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**A. SELVAKUMAR[1], U. SANJITH[2,3], T.R. TAMILARASAN[4],**
**R. MURALIRAJA[5], W. SHA[6], and J. SUDAGAR[7,*]**

[1] VIT Fashion Institute of Technology (VFIT), Vellore Institute of Technology,
Chennai, Tamil Nadu, India
[2] Department of Mechanical Engineering, B.S. Abdur Rahman Crescent
Institute of Science & Technology, Chennai, Tamil Nadu, India
[3] Centre for Sustainable Materials Research and Technology (SMaRT),
School of Materials Science and Engineering, UNSW Sydney, Australia
[4] Department of Automobile Engineering, B.S. Abdur Rahman Crescent
Institute of Science & Technology, Chennai, Tamil Nadu, India
[5] Department of Mechanical Engineering,
Vels Institute of Science Technology and Advanced Studies,
Chennai, Tamil Nadu, India
[6] School of Natural and Built Environment, Queen's University Belfast,
Northern Ireland, UK
[7] Department of Physics, School of Advanced Sciences, VIT-AP University,
Near Vijayawada, Andhra Pradesh, India

*sudagar.jothi@vitap.ac.in

# A CRITICAL REVIEW OF CARBON NANOTUBE-BASED SURFACE COATINGS

The emergence of carbon nanotubes (CNT) has encouraged widespread interest among researchers with many pioneering applications achieved by exploiting the unique properties of carbon allotropes. This article is a general overview of the diversity of applications of CNT and their various forms, particularly, in the area of surface coatings. The different methods, which have been developed and practiced in the preparation, dispersion, functionalization, and metallization of CNT, are elucidated. The composite coatings have been prepared using electrochemical methods such as electroplating and electroless plating. The review presents the mechanical, electrochemical, corrosion, thermal, electrical conduction, tribological, biosensing, magnetic, and microwave absorbing properties of CNT-based composites. The incorporation of CNT substantially affects the coating performance, and the level of influence can be befittingly adjusted to suit the application needs. Various charac-

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terization studies have been conducted on these coatings, emphasizing their properties. The potential of CNT as a versatile material in catering to diverse industrial applications has placed the carbon allotrope among the elite group of materials, drawing the attention of researchers to widen their scope of utilization. The challenges, problems, and ways of the overcoming are also addressed in this review.

**Keywords:** carbon nanotube, electroplating, electroless plating, composite coating, surface roughness, mechanical properties, wear, corrosion.

## 1. Introduction

Surface engineering involves the wide range of technologies considered to modify the surface properties of metallic and non-metallic components for functional and decorative purposes. An increasing number of surface engineering techniques started to reach commercial maturity in the last decade owing to their ability to serve widespread industrial applications. Earlier researchers have studied the optimization of surface and substrate properties with respect to tribological and the corrosion characteristics, coating method adopted, and the coating characterization, which are identified as the three interrelated activities describing surface engineering [1–3].

Surface engineering encompasses techniques and processes capable of developing and modifying surfaces to enhance essential properties such as wear, corrosion, fatigue resistance, and biocompatibility, as listed in Tables 1 and 2 [4, 5]. Modern surface engineering techniques

*Table 1*. **Design attributes and selection criteria [4]**

| Application area | Properties recommended |
|---|---|
| Tribological<br>Mechanical<br>Chemical<br>Thermal<br>Magnetic<br>Electronic and superconducting<br>Optical<br>Optoelectronic<br>Aesthetic | **Coating(s):**<br>Wear resistance, hardness, low coefficient of friction, chemical inertness, and diffusion barriers<br>**Interface(s):**<br>Adhesion, bonding, mechanical<br>**Substrate:**<br>Toughness, strength, fatigue life, lightness, shape |

*Table 2*. **Essential properties of a functional component [5]**

| Properties | Properties |
|---|---|
| Resistance to abrasive wear regardless of the compressive loading<br>Resistance to erosion and corrosion<br>Thermal stability<br>Heat dissipation<br>Lubrication | Resistance to scuffing or seizure<br>Bending or torsional strength<br>Bending or torsional fatigue strength<br>Resistance to mechanical fatigue<br>Resistance to case crushing |

combined together with traditional surface treatments have a profound influence on the desired engineering properties instilled on the coated substrates, listed in Table 2. Presently, the advancements have reached a level wherein surface engineering processes capable of producing multilayer and multicomponent surfaces, graded surfaces with novel properties, and surfaces with highly non-equilibrium structures have been developed.

### 1.1. Electrochemical Deposition Techniques

The electrochemical method is the second most widely accepted method for developing thin composite coatings (thickness ranging from 20 to 180 μm) next to the powder metallurgy techniques. This technique is being adopted for preparing nickel composite coatings in various dimensions especially one-dimensional composites [6]. Deposition by both electro and electroless methods has been extensively used for metal matrix composite fabrication [7].

Electroplating is the process of producing thin or thick coatings of one metal upon the surface of another metal(s). Generally, ferrous or nonferrous materials may be coated by a variety of common (chromium, brass, copper, lead, nickel, bronze, tin, iron, zinc, aluminium, and their combinations) or precious (silver, gold, platinum, iridium, rhodium, indium, osmium, palladium, ruthenium and their combinations) metals. In the process of electrodeposition, metal ions supplied by the dissolution of metal from their anodes are reduced on the coating substrate (cathodes) while in alkaline, acid, or neutral solutions. The electrolytic bath contains metal salts, alkalis, and other bath control compounds in addition to plating metals such as copper, nickel, silver, or lead. Many plating solutions contain metallic, metalorganic, and organic additives to induce grain refining, levelling, or smoothening the plated surface and brighten the deposit.

