A Simple Nickel Activation Process for Electroless Nickel-Phosphorus Plating on Carbon Fiber

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A new nickel activation process was developed for metalizing the carbon fiber (CF) surface with electroless nickel plating. The oxidation and activation processes were examined using X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectrometry (EDS), and X-ray Diffractometry (XRD). XPS analysis showed that HNO_3 oxidation improved the O/C ratio of the CF surface, which resulted in an increase in the amount of oxygen-containing groups. As activation time increased, both Ni^o cluster and Ni-P deposits increased. More than 50 mg of Ni^o clusters formed on the surface of 1g CF. SEM observations illustrated that particles and island-like shapes were developed from the Ni^o cluster, which helped to initiate the electroless nickel-plating on the CF surface. A continuous and compact coating with a thickness of about 2 to 3 µm was obtained. EDS results showed that the nickel and phosphorus content in the deposits was 97.34 wt.% and 2.66 wt.%, respectively. XRD indicated that the Ni-P coating was crystalline and the maximum deposition on 1 g CFs was as high as 9000 mg. As the results of the observations reveal, the activation method is a feasible alternative to Pd activation.

INTRODUCTION

Due to its strength, stiffness, dimensional stability, low coefficient of thermal expansion, biological compatibility, and fatigue resistance, carbon fibers (CFs) are widely used in some special applications such as aerospace, automobile, chemical industry, general engineering, missile, nuclear field, reinforcement in composite material, and textiles (Xu *et al.* 2008; Seo *et al.* 2009; Rezaei *et al.* 2009; Dai *et al.* 2011). However, the bond between CFs and the polymer matrix in composite materials is weak because the surface of CFs is smooth, compact, and lacks polar functional groups (Pittman *et al.* 1997). Therefore, interest in the modification of the CF surface to improve the interfacial adhesion has recently arisen. Electroless plating is a cost-effective technology because it can make a complex surface harder and more uniform. The coating can serve as the medium for the adhesion and the transferring loads. As is well known, an activation process is necessary for electroless plating on a dielectric surface. Conventional activation always involves the metal Pd (Bosko *et al.* 2011; Cheon *et al.* 2011; Park *et al.* 2011), which has high catalysis performance in the electroless plating process. However, the cost is so great that the alternative activation is required to decrease the cost

of the surface modification. Ni activation has received more attention in the past decade in order to reduce the cost of the surface modification. Tang *et al.* (2008) employed chitosan to fix the nickel on the surface of ABS plastic as a means of initiating electroless nickel plating. Li *et al.* (2011) conducted a new Ni activation process in which nickel oxide particles were obtained on the surface of glass fiber through Ni^{2+} adsorption and heat treatment, separately. In our previous work (Li *et al.* 2010), the nickel coating was successfully deposited on a wood surface using the method that wood veneers loaded with $NaBH_4$ were immersed in a plating solution to complete the activation and plating process in one bath due to the porous surfaces and good wettability of wood. It was found that only a small amount of Ni^{2+} ions can be directly absorbed and cannot form enough active sites for initiating the subsequent plating process owing to the smooth and hydrophobic surfaces on CFs.

In the present work, electroless nickel-plating on CFs surface was investigated using a new activation process in order to achieve uniform deposition. In this process, the plating solution was used as an activation solution for absorbing the Ni^{2+}. The process involved lactic acid complexion on the CFs surface and reduction to form Ni^o clusters for initiating the plating reaction.

EXPERIMENTAL PROCEDURES

Materials

The polyacrylonitrile substrate CF used in the present study was obtained from Mitsubishi Company, Japan. Other chemical reagents used were all of analytical grade.

Pretreatment of CFs

Two steps, degreasing and roughening, were used in the pretreatment of CFs. After CFs were cut into a length of about 3.5 cm, the epoxy resin on the surfaces of CFs was removed by acetone in a Soxhlet device at 80^oC for 24 h. Then CFs were immersed in a boiled 1.0 mol/L NaOH solution for 15 min and a following treatment in boiled 1.0 mol/L HCl solution for 15 min. Degreased CFs were ultrasonically cleaned in distilled water until the solution was neutral. Finally, they were dried at 100^oC to a constant weight.

