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High Hardness Nickel - Carbon Nanotubes Composite Electroplating

Bui Hung Thang[1*], Nguyen Xuan Toan[1] and Phan Ngoc Minh[1,2,3]

[1]Institute of Materials Science (IMS), Vietnam Academy of Science and Technology (VAST), A2 Building, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi 122102, Vietnam.
[2]Graduate University of Science and Technology (GUST), Vietnam Academy of Science and Technology (VAST), A2 Building, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi 122102, Vietnam.
[3]Center for High Technology Development (HTD), Vietnam Academy of Science and Technology (VAST), A2 Building, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi 122102, Vietnam.

Authors' contributions

This work was carried out in collaboration between all authors. Author NXT managed the literature searches and designed the study. Author BHT performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author PNM managed the analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

In this paper we present some results on making Ni/CNTs composite by electroplating technique. The work aims to create an advanced nano-composite coating surfaces by taking superior mechanical properties of the CNTs. The Watts solution was used for nickel plating experiments. We utilized two different methods to disperse CNTs in the Watts solution. In the first method, CNTs were mixed in the Watts solution by ultrasonication. In the second one, the CNTs were chemically functionalized by using diazo coupling reaction in sulfanilic acid ($NH_2C_6H_4SO_3H$) and nitrous acid (HNO_2) before mixing in the Watts solution. In order to investigate the role of CNTs additives in coating, nickel was plated onto copper substrates with and without CNTs additives. The Vickers hardness of coatings was measured by Shimadzu Micro Hardness Tester.

**Corresponding author: E-mail: thangbh@ims.vast.vn; thangbh@ims.vast.ac.vn;*

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1. INTRODUCTION

Electroplating involves the coating of an electrically conductive object with a layer of metal by using electrical current through electrolyte solution [1]. In order to satisfy wear resistance and intensify hardness of coating, the electroplating technology with micro/nano size materials such as SiC, Al_2O_3 and carbon powders were utilized. Many researches showed that the coatings have better mechanical properties by adding the smaller and harder nanoparticles [2-3].

Carbon nanotubes (CNTs) were known as one of the strongest materials, both in terms of tensile strength and elastic modulus [4-5]. These special properties of the CNTs are opened a promising way to make Ni/CNTs composite electroplating [6-8]. C.K. Lee et al. [6] indicated that hardness of the Ni–CNTs composite coatings increased when CNTs concentration in the electrolyte increased. The hardness of the specimen that was treated with 30 g/l CNTs was 98.5% higher than that of the pure Ni coating [6]. A. Zhonglie et al. [7] also showed that the hardness of the Ni/CNTs coating increased 1.4 times by adding 2.4% CNTs content. In order to disperse CNTs in the Watts bath, all these studies used surfactants instead of functionalized CNTs, such as sodium dodecyl sulfate (SDS) or poly(diallyldimethylammonium chloride) (PDDA). In this paper, we present a new method for making Nickel/CNTs (Ni/CNTs) composite electroplating by using ultrasonication and chemically functionalized CNTs.

2. MATERIALS AND METHODS

CNTs were produced at the Vietnam Academy of Science and Technology by using the thermal chemical vapor deposition (CVD) method. In this method, we used iron nanoparticles formed on $CaCO_3$ support as catalyst and substrate that was placed in a thermal CVD system in a gas mixture of acetylene, hydrogen and nitrogen [9].

The electroplating system was showed in Fig. 1. It consisted of a computer connected to an Aligent E3640A power supply by RS-232 connection, and the Watts bath was put on a heating magnetic stirrer. The anode was nickel bar and cathode was copper substrate. In order to control and investigate the influence of plating parameters in the electroplating process, we have programmed a software to control the Aligent E3640A by Visual Basic language. The system can work in some modes such as constant current, constant voltage, pulsed current and pulsed voltage.

