

Research Article

The Microstructure of Ni Layer on Single-Walled Carbon Nanotubes Prepared by an Electroless Coating Process

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The single-walled carbon nanotubes (SWNTs, diameter: 2~3 nm), which were obtained in the suspension of purification solution, with Ni-P coating layers were obtained by an electroless deposition process. The SWNTs before and after coating were characterized by transmission electron microscopy (TEM) and energy dispersive spectrometry (EDS). An Ni-P layer on individual nanotube with thickness of 20 nm can be obtained after the deposition process. The X-ray diffraction (XRD) and selected area electron diffraction (SAED) analysis of Ni-P SWNTs before and after heat treatment show that the heat treatment caused the transformation of the amorphous Ni-P layer to the nanocrystalline Ni-P (crystalline Ni and Ni₃P intermetallic compound) layer. The XRD pattern of SWNTs with Ni-P layers after heat treatment revealed that the crystal structures of Ni in plating layer contained: hexagonal close-packed (hcp) structure and face-centered cubic (fcc) structure. The lattice parameters of Ni (fcc) and Ni₃P are larger than the bulk's, indicating that the lattice expansion has taken place. However, the lattice parameter of Ni (hcp) has no difference from the bulk's.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991 [1], much attention has been focused on one-dimensional nanomaterials for their outstanding properties, including high length/diameter ratio, low density, and mechanical properties [2, 3]. Significant interest has been recently focused on CNTs-metal composites. However, the bonding of interface between carbon nanotubes and metal is not strong enough. Metal-coated CNTs increase surface active sites to improve interfacial bonding between CNTs and metal matrix. Ni-P layers have been adopted for an increasing number of CNT applications in recent years.

Electroless deposition is an effective approach for the preparation of the CNTs with Ni-P layers. This means that CNTs can be used as reinforcing fibers for metal matrix composites with surface treatment. It will be essential to achieve good interfacial adhesion. The coated layers can serve as medium for adhesion and transferring loads. There have been studies on the morphology of metallic nanoparticles

as a function of deposition time in electroless deposition of metal on carbon nanotubes [4].

Multiwalled carbon nanotubes (MWNTs) subjected to electroless deposition are produced by CVD which appear to be curved, twisted together, and hard to disperse [5, 6]. Single-walled carbon nanotubes (SWNTs) adopted in this experiment are straight and easy to disperse. SWNTs with Ni-P coating layers could improve the interfacial bonding between SWNTs and metal matrix and the dispersion of SWNTs in metal matrix.

In order to understand the combining mechanism at the interface, it is necessary to investigate crystal structures under heat treatment. Better thermodynamical stability can be achieved through the nanocrystallization process of the metastable amorphous structure in Ni-P layers, leading to an improvement of the composite properties.

In this study, we prepared SWNTs, which were obtained in the suspension of purification solution, with Ni-P layers by electroless deposition processing. The Ni-P layers are thick and smooth. SWNTs with nanocrystalline Ni-P layers were

prepared by heat treatment at 400°C. The samples were characterized with TEM, EDS, SAED, and XRD.

2. Experimental

Single-walled carbon nanotubes were prepared by anodic arc discharging plasma. The purification of SWNTs was conducted by using mixed acid ($\text{HNO}_3:\text{H}_2\text{SO}_4 = 1:3$) to take away amorphous carbon and catalytic nanoparticles. For the purification before further pretreatments for electroless plating, the SWNTs were obtained in the suspension of purification solution, then filtered and washed with deionized water and dried in air at 80°C. Next, the cleaned SWNTs were sensitized in the aqueous solution containing $\text{SnCl}_2 + \text{HCl}$ and activated in the aqueous solution containing $\text{PdCl}_2 + \text{HCl}$ (the so-called two-step process), followed by washing thoroughly with deionized water. Finally, the pre-treated SWNTs were immersed in the electroless plating bath, which contains NiSO_4 , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, and NaH_2PO_2 . Ammonia solution was used as buffer to adjust and maintain pH value between 8.5 and 8.7. The sample was heat treated under argon atmosphere at 400°C for 3 h, where heating rate was 10°C/min. The SWNTs before and after coating were characterized with TEM (JEM-2010) and EDS. The Ni-P-SWNTs before and after heat treatment were studied using XRD (D8) and SAED.

