Controllable synthesis of carbon coils and growth mechanism for twinning double-helix catalyzed by Ni nanoparticle

Xian Jian a, Dingchuan Wang b, Hongyang Liu b, Man Jiang a, Zuowan Zhou a,*, Jun Lu a, Xiaoling Xu a, Yong Wang a, Li Wang c, Zizheng Gong c, Mingli Yang d, Jihua Gou e, David Hui f

aKey Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu 610031, China
bShenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
cChina Academy of Space Technology, Beijing 100094, China
dDepartment of Mechanical, Materials and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, USA
eDepartment of Mechanical Engineering, University of New Orleans, New Orleans, LA 70148, USA

ABSTRACT

A simple approach using ~90 nm Ni nanoparticles to tune the growth of carbon fibers is developed basing on the bottom-up regulation in this study. By adjusting the preparing temperature and atmospheric composition, the nickel-containing catalysts with specific sizes and shapes are alternately prepared from 90 nm to 500 nm. The straight carbon nanofibers and three kinds of carbon coils (single-helix carbon nanocoils, single-helix carbon microcoils and twinning double-helix carbon microcoils) with the coil diameter ranging from 150 nm to 3 μm are achieved by using the as-prepared catalyst. The relationship between the carbon coil and catalyst particle, and the growth mechanism for different kinds of helices are discussed in details. The results suggest that catalytic anisotropy come from growing tendency and rate of carbon deposition on the facets, edges and vertices of catalyst grain. The twinning structure exists in each fiber of the double-helix carbon microcoils regardless of circular or flat fiber, which is separated by the tip of the catalyst particle due to the different rate of carbon deposition at edge and vertex.

Keywords:
A. Carbon fibre
A. Nano-structures
E. Chemical vapour deposition (CVD)
E. Heat treatment

1. Introduction

Since the discovery of carbon helix, the synthesis of carbon coils involving fibers or tubes with helical diameter sized from 16 nm to 30 μm [1,2] has attracted significant attention, not only for fundamental scientific [3,4] interests, but also for their potential applications [5–7]. Though carbon nanofiber or tubes can strength some composites. Part B (2013), http://dx.doi.org/10.1016/j.compositesb.2013.06.010

So far, two main strategies have been developed to synthesize helical structures of carbon coils. One is the “catalyst-component” adjustment depending on the catalytic activity, and the other is the “growth-condition” method being governed by the chemical kinetics. Several helical carbon structures (double/single-helix, micro/nano-coils, helical fibers/tubes, etc.) were obtained by adjusting the component of metallic catalysts (Fe, Co, Ni, Cu, In or their alloys) [22–24]. The advantage of the catalytic activity methods is the production with high pertinent characteristic, but the procedure of preparing the special catalyst seems quite complicated. The chemical kinetic methods can be used to synthesize shape-controlled carbon coils by choosing different carbon sources [24], adding the substrate [25,26] or introducing magnetic/micro-wave field [27,28], but the equipment is usually fussy and the procedure is multi-step. In order to simplify the process to obtain special carbon coils, it is necessary to explore an effective method to combine the catalytic activity with chemical kinetics.

Nickel is one of the typical catalysts for growing the helical carbon fibers (CFs). For example, pure Ni powder sized of ~5 μm [29] or 500 nm [30], activated carbon nanotubes supported Ni ~0.8 μm [31], nickel foam [32] and Ni plate [33] were used to prepare helical CFs with an approximate fiber diameter of 500 nm. It can be noticed that some carbon coils with similar sizes and diameters were prepared using Ni catalyst with different particle size.
Nevertheless, few literatures provided reasonable explanations to the relationship between the initial Ni catalyst size and the diameter of the CFs. In addition, it has been proposed that the driving force for the coiling of vapor grown CFs is the presence of catalytic anisotropy among the crystal facets of the catalyst grain. However, the direct evidence of this presumption has not been reported yet.