Electrodeposition of metals or alloys involves the reduction of metal ions from electrolytes. When the current flows, oxidation (loss of electrons) occurs at the anode, adding metal ions to the solution. Those ions travel on the electric current to the cathode, where reduction (gain of electrons) happens, plating the metal ions onto the substrate. In its simplest form, the reaction in an aqueous medium at the cathode follows the equation ($M^{n+} + ne^- \to M$) with a corresponding anode reaction. At the anode, electrons are supplied to the anions, which migrate to the anode. The anode material can be either a sacrificial anode or an inert anode. In the case of a sacrificial anode, the anode reaction is represented by the following equation ($M \to M^{n+} + ne^-$). In this case, the electrode reaction is electro dissolution that continuously supplies the metal ions replenishing the electrolyte bath.

On the other hand, the electroless coating process does not require any form of external energy. The plating process is carried out by autocatalytic chemical reduction, in which thermochemical decomposition of metallic salts releases metallic ions. The metallic ions are strongly influenced to form binary, ternary, and quaternary alloy layers.

### 1.2. Electrodeposition of Metal Matrix CNT Composite Coatings

Generally, electrodeposition has been one of the most technologically feasible and economically superior techniques for producing metal matrix and nickel composites. The technique typically employs Watts or sulphamate bath for co-deposition of various alloys, metals, and non-metals on the substrate. A lot of research work on the co-deposition of SiC [8], $TiO_2$ [9], $Al_2O_3$ [10, 11], $ZrO_2$ [12, 13], WC [14], $SiO_2$ [15], and CNT [16, 17] have been conducted revealing productive results in order to develop these methods for industrial applications. Of all these co-deposited nanoparticles, our literature concentrates on CNT as these materials have been attracting significant interest as reinforcement in metallic coatings owing to their superior mechanical properties such as high strength, high elastic modulus, and large elastic as well as fracture strain. In addition, CNT have significant interests as reinforcement in various metallic, ceramic, and polymeric materials to impart strength, toughness, and wear-corrosion resistance.

### 1.3. Electroless Deposition of Composite Coatings

Electroless plating is a technique of plating metal by chemical rather than electrical means, in which the piece to be plated is immersed in a reducing agent that, when catalysed by certain materials, changes metal ions to metal that forms a deposit on the piece. This technique is often a better choice because the resulting plated part tends to be of uniform thickness, very hard, and less porous, thereby more resistant to corrosion. While electroplating requires complex filtration equipment and possibly dangerous battery applications, electroless plating uses no extra equipment. The chemicals can be replenished spontaneously, and the operators exercise more control over the deposition process: resulting in a smooth, even application of the nickel plating. They can also vary the thickness and volume of the plating to exacting standards.

The electroless nickel plating of metallic nickel from an aqueous solution in the presence of hypophosphite first occurred as a chemical accident by Wurtz [18]. Though Breteau [19] was the first one to report bright coatings on the surfaces of the reaction vessels, the first patent on electroless plating based on a chemical reaction was granted to Roux [20]. It was observed that the reaction baths decompose spontaneously and form deposits on any surface that is in contact with the solution, even on the inner walls of the vessel. Other researchers studied the existing process, but their interest centred more on the chemical reaction than the plating technique. Brenner and Riddell rediscovered the electroless nickel technology as it is used in recent days [21, 22]. Brenner was the first to refer to the plating technique as electroless plating. Shipley [23] reported that the autocatalytic nature of the plating produces continuous reduction on the substrate regardless of the material (conductive and non-conductive) type and their dimensions. Apart from the usual electroplating, metal matrix composites are developed by electroless applications for getting very thin coatings with enhanced mechanical (hardness, surface roughness, friction, and wear resistance), thermal (thermal conductivity, coefficient of thermal expansion (CTE)), electrical (conductivity), and electrochemical (corrosion resistance) properties.

## 2. Preparation of CNT Composites

The growing awareness in applying CNT in different fields has led to continued efforts to develop dispersion and functionalization techniques. To effectively incorporate CNT in nanocomposites, proper dispersion and appropriate interfacial adhesion between the CNT and matrix have to be guaranteed. This part of the literature briefs the studies conducted on the dispersion, functionalization, and metallization of CNT by employing various methods, and analyses the effect of the addition of surfactants to the plating bath.

### *2.1. Dispersion of CNT*

In order to achieve a harder deposition, the CNT particles were dispersed in the nickel bath by means of ultrasonic agitation. It was found that the CNT was deposited on the metal substrate in an uneven disorderly fashion. A majority of the CNT particles were deposited perpendicularly to the surface of the substrate while the remaining was seen to be deposited in a curved and tilted fashion on the substrate. Chen *et al.* [10] proposed a method of electroplating for fabricating multiwalled carbon nanotubes MWCNT–Ni composite over a metal substrate. A comparative analysis of the friction and wear behaviour of the CNT/Ni composite with the uncoated steel and pure nickel-coated substrates was performed. It can be inferred that the composite coating reinforced with CNT had excellent tribological properties and wear resistance due to the high toughness and self-lubrication properties of CNT. In another study, Wang *et al.* [24] tried to develop a method to improve the concentration of the carbon nanofibers in the nickel matrix using the electroplating process. A pulse-reverse (PR) technique was employed to improve the dispersion and distribution of carbon nanofibers in the nickel matrix. In

