Transactions of the Materials Research Society of Japan 27 [1] 39-42 (2002)

Vapor Phase Preparation of Carbon Microcoils/Nanocoils Using an Electromagnetic Field

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Carbon microcoils were prepared by the catalytic pyrolysis of acetylene with both the application of an external electromagnetic field and static magnetic field (hybrid EM field), and the effects of the hybrid EM field on the coil yield, morphology and some properties of the carbon coils were examined. The application of the hybrid EM field resulted in a decrease of the coil diameters, and the growth of carbon nanocoils with a few hundreds nm coil diameter were observed. The amount of carbon nanocoils increased with the increasing magnetic flux density. The carbon nanocoils were favorably obtained by using a nm-sized Ni powder as a catalyst along with the application of a low hybrid EM field and also by using a μ m-sized Ni powder catalyst with the high hybrid EM field. The carbon nanocoils are generally a single coil while the carbon microcoils are double coils. The density of the carbon coils increased from 1.80-1.83 without application of the EM field to 1.88-1.92 with the hybrid EM field.

Key words: chemical vapor deposition, carbon microcoils, carbon nanocoils, acetylene, electromagnetic field, static magnetic field

1. Introduction

Carbon microcoils, which have a 3D-helica/spiral structure with a coil diameter of a few μ m, can be obtained by the catalytic pyrolysis of acetylene at 750-800℃. The carbon coil can effectively absorb electromagnetic (EM) waves in the GHz regions. Accordingly, it may be reasonably considered that the growth process of the carbon coils is strongly influenced if the EM waves are irradiated into the reaction zone. We usually use an AC electric heater as the heating source for the high temperature reaction processes. In this case, strong EM waves are emitted from the electric heater and irradiated into the reaction zone. It was observed that the growth of the carbon coils was strongly affected by this EM field and/or bias voltage applied in the reaction zone, the coil yield was generally increased and the coil morphology was affected by application of the EM field (1-2). The carbon nanocoils with a coil diameter of a few hundreds to few tens nanometers were obtained using various catalysts with reaction conditions similar to that for carbon microcoils (3-12). The carbon microcoils and nanocoils are very interesting as key materials for nano-technology, because they have various potential applications such as electromagnetic absorbers, hydrogen storage materials, tunable micro/nano-devices, chiral catalysts, etc.

In this study, the carbon nanocoils as well as carbon microcoils were obtained by the catalytic pyrolysis of acetylene at 770℃ with the hybrid application of the outer EM waves and static magnetic field. The effects of the static magnetic field on the coil yield, coil diameter, morphology and growth mechanism were examined.

2. Experiment

A schematic of the reaction apparatus is shown in Fig. 1. The source gas mixture of C_2H_2+H_2+H_2S was vertically introduced into the horizontal reaction tube (quartz, 30 mm i.d.) from the upper gas inlet and purged from the lower gas outlet. The reaction tube was heated from the outside by an AC electric heater. The substrate, on which the metal powder as a catalyst was dispersed, was placed in the central zone of the reaction tube. The yoke (carbon steel, 75-160 mm i.d.) for supporting a permanent magnet (Nd-B-Fe, remanent magnetization: 1.22T) was placed on the outside of the reaction tube. The outer EM field emitted from the outer AC heater and static magnetic field emitted from the outer permanent magnet was simultaneously applied on the substrate surface.

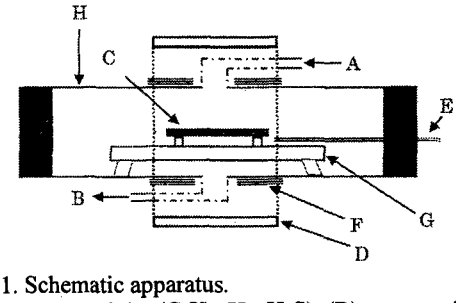

Fig. 1. Schematic apparatus.
(A) Source gas inlet (C_2H_2+H_2+H_2S), (B) gas outlet, (C) substrate (graphite), (D) yoke (carbon steel), (E) thermocouple, (F) AC electric heater, (G) susceptor, (H) reaction tube (quartz, 30 mm i.d.).

The placement pattern of the permanent magnet and the magnetic flux density measured on the substrate surface are shown in Fig. 2. The two permanent magnets were diagonally placed in the inner wall of the yoke. The magnetic flux density from the outer AC heater was 0.03 T. The static magnetic field is superimposed on this outer EM field to form a hybrid electromagnetic field (referred to as "hybrid EM field" hereafter). The hybrid magnetic flux density on the substrate surface was controlled by changing the inner diameter of the yoke, i.e., by changing the distance between the magnet and substrate. The experiment was also carried out without applying the outer EM field in the reaction zone by using a gas heater or applying only an outer EM field emitted from an outer AC electric heater (single EM field). The Ni powder was used as the catalyst unless otherwise stated.