Degreased CFs were oxidized in nitric acid at 30^oC or 80^oC for a certain time, as specified. The roughened CFs were cleaned with distilled water and dried in oven at 100^oC to a constant weight.
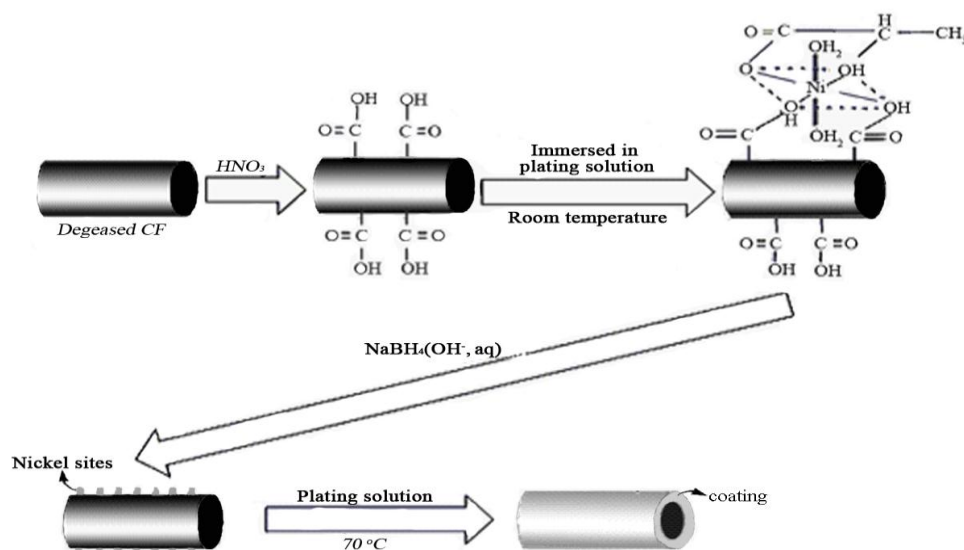
Activation and Electroless Plating

The surface activation was conducted by immersion of 1 g of pretreated CFs in the 200 mL or 500 mL plating solution for certain time followed by immersion in the $NaBH_4$ solution for forming the catalytic sites (Ni^o clusters). After the activation process, the samples were rinsed with distilled water.

The electroless nickel plating was achieved by dipping the pre-nucleated CFs into the plating solution at 70^oC for 20 min. Then, the coated CFs were cleaned with distilled water and dried to a constant weight at 50^oC. The composition of the electroless nickel-plating solution used in both the activation process and the nickel-plating process can be

found in Table 1. The pH value was adjusted by using ammonia solution. The whole process including pretreatment, activation, and plating is illustrated in Fig. 1.

Table 1. Composition of Nickel Plating Solution

Chemicals	Concentration (g/L)
$NiSO_4 \cdot 6H_2O$	35
NaH_2PO_2	35
Lactic acid	18
NH_4Cl	25
pH	8.5

Fig. 1. Electroless nickel plating process on carbon fiber using nickel activation

Measurement of Nickel Amount on CFs

Ni^o clusters or the coatings were redissolved into the nitric acid solution, and the obtained solution was diluted in a constant volume. The concentration of Ni^{2+} ions was analyzed by spectrophotography. The mass of Ni^o clusters or the coatings can be calculated from the concentration and the volume of the solution. The amount of Ni^o clusters and the deposition of the coating can be calculated as below,

$$\text{Ni}^o \text{ cluster amount} = (C_1 \times V_1 \times M_{Ni}) / M_{CF} \qquad (1)$$

$$\text{Deposition} = (C_2 \times V_2 \times M_{Ni}) / M_{CF} \qquad (2)$$

where C_1 and V_1 are the concentration and the volume of the solution from Ni^o clusters; C_2 and V_2 are the concentration and the volume of the solution from the coatings; and M_{Ni} is atomic weight of nickel and M_{CF} is the mass of the carbon fiber.

Characterization Methods

X-ray Photoelectron Spectroscopy (XPS) was used for analyzing the O/C ratio of CFs before and after the pretreatment. Scanning Electron Microscopy (SEM) was used to observe the morphologies of pretreated, activated, and plated CFs surfaces. The Energy Dispersive X-ray Spectrometry (EDS) and X-ray Diffractometry (XRD) methods were used for examining the nickel coating.