To improve the quality of the coating, CNTs must be good dispersion in the electroplating solution. We used both physical and chemical methods to disperse CNTs in the Watts bath. In the physical method, we put CNTs into the Watt bath, then used ultrasonic vibration for 6 hours in order to get the good dispersion of CNTs in the Watt bath. In the chemical method, we used diazo coupling reaction by the following steps:

- Step 1: Dispersing CNTs into HNO_3 solution
- Step 2: Ultrasonication solution in 30 minutes to make defect on CNTs
- Step 3: Filter CNTs from HNO_3 solution
- Step 4: Dispersing CNTs into sufanilic acid ($NH_2C_6H_4SO_3H$) solution at 70^oC
- Step 5: Drop $NaNO_2$ into solution obtained in step 4
- Step 6: Filter and dry CNTs from solution obtained in step 5
- Step 7: Dispersing CNTs into Watts bath by using ultrasonication in 30 minutes.

We found that CNTs were functionalized by the steps above, the CNTs have a better ability to disperse in the plating solution. This can be explained by following reasons: after diazo coupling reaction, the CNTs are remained functional groups of -N=N-C_6H_4-SO_3Na. These functional groups will be dissociated in the plating solution, this leads to CNTs are charged with the same electrical charge, and they will generate propulsive Coulomb force between each other.

We employed Watts solution for nickel electroplating experiments. A standard solution contained: [10]

- 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

The volume of Watts bath was 1 liter with a pH of 4.5. The temperature of Watts bath was kept at 50°C. We used 10 Hz pulse for all plating

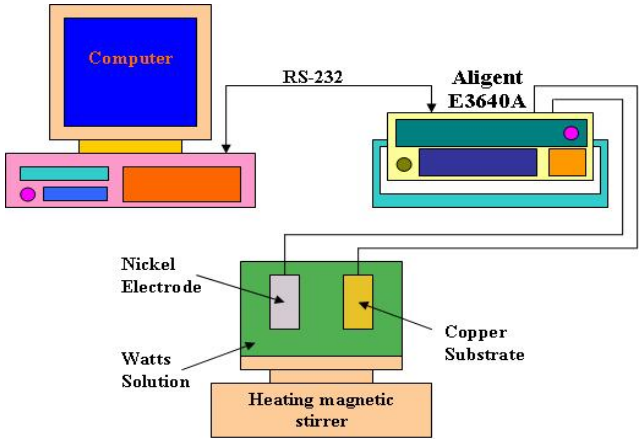

Fig. 1. Diagram of the Ni/CNTs electroplating system

process in the experiment, therein duty cycle for pulsed7 current is 50%, high current density was 15A/dm^2 and low current density was zero. The Watts bath was stirred at 6.5 rps of rotation speed. The plating process with CNTs additives was done using the same conditions above with 5g/l of CNTs-concentration in Watt bath.

3. RESULTS AND DISCUSSION

Fig. 2 is the SEM image of the normal Ni electroplating surface. It is seen that the size of crystal particles of the electroplating layer is relatively large and heterogenous, ranging from 200 nm to 500 nm. Fig. 3 is the SEM image of the Ni/CNTs electroplating surface. The SEM image in Fig. 3a showed that in the case of using non-functionalized CNTs additives, the crystal particles of coating is very homogeneous with size in the range of 100 nm to 150 nm. Besides that, we observed the presence of the CNTs merging into the Ni coating. The SEM image in Fig. 3b showed that in the case of using functionalized CNTs addition, the crystal particles of coating appear unclearly compare to Fig 3a, but there are a lot of CNTs on the plated surface. It also showed that the density of functionalized CNTs on coating (Fig. 3b) was higher than CNTs density of non-functionalized CNTs on coating (Fig. 3a).

The SEM image of non-functionalized CNTs nickel coating at low magnification was shown in Fig. 4a. It is clear that the coating surface is not very smooth and there are some micro CNTs gathering clusters. This means the dispersion of CNTs in the solution was not good enough and the CNTs tend to gather to form micro cluster on the Ni plated surface. The SEM image in Fig. 4b showed that the functionalized Ni/CNTs coating is much smoother compare to non-functionalized Ni/CNTs coating. This is attributed to the better dispersion of the functionalized CNTs in the Watts solution.

