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PII: S0008-6223(15)30358-4
DOI: 10.1016/j.carbon.2015.10.048
Reference: CARBON 10412

To appear in: Carbon

Received Date: 22 July 2015
Revised Date: 11 October 2015
Accepted Date: 13 October 2015


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Temperature-dependent chemical state of the nickel catalyst for the growth of carbon nanofibers

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\textbf{Abstract:} Nickel is one of the most commonly used catalysts for the growth of carbon nanofibers (CNFs) by catalytic chemical vapor deposition (CVD). Nevertheless, the chemical state of nickel catalyst, which may be metallic nickel (Ni), nickel subcarbide (Ni\textsubscript{3}C\textsubscript{1-x}) and nickel carbide (Ni\textsubscript{3}C) during the growth process of CNFs, remains a longstanding issue. We report here the catalytic growth of CNFs by CVD at temperatures ranged from 300 to 600 °C. It is demonstrated that the nickel catalyst has different chemical states during the catalytic growth, including Ni\textsubscript{3}C at 300 °C, composite Ni-Ni\textsubscript{3}C\textsubscript{1-x} from 400 to 500 °C and metallic Ni at 600 °C, which is clearly dependent on the growth temperature. Our findings reconcile the longstanding debate on the contradictory models (i.e. Ni-assisted growth, Ni\textsubscript{3}C\textsubscript{1-x}-assisted growth and Ni\textsubscript{3}C-assisted growth) for the catalytic growth CNFs.

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1. Introduction

Catalytic chemical vapor deposition (CCVD) has been a widely used approach for industrial production of carbon nanofibers/nanotubes (CNFs/CNTs) due to its low cost, high yield and ease of scale-up.[1-4] However, some longstanding and fundamental problems about this method have not yet be clarified, such as the state of the catalysts.[1, 2] In the early 1970s, Baker and co-workers proposed that the formation of CCVD-grown CNFs was induced by the liquid catalyst,[5, 6] and thus triggered the important issue about the state of catalysts, including both physical and chemical states.[1, 7] To date, with the aid of the advanced *in situ* characterization techniques, some general agreements on the physical state, i.e. liquid state or solid state, of the catalyst have been achieved. For example, *in situ* transmission electron microscopy (TEM) confirmed that the Ni particles in a crystalline state could also induce the growth process of CNTs.[8] The recent in-situ Raman analyses also revealed that CNTs could grow from both solid and liquid catalyst Fe, depending on the growth temperature.[9]

The debate on the chemical state of catalysts was originated from the argument in 1980s that the deviation of C equilibrium during the growth process of CNFs could be attributed to the formation of the metastable carbides, $\text{Ni}_3\text{C}$ or $\text{Ni}_3\text{C}_{1-x}$.[7, 10-12] However, the validity of such a carbide-assisted mechanism has been strongly questioned in the past. Because some early experimental results and analyses[13, 14] suggested that carbides should not be active catalysts for the formation of CNFs, and moreover, the convincing evidence for carbide-assisted mechanism was absent until very recent years. The direct evidence for carbide-assisted growth was firstly given by *in situ* TEM observation that $\text{Fe}_3\text{C}$ was able to induce the growth of CNFs at the temperatures of 600 - 700 °C.[15, 16] After that, comparative *ex situ* TEM analyses also demonstrated that both Fe and $\text{Fe}_3\text{C}$ could induce the catalytic growth of CNFs.[17]
Ni is one of the most common catalysts used for the growth of CNFs/CNFs. The chemical state of Ni catalyst exists as metallic Ni during the catalytic growth of CNFs/CNTs at the temperatures of above 500 °C, which has been well demonstrated by both in situ TEM and XPS characterization.[8, 18, 19] However, the possibility of Ni₃C-assisted growth of CNFs/CNTs at temperatures of below 500 °C still cannot be ruled out. In fact, some earlier theoretical research has predicted that the surface carbide, Ni₃C, could induce the growth of CNFs at temperatures of below 400 °C,[20] which was significantly lower than the common Ni-catalytic growth temperatures of above 500 °C.

