



The Formation of Carbon Microcoils Having the Coil-Type Overall Geometry

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Abstract: Carbon microcoils could be synthesized using a thermal chemical vapor deposition process in which C_2H_2/H_2 is used as the source gas and SF_6 as an additive gas. We investigated the formation of carbon microcoils as a function of reaction time to study the growth mechanism of coil-type carbon microcoils, particularly under long reaction time. After the first 5 min of the reaction, wave-like carbon nano coils were formed along with carbon microcoils at certain positions on the sample. An increase in reaction time (60 min) led to the formation of double helix-type carbon microcoils. Further increase in the reaction time (120 min) led to the formation of twist-type carbon microcoils with occasional growth of the coil-type carbon microcoils on the sample. However, at the longest reaction time (180 min) investigated in this work, we observed a decrease in the density of the carbon microcoils. Based on these results, we determine the optimal reaction time for the growth of double helix-type carbon microcoils and suggest the growth mechanism of the coil-type carbon microcoils with a focus on long reaction time.

Received on 16-10-2015
 Accepted on 17-11-2015
 Published on 05-01-2016

Keywords: Coil-type Carbon Microcoils, Growth Mechanism, Coil Geometry, Reaction Time, Thermal Chemical Vapor Deposition.

DOI: <http://dx.doi.org/10.6000/2369-3355.2015.02.03.5>

1. INTRODUCTION

Unique geometries of carbon microcoils have attracted considerable attention as a promising material in nano-/microelectronic or mechanical devices [1-5]; however, the growth mechanism of carbon microcoils is not yet fully understood. Chen and Motojima reported the growth pattern and morphology development of carbon microcoils as a function of reaction time from 5 to 120 min [6]. Their study indicated that the initial reaction stage during carbon microcoil formation could play an important role in determining the geometry of the carbon microcoils. In general, metal catalysts are considered indispensable in the growth of carbon microcoils [7-10]. The catalytic anisotropy of the different crystal faces of the catalyst grain was proposed as the initial driving force to form the microcoil geometry [9] following a quasi-vapor liquid solid (VLS) mechanism [10].

A plausible growth mechanism of the carbon microcoils was also reported in our previous work [11-13]. Park *et al.* confirmed the initial stage of the reaction as being the most effective for the formation of the double helix-type carbon microcoils [11]. Thus, the growth mechanism of the carbon microcoils was investigated from the preheating stage of the

reactor by Jeon *et al.* [12]. In their study, circular-type nickel clusters were formed when the substrate temperature was set to $750\text{ }^{\circ}\text{C}$ followed by the formation of carbon nanofilaments after a reaction time of 30 s. Jeon and Kim revealed that the twin carbon nanofilaments transformed into wave-like carbon nano coils with an increase in the length of the carbon nanofilaments [13]. In spite of these reports, more in-depth investigation is still needed for complete understanding of the formation and growth mechanism of the carbon microcoils.

In this work, the surface morphology of the samples was investigated as a function of reaction time to study the growth mechanism of the carbon microcoils with various geometries at long reaction times. The evolution of the coil-type carbon microcoils from the double helix-type carbon microcoils was observed, particularly, at longer reaction time. To this end, we present a systematic growth model for the coil-type carbon microcoils with a focus on long reaction time.

2. EXPERIMENTAL

Silicon oxide (SiO_2) substrates used in this work were prepared by the thermal oxidation of $2.0\text{ cm}\times 2.0\text{ cm}$ p-type Si (100) substrates. The thickness of the SiO_2 layer on the Si substrate was estimated to be about 300 nm. About 0.01 g of nickel (Ni) powder (99.7%) was evaporated for 1 min to form the Ni catalyst layer on the substrate using a thermal

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Table 1: The Detailed Reaction Conditions for the Formation of Carbon Microcoils

Samples	C ₂ H ₂ Flow Rate (sccm)	H ₂ flow Rate (sccm)	SF ₆ Flow Rate (sccm)	Substrate Temp. (°C)	Total Pressure (Torr)	Reaction Time(min)	Source/Additive Gas Flow Time (min)		
							C ₂ H ₂	H ₂	SF ₆
A	15	35	35	750	100	1.0	1.0	1.0	1.0
B	15	35	35	750	100	5.0	5.0	5.0	5.0
C	15	35	35	750	100	60.0	60.0	60.0	5.0
D	15	35	35	750	100	120.0	120.0	120.0	5.0
E	15	35	35	750	100	180.0	180.0	180.0	5.0

evaporator. The estimated thickness of the Ni catalyst layer on the substrate was about 400 nm, as measured by cross sectional field emission scanning electron microscopy (FESEM).

