Original Research Article

Nickel/CNTs Composite Electroplating

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ABSTRACT

In this paper we present some results on making Ni/CNTs composite by electroplating technique. The work aimed creating an advanced nano-composite coating surfaces by taking advantaged mechanical properties of the CNTs. The Watts solution was used for nickel plating experiments. We utilized two different methods in dispersion 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.

Keywords: Nickel, Carbon Nanotubes, Nanocomposite, Electroplating, Coating

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 open a promising way when we use CNTs to make Ni/CNTs composite plating [6-7]. In this paper, we present some results on fabrication Nickel/CNTs (Ni/CNTs) nanocomposite by electroplating technique.

2. MATERIAL AND METHODS

The CNTs was used in this research production by CVD method at the Institute of Materials Science. 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 [8].

The electroplating system was built as the outline in figure 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 programmed software for control the Aligent E3640A by Visual Basic language. The system can be worked at some modes such as constant current, constant voltage, pulsed current and pulsed voltage.

An important requirement is carbon nanotubes have to be settled before plating to increase dispersion ability in the solution and against gathering. We used both physical and chemical methods for well dispersion of CNTs in Watts bath. In the physical method we put CNTs into the Watt bath, then used ultrasonic vibration for 6 hours in order to get well dispersion of CNTs in the Watt bath. In the chemical method, we used diazo coupling reaction by the following steps:

1) Put CNTs into HNO_3 solution.
2) Use Ultrasonic vibration for 30 minutes to make up defect on the CNTs.
3) Use filter paper to filter CNTs from HNO_3 solution.
4) Mix the CNTs with aqueous solution of sufanilic acid ($NH_2C_6H_4SO_3H$) at $70^{o}C$.
5) Drop the solution of sodium nitrite (HNO_2) into the solution in step 4 and keep stirring.
6) Filter and dry CNTs.

We found that after functionalizing by above steps, the CNTs have a better ability to disperse in the plating solution. This can be explained as following: after diazo coupling reaction, the CNTs remained function groups of $-N{=}N{-}C_6H_4{-}SO_3Na$. These function groups will be dissociated in the plating solution. The CNTs will be charged the same electrical charge, and they will generate Coulomb propulsive force between each other.

We employed Watts solution for nickel electroplating experiments. A standard the solution contained: [9]

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 $50^{\circ}C$. We used 10 Hz pulsed current for all plating process in the experiment, therein duty cycle for pulsed 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.

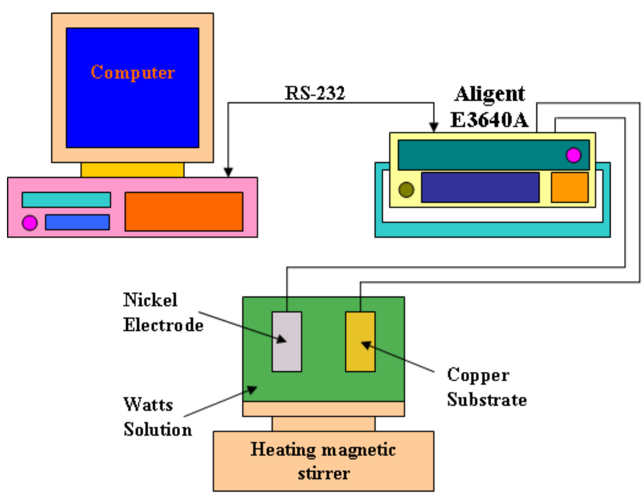

Fig. 1. Schematics of the Ni/CNTs electroplating system

3. RESULTS AND DISCUSSION

Figure 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 un-uniform, ranging from 200 nm to 500 nm. Figure 3 is the SEM image of the Ni/CNTs electroplating surface. The SEM image in figure 3a showed that in the case of using non-functionalized CNTs additives, the crystal particles of coating is very uniform with size in the range from 100nm to 150nm.

Besides that, we observed the presence of the CNTs merging into the Ni coating. The SEM image in figure 3b showed that in the case of using functionalized CNTs additive, the crystal particles of coating appear unclearly, but there are a lot of CNTs on the plated surface. It also showed that the density of functionalized CNTs on coating (figure 3b) was higher CNTs density of non-functionalized CNTs on coating (figure 3a).