In our recent work, we successfully synthesized CNFs at 300 °C by metal-organic CVD, and demonstrated that the Ni catalyst appeared as Ni₃C, instead of metallic Ni during the catalytic growth process.[21] It is known that metastable Ni₃C is sensitive to the environmental temperature and decomposes totally at temperatures of above 500 °C.[22] It is therefore quite reasonable to expect that the chemical state of Ni catalyst will be dependent on the growth temperature. In this work, we systematically investigate the chemical state of Ni catalyst at the catalytic growth temperatures ranged from 300 to 600 °C, and find that the chemical state of Ni catalyst might shift from Ni₃C to Ni₃Ni₃C_{1-x}, and finally to metallic Ni as the increase of the growth temperature.

2. Experimental Details

CNFs were synthesized by metal-organic CVD in a horizontal tube furnace. Nickel(II) acetylacetonate (Ni(acac)_2, Aldrich Chemical Co., 95%), as the precursor, was loaded in the quartz tube that was located at the upstream of the furnace with a temperature of 150 °C. The SiO₂ wafer (4 cm × 15 cm) was mounted at the downstream of the furnace with a temperature of 300 - 600 °C, as the substrate for collecting the synthesized products. During the deposition process, the pressure and flow rate of the carrier gas, H₂, in the furnace tube were set up to be
50 Pa and 200 standard cubic centimeters per minute, respectively. The temperature of the furnace was calibrated right before and after each synthesis. The detailed information on the experimental set-up can be found in our works reported previously.[21, 23-26]

The collected products were characterized using X-ray diffraction (XRD, Rigaku D max 2500 VB), scanning electron microscope (SEM, JEOL JSM-7800F, operated at 5 kV), TEM (JEOL JEM-2100F and FEI Tecnai F20 operated at 200 kV) equipped with energy dispersive spectroscopy (EDS, EDAX Genesis XM2).

3. Results and Discussion

3.1 Morphological and structural characteristics of CNFs

The phase compositions of the products synthesized at different temperatures were examined by XRD, as shown in Figure 1. It is seen that the main diffraction peaks of the product obtained at 300 °C are located at 39.2°, 41.6°, 44.6° and 58.5°, which match well with the indexes of the (110), (006), (113) and (116) crystal planes of Ni₃C with a rhombohedral structure (JCPDS 06-0697; \(a = 0.458 \text{ nm}, \ c = 1.299 \text{ nm}\)), respectively. There exists a broadened peak ranged from 20 to 30°, which should come from the amorphous C. For the product obtained at 400 °C, besides the peaks from Ni₃C, both face-centered-cubic (fcc) Ni (JCPDS 04-0850, \(a = 0.353 \text{ nm}\)) and graphite (JCPDS 41-1487, \(a = 0.2470, \ c = 0.6724 \text{ nm}\)) appeared. The diffraction peaks of Ni₃C disappeared in the product synthesized at 500 °C, where only fcc-Ni and graphite could be detected. The XRD spectrum of the product synthesized at 600 °C is almost the same to that at 500 °C, but the intensity of the graphite peaks is significantly stronger. It should be noted that no trace of nickel oxide, such as NiO (JCPDS 44-1159; \(a = 0.296 \text{ nm}, \ c = 0.723 \text{ nm}\)) and Ni₂O₃ (JCPDS 14-0481; \(a = 0.461 \text{ nm}, \ c = 0.561 \text{ nm}\)), could be detected from these samples.
Figure 1. The XRD diffractograms of the products synthesized at 300, 400, 500 and 600 °C.

Figure 2. The CNFs obtained at 300 °C. (a) SEM image of the as-synthesized CNFs, (b) TEM image of a faceted catalyst particle and the corresponding induced CNFs, (c) HRTEM image and (d) the corresponding SAED pattern of the catalyst particle in (b). The insert in (b) shows the corresponding EDS spectrum of the catalytic particle.