A thermal chemical vapor deposition (CVD) system was used to grow carbon coiled structures, with acetylene (C₂H₂) and H₂ as the source gases. SF₆, an incorporated additive gas, was injected into the reactor during the reaction. The flow rate for C₂H₂, H₂, and SF₆ were fixed at 15, 35, and 35 standard cubic centimeters per minute (sccm), respectively. The reaction processes were terminated at the desired reaction times. The substrate temperature and total pressure in the reactor were set to 750 °C and 100 Torr, respectively. The detailed reaction conditions for the formation of carbon microcoils are described in Table 1.

To elucidate the growth mechanism of the carbon microcoils at long reaction time, five samples (samples A–E) with different reaction times (1, 5, 60, 120, and 180 min) were prepared. Detailed morphology of the deposited carbon microcoils on sample substrates (A–E) was investigated by using FESEM (Hitachi S-4200).

3. RESULTS AND DISCUSSION

Figure 1 illustrates FESEM images of the surface morphologies of sample A. As seen in Figure 1a, a 1 min reaction resulted in the formation of carbon nanofilaments

covering the entire surface area of sample A. The magnified images show several lumps (see Figure 1b) as well as the linear-type carbon nanofilaments which appeared to have a twin structure (see dotted circle in Figure 1c). Indeed, most of the carbon nanofilaments formed under this condition showed twin-structured carbon nanofilaments attached to each other, as discussed in our previous reports [12, 13]. In addition, many bright spots comprised of the Ni catalyst-incorporated carbon species, such as Ni₃C were observed around the lump area [14].

Figure 2 shows FESEM images of the surface morphologies of sample B. After 5 min of the deposition reaction, we observed not only the formation of numerous wave-like carbon nanocoils but also the initial growth of the carbon microcoils on sample B (see areas marked by arrowheads in Figure 2b). We noticed that the formation of the carbon microcoils was initiated from the wave-like carbon nanocoils [12, 13].

As shown in Figure 3, after 60 min of the reaction, well-developed carbon microcoils were formed on the entire surface of sample C. These carbon microcoils show the typical double helix geometry [12, 15] with lengths in the range of several tens of micrometers.

After 120 min of the reaction, double helix-type carbon microcoils were still observed on the surface of sample D, as seen in Figure 4. However, the density of the carbon

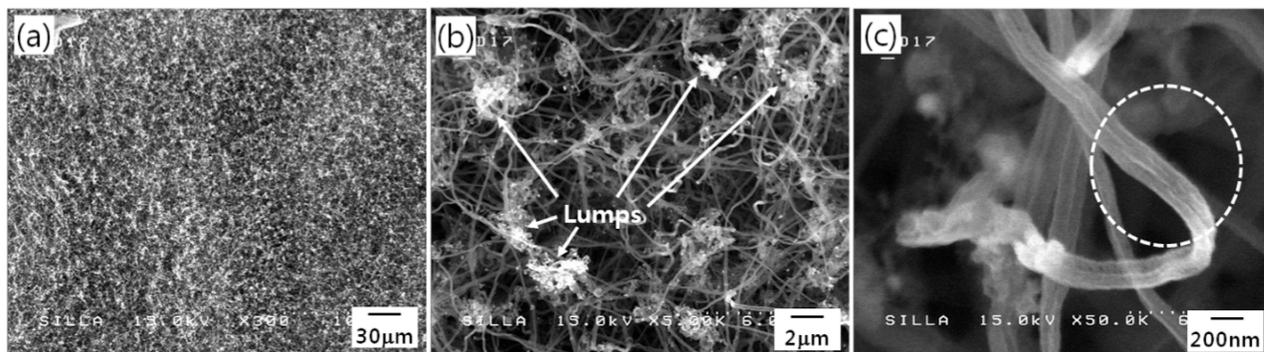


Figure 1: FESEM images of the surface morphologies for sample A under the magnification of (a) 300, (b) 5,000, and (c) 50,000.