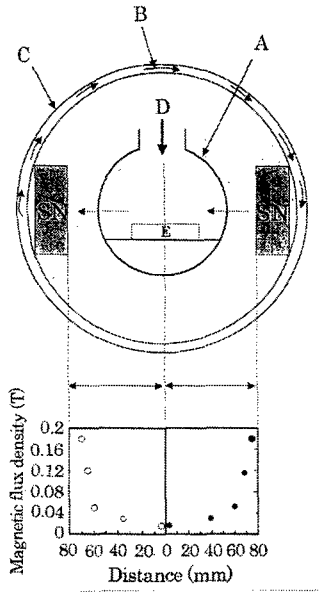

Fig. 2. Placement pattern of permanent magnet and magnetic flux density on the substrate surface.
(A) Reaction tube, (B) line of magnetic force, (C) yoke, (D) source gas inlet, (E) substrate.

3. Results and discussion

3.1. Effect of magnetic flux density on the coil yield:

The coil yield was obtained from the weight ratio between the obtained carbon coils and the introduced carbon contained in the source acetylene. The coil yield increased by 1.1-1.2 times with application of the hybrid EM field of 0.003T-0.03T.

3.2. Effect of magnetic flux density on the coil diameter:

The effect of the hybrid magnetic flux density on the coil diameter is shown in Fig. 3, in which Ni catalysts with 5 μ m (μ m-Ni) and 50 nm (nm-Ni) average diameter were used. The average coil diameter did not change with the application of the outer single EM field by the AC heating, and was about 3.5 μ m with and without the single EM fields. On the other hand, the average coil diameter decreased from 3.5 μ m without the EM field or with the single EM field to 1.5-2 μ m with the hybrid EM field of 0.015-0.3T. Using Nb or Ta metal powder as the catalyst, the average coil diameter of 5 μ m without the EM field gradually decreased with increasing hybrid magnetic flux density and attained 2.5 μ m with the hybrid magnetic density of 0.03T as shown in Fig. 4. The coil diameter is determined by the catalytic anisotropy of the catalyst grain, and the small coil diameter can be attained by the higher anisotropy. That is, these results indicate that the anisotropy of the catalyst increases with the increasing magnetic flux density which results in decreased the coil diameters.

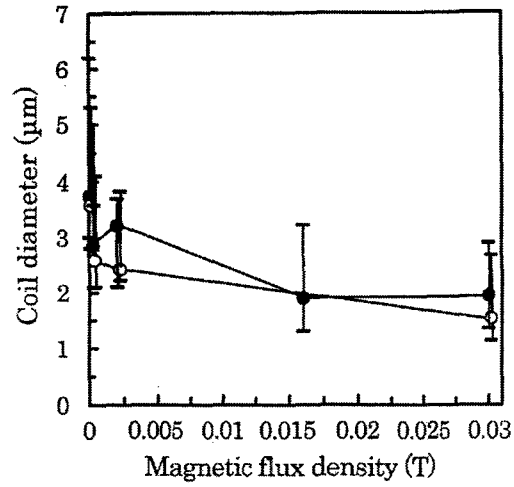

Fig. 3. Effect of magnetic flux density on the coil diameter.
Catalyst: (●) μ m-Ni powder, (○) nm-Ni powder.

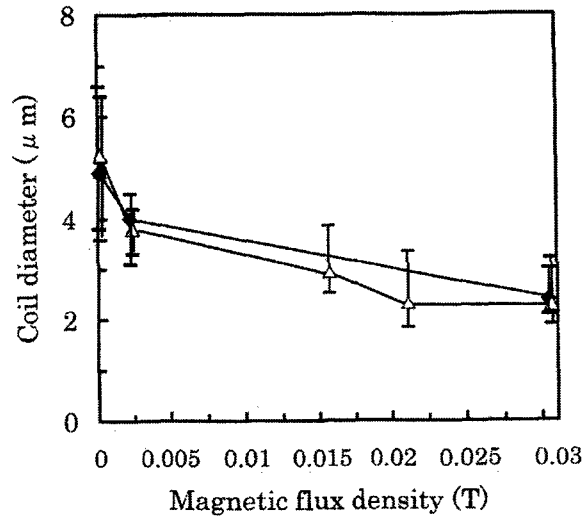

Fig. 4. Effect of magnetic flux density on the coil diameter.
Catalyst: (▲) Nb powder, (△) Ta powder.