Figure 2(a) shows the SEM image of the product obtained at 300 °C, where curly CNFs with lengths ranged from several hundred nanometers to several micrometers can be observed. The TEM examination revealed that the CNFs had a bi-directional structure with a catalyst particle in the middle, as shown in Figure 2(b). The EDS analysis confirmed that only the elemental Ni, C and Cu (from the TEM grid) existed (see the insert in Figure 2(b)), indicating
that the growth of CNFs was induced by Ni catalyst. From the high resolution TEM (HRTEM) image of the catalyst particle shown in Figure 2(c), it can also be found that the lattice spacings are 0.23 nm and 0.43 nm, which agree with those of the (110) and (003) planes of Ni₃C. The corresponding selected area electron diffraction (SAED) pattern in Figure 2(d) confirmed this. The EDS, HRTEM and SAED analyses clearly demonstrated that the chemical state of the Ni catalyst was Ni₃C.

Figure 3. The CNFs obtained at 400 °C. (a) SEM image of the as-synthesized CNFs, (b) TEM of the typical bi-directional CNFs with a catalyst particle at the center, (c) the HRTEM image taken from the dashed square C in (b), (d, e) the FFT patterns acquired from the inside and at edge of the particle in (c), (f) the HRTEM image taken from the dotted square F in (b). The insert in (b) is the corresponding EDS spectrum of this particle.
Figure 3(a) shows the typical SEM image of the product obtained at 400 °C, where the CNFs have lengths of up to tens of micrometers. The TEM analyses revealed that the CNFs were grown from two of the four corners of the diamond-shaped catalyst particle, as shown in Figure 3(b). Although the catalyst particles generated at 400 and 300 °C appear to have different morphologies and shapes, they are composed of the same chemical compositions of Ni and C, as evidenced by the similar EDS patterns inserted in both Figures 2(b) and 3(b). Figure 3(c) is the HRTEM image taken from the dashed square in Figure 3(b). HRTEM image and the corresponding fast Fourier transformation (FFT) pattern in Figure 3(d) reveal that the lattice fringes at the corner of the catalyst particle have spacings of 0.24 nm and 0.25 nm with an interfacial angle of ~ 70°. Obviously, this lattice fringes with relatively large spacings are definitely not from fcc-Ni. On the other hand, the observed lattices are also not well consistent with the most possible two planes of Ni₃C, (1-14) and (-104), \( d_{(1-14)} = d_{(-104)} = 0.25 \text{ nm} \) with the interfacial angle of ~ 67°. Inside the catalyst particle, the lattice fringes have spacings of 0.20 nm and 0.18 nm, which agree with those of the (111) and (200) crystalline planes of fcc-Ni. This is also supported by the corresponding FFT analysis, as shown in Figure 3(e). Figure 3(f) is the HRTEM image taken from the area marked by the dotted square in Figure 3(b). In Figure 3(f), one pair of the lattice fringes are with spacings of 0.30 and 0.32 nm has an interfacial angle of ~ 70 °C, and the other pair of lattice fringes are with spacings of 0.30 and 0.25 nm has an interfacial angle of ~ 53 °C. Detailed analyses suggest that these lattice fringes should not belong to NiO (JCPDS 44-1159) or Ni₂O₃ (JCPDS 14-0481). This is further supported by the EDS analysis that no elemental O could be detected in the catalyst particle (see the inset in Figure 3(b)). Again, the observed lattices are also not well consistent with the possible planes in Ni₃C \( d_{(013)} = 0.29 \text{ nm} \) and \( d_{(01-2)} = 0.33 \text{ nm} \) with an angle of 74°, \( d_{(-114)} = 0.25 \text{ nm} \) and \( d_{(012)} = 0.33 \text{ nm} \) with an angle of 48°, respectively. For Ni-C binary system, metallic Ni is the only stable phase, Ni₃C is the only metastable phase with a definite crystalline structure, and
metastable Ni$_3$C$_{1-x}$ does exist but does not have a definite crystalline structure.[27, 28] In particular, we observed directly the obvious distorted lattices and defects in the carbide (Figures 3(c) and 3(f)). It is therefore reasonable to presume that the observed unknown phases are highly possible to be distorted Ni$_3$C or unstable Ni$_3$C$_{1-x}$. [27-31]

