis and elemental distribution of the coatings are studied using SEM equipped with EDS, TEM and Raman spectrum. XRD is employed to determine phase changes. The appearance of the coated surface probably results from the nucleation of nanoparticles and is shown in the SEM images. The non-uniformity of the active sites on the surface of the MWCNTs may be caused by the discontinuous of the coating layers. It is declared that the density of active sites should be increased to obtain a better coating layer \[21\]. A curved surface structure of MWCNTs has also an important effect on the coating layer and the aggregation tendency of the coating. The coating characteristics of the two types of coating

| Bath       | Solution  | Concentration |
|------------|-----------|---------------|
| Sensitization | SnCl₂     | A 10.8 g l\(^{-1}\) | B 21.6 g l\(^{-1}\) | C 32.4 g l\(^{-1}\) |
|            | HCl       |               | 3.5 ml l\(^{-1}\)  | 7.0 ml l\(^{-1}\)  | 10.5 ml l\(^{-1}\) |
| Activation | PdCl₂     | A 0.1 g l\(^{-1}\) | B 0.2 g l\(^{-1}\) | C 0.3 g l\(^{-1}\) |
|            | HCl       | A 8.8 ml l\(^{-1}\) | B 17.6 ml l\(^{-1}\) | C 26.4 ml l\(^{-1}\) |
| Coating    | NiSO₄ · 6H₂O | A 23 g l\(^{-1}\) | B 46 g l\(^{-1}\) | C 69 g l\(^{-1}\) |
|            | NaH₂PO₄·H₂O | A 8.6 g l\(^{-1}\) | B 17.2 g l\(^{-1}\) | C 25.2 g l\(^{-1}\) |
|            | Na₅C₆H₅O₇·5H₂O | A 51 g l\(^{-1}\) | B 102 g l\(^{-1}\) | C 153 g l\(^{-1}\) |
|            | NaOH      | pH adjuster   |               |               |               |

Table 7. EDS analyses for various concentration.

| Concentration/Element | C | O | Si | P | Ni | Br | Pd | Sn | Al | Na | S | Total |
|-----------------------|---|---|----|---|----|----|----|----|----|----|---|-----|
| A                     | 16.51 | 34.74 | 0.19 | 2.33 | 17.34 | 1.26 | 0.76 | 26.87 | —   | —   | — | 100  |
| B                     | 18.40 | 24.68 | —   | 2.85 | 30.96 | —   | —   | 21.67 | 0.26 | 1.18 | — | 100  |
| C                     | —   | 33.09 | —   | 3.72 | 35.25 | —   | 0.70 | 20.44 | 0.42 | 6.08 | 2.30 | 100  |
The increase in the deposition bath time increases the coating thickness for Co within the trend. The four principal mechanisms were proposed for electroless plating, that is, the hydrogen (atomic) mechanism, hydride transfer mechanism, electrochemical mechanism and metal hydroxide mechanism [22–28]. In the hydrogen mechanism, the actual reductant is hydrogen formed by the reaction of water with hypophosphite and absorbed at the catalytic surface. The ions obtained the electrons unrestrained from the hydrogen and are decreased to the metallic element. Besides, the mechanical force mechanism due to the done magnetic stirring has an important effect on coating [29]. The deposition contains phosphorus and is not pure nickel which was confirmed with EDS results and apparent evidence of the proposed mechanism. It is noted that the non-uniformity coating structure is linked to hydrogen gas which enhances the porosity concentration [30]. Additionally, the high bath temperatures cause the bad uniformity plate and the porosity in the coating.

Figure 8. FTIR spectra of (a) uncoated MWCNTs, (b) Ni-coated particles and (c) Co-coated particles.
A higher amount of MWCNTs inclusion in the bath might be affected by the chances for the formation of oxides. The intensity of the diffraction peaks changed with the various coating parameters. The holding time in the coating bath from 15 min to 60 min affects the structure of the deposition and morphology of coating. The formation of different phases or compounds can be attributed to amorphous characteristics of the process. The oxidative reaction or the formation of different oxides may affect the intensity by vibrational characteristics as declared in the works [31, 32]. The coating thickness might also be affected by oxides. It is stated that the oxidation formation decreased the quality and thickness of the coating [33]. The agglomeration and adhesion of particles in the pre-treatment process hinder the deposition rate. The coating structure and oxidation changed the peak intensity of XRD samples. It is declared that after the metallic coating, the peak intensity is reduced particles in the pre-treatment process hinder the deposition rate. The coating structure and oxidation changed declared in the works [33, 34]. The intensity of the diffraction peaks changed with the various coating parameters. The holding time in coating bath from 15 min to 60 min affects the structure of the deposition and morphology of coating. The oxidation might also be affected by oxides. The presence of palladium and nickel in the nickel coated samples and in cobalt coated samples for 30 and 60 min indicate that the successfully activated samples were well coated. Besides, the palladium rate in the composition should be increased to improve the activation process. The control of coating parameters in pre-treatment, sensitization, and activation steps is precisely carried out to get good quality. The incorrect selection of parameters causes the improper coating of nanotubes. The pre-treatments make the conditions proper for electroless coating. If the pre-treatment process is not performed agreeably, the electroless coating can’t be carried out in large. The increase in pH results in the acceleration in the reaction of Ni reduction. It is declared that a good adhesion was observed between the coating and the surfaces at a high pH level [35]. The effect of bath temperature is another parameter for an electroless deposition that is an endothermic reaction that needs to absorb energy from the surrounding. High temperatures contributed to improving deposition thickness and speed. The parameters and used chemicals improved the cohesion of coatings and make the surface more chemically active and affect the quality of plating layers.