3.3. Effect of the application of hybrid EM field on the coil morphology:

The carbon coils grew with a constant coil diameter and coil pitch from the bottom to the top, and attained a 3-8 mm length after a 2-hr reaction time. The shape of the cross section of the carbon fibers, which make up the carbon coils, is strongly affected by the outer EM field.

The carbon coils obtained without the outer EM field have a circular fiber cross-section (referred to as "circular coils" hereafter) as shown in Fig. 5(a). On the other hand, the carbon coils obtained with the outer EM field have a flat or ribbon-like fiber cross-section (referred to as "flat coils" hereafter) as shown in Fig. 5(b). The shape of the cross-section of the carbon fibers grown from a catalyst grain is generally determined by the form of the catalyst grain. That is, the circular coils and flat coils can be obtained from a coaxial and long-shaped catalyst grain, respectively. It may be considered that, during the application condition of the EM field, the flat and long-shaped catalyst grain is effectively used for the growth of the carbon coils because of the higher magnetic moment than that of a coaxial catalyst grain. However, using a very fine Ni catalyst of ca. 50 nm grain diameter, the circular coils were usually obtained due to the coaxial form of the catalyst fine grain as shown in Fig. 6. It was observed that during the application of the hybrid EM field, very fine deposits were observed in several spots among the carbon microcoils as shown in Fig. 7. The enlarged view of the fine deposits is shown in Figs. 8 and 9. We found that these fine deposits are also carbon coils with fine coils with a few hundreds to few tens nm coil diameter. We call these coils carbon nanocoils. Fig. 8 shows the carbon nanocoils obtained in the hybrid magnetic field of 0.002T. Using a nm-Ni catalyst, a large amount of carbon nanocoils grew among the carbon microcoils, while a very small amount of carbon nanocoils grew using a μ m-Ni catalyst. However, during the application of the higher hybrid EM field of 0.03T, a large amount of nanocoils grew using a μ m-Ni catalyst.

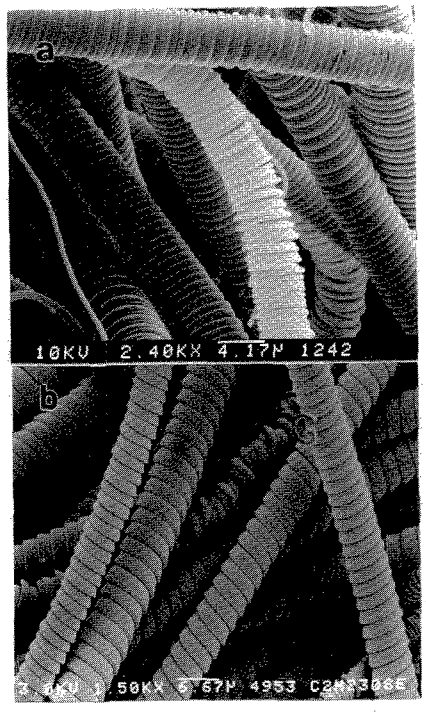

Fig. 5. Morphology of the carbon coils (1). (a) Without application of the EM field (gas heating), (b) with EM field (AC electric heating).

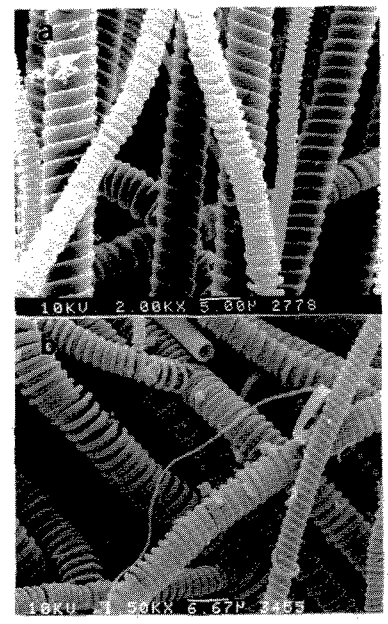

Fig. 6. Morphology of the carbon coils (2). Catalyst: (a) μ m-size Ni powder, (b) nm-size Ni powder.

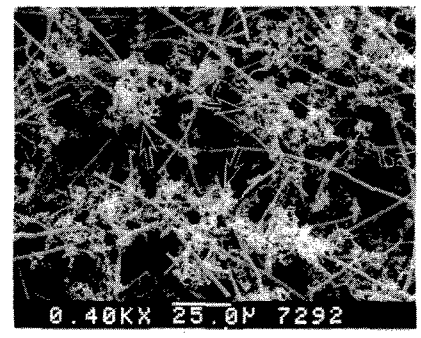

Fig. 7. Fine deposits among the carbon microcoils obtained in the hybrid EM field.