![Figure 4](image)

**Figure 4.** The CNFs obtained at 500 °C. (a) The SEM image of the as-synthesized CNFs, (b) the TEM image of the catalyst particle, (c) the HRTEM image of the dotted square C in (b), (d,e) the FFT patterns acquired from the upper and the lower parts of the particle in c), (f) the HRTEM image of the dashed square F in (b), and (g,h) the FFT patterns of the inner part and the edge of the particle in (f).

The CNFs obtained 500 °C exhibit the similar bi-directional structure as those obtained at 400 °C (Figures 4(a) and 4(b)). As seen in the HRTEM image and the corresponding FFT patterns of the catalytic particle (Figures 4(d) - 4(e)), the defects formed at 500 °C are the
common (111) twins in fcc-Ni,[32-34] unlike those observed in Figure 3. The detailed TEM analyses also revealed that a different crystalline structure exists around the edge of the diamond-shaped Ni-particle, as shown in Figure 4(f). The structure has the lattice spacings of 0.25 nm and 0.37 nm and an interfacial angle of ~ 90°, which are definitely not from metallic Ni. Again, the spacings and angle of those planes do not well match those of the most possible planes in Ni$_3$C, $d_{(011)} = 0.38$ nm and $d_{(-104)} = 0.25$ nm with an angle of 94°. As not elemental O could be detected (not shown here), the most possibility is that the lattice fringes are also from the distorted Ni$_3$C or the unstable Ni$_3$C$_{1-x}$.[27-31]

The morphology and structure of the CNFs at 600 °C are similar to those obtained 500 °C, though rare defects can be detected within the catalytic particles, as shown in Figures 5(a) and 5(b). Detailed TEM analyses confirmed that the catalytic particle was pure fcc-Ni, and no other phase could be detected at the edge of the catalyst particles. This is also supported by the EDS result that no elemental O could be detected in catalytic particles (not shown here) and no nickel oxides could be detected by XRD (Figure 1).

![Figure 5](image)

**Figure 5.** The CNFs obtained at 600 °C. (a) The SEM image of the as-synthesized CNFs, (b) the TEM image of a typical catalytic particle, (c) the HRTEM image taken from the dashed square C in (b). The inset in (c) shows the corresponding SAED pattern of the catalytic particle.
Figure 6. HRTEM images of the C layers and the ends of the catalyst particles obtained at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C, respectively. The inset in each image shows the corresponding FFT pattern of the end of the catalyst particle.

From the above-mentioned TEM results, we find that the catalyst particles are basically diamond-shaped at 400, 500 and 600 °C and are hexagonal at 300 °C. To obtain the further structural information about the CNFs and the corresponding catalysts at different temperatures, we performed intensive TEM analyses on the C layers and the ends of the corresponding catalyst particles, and presented the typical HRTEM images in Figure 6. According to the TEM results, the crystallinity of the C layers, although relatively low, increase with the growth temperature ranged from 300 to 600 °C. Moreover, the C layers are all basically parallel with the C/catalyst interfaces, i.e., the C layers may exhibit different angles to the growth directions of the corresponding CNFs, roughly depending on the tip angles of the catalyst particles. At 300 °C, the end of the Ni$_3$C particle is smooth and flat, and C layers are therefore roughly
perpendicular to growth direction of the CNF (Figure 6(a)). On the other hand, the tip angle of the diamond-shaped catalyst particle become sharper with the increase of the growth temperature from 400 to 600 °C, the angle between the C layers and growth direction of the corresponding CNF is thus become smaller, as shown in Figures 6(b)-6(d).

