Vietnam Journal of Science and Technology ***56*** *(3B) (2018) 144-151*

NICKEL-BASED MULTIWALLED CARBON NANOTUBE COMPOSITE COATINGS

Bui Hung Thang[1, *], Nguyen Xuan Toan[3], Nguyen Viet Phuong[1], Tran Van Hau[1], Nguyen Thi Hong[4], Nguyen Ngoc Trac[4], Vu Dinh Lam[1, 3], and Phan Ngoc Minh[1, 2, 3, *]

[1]*Institute of Materials Sciences, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

[2]*Center for High Technology Development, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

[3]*Graduate University of Science and Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

[4]*Hue Industrial College, Ministry of Industry and Trade, 70 Nguyen Hue Street, Hue City*

[*]Email: *thangbh@ims.vast.vn, pnminh@vast.vn*

Received: 12 July 2018; Accepted for publication: 7 September 2018

ABSTRACT

Carbon nanotubes (CNTs) have been widely known as nanomaterials with excellent mechanical properties. Previous studies reported that the tensile strength of multi-walled carbon nanotubes (MWCNTs) was up to 63 GPa and single-walled carbon nanotubes (SWCNTs) could reach 150 GPa while the highest tensile strength of the steel was found to be about 1.8 GPa. SWCNTs could have Young's modulus up to 1000 GPa that was much greater than the value of 209 GPa of steel. Therefore, there is a great potential to utilize CNTs as reinforced materials for composites in general and Ni electrodeposition coating in particular to improve hardness, durability, corrosion, and other physical and mechanical properties. This paper presents results of preparing and examining characteristics of the Nickel electrodeposition coatings containing MWCNTs (Ni-MWCNTs). The Ni-MWCNTs composite coatings deposited on a steel plate with the area of 0.4 dm^2 using bipolar pulses at 470 Hz and 50^oC in a 5-liter bath. Amount of CNTs varying from 1 g/l to 3 g/l was dispersed into the solution by using surfactants and ultrasonic vibration. CNTs used in the study was MWCNTs diameters in the range from 20 to 90 nanometers and few micrometers in length. The SEM, EDS, hardness and adhesion tests were conducted to analyze the properties of the electrodeposition coatings. The obtained results indicated that the hardness and adhesion of the Ni-CNTs coating were 1.5 and 1.46 times, respectively, higher than those of the Ni coating. In addition, adhesion of the Ni-CNTs coating was significantly improved.

Keywords: electrodeposition, Nickel, reinforcement, carbon nanotubes, CNTs.

1. INTRODUCTION

The aim of preparing composite coatings on the substrates is to protect the materials from corrosion and enhance the surface properties. There are several methods to prepare composite coatings such as chemical vapor deposition, physical vapor deposition, laser melt injection, and electrodeposition. In these methods, electrodeposition has been most widely used because of its simplicity and economic efficiency.

In order to enhance physical and mechanical properties including micro-hardness, corrosion resistance, adhesion as well as to improve other properties of the electrodeposition coatings, reinforced materials of SiC, Al_2O_3, or graphene with the grain size of μm have been employed in the electrodeposition process. Many studies demonstrated that physical and mechanical properties of the electrodeposition coatings were markedly improved by the presence of small reinforced grains, especially grain size of nm [1-5]. With outstanding characteristics required for anticorrosion coatings such as low density, high tensile strength, and the greatest durability, the diameter of less than 100 nm, etc. [6-8], carbon nanotubes (CNTs) are potential reinforcement materials for the composite electroplating technology in order to enhance the properties of electrodeposition coatings [9, 10].

The advantages of the pulse reverse current technique in electrodeposition have been investigated in the studies of Chandrasekar et al. [11], Pavithra et al. [12], and William Arnulfo et al. [13]. The coatings obtained by the pulse reverse current technique showed a decrease in the grain size and a more uniformity in the deposit thickness compared to the coatings prepared by the direct current technique.

Therefore, this paper presents results of studies of the Nickel electrodeposition coating containing CNTs (Ni-CNTs) on the steel plate produced by a pulse reverse electrodeposition method.

2. EXPERIMENT

Carbon nanotubes with diameters varying from 20 to 90 nanometers and few micrometers in length produced by the thermal-CVD method at Institute of Materials Science [14] were used as reinforcement materials for Nickel-CNTs electrodeposition coatings.

Schematic diagram of experimental setup used for electrodeposition process is shown in Figure 1. The electrodeposition system includes a Watts bath placed on a magnetic stirrer and a pulse generator [15].