In this work, we reported the size control of Ni catalyst by chemical reduction and the rational synthesis of several different carbon coils by catalytic chemical vapor deposition (CCVD) method using acetylene as carbon source. The as-synthesized CFs could be controlled into linear carbon nanofibers (CNFs) and carbon coils including single-helix carbon nanocoils (SH-CNCs), single-helix carbon microcoils (SH-CMCs) and twinning double-helix carbon microcoils (TDH-CMCs). In addition, the existence of catalytic anisotropy was experimentally approved and the expounded growth mechanism for these carbon species was preliminarily suggested.

2. Experimental section

For the synthesis of Ni catalyst, the mixed solution containing 20 mL of 0.8 mol/L (M) sodium hydroxide solution, 20 mL of 6 M hydrazine hydrate aqueous solution and 1 g polyvinylpyrrolidone (PVP-K30) was firstly prepared. Then 20 mL of 1 M nickel sulfate aqueous solution was slowly added to the mixed solution. Finally, Ni nanoparticles were prepared by chemical reduction with hydrazine hydrate in distilled water at 70 °C with magnetic stirring for 1.5 h. Ni nanoparticles, namely the black precipitates, were separated from the mother liquor by magnetic separation, and washed several times with distilled water and acetone, respectively, until the pH was 7. The obtained Ni nanoparticles, grey–black powder, were dried in vacuum at 25 °C.

The Ni catalyst (30 mg/cm²) supported by graphite plate was placed in the central part of a horizontal reaction tube (quartz, 24 mm i.d.), which was heated from the outside by an electrically heated horizontal furnace. Then linear and helical CFs were prepared on the graphite plate using a gas mixture of C₂H₂, H₂ and N₂ containing a small amount of thiophene as catalytic auxiliary. The furnace was firstly flushed until 600 °C at the rate of 5 °C/min under nitrogen, and it was unceasingly flushed from 600 to 750 °C at 3 °C/min under hydrogen. Acetylene along with thiophene vapor was allowed to slowly enter the furnace at a rate of 20 mL/min. Thiophene was introduced at a rate of about 80 mg/min by bubbling acetylene through a vessel containing thiophene at 40 °C. Meanwhile, the flow rate of H₂ was fixed at 60 mL/min. Nitrogen was used as the carrier gas at a given rate from 100 to 140 mL/min. The fluffy products of various CFs including linear CNFs, SH-CNCs, SH-CMCs and TDH-CMCs were synthesized without further treatment.

The crystal structure of the catalyst particles and the helical CFs was investigated using X-ray diffraction (XRD, Panalytical X’Pert PRO diffractometer with Ni-filtered, the Netherlands). The size and morphology analyses of the nickel particles and the CFs were performed using scanning electron microscope (SEM, Fei, Quanta 200 and Inspect-F) with an accelerating voltage of 20.0 kV and transmission electron microscopy (TEM, H-700H) at an accelerating voltage of 160 kV.