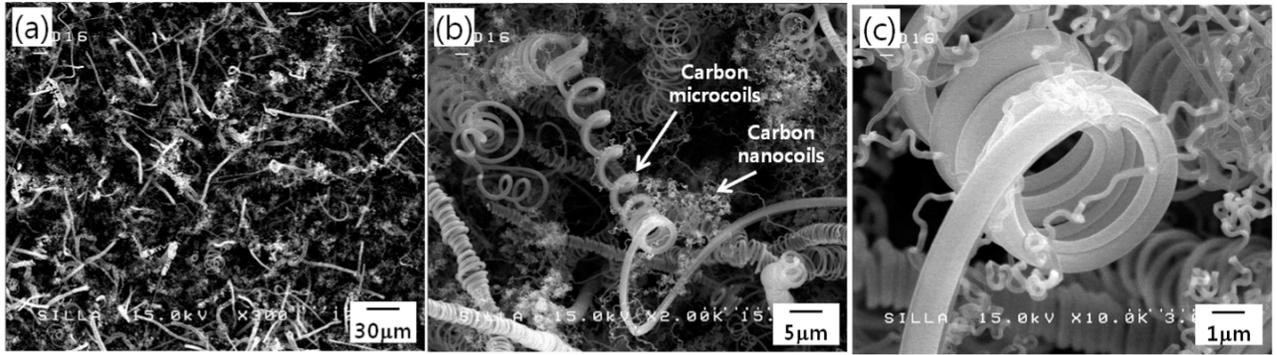


Figure 2: FESEM images of the surface morphologies for sample B under the magnification of (a) 300, (b) 2,000, and (c) 10,000.

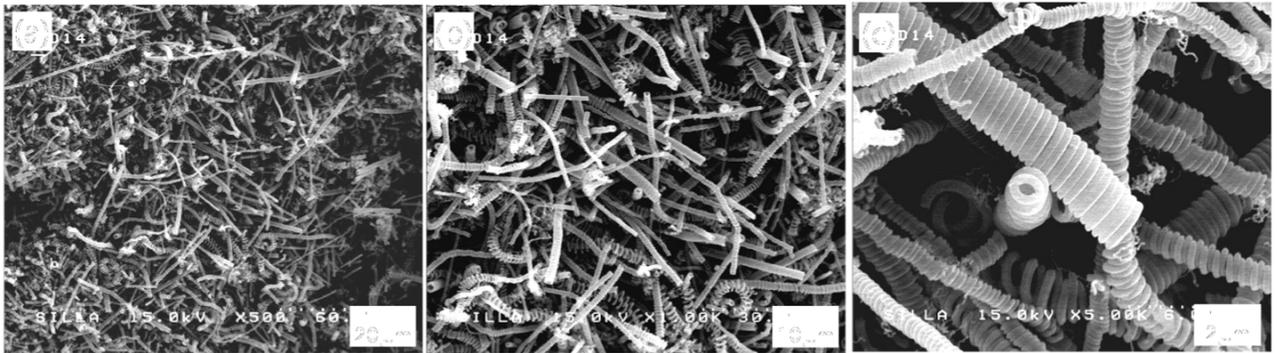


Figure 3: FESEM images of the surface morphologies for sample C under the magnification of (a) 500, (b) 1,000, and (c) 5,000.

microcoils was decreased compared to that observed after 60 min (compare Figures 4b and 3b). In this case, many wave-like carbon nanocoils were also formed around the carbon microcoils as shown in Figure 4d. In addition, compared to sample C, the length of the carbon microcoils in sample D increased and reached more than several hundreds of

micrometers (compare Figures 4a and 3a). Besides the length difference, the overall geometry of the carbon microcoils was slightly different between sample C and sample D. Specifically, the twist-type overall geometry for the carbon microcoils was commonly observed (see the dotted circle areas in Figures 4b and 4c) along with occasional coil-