## RESULTS AND DISCUSSION

HNO_3 Oxidation

In order to obtain oxygen-containing groups, CFs were oxidized in nitric acid. XPS was used for measuring the O/C ratio to evaluate the amount of oxygen-containing groups on carbon fiber surfaces. As shown in Table 2, the element nitrogen was from the polyacrylonitrile substrate prior to carbonization. The O/C ratio was only 0.17 in degreased CF and increased after HNO_3 oxidation. When the oxidation temperature increased from 30 to $80^{\circ}C$ and time increased from 40 to 60 min, the O/C ratio remained unchanged. Moreover, high-resolution XPS C1s spectra of CF before and after HNO_3 oxidation were analyzed, and results are shown in Fig. 2 and Table 3. It was found that the C 1s peaks could be fitted to four smooth distribution functions corresponding to different binding energies. The different binding energy peaks were assigned to C-C, C-O, C=O, and O-C=O groups. After HNO_3 oxidation, the results showed that the relative amount of C-C groups decreased but that of C=O and O-C=O increased, which indicated that some C-C groups were transformed to C=O or O-C=O groups in the oxidation process. It has been suggested that HNO_3 oxidation can lead to oxygen-containing groups on carbon fiber surface which has been proved carboxyl groups, phenolic groups, quinines, and lactones in previous work (Pittman *et al.* 1997). Such groups favor the adsorption of Ni^{2+} in the plating solution for the activation because of complex formation.

Table 2. Element Composition on Oxidized CF Surface

Sample	Oxidation condition	N	C	O	O/C
1	None	3. 09	82. 99	13. 92	0. 17
2	40 min, $30^{\circ}C$	3. 66	79. 63	16. 71	0. 21
3	60 min, $30^{\circ}C$	3. 09	80. 39	16. 52	0. 21
4	40 min, $80^{\circ}C$	3. 53	80. 8	15. 67	0. 20
5	60 min, $80^{\circ}C$	2. 72	79. 46	17. 82	0. 22

Table 3. C1s Binding Energy (BE) and Relative Amounts of Different Components (RA) of CF Before and After HNO_3 Oxidation (samples 1 and 5)