3. Results and discussion

3.1. Preparation and characterization of Ni catalyst

Generally, catalyst plays an important role in the control of helical carbon materials with desired category and morphology. For example, three-dimensional spring-like carbon nanocoils are obtained with high purity by the catalytic pyrolysis of acetylene at 750–790 °C using a Fe-based catalyst, and the nanocoils have a nanotube of 10–20 nm [34]. Besides, the carbon nanocoils with coil diameters of 50–450 nm can be obtained using sputtered thin films of Au and Au/Ni as catalysts [27]. Considering that Ni particle is one of the typical catalysts for the mass production of carbon microcoils (CMCs), we prepared high-purity and monodispersed Ni nanoparticles by the reduction of a nickel salt with hydrazine hydrate employing the surfactant of PVP to prevent agglomeration of the nanoparticles. The effects of reaction temperature (Fig. S1 in Supporting information), NaOH concentration (Fig. S2) and reaction time for the preparation of nickel powders were systematically investigated. Spherical and relatively uniform Ni particles (Fig. 1a) were obtained under the optimal condition that the molar concentration of NaOH solution was 0.8 M at 70 °C with magnetic stirring for 1.5 h. Particle-size distribution (Fig. 1c) of the obtained monodispersed Ni nanoparticles was determined by software of Nano Measurer [35] program based on the corresponding SEM images. The average particle size was 90.12 nm with a relatively narrow distribution. The TEM image of the as-prepared Ni nanoparticles placed in ethyl alcohol is shown in Fig. 1b. It could be seen that sometimes Ni nanoparticles adhered to each other forming into some larger Ni grains of about 150 nm, which might be due to the ferromagnetism of them. The XRD pattern of the nanoparticles, shown in Fig. 1d, revealed an fcc Ni crystalline structure. In the XRD profile, the three characteristic diffraction peaks corresponding to the (1 1 1), (2 0 0) and (2 2 0) diffraction planes of only cubic Ni phase over 40° were clearly observed, which was well in agreement with the standard nickel diffraction pattern (ICDD, PDF file No. 01-070-1849). The crystallite size of Ni for the most intense peak (1 1 1) plane was determined from the X-ray diffraction data using the Debye–Schererr formula, and the average value was about 5.07 nm when the concentration of NaOH was 0.8 M. In addition, it could be found that the particle size calculated from the XRD pattern was rather smaller than that determined from the SEM image. The results suggested that the spherical nickel particles contained a number of ultra-fine crystals of about 5 nm, which agreed with the TEM observation of Ni particles’ morphology.

3.2. Rational synthesis of CFs

The CMCs are usually prepared using typical nickel catalyst such as Ni plate [33] and Ni powder with particle sizes from 0.5 to 5 μm [29–31]. Besides, Ni particles with a particle size below 50 nm [36] or about 500 nm [37] have also been chosen for the catalyst to prepare CMCs. It is can be seen that the Ni catalyst are of various kinds and their original size does not determine the fiber diameter of the corresponding carbon coil. The cause of this case might be that it was difficult to obtain carbon nanocoils on Ni nanoparticles below 100 nm. Similarly, we obtained linear CNFs without helical shape using the as-prepared Ni nanoparticles as the catalyst under the reaction conditions that the bath temperature of thiophene was 40 °C and the flow rate of C₂H₂, H₂ and N₂ was 20, 60 and 100 mL/min, respectively, at the reaction temperature of 660 °C for 3 min. A typical SEM image of the linear CNFs (Fig. 2) displayed an almost uniform fiber diameter of about 100 nm. This was due to the presence of an almost uniform size of catalyst particles and confirmed that the linear CNFs diameters depended on the size of the Ni particles in chief. The linear CNFs were straight or complexly curved, and interlaced with each other. This might be associated with the real-time shape of crystalline metallic Ni particles with symmetric or asymmetric shape during the growth of the CFs [38]. Since spherical catalyst particle has symmetric planes on condition that they pass through any diameter of the Ni nanoparticles, and the anisotropic behaviors of the catalyst do not show. Then straight CFs could be obtained using...
fine Ni particles with spherical shape, and curved CFs formed on the asymmetric spheroidal Ni particles. From the early study [39], linear CFs were synthesized using the catalyst containing Co or Fe alloy. This is a supplementary method for the synthesis of linear CFs, differing from the noodle-like twin fibers obtained at 700°C [40] by Chen and Motojima. Compared with the linear fibers, the fiber diameters of SH-CNCs were generally larger. The probable reason for this phenomenon was that the Ni particles underwent a growing-up experience by agglomerating and/or recrystallizing as the reaction temperature increased from 660 to 750°C. The fiber diameters of CFs depend on the size of Ni particles, thus the SH-CNCs have a little thicker fibers than linear CFs at relatively higher temperature of 750°C.