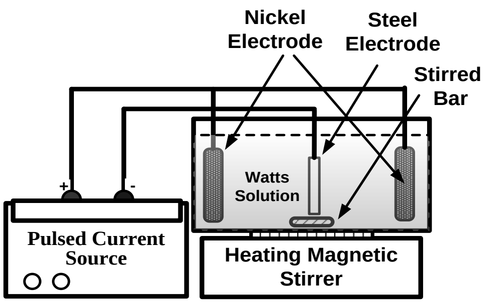

Figure 1. Schematic diagram of the electrodeposition system.

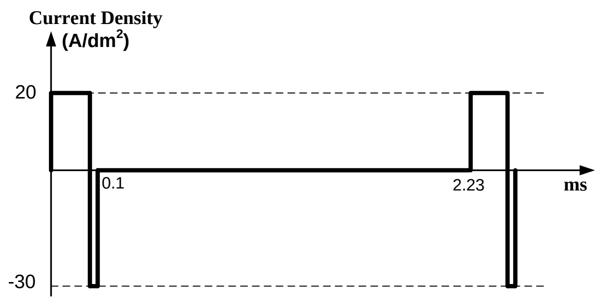

Figure 2. Bipolar pulses used in the electrodeposition process.

The generator was adjusted to supply 470-hertz bipolar pulses throughout the electrodeposition process with positive pulse current density set to 20 A/dm^2 for 0.08 ms, negative pulse current density set to -30 A/dm^2 for 0.02 ms and zero current density set for 2.03 ms (Figure 2).

Cathode was a steel plate with an area of (5 × 4) cm^2. In order to improve quality of the coating, two Nickel plates (99.9 %) located on either side of the cathode were used as anode.

The homogeneous Watts solution used in the electrodeposition process was contained in the bath with volume of 3 liters and consisted of the following components:

300 g/l Nickel sulfate, $NiSO_4.6H_2O$

50 g/l Nickel chloride, $NiCl_2.6H_2O$

40 g/l Boric acid, H_3BO_3 [16].

Amount of CNTs in the range from 1 g/l to 3 g/l was examined in this study. Before added into the Watts solution, CNTs were functionalized with Azo group and treated by DBSA surfactant. The temperature and pH of the electroplating solution were maintained at 30 °C and 4.5, respectively. During the process, the Watts solution was stirred by a magnetic stirrer at the speed of 6.5 rps.

3. RESULTS AND DISCUSSION

3.1. Coating structure

Figure 3 is the SEM image of CNTs used in this study. Figure 3 shows that CNTs had a fairly uniform diameter with an average value of 50 nm.

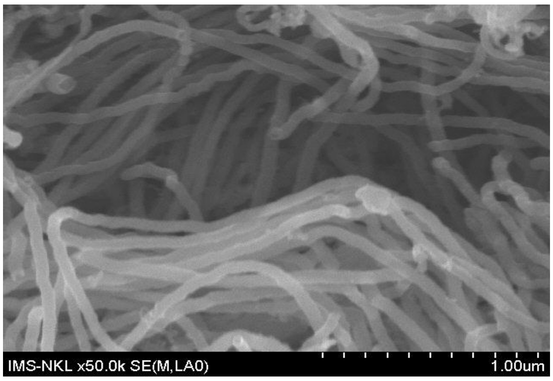

Figure 3. The SEM image of CNTs.

SEM micrograph from the surface of the pure nickel coating is presented in Figure 4. Particles of the Ni coating are uneven in size and dramatically varies from 100 nm to 500 nm. The large and uneven grain size may make a negative impact on mechanical properties of the coating.

Figure 5 represents a SEM image of the Ni-CNTs composite coating with concentration of CNTs 3 g/l in the Watts solution. Due to the presence of CNTs, the grain size of the Ni-CNTs composite coating is more uniform than that of the Ni coating using similar electrodeposition parameters. The diameter of the grain is in the range from 300 nm to 500 nm and CNTs is exposed on the coating surface.

The cross-sectional images of Ni and Ni-CNTs composite coatings are illustrated on Figure 6. The result indicates that coating thickness is about 45 µm. Therefore, the thickness of Ni and Ni-CNTs composite coatings using similar electrodeposition conditions are equivalent.