Component	sample 1		sample 5		Assignment
	BE	RA (%)	BE	RA (%)	
C_1	284.16	67.11	284.23	65.79	C-C
C_2	285.64	13.42	285.67	13.82	C-O
C_3	286.53	6.71	286.92	7.24	C=O
C_4	288.44	12.75	288.56	13.16	O-C=O
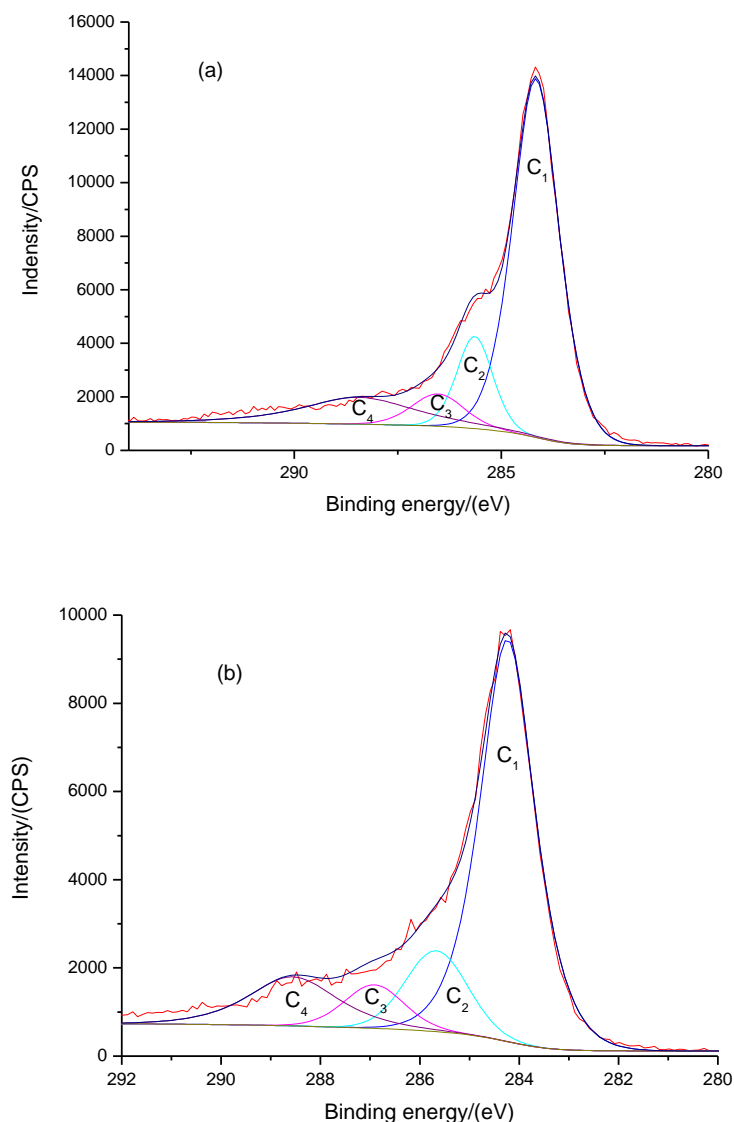
Fig. 2. High-resolution XPS C1s spectra of CF before (a) and after (b) HNO_3 oxidation at 80 ^{o}C for 60 min
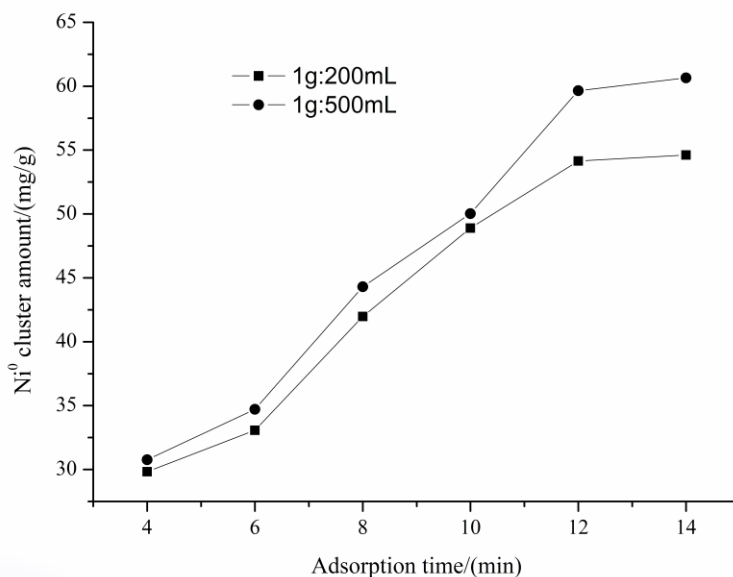
Activation Process

The adsorption process is very important because the aim of activation in this study is to form catalytic Ni^0 sites. The reaction in the activation process can be written as:

$$BH_4^- + 4Ni^{2+} + 8OH^- \rightarrow 4Ni^0 \downarrow + BO_2^- + 6H_2O \tag{3}$$
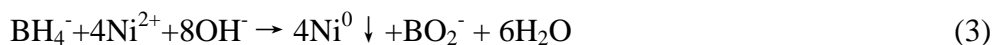
Higher adsorption of Ni^{2+} can provide more active sites to initiate the plating process. The result of the activation can be influenced by the adsorption time and the ratio of CF mass to the volume of the solution. The amount of Ni^o clusters on carbon

fiber was measured under various conditions. As shown in Fig. 3, the amount of Ni^o (as clusters) increased from 29.8 mg to 54.6 mg on 1g CF as the absorption time increased from 4 min to 12 min in a 200 mL solution. A slight change was observed when the absorption time was longer than 12 min. Under the same adsorption time, the more volume of solution can lead to more Ni^o clusters.