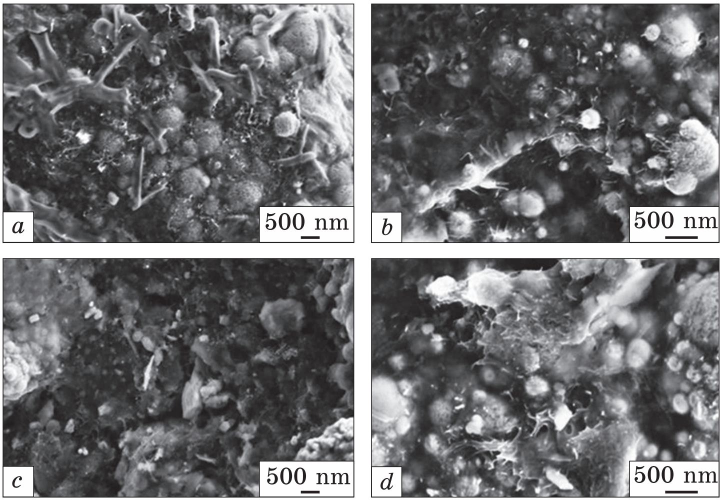

*Fig. 1*. FESEM images of NiP–MWCNT composite with varying MWCNT concentration: (*a*) 100, (*b*) 200, (*c*) 300 and (*d*) 400 mg/L [25]. The diagrams were reproduced with the permission from © Institute of Materials, Minerals and Mining, reprinted by permission of Informa UK Limited, trading as Taylor & Francis Group

the plating process, the carbon nanofibers were pre-treated in a bath containing cationic polymer with high molecular weight (poly (diallyl dimethylammonium chloride)) as the dispersing agent. The bath was agitated with ultrasonic waves followed by electrodeposition using the PR technique that enabled partial dissolution of the deposited metal. As found, the carbon nanofiber concentration improves substantially in the PR electrodeposition method. The microstructural studies of the composite also confirmed the co-existence of carbon nanofibers and Ni. The effectiveness of pulse-reverse electrodeposition for synthesizing metal–carbon fibre composites with higher fibre concentration was demonstrated in the study. Figure 1 shows the images that the reinforcement of MWCNT with the nickel matrix increases with the increase in the concentration of MWCNT in the electroless bath. This can be explained by the high binding energy and the affinity of MWCNT towards the nickel matrix for nucleation augmentation. The increased percentage of MWCNT is expected to improve the tribological properties of the metals [25].

Chen *et al*. [26] studied the preparation and deposition of Ni-carbon nanotube composite coatings on carbon steel substrate using the electrodeposition technique. The notable aspect of the study was the analysis of deposition for two forms of CNT, namely; (1) Ball milled short CNT and (2) Purified long CNT. Solutions of the saturated concentration of CNT were selected for their dispersion in the nickel bath. Results reveal that better dispersion is evident with shorter CNT; concentration of 1.2 g/L for unmilled CNT and 1.9 g/L for milled CNT of

10 hours deposition time is witnessed. The quantum of CNT deposition in the nickel matrix increases linearly with the increase in the bath concentration up to a certain limit beyond which the deposition rate becomes non-linear. The maximum CNT deposition rate was observed for the concentration of 1.9 g/L for short CNT and 1.1 g/L for long CNT. It was found that the CNT in the deposit was influenced by CNT concentration in the bath, agitation rate, particle surface charge, and current density. The current density highly influences the co-deposition rate of CNT due to the electrostatic attraction between the CNT and the cathode and the electrical conductivity of CNT. The maximum content of CNT is obtained at the current density of 3.0 A/dm$^2$ for short CNT and 2.4 A/dm$^2$ for long CNT. It was observed that an agitation rate of 150 rpm for short CNT and 120 rpm for long CNT resulted in higher CNT concentration on the deposit in the study.

Németh *et al.* [27] studied the formation of a proper coating on the surface of MWCNT for homogenous coverage using precursor compounds (titanium (IV) bromide and titanium (IV) chloride). The surface of CNT was coated under either solvent-free or solution conditions. The resulting material can be used in further processes, such as CNT-based polymer composites and photocatalytic reactions as CNT–$TiO_2$ composite catalysts. In this study, the sample was prepared with three kinds of solvent with a fixed concentration of MWCNT. Then precursors were added to the suspension, and the bath chemicals were sonicated for 1 hour. It was observed that the TiBr precursor has a higher affinity towards the MWCNT surfaces and produces homogeneous coverage of MWCNT surface regardless of the solvent used. This is relatively more significant than the result obtained with TiCl precursor.

CNT are often functionalized with various kinds of industrially significant polymers to enhance the properties of the end material. The full potential of CNT as reinforcements has been severely limited due to poor interfacial interaction, van der Waals interaction between CNT and polymer matrix. To overcome these shortcomings in utilizing the complete potential of CNT, researchers have been directed towards developing methods to modify the surface properties of CNT by functionalization. Carpenter *et al.* [28] studied the dispersion ability of CNT in the Watts nickel bath for electroplating. The CNT were functionalized with nitric acid prior to electroplating. Electrodeposition was carried out using pure nickel as an anode and mild steel as a cathode with continuous magnetic stirring. During electrodeposition, effective dispersion of CNT was witnessed at lower sonication, thereby improving the CNT content in the nickel matrix. It was observed that the functionalized CNT improved the homogeneity in the nickel coatings with less agglomeration for the electrodeposition process. On the other hand, the raw CNT is not uniformly distributed in the nickel due to agglomeration.