3.2 Growth mechanism of CNFs

It is generally argued that the observed Ni$_3$C or Ni$_3$C$_{1-x}$ nanoparticles might be formed from the metallic Ni during the cooling process, rather than the “true catalytic particle” for the growth of CNFs.[35] In our experiments, provided that the observed nickel carbide in the samples obtained at temperatures of 300 to 500 °C was generated during cooling, it should also exist in the samples that were cooled down from 600 °C, because all samples were cooled at the same rate, and the catalytic particles at the 600 °C should have a higher solubility of C.[35, 36] As the temperature ceiling for metastable Ni$_3$C is ~ 500 °C, and no nickel carbide is detected in the catalytic particles obtained at 600 °C. It is reasonable to conclude that the observed nickel carbide should be generated at the initial stage of the synthesis and assist the growth of the CNFs, but not generated during the cooling process.

According to the C-Ni phase diagram,[37] there are no stable carbides in the C-Ni system, but the metastable carbide, Ni$_3$C, can exist at a temperature up to ~ 1000 °C. However, the phase transitions in C-Ni nanoscale system are quite different the bulk counterpart.[38] Itoh and Robert detected a weak broad peak below 500 °C when characterizing the Ni-C nanostructure by differential scanning calorimetry, and then confirmed that the thermal decomposition of metastable Ni$_3$C started at 300 °C and accomplished at ~ 500 °C using in-situ annealing in a TEM.[39] Similar phase transitions for Ni-C nanoscale system were later also observed by some other groups, and also well consistent with our XRD and TEM results.[22, 28, 30, 31, 40] It is therefore reasonable to presume that the chemical state of Ni catalyst should be Ni$_3$C at
300 °C, and then shift to Ni-Ni$_3$C$_{1-x}$ composite at 300 to 500 °C, and eventually transform into the common metallic Ni at temperatures higher than 500 °C. More detailed processes of the catalytic growth process at different temperature are sketched as follows (Figure 7).

The growth of the CNFs obtained at 300 °C, as suggested in our previous work, is controlled by the Ni$_3$C-assisted mechanism with the following basic steps (Figure 7a).[21] (1) Decomposition gaseous precursor Ni(acac)$_2$ and formation of Ni atomic-clusters and C-contained gases.[41, 42] (2) Formation of Ni$_3$C nanoparticles due to the aggregation of Ni$_3$C molecule-clusters generated by the catalytic reaction between the pre-formed Ni clusters and C-contained gases.[43] (3) Nucleation of C layers on the surface of Ni$_3$C nanoparticles due to the thermal decomposition of Ni$_3$C molecules.[30, 44] (4) Growth of CNFs from Ni$_3$C nanoparticles due to the continuous decomposition-formation cycle of Ni$_3$C molecules.[45, 46] It should be noted that the concept of carbide cycle is based on the previous in-situ TEM observation that the formation and decomposition of metastable Ni$_3$C could simultaneously take place at different parts of the Ni-C film at about 300 °C.[39]

The growth of CNFs obtained at the temperatures ranged from 300 to 500 °C is presumed to be induced by the composite-assisted mechanism with the following fundamental process (Figure 7b). (1) The gaseous precursor Ni(acac)$_2$ was thermally decomposed and Ni atomic-clusters and C-contained gases were formed. (2) Ni-Ni$_3$C$_{1-x}$-C composite nanoparticles[27, 28, 47] were formed from the aggregation of Ni$_3$C$_{1-x}$ molecule-clusters and small Ni-C clusters, which were generated by the catalytic reaction between the pre-formed Ni atomic clusters and C-contained gases. It should be noted that the existence and the detailed chemical state of Ni$_3$C$_{1-x}$ considerably rely on the temperature and the atmosphere in a specific reaction.[48, 49] and the resultant nanoparticles are therefore expected to exhibit an complex and uncertain phase constituents and crystalline structures, as observed in our TEM
examination (Figures 3(c), 3(f) and 4(f)). (3) C layers nucleated on the outer surface of metallic Ni within the composite nanoparticle and the difference of C concentration between Ni$_3$C$_{1-x}$ and Ni within the composite nanoparticles was established. (4) CNFs were grown continuously from metallic Ni/C interfaces.[50, 51] In this step, C atoms were firstly adsorbed onto the surface of Ni$_3$C$_{1-x}$ exposed to the atmosphere. Then, they were dissolved into Ni$_3$C$_{1-x}$ and further diffused through the interface between Ni$_3$C$_{1-x}$ and Ni, due to driving force from the huge concentration gradient at the interface. Eventually, C atoms were precipitated from the Ni/C interface, thus leading to the growth of CNFs.