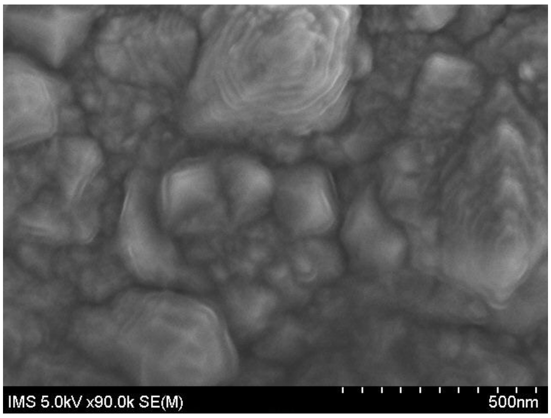

Figure 4. The SEM image of the Ni coating.

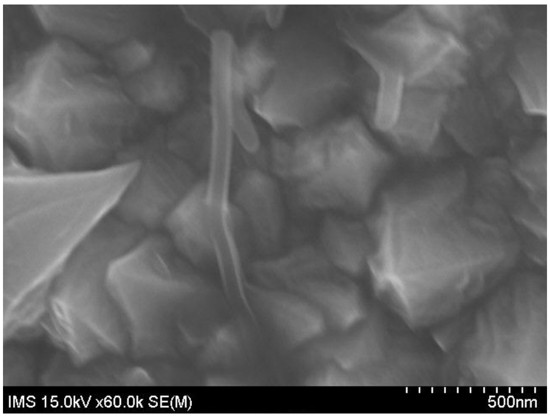

Figure 5. The SEM image of the Ni-CNTs coating.

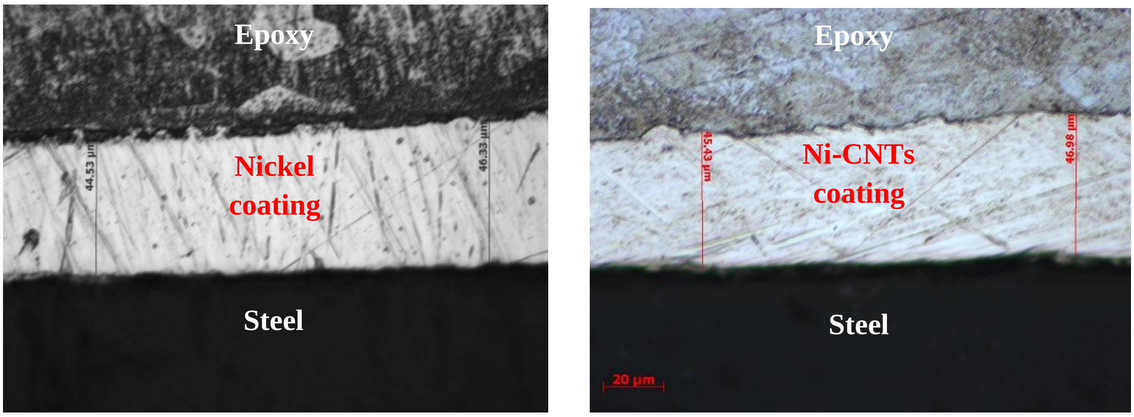

Figure 6. The cross-sectional images of Ni (a) and Ni-CNTs (b) coatings.

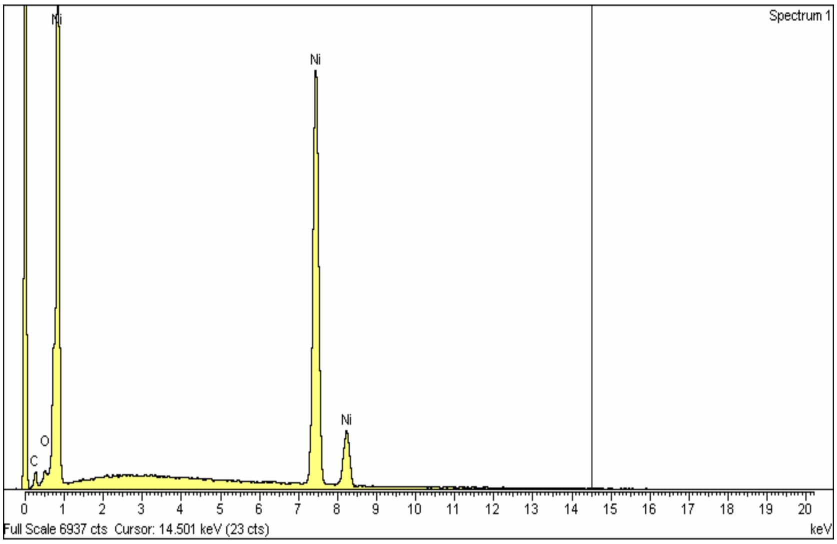

Figure 7. The EDS results of the Ni-CNTs electrodeposition coating with 3 g/l CNTs in the Watts solution.