### 2.2. Metallization of CNT

The process of metallization has been witnessing burgeoning industrial interest in the last decade. As the incorporation of metallized powder-like particles into metals, alloys, ceramics, or plastics are known to increase their strength, microhardness, tribological properties significantly, wear resistance, temperature, and radiation stability, research efforts to channelize the process for property-specific applications are being encouraged. A new method for growing carbon nanotubes on a porous anodic aluminium oxide (AAO) template through the electrochemical process was proposed by Xu *et al*. [29]. Nickel was coated in a controlled manner in continuous layers on the well-aligned CNT structure that was grown on the AAO template. The coating was realized without any surface treatment of CNT as the deposition was carried out on AAO pores. The length, diameter, and thickness of nickel on nanowires are influenced by the size of the pores and its widening time. This method possibly will facilitate a new method to coat different alloys over the carbon nanotubes to the desired size and thickness.

Studies were carried out by Arai *et al*. [30] to prepare MWCNT–Ni composite powder by an electrodeposition technique. The MWCNT were dispersed in a dull Watt's bath solution containing polyacrylic acid (with a mean molecular weight of 5000) with continuous stirring to break the MWCNT cluster and maintain a consistent deposition process. The electrodeposition was carried out with pure nickel plate as an anodic substrate and pure copper plate as cathodic substrate at ≈300 K under galvanostatic conditions. The electrodeposits were separated from the cathode by ultrasonic irradiation in a bath containing acetone. The MWCNT–Ni composite was separated as powders in skewered dumpling-like structures with the MWCNT strongly bonded to the deposited Ni.

Sandeep Mani Tripathi *et al*. [31] reported the applications of metalized (iron nanoparticle coated) carbon nanotubes fabricated through RF-powered plasma enhanced chemical vapour deposition technique. The surface properties of the metal-coated and non-coated carbon nanotubes were compared by synthesizing field emitting transistors (FETs) whose dimensions are ranged in nanoscale. The investigations inferred that the metalized carbon nanotubes have reliable magnetic and electrical properties that are highly suitable for fabricating AFM tips, FETs, magnetic recording tapes, and current-carrying tubes.

### 2.3. Interfacial Bonding of CNT

A comparative analysis of interfacial bonding between CNT and CNT-based nickel matrix composite materials (Ni/SWCNT & Ni/MWCNT) fabricated through the electroplating method was performed by Sun *et al*. [32]. The analysis reports that the good reinforcement of CNT in the nickel phase is attributed to the good bonding at interfaces. The Ni/SWCNT has a very high tensile strength of 2 GPa and is higher than three times that of the nickel coatings. The mechanical strength of the Ni/CNT composite is predominantly due to the concentration of CNT in the nickel matrix. On the other hand, the magnitude of fracture strain of the composites shows a similar trend or sometimes better than that of the nickel coatings. The shreds of evidence of the study proved that the CNT are not deformed and are not separated easily from the nickel matrix due to their interfacial bonding strength.

## 2.4. Addition of Surfactants

Surfactants are surface-active agents. It is categorized by the presence of formally charged groups in its head. In general, there are two types, namely ionic and non-ionic surfactant. A non-ionic surfactant has no charged groups in its head. The head of the ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterion by Salager [33].

Xiaohua Chen *et al.* [34] proposed a surfactant employed method for depositing CNT/Ni–P composite over carbon steel substrate employing

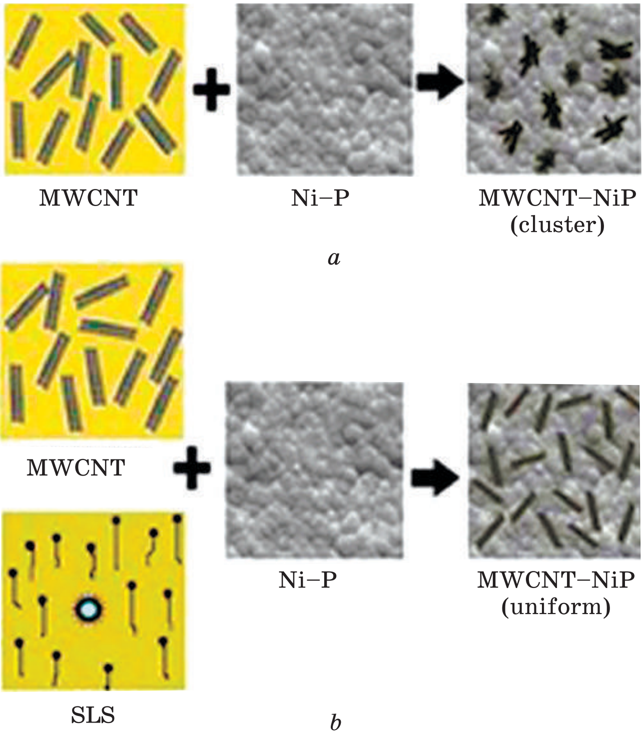

*Fig. 2.* Schematic representation of MWCNT reinforcement with nickel phase: (*a*) without surfactant; (*b*) with surfactant [25]. The diagrams were reproduced with the permission from © Institute of Materials, Minerals and Mining, reprinted by permission of Informa UK Limited, trading as Taylor & Francis Group

electroless nickel sulphate bath. The raw CNT are functionalized with a solution of 65% $HNO_3$ or HCl, followed by washing of the refluxed CNT to remove the impurities. The functionalized CNT have many side groups: a carbonyl group, O–H, and C–O bonds. These side groups impart hydrophilic properties to the CNT that aid to disperse directly in the solution with a negative charge. The addition of cationic surfactant (cetyltrimethyl ammonium bromide with the amidocyanogen group) imparts a positive charge over the CNT surface that enables reduction of the formation of CNT clusters. It was found that the microhardness of the CNT/Ni–P composite is 946 *HV* at 200 N loads; it is higher than that of the Ni–P and SiC–Ni–P composite. The friction coefficient of the CNT/Ni–P composite is comparatively lower (0.088) than the SiC–Ni–P composite and pure Ni–P. This improvement could be due to the uniformity in CNT distribution and their concentration in the nickel matrix. Figure 2 shows the formation of Ni–P–MWCNT composite coating (*a*) without the addition of surfactant, whereas the uniform distribution of MWCNT is achieved with the addition of surfactants (*b*) [25].