3. Results and Discussions

3.1. Morphological Features of Ni-Coated SWNTs. Figure 1 shows the TEM image of SWNTs after purification, which shows that the CNTs are straight. The diameter of SWNTs is almost 2.6 nm. The purification processing has two effects: taking away the impurities and introducing functional groups on SWNTs surface, such as carboxyl ($-\text{COOH}$) and hydroxyl ($-\text{C}-\text{OH}$) [7]. These functional groups change the surface state of SWNTs, which plays an important role in electroless deposition [8, 9]. The SWNTs have to be oxidized to introduce high density and distributed homogeneously functional groups on their surface. This would subsequently lead to a sufficiently high density of adsorbed activator nuclei and a correspondingly distribution of growing Ni metal nuclei. The growth of Ni would be insufficient to cover the whole tube surface unless the initial density of catalytic sites is very high and homogenous.

Figure 2 shows the representative TEM image of SWNTs with Ni-P coating layers, which clearly indicates that the Ni-P layers coat the tube surface uniformly. The electrolessly deposited Ni-P layers are distributed on the individual tube homogeneously. The thickness of the coating layer is more than 20 nm and as ten times as the semidiameter of the nanotube. The coating thickness can be controlled via reaction time of plating. The layer is symmetric around the SWNTs. Compared to SWNTs produced by CVD, SWNTs adopted in this experiment are straighter, leading to the fewer defects exist on the surface of SWNT. The preparation of tubes with continuous and smooth coating layer has been influenced by two crucial factors: the curvatures of tube [10, 11] and the distance between catalytic centers [12].

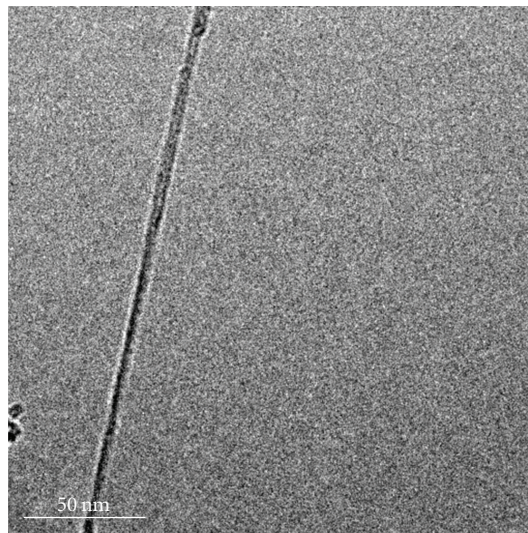


FIGURE 1: TEM image of purified SWNTs.

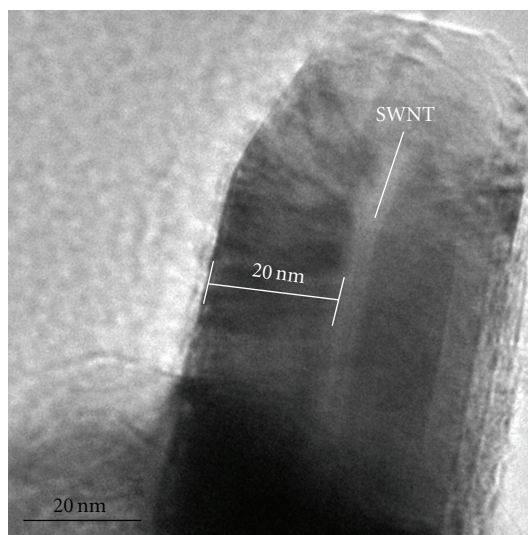


FIGURE 2: TEM image of the end of as-coated SWNTs.

Figure 3 shows the representative TEM, EDS image of SWNTs with Ni-P layers. The EDS shows the major component in deposited layer is Ni, with a little P and Pd. The peak of Cu is due to the grid used in TEM.