3.2. Chemical component of the coatings

Energy dispersive spectroscopy (EDS) analysis was applied to examine and confirm the presence of CNTs in the Ni-CNTs composite coatings. The EDS results of the Ni-CNTs electrodeposition coating shows signature of C, O, and Ni peaks as illustrated on Figure 7.

The detailed weight percentage of elements of the Ni-CNTs electrodeposition coating is presented on the Table 1. The result shows that carbon content is 5.51 %wt in the Ni coating and 9.19 %wt in the Ni-CNTs coating with 3 g/l CNTs in the Watts solution. With similar electrodeposition parameters, hence, the significant increase of carbon content in the electrodeposition coating led by the presence of CNTs in the Watts solution contributes to confirm dispersion of CNTs into the Ni-CNTs coating.

Table 1. The detailed percentage of elements of the electrodeposition coating.

Element	**Ni coating (weight %)**	**Ni-CNTs coating (weight %)**
C	5.51	9.19
O	1.19	1.96
Ni	93.30	88.95
Total	100.00	100.00

3.3. Hardness

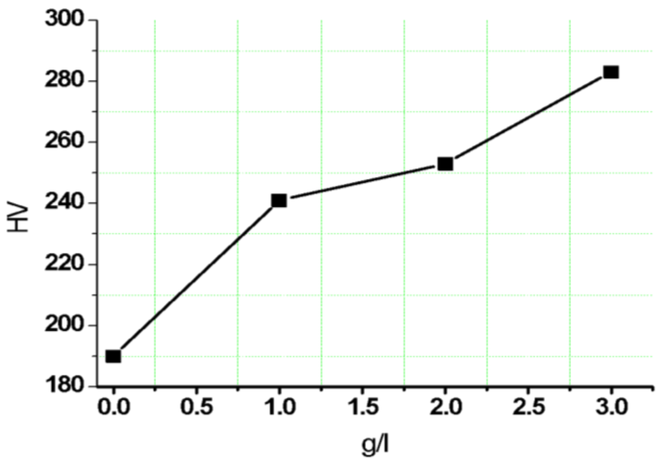

Figure 8. The hardness of the Ni-CNTs coating.

The hardness of the Ni-CNTs electrodeposition coating was determined by using Shimadzu Micro Hardness Tester. Figure 8 shows the measurement result of hardness as a function of CNTs concentration in the electroplating solution. The result indicates that the hardness increases with the increase of the CNTs content in the Watts solution: approximate 190 HV with 0 g/l CNTs (the Ni coating), approximate 241 HV with 1 g/l CNTs, and 283 HV with 3 g/l CNTs. In the other word, the hardness of the Ni-CNTs coating is 1.5 times higher than that of the Ni coating. This demonstrates the presence of CNTs with excellent characteristics plays an important role in enhancing the hardness of the electrodeposition coating.

3.4. Adhesion

Pull-Off Adhesion is a common and effective method to evaluate adhesive ability of the coating. In this method, a specialized glue was used to stick a plate with a certain area on the prepared coating. An increasing force is applied to pull the coating off the surface. The adhesion of the coating is determined by using the following equation:

$$K = \frac{F}{S} \tag{1}$$

with: K is adhesion (Pa); F is the force at the coating off the surface (N); S is the area of the plate (m^2).

Table 2. The measured values of adhesion of the Ni and Ni-CNTs coatings.

Parameter	**Ni coating**	**Ni-CNTs coating**
Area (S)	6.36×10^{-5} m^{-2}	6.36×10^{-5} m^{-2}
Force (F)	15.11 N	22.05 N
Adhesion (K)	0.237 MPa	0.346 MPa

The measurement results are shown on the Table 2. By using a plate with area equal to 6.36×10^{-5} m^2, the measured values of adhesion of the Ni and Ni-CNTs coatings were 0.237 MPa and 0.346 MPa, respectively. This indicates that adhesive ability of the Ni-CNTs electrodeposition coating is 1.46 times higher than that of the Ni coating.

3.5. Corrosion resistance

Ni-CNTs

Ni

Figure 9. The variation of the corrosion potential with time.

Corrosion resistance of the prepared coatings was estimated by examining the variation of the corrosion potential as a function of time. The corrosion potential was conducted in the 5 %wt NaCl solution for 5 days. The obtained results show that the corrosion potential of the Ni-CNTs coating is always higher than that of the Ni coating as shown on Figure 9. Therefore, the Ni-CNTs composite coating has better corrosion resistance than the nickel coating.