## 3. Properties of CNT-Based Composite Coatings

### 3.1. Electrochemical and Corrosion

Prasannakumar *et al.* [35] investigated the corrosion resistance of Ni–P/MWCNTs nanocomposite prepared through the electroless plating process. The CNT nanoparticles were ultrasonically dispersed in a separate bath and then loaded into the electroless nickel bath. The Ni–P–MWCNT composite was deposited on a steel rod with varying concentrations of CNT. A noteworthy improvement in the electrochemical resistance could be observed due to the formation of the effective protective coating by the homogeneous reinforcement of MWCNT in the nickel phase and having a good anti-corrosion coating for mild steel in flowing chloride media. This can be recommended for long-time flow applications due to its high resistance against the corrosive flow environment though care should be engaged at flow conditions above 240 rpm.

### 3.2. Strength and Hardness

Chen *et al.* [34] have proposed a method for fabricating Ni–P–CNT composite coatings. The Ni–P–SiC and Ni–P–graphite coatings are made on a medium carbon steel ring. The coating is prepared in two stages: first, the electroless Ni–P coating is achieved to a thickness of 5 µm, and secondly, the Ni–P–CNT composite layer is obtained by electroless plating to the thickness of 25 µm. Similar to the Ni–P–CNT composite deposition, Ni–P–SiC and Ni–P–graphite composite are obtained over the test ring. All samples are annealed at 473 K for 1 hour and 673 K for 2 hours to avoid hydrogen brittleness and improve microhardness. The microhardness of the Ni–P–SiC and Ni–P–CNT composites is increased by about two times at 673 K for 2 hours compared to the heat treatment process at 473 K for 1 hour, as shown in Table 3. The CNT volume fraction (5.3%) is lower than the SiC volume fraction (6.1%). The friction and wear properties had substantially improved, as shown in Table 4 [36–38].

The Ni–P–CNT composite has a very low mass loss and friction coefficient (0.063) compared with Ni–P, Ni–P–SiC, and Ni–P–graphite composite. The enhancement of the mechanical properties is attained due to the excellent lubrication and strength of CNT. Yang *et al.* [39] have studied the mechanical properties of the Ni/P/SWCNT composite prepared and deposited on a carbon steel substrate by employing sodium hypophosphite reduced electroless plating. Three levels of SWCNT concentration (1 g/L, 2.5 g/L, and 5 g/L) were taken for preparing the composite with a thickness of 25 μm. An ultrasonic agitator was integrated in the plating bath to obtain a uniform SWCNT dispersion in the solution. A huge number of nucleation augmentations of the nickel phase were developed. The SWCNT reinforces the matrix. The hardness of the composite is improved due to the formation of the crystalline region and $Ni_3P$ phase by annealing process (at 673 K and 773 K for

*Table 3.* **Microhardness of electroless composite coatings [35–38]**

| Electroless coating | At 473 K for 1 h | At 673 K for 2 h | Electroless coating | At 473 K for 1 h | At 673 K for 2 h |
|---|---|---|---|---|---|
| Ni–P | 467 | 860 | Ni–P–graphite | 472 | 980 |
| Ni–P–SiC | 550 | 1060 | Ni–P–CNT | 520 | 1035 |

*Table 4.* **Wear and friction properties [35–38]**

| Coating | Treated at 473 K for 1 h | |
|---|---|---|
| | Mass loss | Friction coefficient |
| Ni–P | 32.4 mg (100%) | 0.102 μ (100%) |
| Ni–P–SiC | 74% less that of Ni–P | 21% more that of Ni–P |
| Ni–P–graphite | 68% less that of Ni–P | 25% less that of Ni–P |
| Ni–P–CNT | 81% less that of Ni–P | 39% less that of Ni–P |
| | Treated at 473 K for 2 h | |
| | Mass loss | Friction coefficient |
| Ni–P | 15.6 mg (100%) | 0.090 μ (100%) |
| Ni–P–SiC | 78% less that of Ni–P | 0.2% more that of Ni–P |
| Ni–P–graphite | 73% less that of Ni–P | 26% less that of Ni–P |
| Ni–P–CNT | 84% less that of Ni–P | 33% less that of Ni–P |

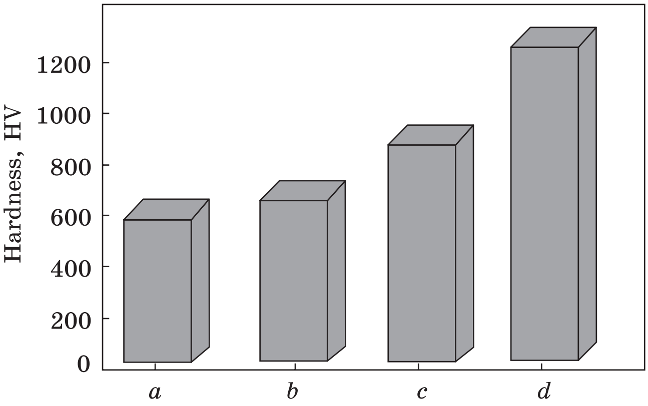

*Fig. 3*. Bar diagram represents the microhardness values of the composite coatings: (*a*) as prepared Ni–P coating; (*b*) as prepared Ni–P–CNT composite coatings; (*c*) Ni–P coating after heat treatment; (*d*) Ni–P–CNT composite coatings after heat treatment [40]

1 hour, respectively). The hardness value reaches about 1204 *HV* after annealing at the temperature of 673 K, beyond which the hardness value starts decreasing. This may be due to the formation of a cluster of SWCNT at higher concentrations. The measurement of the tribological properties was carried out under non-lubricated conditions. It was found that the friction and wear properties are significantly improved in comparison with Ni–P, as listed in Table 5.