Fig. 3. The proportion of nickel deposits and CF changing along with adsorption time in activation process

Figure 4(a) shows that the many gaps and cracks on the carbon fiber surface were compact and clean. After activation, many particles or island-like materials were observed on the surface (Figs. 4b and c). Moreover, it was found that Ni^o particles were distributed uniformly in the cracks under the activation in a 200 mL solution for 12 min. However, when the solution volume was increased to 500 mL, some Ni^o particles bonded into island-like shapes, which worsened the uniformity.
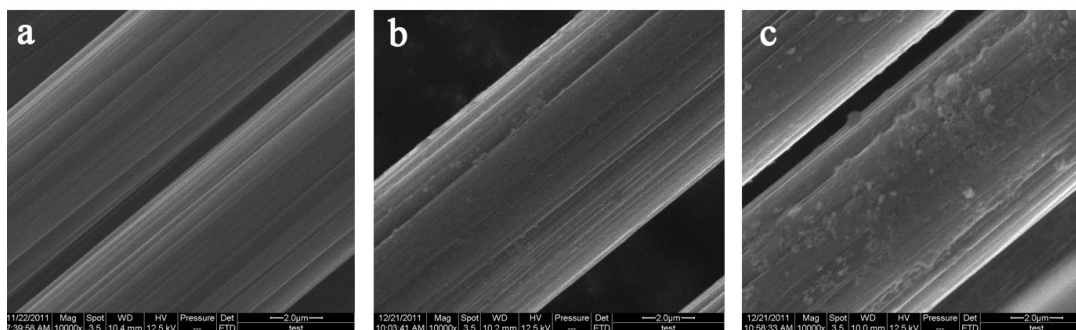
Fig. 4. SEM photographs of CFs before activation (a) and after activation for 12 min in 200 mL (b) and 500 mL solution (c)

Electroless Nickel Plating

The effect of activation time on deposition amount is shown in Fig. 5. With an increase in activation time from 4 min to 12 min, the deposition increased from 6000 mg/g CF to 9000 mg/g CF. The rate of increase was slowed down after 12 min. The amount of auto-catalyst Ni^o increased with an increase in activation time. Therefore, more Ni^o can rapidly initiate and accelerate the electroless plating process, resulting in more deposition. Comparing the deposition under the different volumes of solution in the activation process, the effect of the 500 mL solution was a little better than that of 200 mL. When the activation time was up to 14 min, almost same amount of deposition was obtained for both solutions. This indicated that almost all the Ni^{2+} in the plating solution were reduced and deposited on CF surface because the volume of plating solution was fixed.
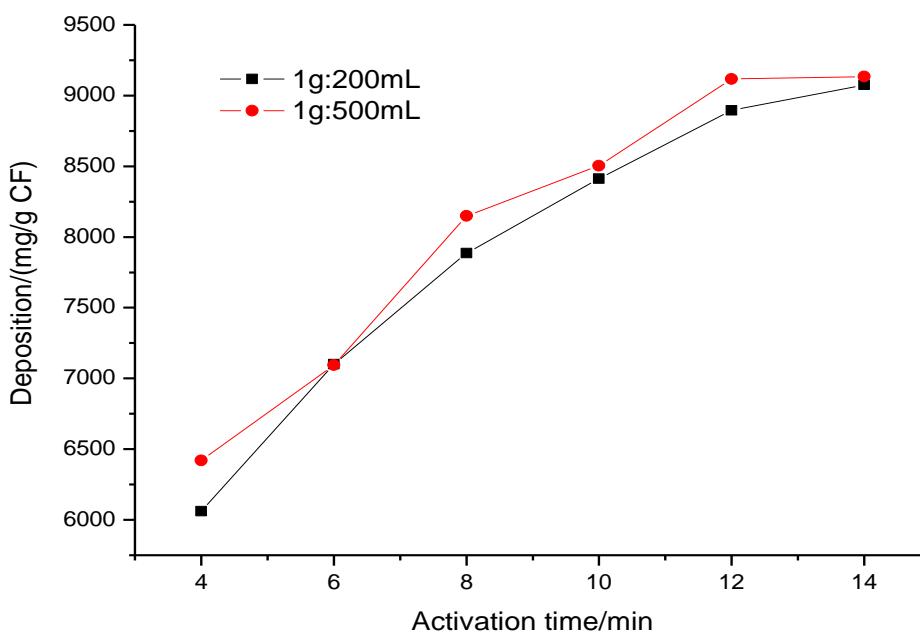