The properties of MWCNTs are dependent upon the degree of order within the nanotube wall. It is seen that the D and G bands intensities ratio (ID, uncoated/ID, coated) decreases with increasing bath time for Ni coated samples, but remains unchanged in the band’s intensities ratio (I_D/I_G) significantly. In Co-coated samples, because there are no significant changes in the quality of uncoated and coated MWCNT nanoparticles the spectra and the ratio (ID, uncoated/ID, coted) are observed to be identical. The two bands -D and G- reflect the high-density zones for zone-edge and mid-zone phonons, respectively [19, 30]. Raman spectra for MWCNTs exhibited polycrystalline graphite structure which indicates that Ni and Co-coated CNTs have a good extent of graphitization.

The absence of the Carbon element for C concentration shows that all surfaces are successfully coated by Nickel. In particular, it is confirmed that the presence of the Oxygen element which cannot be completely prevented and the presence of compounds such as NiO may occur with nickel. The use of sodium hypo-phosphate as the reductant agent is considered to be the phosphorus content and represents the possible Ni_3P or Co_3P compounds [36, 37]. In addition, all samples according to phosphorus content, it can be classified as low phosphorus [38]. The different functional groups are revealed using the FTIR spectra. The FTIR spectrum of MWCNTs is recorded in the range of 4000–500 cm⁻¹ wavelength. The weak bands at around 500–1000 cm⁻¹ can be due to Co–O or Ni–O stretching modes. The peak seen between wavenumber of 1000 and 1500 cm⁻¹ is assigned to the vibration of C–O(H) or C–C–C chemical bonds which is also a strong peak, around 1600 cm⁻¹ to C–C (the carbonyl group) and around 3000 cm⁻¹ to C–H group that is very strong peak [39, 40]. Several peaks at 1000 and 1500 cm⁻¹ found in Ni-P and Co-P/CNT samples are well segmented into the typical peaks owing to the oxidation in air contact [41]. Ni-coated CNTs exhibited a broadband structure comparing cobalt coated samples.

The chemical reactions that are necessary to coat Ni and Co into the medium are given by the following equations:

Sn^{2+} + Pd^{2+} → Sn^{4+} + Pd^{0}  \quad (1)

Ni^{2+} + H_2PO_3^- + H_2O → Ni + H_2PO_3^- + 2H^+  \quad (2)

Co^{2+} + H_2PO_3^- + H_2O → Co + H_2PO_3^- + 2H^+  \quad (3)

H_2PO_3^- + H_2O → H_2PO_3^- + H_2  \quad (4)

Ni^{2+} + Pd → Pd^{2+} + Ni  \quad (5)

Co^{2+} + Pd → Pd^{2+} + Co  \quad (6)

The stages of the coating procedure are given in these equations. MWCNT particles are adsorbed Sn ions onto the surface and Pd^{2+} is reduced to Pd^{0}. Then, the surfaces show the catalytic activity for the Ni^{2+}/Co^{2+} to Ni^{0}/Co^{0}. It is well known that there are a lot of variables affecting the electroless coating process. The model
suggested by Brenner patented the technology for the deposition of several metals [12], describes the deposition rate as

\[ D = F \left( T, \, pH, \, C_{Ni^{2+},Co^{2+}}, \, Red, \, C_{Red}, \, \frac{O}{V}, \, n_i \right) \]  

(7)

where the parameter D is deposition rate, T is temperature, \( C_{Ni^{2+}} \) or \( C_{Co^{2+}} \) is the concentration of Ni or Co in solution. The reducing agent is referred to as \( \text{Red} \), \( C_{\text{Red}} \) is the reducing agent concentration, \( O/V \) is bath load and \( n_i \) was an agitation factor. To maintain a fixed pH value (pH = 8.5) ammonia/ammonium chloride (\( \text{NH}_3/\text{NH}_4\text{Cl} \)) is used as a buffer solution. The density of the Ni and Co elements, the surface area of particles, and coating weight are the other parameters that affect the deposition rate [13]. All processes are carried out with continuous stirring at 300 rpm. The deposition rate increases the increase in the temperature and pH level which accelerates the reaction and decreases the phosphorus content of the coating as seen in this work. Bath loading is the ratio of the surface of the working piece to the volume of solution in the cup. The decreasing of the bath loading increased the deposition rate. The results showed that the Ni and Co can be deposited on surfaces of MWCNTs under optimal conditions. It is observed improving some properties of matrix material with the addition of CNT. The conductivity of composites have been shown to increase with a higher loading of SWCNT [2]. The mechanical properties of Ni-coated composites improved with CNTs. Al-Ni-coated CNTs composites displayed an increase of 27% in hardness in comparing with Al-CNTs composites [42]. Besides, the distribution and stabilization of CNTs in Al-Ni-coated CNTs composites improved the extra addition of Ni. The Ni-coated CNTs improved the wear resistance of the composites [18]. The maximum corrosion resistance is obtained at the Ni–P–TiC coated steel [43].

5. Conclusion

In this study, the multi-walled carbon nanotubes are coated by Nickel and Cobalt using the electroless coating method. The coatings are characterized by SEM, elemental mapping, EDS, XRD, Raman and TEM analyses. The following conclusions from this work can be drawn;

- The deposition of nickel and cobalt on MWCNTs can be achieved under favorable conditions.
- The sensitization and activation processes affect the coating process and quality.
- The process parameters of the coating should be adjusted carefully.
- The high bath load and high specific surface area of MWCNTs decrease the deposition rate.
- The increase in the holding time contributes to the increasing of deposition rate. The optimum holding time is observed to be 60 min.
- A higher concentration of the MWCNTs in the bath can be culminated by a high agglomeration, poor cohesion and non-uniformity layers of the coating.
- FTIR spectrum revealed that the bond structure and intensity of samples varied with the Nickel and Cobalt coatings where strong bond types are observed.

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13
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