Yang *et al*. [40] have investigated the microhardness and corrosion behaviour of electroless Ni–P–carbon nanotube composite material compared to Ni-P at a constant heat-treatment process. The microhardness of the composite was compared before and after the annealing process at 673 K temperature for 1 hour, and the results are represented in Fig. 3. The corrosion behaviour of CNT incorporated composite coatings is enhanced due to the poor chemical reactivity of CNT and by the formation of the passive film. Wu *et al*. [41] have studied the properties of Ni–Cu–P/CNTs quaternary composite fabricated on a carbon steel substrate through electroless plating technique. It was found that the hardness of the Ni–Cu–P/CNTs composite increased (1500 *HV*) after heat treatment process at 673 K for 1 hour (at hydrogen-free atmosphere) compared to the as-plated Ni–Cu–P composite (500 *HV*); in addition, properties of

*Table 5*. **Comparison of wear and friction properties of Ni/P coating and Ni/P/SWCNT composite coatings treated at 673 K for 1 hour [39]**

| | Wear volume | Friction coefficient |
|---|---|---|
| Substrate | $20.5\times10^{-4}$ mm$^3$ (100%) | 0.64 μ (100%) |
| Ni/P | 48% less that of Substrate | 13% less that of Substrate |
| Ni/P/1% SWCNT | 85% less that of Substrate | 61% less that of Substrate |
| Ni/P/2.5%SWCNT | 83% less that of Substrate | 58% less that of Substrate |
| Ni/P/5% SWCNT | 77% less that of Substrate | 50% less that of Substrate |

smoothness and corrosion resistance also show improvement. The heat treatment process yields improved hardness due to the formation of intermetallic phases such as $Ni_3P$ and $Cu_3P$ phases. However, the hardness has decreasing trend beyond the CNT concentration of 1.6 g/L, due to its conglomeration nature.

Arai *et al.* [42] have investigated the adhesion strength and frictional properties of Ni–P alloy/MWCNT composite deposited on acrylonitrile butadiene styrene (ABS) resin by the electroless plating technique. The composite was prepared with various forms of MWCNT (vapour-grown MWCNT, vapour-grown carbon fibres, and vapour-grown carbon nanofibers and varying phosphorus content). It was found that the adhesion strength between the resin and Ni–P alloy/MWCNT is higher than 1300 N $cm^{-2}$, and the coefficient of friction is much lower for phosphorus content of 12 mas.%. The authors recommend an electroless plating method for producing CNT-based metal composites (for insulators such as ceramics) by optimizing the MWCNT concentration and phosphorus content. Maqbool *et al.* [43] have studied the mechanical properties of Cu coated CNT reinforced aluminium matrix composite fabricated by an electroless plating process. The microhardness and tensile properties of the uncoated and Cu-coated CNT/Al composites were compared with pure Al. It was observed that the microhardness of the uncoated and Cu–CNT/Al composite had improved and was higher (44% for uncoated composite and 103% for Cu–CNT/Al composite) than the pure Al. The tensile strength of the uncoated composite and Cu–CNT/Al composite had also considerably improved, by 121% and 107%, respectively. Ma *et al.* [44] have examined the influence of the heat treatment process on Ni–P–SiC nanocomposites fabricated through electroless plating technique. For this analysis, four levels of temperature range were chosen with constant treatment time. The mean grain size of the Ni–P–SiC nanocomposite was determined to be 0.16 μm. The microhardness of the nanocomposite is increased to a maximum of 968.3 *HV* after heat treatment at 673 K due to the formation of the intermetallic layer and the homogeneous distribution of SiC particles in the nickel matrix. The corrosion current density of the composite sample is observed to be very low for samples heat-treated at 673 K.

### 3.3. Tribological Properties

Many researchers showed a great deal of interest in exploiting the exceptional mechanical properties of carbon nanotubes in electroless Ni–P coatings, as these materials revealed outstanding tribological behaviour when incorporated in the electrodeposition process. As a result, several experiments were conducted in attempts to co-deposit CNT in the electroless Ni–P matrix anticipating an enhancement in the wear and fric-

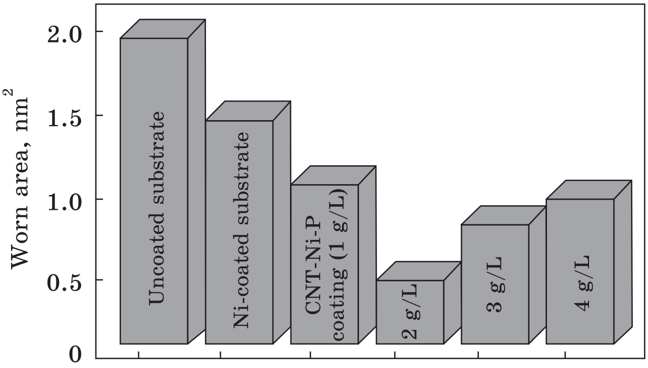

*Fig. 4*. Wear behaviour of various coated and uncoated substrates [48]

tion behaviour. This part highlights the studies carried out to improve the tribological characteristics of electroless Ni–P–CNT coatings.