4. CONCLUSIONS

The SEM and EDS results confirmed the presence of CNTs in the Ni-CNTs electrodeposition coating. The fine and uniform grain size as well as the presence of CNTs in the electrodeposition coating improved the mechanical properties of the Ni-CNTs coating compared to the Ni coating. The measurement results showed that the hardness and adhesion of the Ni-CNTs coating is 1.5 and 1.46 times, respectively, higher than those of the Ni coating. The study also presented that the Ni-CNTs composite coating has better corrosion resistance than that of the nickel coating. The obtained results has significantly contributed to affirm the great potential application of carbon nanotubes in the composite electroplating technology in order to create coatings with hardness, adhesion, and corrosion resistance reinforced.

Acknowledgements. Authors would like to thank the financial support from FIRST under Subproject "Research on the application of carbon nanomaterials for improving the mechanical properties of industrial electroplating".

REFERENCES

1. He P., Huang S., Wang H., Huang Z., Hu J., Cheng X., Pan C. - Electroless nickel-phosphorus plating on silicon carbide particles for metal matrix composites. Ceramics International **40** (10 B) (2014) 16653-16664.
2. Sun X. J., Li J. G. - Friction and Wear Properties of Electrodeposited Nickel–Titania Nanocomposite Coatings. Tribology Letters **28** (3) (2007) 223-228.
3. Singh R., Kumar D., Tripathi C. C. - Graphene: Potential Material for Nanoelectronics Applications. Indian Journal of Pure and Applied Physics (53) (2015) 501-513.
4. Kiran N. U., Dey S., Singh B. P., Besra L. - Graphene Coating on Copper by Electrophoretic Deposition for Corrosion Prevention. Coatings **7** (12) (2017) 214.
5. Szeptycka B., Midzialek A. G., Babul T. - Electrodeposition and Corrosion Resistance of Ni-Graphene Composite Coatings. Journal of Materials Engineering and Performance **25** (8) (2016) 3134-3138.
6. Yu M. F., Lourie O., Dyer M. J., Moloni K., Kelly T. F., Ruoff R. S. - Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes under Tensile Load. Science **287** (2009) 637-640.
7. Coleman J. N., Khan U., Gun'ko Y. K. - Mechanical Reinforcement of Polymers Using Carbon Nanotubes. Advanced materials **18** (6) (2006) 689-706.
8. Collins P. G., Avouris P. - Nanotubes for Electronics. Scientific American, (December, 2000), 62-69.
9. Zhao G., Deng F. - Electroless Plating of Ni-P-CNTs Composite Coating. Key Engineering Materials **280-283** (2007) 1445-1448.
10. Tan J., Yu. T., Xu B., Yao Q. - Microstructure and Wear Resistance of Nickel–Carbon Nanotube Composite Coating from Brush Plating Technique. Tribology Letters **21** (2) (2006) 107-111.
11. Chandrasekar M. S., Pushpavanam M. - Pulse and pulse reverse plating - Conceptual, advantages and applications. Electrochimica Acta **53** (8) (2008) 3313-3322.

12. Pavithra C. L. P., Sarada B. V., Rajulapati K. V., Rao T. N., and Sundararajan G. - Process Optimization for Pulse Reverse Electrodeposition of Graphene-Reinforced Copper Nanocomposites. Materials and Manufacturing Processes **31** (11) (2016) 1439-1446.
13. Aperador C., William A., Lopez E. V. - Electrodeposition of nickel plates on copper substrates using PC and PRC. Revista Matéria **12** (4) (2007) 583 – 588.
14. Dung N. D., Chuc N. V., Tam N. T. T., Quang N. H., Khoi P. H. and Minh P. N. - Carbon-Nanotube Growth over Iron Nano particles Formed on CaCO3 Support by Using Hydrogen Reduction. Journal of the Korean Physical Society **52** (5) (2008) 1372-1377.
15. Mimani T., Mayanna S. M., Munichandraiah N. - Influence of Additives on the Electrodeposition of Nickel from a Watts Bath: a Cyclic Voltammetric Study. Journal of Applied Electrochemistry **23** (4) (1993) 339-345.
16. Wang Q. F., Zhang P. C., Wang X. H., Ren D. P., Lang D. M., Zhang Y. Z. - Microstructure of Nanocrystalline Nickel Deposit Pulse-plated on Depleted Uranium Surface. Journal of Metastable and Nanocrystalline Material **23** (2005) 191-194.