3.2. The Transformation of Crystal Structures of Ni-P Layers. The electroless deposition Ni is a metastable and supersaturated alloy consisting of P atoms between Ni atoms. The face-centered cubic (fcc) structure of Ni may be maintained within small grains. The structure is essentially amorphous in the regions where the fcc structure cannot be maintained at all [13]. The as-coated SWNTs have been confirmed to be the SWNTs with the amorphous Ni-P layers, and the SWNTs with nanocrystalline Ni-P layers can be prepared by the heat treatment at 400°C.

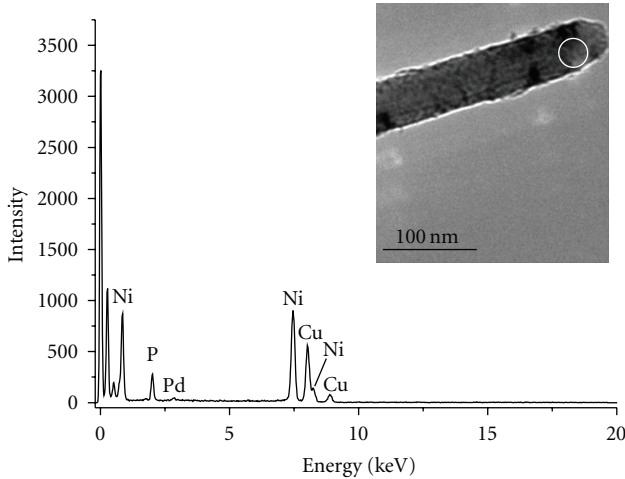


FIGURE 3: TEM image of as-coated SWNTs and EDS, which was selectively taken on the edge of SWNTs with Ni-P layers.

In order to observe the nanocrystallization structures, the SWNTs with Ni-P deposition layers were analyzed by XRD method. In addition to XRD, the SAED analysis was also performed to determine the phase transformation. Figure 4 shows the results.

The XRD pattern of as-coated SWNTs afforded only a broad peak showing the amorphous phase structure [14, 15]. And the SAED is a broad ring characteristic of an amorphous phase without any trace of crystalline phases. Under heat treatment, the Ni and Ni₃P (intermetallic compound) peaks became sharp [16, 17]. The SAED shows a polycrystalline structural feature, which is in agreement with the results of the XRD analysis. These results have demonstrated that the SWNTs with nanocrystalline Ni-P layer can be prepared by heat treatment at 400°C using the SWNTs with amorphous Ni-P layers as the precursors.

3.3. Microstructure of Ni-P Layers under Heat-Treatment.

Figure 5 shows the part of XRD pattern of SWNTs with Ni-P layers under heat treatment. $2\theta = (40^\circ, 56^\circ)$. There is one sharp and intense peak of Ni₃P at $2\theta = 41.65^\circ$, several weak peaks are observed, and these peaks correspond to the (231), (330), (112), (141), (222) and (132) planes of body-centered tetragonal structure of Ni₃P. The XRD pattern clearly shows that Ni has two crystal structures in deposition layers after heat treatment: hexagonal close-packed (hcp) structure and face-centered cubic (fcc) structure. The peaks at $2\theta = 45.07^\circ$ and at $2\theta = 44.37^\circ$ correspond to the (011) plane of Ni (hcp) and (111) plane of Ni (bcc), respectively. As we know, there are three crystal structures of Ni: face-centered cubic (fcc), hexagonal close-packed (hcp) and body-centered cubic (bcc). The Ni (hcp) is metastable, but Ni (hcp) stably exists in the deposition layers under heat treatment.

As shown in Figure 6, there is an obvious phenomenon in XRD pattern. The crystal plane distance calculated from XRD spectrum is different with the bulk's value, which reflects the change of lattice parameter.