When the flow rate of N₂ reduced to 120 mL/min, the SH-CMCs (Fig. 3b) could be observed and they had a fiber diameter of 500–600 nm and a coil pitch of 2–3 μm. Different from conventional SH-CNCs, the coil pitch was generally quite large while the coils still kept the regular helical forms. Besides, the SH-CMCs contain an abnormal interlayer of a wavy morphology in the middle part of the fibers, which is similar to the spring-like carbon coils with wave-form laces obtained by changing the composition and the solid state conditions of the catalysts (71Fe–18Cr–8Ni–3Mo) supported on ceramic nano-powders [34]. Then, it is suggested that the SH-CMCs can be obtained just by controlling the flow rate of the carrier gas at 120 mL/min in this case.

Conventional DH-CMCs are usually prepared by the catalytic pyrolysis of acetylene using Ni powder of several micrometers in diameter. For example, Kawaguchi prepared double helix regular carbon microcoils with the catalyst of Ni powder having an average diameter of 5 μm [42]. Here we designed the process of getting the larger Ni particles by the bottom-up method, which is useful for...
The growth mechanism for the three kinds of helical carbon materials will be discussed in the next section.

3.3. Analysis and mechanism for carbon coils

Amelinckx et al. proposed a formation mechanism for catalytically growing of helix-shaped graphite nanotube [43]. They reported the geometrical parameters of the resulting helix could be expressed in terms of the extreme values $V_M$ (maximum velocity), $V_m$ (minimum velocity) of the extrusion velocity and of the inclination angle. The growth mechanism could also be sufficiently general to account for the variability in pitch of helices. About the CFs, the size of its diameter depended on the particle size of the catalyst, and the pitch and diameter of the coil were decided by the extrusion speed of $V_M$, $V_m$ and the inclination angle. Then it can be speculated that the direct cause for the discrepancies of the three kinds of helical fibers is the differences of the size and the anisotropy catalysis of the catalysts. Three kinds of carbon coils can be rationally synthesized by adjusting the flow rate of $N_2$ demonstrating that the flow rate makes huge effects on the catalytic performance of Ni particles.

Nitrogen flow rate seems to be the only changed parameter during synthesizing, which results in different carbon coils under the corresponding condition. However, the change of $N_2$ flow rate is not the essential cause, because $N_2$ is non-active and does not take part in the chemical reaction. Moreover, the $N_2$ flow rate does influence the quantity of carbon source and $H_2$ for a certain period of time. From the difference of the diameters of helical CFs, it can be reasonably speculated that the fine Ni particles happen to form larger agglomerates. For example, as the fine Ni particles of ~100 nm have the volume of $V_0$, they can grow up into larger particles sized of 150 nm ($\sim 3.375V_0$) or 500 nm ($\sim 125V_0$). Though it can be noticed that hydrogen plays an essential role in the formation of helical CFs, it is difficult to in situ observe the changing process of the catalyst particles and the forming course of the carbon coils. To elucidate the mystery, the effects of hydrogen on catalyst particles were investigated and the results displayed that the fine Ni particles changed not only their particles sizes, but also the exposed crystal facets and the topography after heat treatment under $H_2$ at 750 °C for 1 h as shown in Fig. 4. The fine Ni particles grew into larger particles by recrystallization. Meanwhile, some concavity formed on the surface of the aggregative Ni particles highlighted by the small ellipse in Fig. 4a, and some of them had polyhedral shape as shown in Fig. 4b. These changes might be ascribed to two reasons. One is the changes of surface energy under $H_2$. From the energy’s point of view, the Ni facets with lower surface energy tend to expose and wrap around the catalyst particle. The other reason might be the existence of the reaction between $H_2$ and Ni, which causes forming the new species of NiHx. Then the role of $H_2$ during the growth of carbon coils can be summed up in terms of three major points. Firstly, the flowing $H_2$ adjusts the rate of the reaction of $C_2H_2 = 2C + H_2$, by diluting the concentration of the carbon source gas, and accordingly affects the growth rate of the CFs. Secondly, hydrogen prevents the catalyst from poisoning, and reactivate the poisoned catalyst particles according to this work. The main reaction are shown in Fig. 5, where $Ni_xC$ is some poisoned catalyst particles and the $Ni_3C_2$ is the activated catalyst such as $Ni_3C$ [44]. Thirdly, hydrogen induces reconstruction of the catalyst particles and control the exposed metal faces [45], which influences the size, the exposed crystal facet and topography of the catalyst particles [46] and the presence of $H_2$ during synthesis was found to have a positive effect on CCF formation at given condition [47].