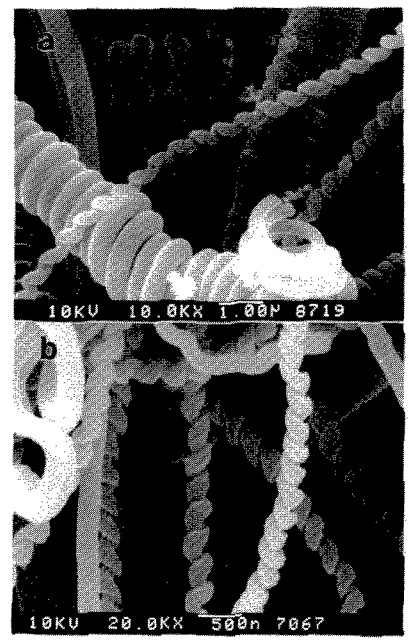

Fig. 8. Carbon nanocoils obtained by application of hybrid EM field (1). Catalyst: (a) μ m-Ni powder, (b) nm-Ni powder, Magnetic flux density: 0.002T.

The grown carbon nanocoils are generally a single coil while the microcoils are generally double coils. However, using the nm-Ni catalyst, the well-formed carbon nanocoils could not be obtained as shown in Fig. 9(b). The reason for this result is not yet known. The carbon nanocoils show two kinds of coiling patterns, a regular spring-like coiling pattern and a twisted pattern as shown in Fig. 10. Furthermore, the carbon nanocoils with various coil gaps, from nearly zero to a highly stretched, nearly straight form, were observed. Almost, all of the carbon nanocoils were a single coil.

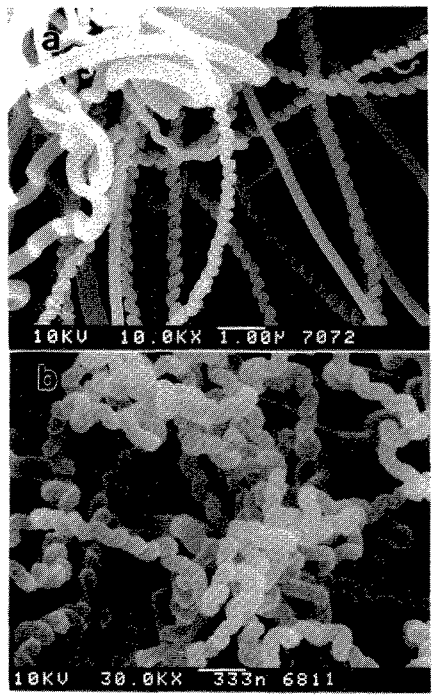

Fig. 9. Carbon nanocoils obtained by application of hybrid EM field (2).
Catalyst: (a) μm-size Ni powder, (b) nm-size Ni powder. Magnetic flux density: 0.03T.

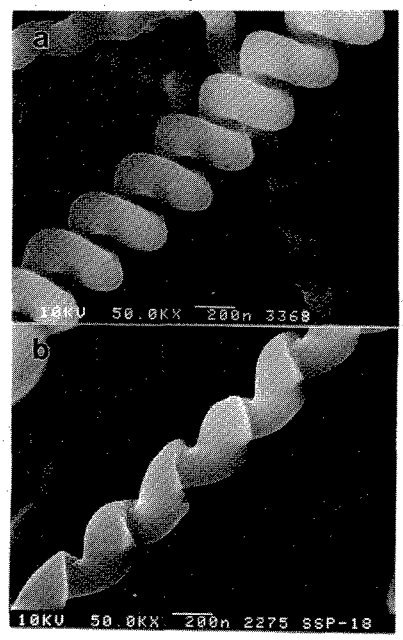

Fig.10 .(a) Spring-like carbon mono coil, (b) Twisted carbon mono coil.

3.4. Some properties

Table 1 shows the density and specific surface area of the carbon coils obtained with or without the hybrid EM field. It was observed that the density increased by application of the hybrid EM field irrespective of the kind of the catalyst used. On the other hand, the specific surface area was not influenced by the application of the hybrid EM field.

Table 1. Density and specific surface area of the carbon microcoils obtained by application of hybrid EM field.

Catalyst		Magnetic field	Density (g/cm^3)	Specific surface area (m^2/g)
Ni	Nano-size	without	1.82	60-100
	Nano-size	with	1.92	100-110
Ta		without	1.83	80-90
		with	1.93	90-100
Nb		without	1.80	84-90
		with	1.88	95-110

Acknowledgement

This work was partly supported by a Grant-in Aid for the Innovative Technology (No. 13506) and a Grant-in Aid for Scientific Research (No. 13555171) from the Ministry of Education, Culture, Sports, Science and Technology.

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(Received December 21, 2001; Accepted January 30, 2002)