Wang *et al*. [45] have investigated the nickel-based carbon nanotubes coated using the electroless method on medium carbon steel for varying concentrations of CNT (volume fraction range: 5–12%). The friction and wear properties were assessed employing a pin-on-disc instrument for a sliding speed of 0.0623 $m \cdot s^{-1}$ under a normal load of 20 N in an unlubricated condition. The friction and wear behaviour of the Ni-based CNT composite were compared with respect to the various level of the volume fraction of CNT. The wear rate of the composite decreases steadily with an increasing CNT volume fraction up to 11.2%. Beyond this level of CNT concentration, the wear rate increases. Furthermore, the microstructure of the worn surface has to crack and spall for the higher volume fraction of CNT during the wear test, which is attributed to the higher volume fraction of CNT creating agglomeration in the reinforcement.

A new method of preparing Ni–P–carbon nanotube and carbon nanotube/copper matrix composite through electroless plating and powder metallurgy technique was proposed by Chen *et al*. [46]. The Ni–P–CNT composites exhibit a very low friction coefficient and higher wear resistance as compared to Ni–P–SiC and Ni–P–graphite. The heat treatment of the Ni–P–CNT composite was carried out at 476 K for 2 hours in order to develop the crystalline structure and the $NiP_3$ forms in the nickel phase. A similar study to understand the wear behaviour of Ni/CNT composite deposited on a carbon steel plate through electroless

*Table 6*. **Depth of worn scar of coatings [47]**

| Coatings | Depth | Coatings | Depth |
|---|---|---|---|
| Ni<br>Ni/SiC | 17.4 μm (100%)<br>36% less that of Ni | Ni/graphite<br>Ni/CNT | 22% less that of Ni<br>63% less that of Ni |

deposition was performed by Chen *et al.* [47]. Hardness tests revealed a higher value of 865 *HV* of Ni/CNT than that of SiC and graphite-reinforced nickel composite. The wear scar analysis supports the trend observed by wear resistance values affected by the CNT present in the nickel matrix, as shown in Table 6. Overall, a reasonable improvement in the wear resistance and a lower coefficient of friction of the Ni/CNT composite is observed due to the excellent mechanical and self-lubricating nature of CNT in the nickel matrix.

Li *et al.* [48] performed a comparative analysis of the wear behaviour of the CNT–Ni–P composite prepared with different concentrations of CNT content. The composite was deposited on a steel grade of 45# through the electroless plating technique. The composite was annealed at 673 K for reducing the hydrogen brittleness before wear analysis. The wear of CNT–Ni–P composite with varying CNT concentration from 1 g/L to 4 g/L is represented in the bar chart in Fig. 4. As found, the optimum concentration of the CNT in the electroless bath is 2 g/L.

The wear rate of all CNT incorporated samples is much lower compared to that of nickel coatings, and the friction coefficient decreased with increasing applied load and duration of the experiment run. Alishahi *et al.* [49] examined the effect of reinforcement of CNT in the nickel phase with respect to the corrosion and tribological properties. The Ni–P–CNT composite and Ni–P coatings were fabricated on a copper substrate through the electroless plating technique. It was found that the corrosion and tribological properties of Ni–P–CNT composite noticeably improved (particularly for CNT concentration of 2 g/L) than that of Ni–P coatings. In addition, annealing (at 673 K for 2 hours) of Ni–P–CNT composite developed an intermetallic phase and a nanocrystalline structure. The tribological behaviour of composite fabricated with the components of Ag and CNT was investigated [50]. The fabrication process comprised of two segments: deposition of CNT on a silicon wafer by spin-coating, and then, the Ag particles were deposited over the CNT coated wafer by electroless plating. It was observed that the dual-layer Ag–CNT composite (with 65 nm Ag thickness) shows a significant reduction (10 times smaller than pure CNT coating) of wear rate at 10 mN of the applied load. It was found that the friction coefficient is very low in the range of 0.65–0.73 for pure CNT coated and Ag–CNT composite regardless of the magnitude of applied load (10–30 mN).

### 3.4. Magnetism and Microwave Absorbing Properties

An attempt by Arai *et al.* [51] to comparatively study the magnetic properties of Ni–P–MWCNT composite, and pure-nickel-coated multi-walled carbon nanotubes fabricated through electroless deposition method revealed that the microstructure of the pure nickel-coated MWCNT

*Table 7.* **Recent developments in the CNT/composite coating with electro deposition and electroless [53]**

| Electro deposition | | | |
|---|---|---|---|
| Metal–CNT | Pre-treatment of CNT | Surfactant | Year & Ref. |
| Ni–MWCNT | Chemical treatment | Sodium lauryl sulphate | 2020 [54] |
| Ni–MWCNT | Wrapped by polydopamine | – | 2019 [55] |
| Ni–Co/MWCNT | Chemical treatment | – | 2019 [56] |
| Cu/MWCNT | Chemical treatment | – | 2021 [57] |
| Cu/MWCNT | Chemical treatment | – | 2020 [58] |
| Cu/MWCNT | – | Stearyltrimethylammonium chloride | 2020 [59] |
| Cu/MWCNT | – | Sodium lauryl sulphate | 2019 [60] |
| Cu/MWCNT | – | Polyacrylic acid | 2019 [61] |
| Zn/MWCNT | Chemical treatment | Cetyltrimethylammonium bromide | 2021 [62] |
| Cr/MWCNT | – | Sodium lauryl sulphate | 2020 [63] |
| Ag/MWCNT | – | Poly (N-vinyl pyrrolidone) | 2021 [64] |
| Al/MWCNT | Acid treatment | – | 2020 [65] |
| Electroless deposition | | | |
| Ni–P/MWCNT | – | Sodium lauryl sulphate | 2021 [66] |
| Ni–P/MWCNT | $Sn^{2+}$ sensitization + $Pd^{2+}$ activation | – | 2020 [67] |
| Ni–P/MWCNT | Introduction of COOH on CNT + $Pd^{2+}$ | – | 2020 [68] |