As the reaction temperature increases from 600 to 750 °C under $H_2$, the Ni particles grow up to larger ones until they reach a stabilized state. Accordingly, the variable size and shape of the catalyst
particles from spherical particle (~100 nm) or special particle (~150 nm) to polyhedral micro-particle (~500 nm) could be adjusted by N₂ flow. Thus the three kinds of helical CFs can be rationally prepared with the same Ni nanoparticles just by controlling the reaction temperature and the N₂ flow. Fig. 6 depicts the formation of the linear CFs, SH-CNCs, SH-CMCs with lace and TDH-CMCs, and the corresponding Ni particles. To lower their surface energy, the small-sized nanoparticles tend to adopt spherical structures and exhibit catalytic isotropy, resulting in the formation of linear CFs. As the Ni particles growing up, their sizes become larger and their shapes turn to be more regular. Then various carbon coils formed on the corresponding nanoparticles of anisotropic catalysis. Apart from the familiar morphologies of SH-CNCs and TDH-CMCs, sometimes, SH-CMCs with lace grow on the asymmetric catalyst grain such as the one composed of hemisphere and a hexahedron. The suggestion will be verified in the future study.

It was reported that the driving force of curling and spiral coiling of the carbon coils was the catalytic anisotropies between catalyst crystal faces [30]. However, the catalytic anisotropy of the catalyst grain is not well defined, and the origin of the catalytic anisotropy is not well described yet. Boskovic et al. reported that carbon flowed to the nanofiber on the surface of the catalyst particle rather than diffuse through the particle [48]. Then the catalytic anisotropy mainly depends on the catalyst surface, leading to formation of various carbon coils with different cross section. In addition, Boskovic et al. observed that graphene layers were oriented parallel to the facets of the catalyst particle, while the middle part of the CNFs was composed of amorphous carbon corresponding to the edge-zone of the catalyst particle. Shen et al. proposed a mechanism for the regular coiled carbon nanotubes [49], basing on their mechanism analysis, a suggestion is put forward that the catalytic anisotropy is the discrepancy of forming carbon atoms on the surface of the catalyst, and the catalytic anisotropy origins from the atomic density of the catalyst surface and reflects in the form of facets, edges and vertices of the catalyst grain. In general, the formation of carbon coils is often related to the existence of polyhedral catalyst grain no matter microcoil [50] or nanocoil [51]. In order to analyze the polyhedral Ni compound particles, three kinds of typical regular polyhedrons, namely octahedron, hexahedron and dodecahedron, are sketched in Fig. 7a, b, and c, respectively. The cuboid has the sectional plane of symmetry more or less. For instance, the regular hexahedron divides into two comparative parts by the diagonal plane as presented in the shadow tetragon of Fig. 7b. Two main CFs (X and Y in Fig. 7e) grow bi-directionally

![Fig. 4. SEM images of Ni particles after heat treatment under H₂ at 750 °C for 1 h. (a) Some concavity formed on the surface of the aggregative Ni particles and (b) the district of the Ni particle with polyhedral shape.](image1)

![Fig. 5. The related reactions during the poisoned catalyst particles changing into activated ones under the effects of hydrogen, where NiₙCₜ is some poisoned catalyst particles, the NiₙCₜ is the activated catalyst such as Ni₃C.](image2)