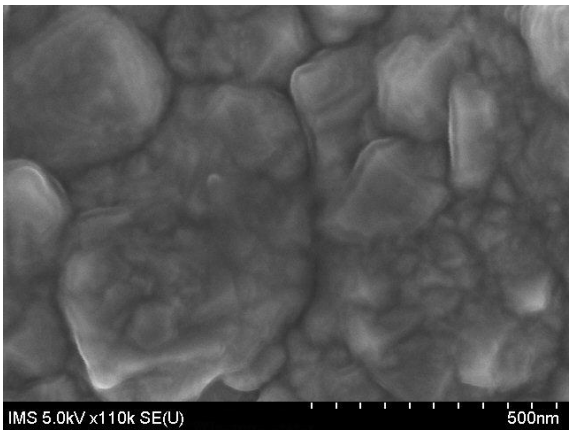

Fig. 2. The SEM image of normal nickel coating surface

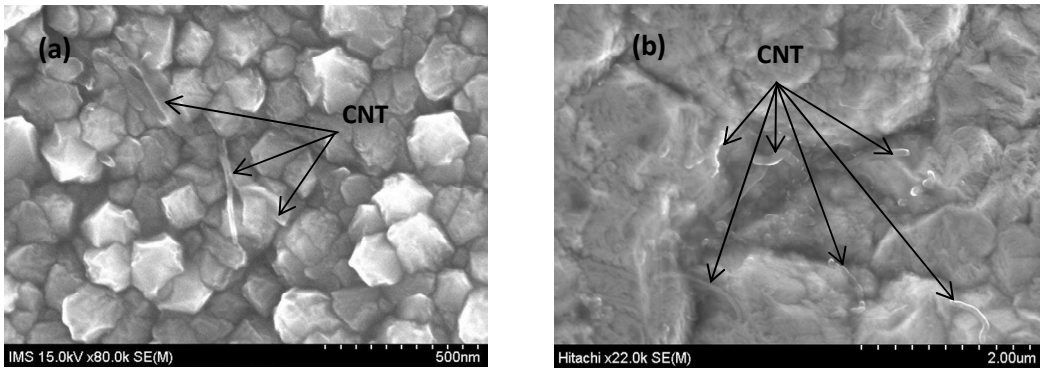

Fig. 3. The SEM image of non-functionalized Ni/CNTs coating surface (a) and functionalized Ni/CNTs coating surface (b)

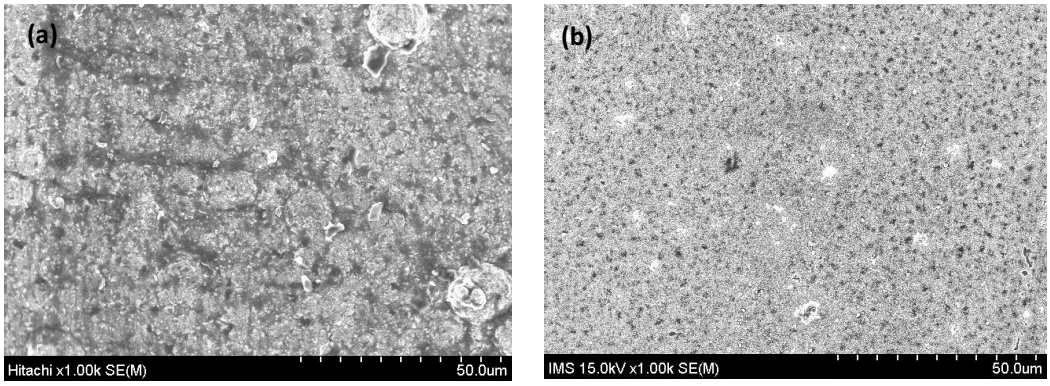

Fig. 4. The SEM image at low magnification of non-functionalized Ni/CNTs coating surface (a) and functionalized Ni/CNTs coating surface (b)

Table 1 is the result of EDS analysis on copper substrate, the result showed that the substrate was copper alloy with 64.32%wt Cu, 32.56%wt Zn and 3.12%wt O of composition.