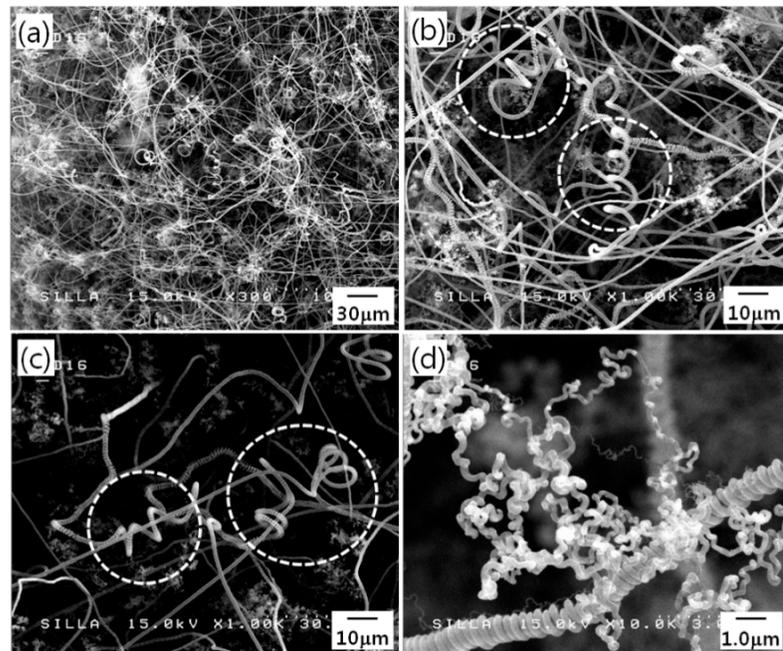


Figure 4: FESEM images of the surface morphologies for sample D under the magnification of (a) 300, (b) 1,000, (c) 1,000, and (d) 10,000.

type carbon microcoils on sample D as shown in Figure 5. Our conclusion from the above observations was that the coil-type geometry evolved from the twist-type geometry.

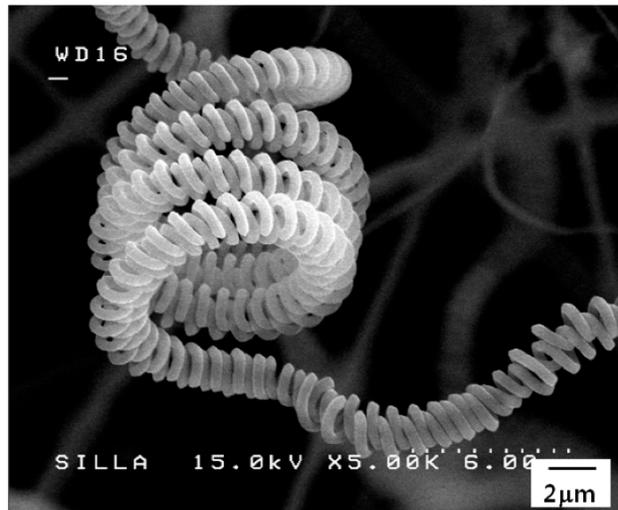


Figure 5: FESEM images of the carbon microcoil having the coil-type overall geometry.

Based on the results of Figures 1-5, we propose the following growth mechanism of carbon microcoils with a coil-type

overall geometry from carbon nanofilaments with increasing reaction time: according to the dissolution-diffusion-precipitation model [10, 16], the precipitated carbon atoms are the origin for the growth of the carbon nanofilaments. In case of the formation of the carbon microcoils, the two carbon nanofilaments building up the double helix-type geometry were initiated from the coil's head with almost opposite growth direction [11]. The balance axis of the metal catalyst located on the coil's head was collapsed by the different growth rates of the two carbon nanofilaments. As a result, it caused twisting of the coil's head, further leading to the spinning of the coil's head. Moreover, the height difference between the starting points of the two carbon nanofilaments and the coil's head alternated for each carbon nanofilament as the coil's head advanced in its growth direction. The preceding steps led to the creation of carbon microcoils with double helix geometry. Further growth of the carbon microcoils causes twisting due to continuous spinning of the coil's head. Eventually, it leads to the formation of the coil-type overall geometry for the carbon microcoils. Figure 6 shows the systematic model for the formation of the carbon microcoils with the coil-type overall geometry.

For the longest reaction time (180 min) investigated in this work, sample E mainly showed linear-type carbon nanofibers