For example, $d_{(111)}$ of Ni (fcc) is 2.04006 Å in Figure 6 and is larger than the bulk's value $d_{(111)0} = 2.01000$ Å indicating

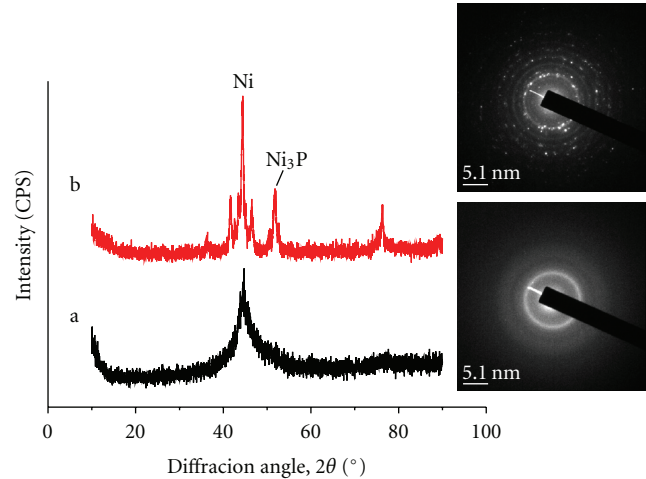


FIGURE 4: XRD and SAED image of SWNTs with Ni-P layers: a as-coated, b under heat treatment.

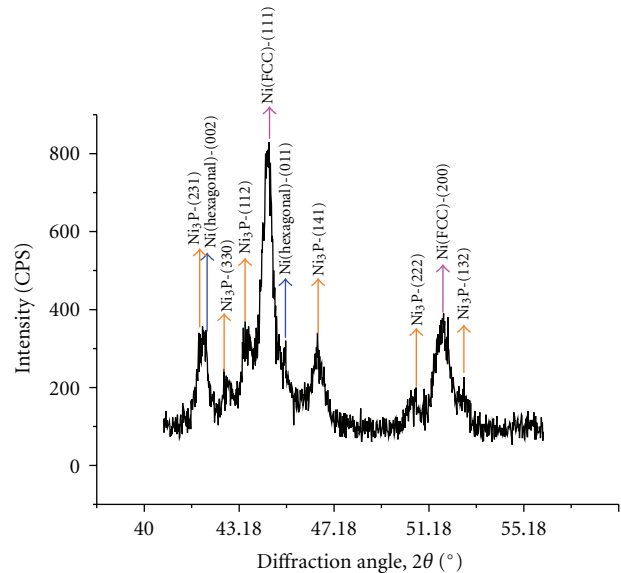


FIGURE 5: Partly of XRD pattern of SWNTs with Ni-P layers under heat treatment.

the emergence of lattice expansion. The rate of the change of crystal plane distance is $(d_{(111)} - d_{(111)0})/d_{(111)0} = 1.5\%$. And $d_{(231)}$ of Ni₃P (body-centered tetragonal) is 2.16654 Å, but the bulk's value $d_{(231)0} = 2.16100$ Å. The rate of the change of crystal plane distance is $(d_{(231)} - d_{(231)0})/d_{(231)0} = 0.26\%$.

While the lattice of Ni (fcc) and Ni₃P (bct) has expanded, the lattice of Ni (hcp) has no change nearly. The change of the lattice parameters of Ni (hcp) can be ignored.

The change of crystal plane distance shows that the lattice of Ni (fcc) and Ni₃P (bct) has expanded. There is a reason as following: the relationship between the lattice parameter and the grain size has been studied by Wei Zhi-Qiang and Lu Ke using the experiment. These studies indicate that the lattice parameter increase significantly with the decrease of the grain size [18, 19]. So the lattice parameter of nanocrystalline