Figure 7. Three different chemical states of Ni catalyst at different temperatures: (a) Ni$_3$C at 300 °C, (b) Ni-Ni$_3$C$_x$-C composite at 400 and 500 °C, and (c) metallic Ni above 500 °C.

The formation of CNFs generated above 500 °C was believed to be governed by the well-known dissolution-precipitation process of C atoms through the metallic Ni particles, as illustrated in Figure 7(c).[51-53] The temperature ceiling of ~ 500 °C for the existence of metastable Ni$_3$C is well accepted, though the thermal decomposition of Ni$_3$C is also dependent on the specific atmosphere.[22] This is also supported by our XRD and TEM results that the catalyst particles are metallic Ni. Moreover, the Ni-catalyzed mechanism is consistent with the *in situ* TEM observation that the catalyst was metallic Ni at the temperatures above 500 °C.
The differences in the chemical states and shapes of the catalyst particles have an obvious effect on the morphology of the CNFs, although all CNFs are basically coiled. The coiled morphology can be intuitively attributed to the asymmetric supply of C atoms during the catalytic growth of CNFs, but is essentially controlled by the asymmetrical morphology and structure of the catalyst particles. At 300°C, the diameters of the CNFs are much smaller than those of the corresponding catalyst particles, and the CNFs normally do not initiate from the centers of the corresponding flat Ni$_3$C surfaces (Figure 2(b)). This will lead to the significant difference in the C supply at the CNF/Ni$_3$C interfaces along different directions. As a result, the CNFs are heavily coiled. At temperatures above 300°C, carbide is asymmetrically located at the side edges of the catalyst particles. With the increase of the temperature, the content of carbide decreases gradually, and the carbide tends to distribute symmetrically at the side edges (Figures 3(b) and 4(b)). In addition, the catalytic particles usually do not have a symmetrical diamond-like shape. The as-grown CNFs are therefore also coiled, but are relatively straighter than those at 300 °C. At 600°C, no trace of carbide could be detected in the catalyst particles, but the diamond-shaped Ni catalyst particles are still asymmetrical (Figure 5(b)). This will definite affect the symmetric supply of C atoms, and thus the CNFs remain coiled to some extends, but are much straighter than those obtained at 300 to 500 °C.

4. Conclusion

The CNFs were synthesized by use of catalytic CVD at temperatures ranged from 300 to 600 °C. It was found that the chemical state of Ni catalyst was dependent on the growth temperature, i.e., Ni$_3$C at 300 °C, Ni$_3$C$_{1-x}$-Ni at 400 and 500 °C, and metallic Ni at 600 °C. This suggested that the growth of CNFs at different temperatures should be controlled by different growth models, Ni$_3$C-assisted model, composite-assisted model and Ni-assisted model. This work not only provided the fundamental knowledge for the controllable fabrication of CNFs, but also
unified the different models on the catalytic growth of CNFs, which has been a longstanding issue on this topic.

Acknowledgements

This study is financially supported by the National Natural Science Foundation of China (51074188, 11502080), Research Funding of Central South University (2014JSJ024) and the Australia Research Council (ARC) under the Discovery Project program (DP130101828).

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