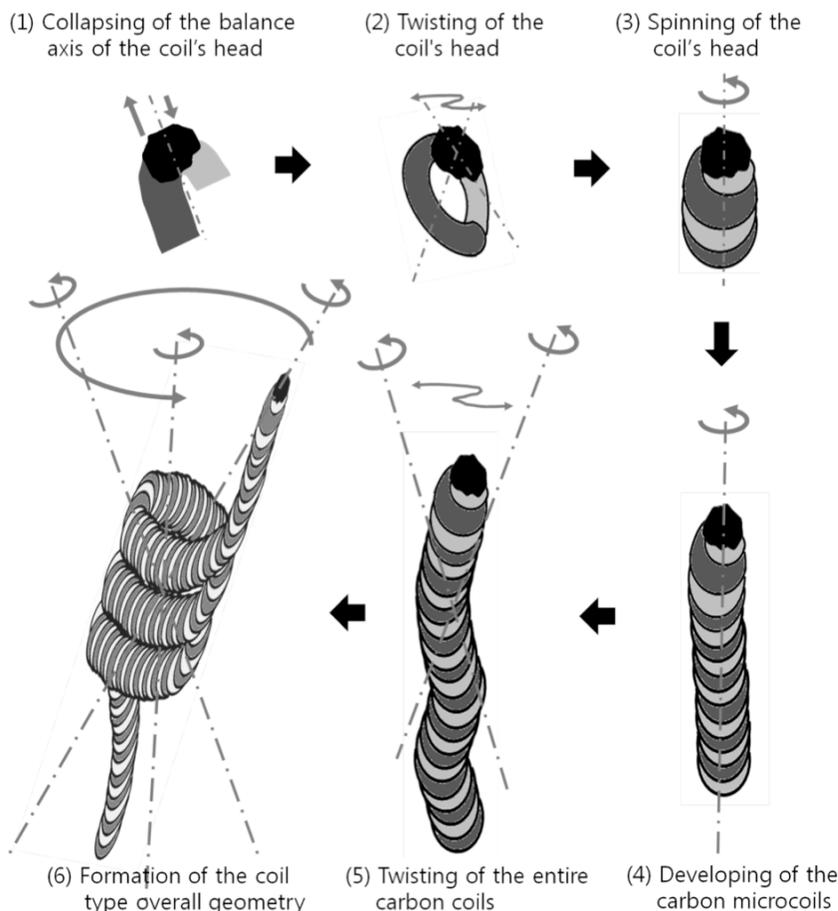


Figure 6: The systematic model showing the growth mechanism of the carbon microcoil with the coil-type overall geometry.

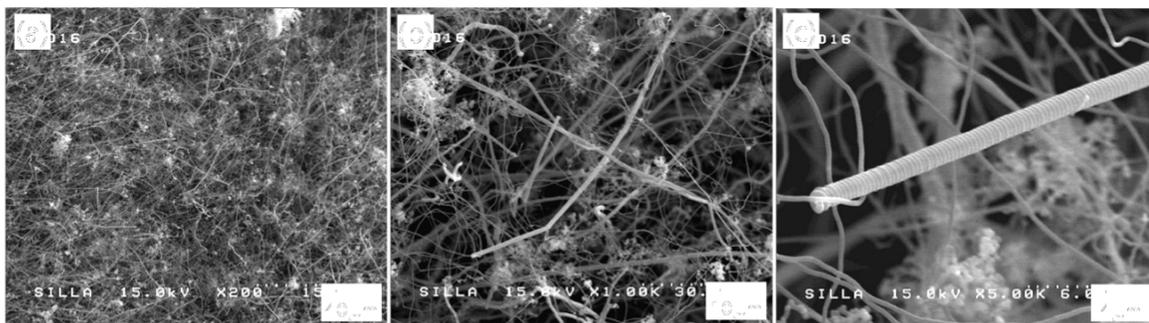


Figure 7: FESEM images of the surface morphologies for sample E under the magnification of (a) 200, (b) 1,000, and (c) 5,000.

with few carbon microcoils (Figure 7). These linear-type carbon nanofibers were formed *via* the release of the carbon microcoils. The release of the carbon microcoils was due to the continuous carbon feeding from the source gas (C_2H_2), which consequently disrupted the spinning of the coil's head by the cumulative production of carbon materials on the head area. These results indicate that a reaction time of 180 min is not suitable for the formation of double helix-type carbon microcoils.

CONCLUSIONS

At the initial reaction stage (1 min), twin-structured carbon nanofilaments were observed. At a reaction time of 5 min, the formation of carbon microcoils was initiated among wave-like carbon nanocoils. At a reaction time of 60 min, double helix-type carbon microcoils were formed with a higher density than any other stage of the reaction. At a reaction time of 120 min, the length of the carbon microcoils was increased and carbon microcoils having the twist-type overall geometry were formed. The twist geometry led to the formation of coil-type overall geometry due to the continuous spinning of the coil's head. We propose a systematic model for the formation of carbon microcoils with the coil-type overall geometry. At a reaction time of 180 min, the density of the carbon coils was decreased, and instead, a large population of the linear-type carbon nanofibers was observed. These linear-type carbon nanofibers were formed due to uncoiling and untwisting of the carbon microcoils.

ACKNOWLEDGEMENTS

This work was supported by the Human Resource Training Program for Regional Innovation and Creativity through the Ministry of Education and National Research Foundation of Korea (2014H1C1A1066859).

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