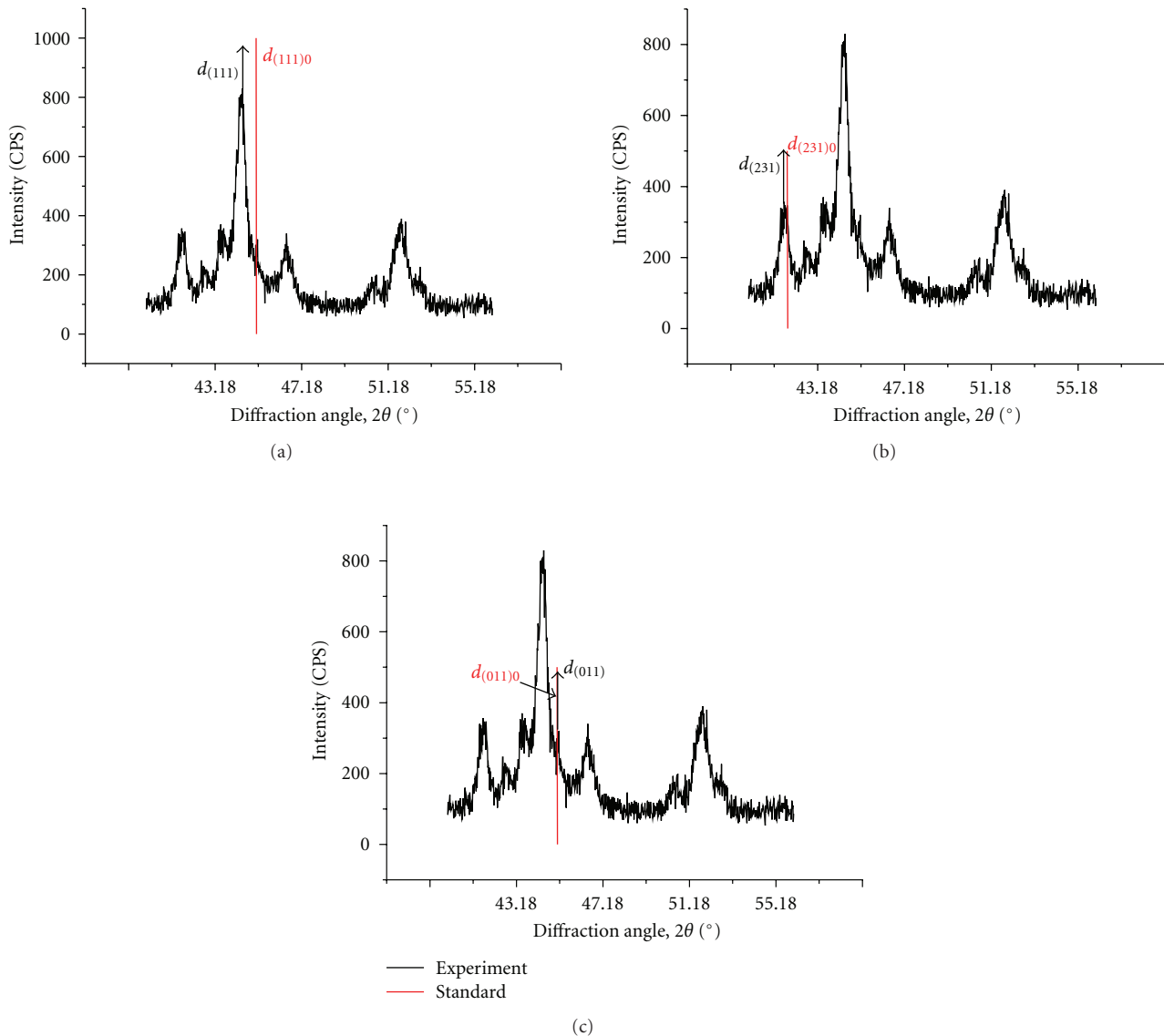


FIGURE 6: The change of crystal plane distance: a-Ni (fcc); b-Ni₃P; c-Ni (hcp).

in Ni-P layers will increase when they are in nanometer scale due to the grain refinement of nanocrystalline.

4. Conclusion

In this paper, the one-dimensional SWNTs with continuous and dense coating layer have been successfully synthesized by an electroless deposition process. The thickness of the coated layer is more than 20 nm. It has been found that the heat treatment can convert the amorphous Ni-P coating layers into the nanocrystalline Ni-P (Ni and Ni₃P) layers. Our results show that the lattice of Ni (fcc) and Ni₃P (bct) has expanded but the rates of expansionary not equal. At the same time, the lattice of Ni (hcp) has contracted and the the change could be ignored.

Acknowledgments

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