![Fig. 6. Diagrams of the growth of four kinds of CFs on Ni particles with different size and shape: (a) small sphere (~80 nm), (b) small regular polyhedron (~150 nm), (c) quasi-regular polyhedron (~500 nm), and (d) regular polyhedron (~500 nm).](image3)
from the symmetric catalyst grain and then entwine with each other to form helical pattern of the conventional DH-CMCs. Similarly, two twinning fibers developed with the catalysis of a quarter of the catalyst particles. The cross section of the DH-CMCs forms according to the topography of the corresponding Ni particles. So the circular (Fig. 7d) and rectangular (Fig. 7e) cross sections of the carbon coils usually exist and are reported with adjusting some reaction condition [52]. Besides, the carbon coils having pentagonal fiber are presented in Fig. 7f. This is in good agreement with the experimental observation of the ruptured tip and of various graphite coils [53].

Kawaguchi et al. suggested that each crystal plane of a Ni seed had different catalytic ability for the growth of coiled fibers. Two CFs began to grow in opposite directions from each pair of planes (X and Y) on the Ni catalytic surface [42]. In the low magnification image (Fig. 8a) of typical DH-CMCs, they seemed to be made up of two circular fibers. The as-prepared regular TDH-CMCs could extend to 3–8 times of its original length as shown in Figs. S4 and S5.
8b. The extension characteristics was better than conventional DH-CMCs reported by Motojima et al. [33], but smaller than the super-elastic carbon microcoils [54]. Interestingly, we found the TDH-CMCs containing four small CFs as shown in Fig. 8b. The thick fiber Y consists of two fibers (Y1 and Y2) as shown in the high magnification image. Besides, some obscure scoop channel was also found in flat carbon filaments (Figs. 8c, d and S6). Thus, the growth mechanism proposed by Kawaguchi et al. [42] could not be applied to the growth of twinning double helical fibers. We then proposed an anisotropically carbon deposition on the facets, edges and vertices of catalytic polyhedron as the growth mechanism for carbon coils. The number of the branching fiber is mostly two [45] and three [50], sometimes is four and six [53], which determined by the anisotropical level of the catalyst grain. The catalyst particles had the sectional plane of symmetry in terms of catalytic ability for the growth of the fibers. Take the helical flat CFs as an example, the fiber M and fiber N grew on each comparative part of the catalyst particle. Due to the different forming rate of carbon atoms on the facet, edge and vertex of catalyst grain, two pieces of CFs grew more quickly on the crystal plane than at the edge or vertex, and the fibers twisted with each other leading to forming two coils. The diameter of the coil depended on the diversity of each comparative part of the catalyst grain. Similarly, fibers M1 and M2 generate on quarter part of catalyst grain and they lightly separate from each other due to the smaller different rate of carbon deposition at edge and vertex.

4. Conclusion

Linear CFs and three kinds of carbon coils were rationally prepared by gas-adjusting method using regular spherical Ni nanoparticles (~50 nm) as catalyst obtained by liquid phase reduction with hydrazine hydrate. The nano-scaled linear CFs often grow on spherical Ni particle in the form of straight and curved shape. Three kinds of carbon coils, namely, SH-CNCs, SH-CMCs and TDH-CMCs are rationally prepared by controlling the flow rate of N2 ranging from 100 to 140 ml/min. The morphological differences of the carbon species are caused by the characteristic of the real-time Ni catalyst, involving size, shape and external planar face. The catalytic anisotropy reflects in the form of facets, edges and vertices of the catalyst grain. The conventional DH-CMCs consisting of circular and flat DH-CMCs in this work had the twinning structure, from which a mechanism is proposed based on different growth rate of carbon nanoparticles on the facet, edge and vertex of catalyst grain. The mechanism is also useful for predicting the existence of some novel carbon coils, such as DH-CMCs with pentagonal cross section.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Nos. 51173148 and 90350003) the Special Research Fund for Doctoral Program of Higher Education (No. 20060613004), the NBRP (Grant No. 2011CB606200), the 2011 Doctoral Innovation Funds of Southwest Jiaotong University and the Fundamental Research Funds for the Central Universities (Nos. 2010XS31 and SWJTU11ZT10).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.compositesb.2013.06.010.

References