Fig. 5. The effect of activation time on deposition amount on CF surface

Figure 6 shows the SEM images of CF after electroless nickel plating. A uniform, smooth, and compact layer was observed in the photograph of the coating surface. The cross-section image reveals that the thickness of the coating was around 3 μm in Fig. 6 (b) and around 2 μm in Fig. 6 (d). This result is accordance with the conclusion from Fig. 5. The EDS spectrum of cross-section of the plated CF surface is shown in Fig. 7. The high content of the element carbon was from the CF itself. The contents of nickel and phosphorus in the coating were 97.34 wt.% and 2.66 wt.%, respectively.
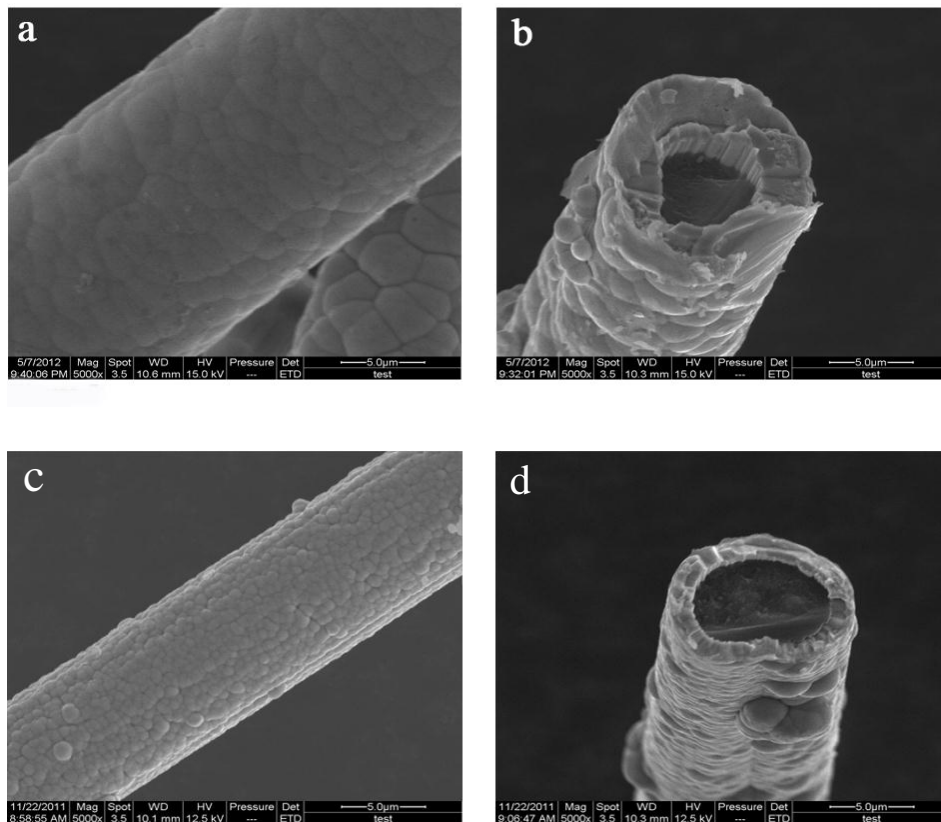
Fig. 6. SEM images of CF after plating under activation in 500 mL and 200 mL solution for 12 min (a, c) the plated CF surface (5000×) and (b, d) the cross-section of the plated CF (5000×)
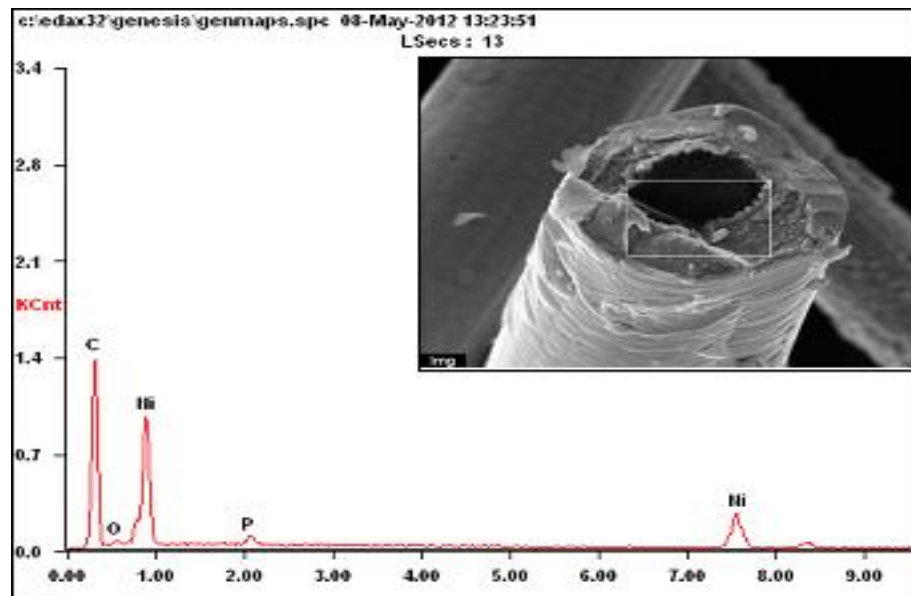
Fig. 7. EDS spectrum of the cross-section of plated CF