Table 1. Concentration of elements on copper substrate by EDS analysis

Element	Weight%
O K	3.12
Cu K	64.32
Zn K	32.56
Total	100.00

Table 2 is the result of EDS analysis on non-functionalized Ni/CNTs coating. We can see presence of Ni, C, O elements corresponding to the 11.59% wt C, 86.7% wt Ni, and 1.71% wt O of composition. This confirmed the presence of the CNTs on the non-functionalized Ni/CNTs coating. Table 3 is the result of EDS analysis on functionalized Ni/CNTs coating. Apart from Zn and Cu from copper substrate, we see presence of C, O, N elements corresponding to the 12.51% wt C, 5.77%wt N, 15.63%wt O of composition. This also confirmed the presence of CNTs on the coating and also confirmed the presence of N from -N=N- dimidiate functional groups. From the EDS analysis result in Table 2 and Table 3, the ratio of C weight over Ni weight in the functionalized Ni/CNTs coating and the non-functionalized Ni/CNTs coating are 0.86, 0.13 respectively. So, it is concluded that the functionalized Ni/CNTs coating have more CNTs than that of the non-functionalized Ni/CNTs coating. This is consistent with the observing result by SEM.

Table 2. Concentration of elements on non-functionalized Ni/CNTs coating by EDS analysis

Element	Weight%
C K	11.59
O K	1.71
Ni K	86.70
Total	100.00

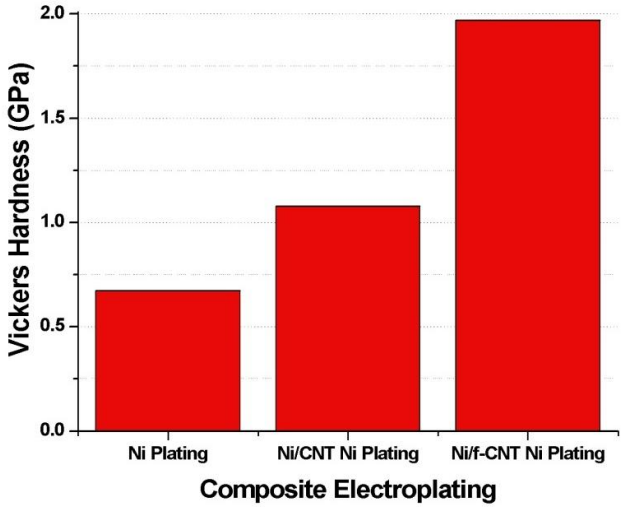

Fig. 5. The Vickers hardness of the electroplating coating

Table 3. Concentration of elements on functionalized Ni/CNTs coating by EDS analysis

Element	Weight%
C K	12.51
N K	5.77
O K	15.63
Ni K	14.61
Cu K	35.58
Zn K	15.91
Total	100.00

We have used Shimadzu Micro Hardness Tester to measure Vickers hardness of the coatings. The results in Fig. 5 showed that the hardness of the normal Ni coating, non-functionalized Ni/CNTs coating and functionalized Ni/CNTs coating were 0.672GPa, 1.08 GPa, 1.97 Gpa, respectively. The results showed that the non-functionalized Ni/CNTs coating is 1.8 times harder than the normal Ni coating, and the functionalized Ni/CNTs coating is nearly 3 times harder than the normal Ni coating. This is explained by the concentration of CNTs in functionalized Ni/CNTs coating was greater than that of normal Ni coating and non-functionalized Ni/CNTs coating. The results showed that CNTs are superb additive components for Ni/CNTs nanocomposite electroplating.

4. CONCLUSION

The SEM images and EDS results affirmed the presence of CNTs on the Ni/CNTs coating. The functionalized Ni/CNTs coating has higher CNTs density than that of the non-functionalized Ni/CNTs coating. The functionalized Ni/CNTs coating is much smoother compare to the non-functionalized Ni/CNTs coating. The hardness of the non-functionalized Ni/CNTs coating and of the functionalized Ni/CNTs coating is 1.8 and 3 times greater than the normal Ni coating, respectively. The results showed that CNTs superb additive components for Ni/CNTs nanocomposite electroplating.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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