deposit is comparatively less smooth than that of the Ni–P–MWCNT composite. Moreover, the former coating had higher magnetization and coercivity. The surface smoothness of the pure-nickel coating also improved due to the heat-treatment process. Park *et al.* [52] studied the microwave absorption properties of hybrid composites made with Ni and Fe coating on the carbon nanofibers. The hybrid composites (Ni–Fe coated carbon nanofiber composite) were successfully prepared by electroless plating at controlled bath conditions. The results of the microwave absorption behaviour at standard testing conditions showed that the hybrid composites showed about 26% improvement over the dielectric composites.

## 4. Recent Developments

In this section, the most recent developments are described/tabulated in Table 7. The developments focus on the composite plating by electrodeposition and electroless deposition; in this composite plating, homogeneous dispersion of CNT in plating baths is crucial and, subsequently, various processes, such as the addition of dispersants and introduction of hydrophilic groups (surfactants) on CNT, have been studied in detail in the reference cited in Table 7. Numerous articles on Ni/CNT or Ni–P alloy/CNT composites by composite plating have been published, wherein outstanding tribological properties and superior corrosion resistance have been reported to be observed. Further, the Cu/CNT composites have also been investigated, and their properties, such as electrical conductivity, have been researched etc. (for instance, Cr, Co, Al). A detailed understanding of the mechanism of the CNT composite plating process is crucial for diversifying the applications of CNT by studying more combinations in the near future.

The presence of any amount of macroscopic (curvature, twist and heterojunction kink) and atomic scale (vacancies, impurities, perturbation and Stone–Wales) defects in CNT can be aimed to modify drastically different properties of these nanosystems [69, 70] as well as other carbon-based quasi-two-dimensional materials [71–76].

## 5. Conclusions

This review has aimed to give a broad spectrum of surface-coated CNTs applications in various fields. These coatings may offer an imperative technology platform for enhanced protective systems in an environment demanding a superior behavioural response. Despite the researchers' burgeoning interest in working on CNT-based coatings, the feasibility of applying these coatings to the commercial level is a challenge. However, the unique structure and excellent mechanical properties of CNT have roused the curiosity of the scientific community, driving them to explore the complete potential of CNT in the coating industry. It is envisaged that CNT can become a vital ingredient to the future world of coatings.

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*А. Сельвакумар*[1], *У. Санджіт*[2,3], *Т.Р. Таміларасан*[4],
*Р. Мураліраджа*[5], *В. Ша*[6], *Й. Судаґар*[7]

[1] Інститут технології моди, Технологічний інститут Веллора,
Ченаї, Таміл Наду, Індія
[2] Кафедра машинобудування, Інститут науки і технології
Абдура Рахмана Кресент, Ченаї, Таміл Наду, Індія
[3] Центр досліджень і технологій стійких матеріалів,
Школа матеріялознавства та інженерії, Сідней, Австралія
[4] Кафедра автомобільної техніки, Інститут науки і технології
Абдура Рахмана Кресент, Ченаї, Таміл Наду, Індія
[5] Кафедра машинобудування,
Інститут наукових технологій та передових досліджень
Велса, Ченаї, Таміл Наду, Індія
[6] Школа природнього та штучного середовища,
Університет королеви Белфаста, Північна Ірландія, Великобританія
[7] Кафедра фізики, Школа передових наук, Університет ВІТ-АП,
поблизу Віджаявади, Андхра-Прадеш, Індія

## КРИТИЧНИЙ ОГЛЯД ПОВЕРХНЕВИХ ПОКРИТТІВ НА ОСНОВІ КАРБОНОВИХ НАНОТРУБОК

Поява карбонових нанотрубок (КНТ) викликала широкий інтерес серед дослідників; багато новаторських застосувань було досягнуто завдяки використанню унікальних властивостей вуглецевих алотропів. Ця стаття є загальним оглядом різноманітності застосувань КНТ та їхніх різноманітних форм, зокрема, в області поверхневих покриттів. З'ясовуються різні методи, які були розроблені та застосовувані для одержання, дисперґування, функціоналізації та металізації КНТ. Композитні покриття виготовлені з використанням електрохімічних методів, таких як ґальванічне (електроосадженням) та хімічне покриття. В огляді представлено механічні, електрохімічні, корозійні, теплові, електропровідні, трибологічні, біосенсорні, магнетні та мікрохвильові поглинальні властивості композитів на основі КНТ. Втілення КНТ істотно впливає на продуктивність покриття, а рівень впливу можна реґулювати відповідно до потреб застосування. Для цих покриттів було проведено різноманітні дослідження характеристик, що підкреслюють їхні властивості. Потенціал КНТ як універсального матеріялу для різноманітних промислових застосувань поставив вуглецеві алотропи в елітну групу матеріялів, привернувши увагу дослідників до розширення сфери їхнього використання. У цьому огляді також розглядаються виклики, проблеми та шляхи їх подолання.

**Ключові слова:** карбонова нанотрубка, електролітичне осадження, неелектролітичне осадження, композитне покриття, поверхнева шерсткість, механічні властивості, зношення, корозія