Figure 8 (a) shows a strong peak at $2\theta = 26.18^o$, which is the characteristic peak of carbon in CF. After plating, a series of peaks were apparent. As shown in Fig. 8 (b), peaks at $2\theta = 44.5^o$, 51.8^o, and 76.3^o, which are attributable to Ni(111), Ni(200), and Ni(220), respectively, indicated the presence of the face-centered cubic phase of nickel (JCPDS 04-0850) and the crystalline nature of the layer. This result can be largely attributed to the fact that there was little distortion of the crystalline of Ni caused by P atoms because of low P content. It was found that the characteristic peak intensity of CF significantly decreased after plating. In accordance with the results from SEM observation, it was found that the CF surface was entirely and compactly covered by the Ni-P coating and the thickness of the coating reached at least several micrometers.
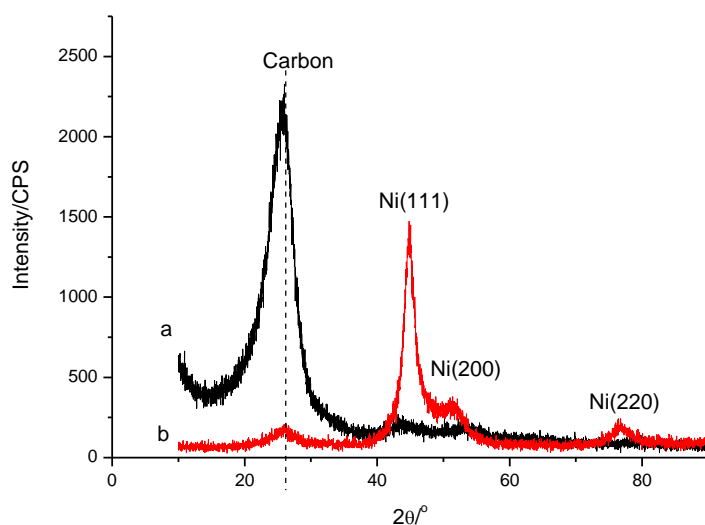
Fig. 8. XRD patterns of CF before (a) and after (b) electroless nickel plating

CONCLUSIONS

In this study, electroless nickel-plating on CF surface catalyzed with a new activation was investigated. The plating solution was used for both activation and plating process. The hydrophilicity of CF surface was improved by HNO_3 oxidation at 30^oC for 40 min. By dipping 1 g CFs in a 500 mL plating solution for 12 min for activation and 20 min for plating, a uniform and continuous coating was deposited on the CF surface. The maximum deposition reached more than 9000 mg Ni-P alloy. The thickness of the coating was around 2 to 3 μm. Moreover, the film was crystalline and contained 97.34 wt.% and 2.66 wt.% of the nickel and phosphorus, respectively. It was confirmed that the method was an effective and promising alternative to the conventional Pd activation.

ACKNOWLEDGMENTS

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