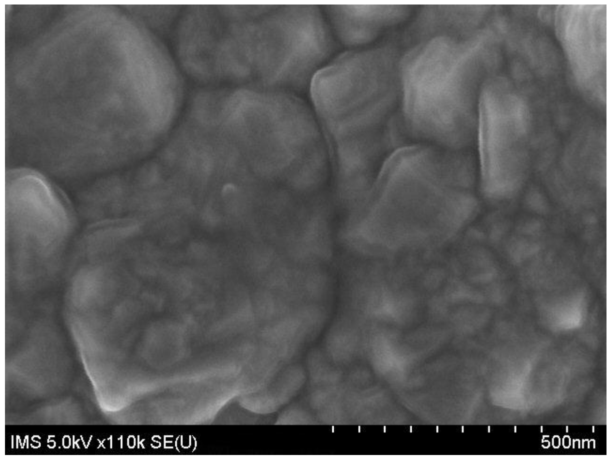

Fig. 2. The SEM image of normal Nickel coating surface

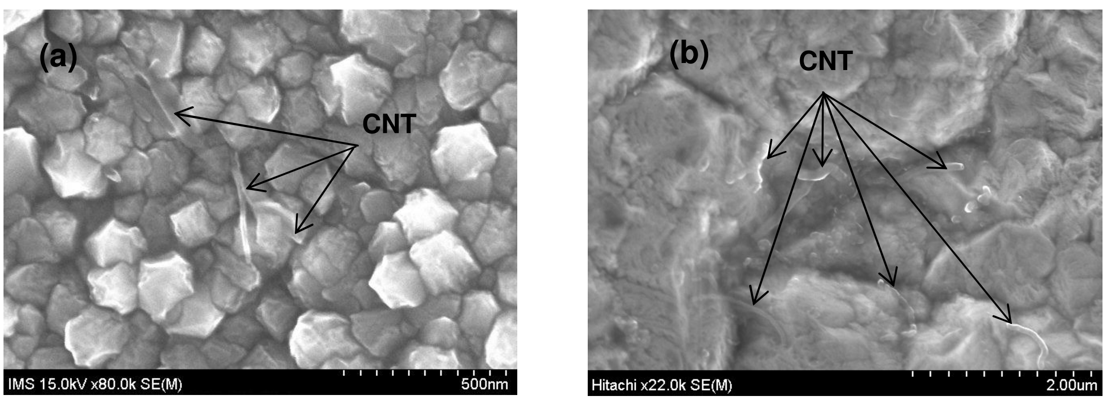

Fig. 3. The SEM image of non-functionalized Ni/CNTs coating surface (a) and functionalize Ni/CNTs coating surface (b)

The SEM image of non-functionalized CNTs nickel coating at low magnification was shown in figure 4a. It is clear that the surface of coating 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 each other to form micro cluster on the Ni plated surface. The SEM image in figure 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.

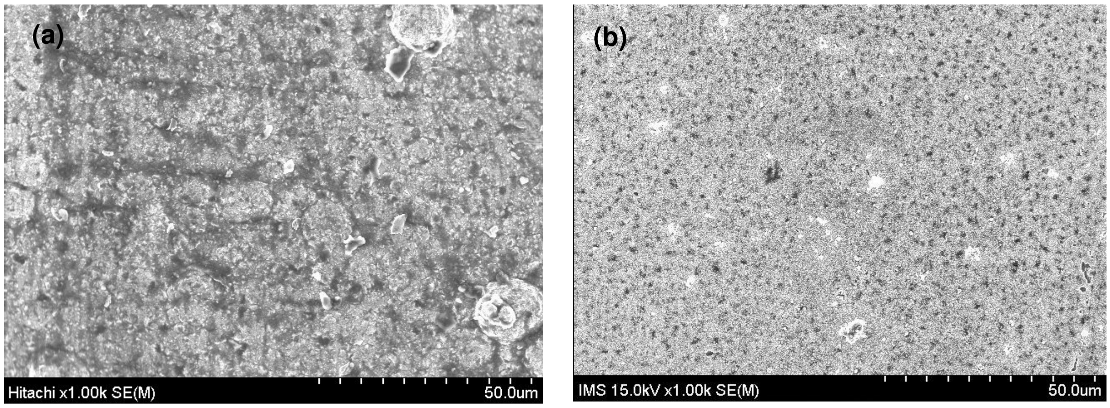

Fig. 4. The SEM image at low magnification of non-functionalize Ni/CNTs coating surface (a) and functionalize Ni/CNTs coating surface (b)

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
Totals	100.00

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
Totals	100.00

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
Totals	100.00

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 2 is the result of EDS analysis on non-functionalized Ni/CNTs coating. We can see presence of Ni, C, O, N 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 in consistence with the result observing by SEM.

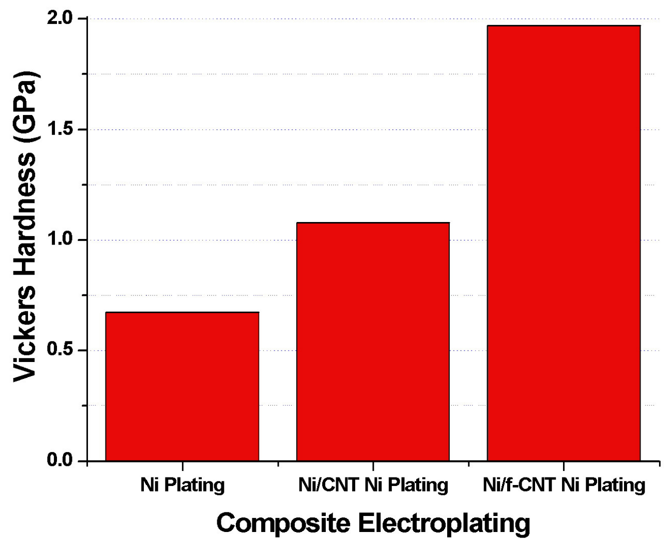

Fig. 5. The Vickers hardness of the electroplating coating

We used Shimadzu Micro Hardness Tester to measure Vickers hardness of the coatings. The results in figure 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. It concluded 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 content of CNTs in functionalized Ni/CNTs coating was higher than that of normal Ni coating and non-functionalized Ni/CNTs coating. The results showed that CNTs is as great promising of additive components for Ni/CNTs nanocomposite electroplating.

4. CONCLUSION

The SEM images and EDS results affirmed the presence of the 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 also enhance in 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 harder than the normal Ni coating, respectively. The results showed that CNTs is as great promising of additive components for Ni/CNTs nanocomposite electroplating.

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