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Vapor Phase Preparation of Carbon Microcoils by Applying Ultrasonic Waves

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Carbon microcoils were prepared by the ultrasonic wave CVD process, in which ultrasonic waves of 23-400 kHz irradiated the growing zone of carbon microcoils. The irradiation effects of the ultrasonic waves on the activation of the pyrolysis of acetylene, coil yield, morphology and some properties of the carbon microcoils were examined. The pyrolysis of acetylene was promoted by the ultrasonic wave irradiation, resulting in a high coil yield. The average coil diameter was increased by using ultrasonic waves, probably caused by the reduction of the difference in the chemical composition, which determines the anisotropic characteristics, between the respective catalyst crystal faces. The effect of ultrasonic wave irradiation is more promoted when using a multi-source-gas-inlet reaction tube compared to a single-gas-inlet reaction tube.
Keywords: Carbon microcoils, ultrasonic waves, acetylene,

1. Introduction

Recently, the sono-chemical process, in which an ultrasonic wave irradiates the atmosphere of chemical processes within a solution, has attracted much attention because the ultrasonic wave can produce a critical field of super high temperature/high pressure (5000 K and 1000 atm) within critical short times followed by super rapid cooling due to the ultrasonic wave cavitation. Itoh et al. first applied ultrasonic waves for the preparation of TiN, TiB_2, and TiC coatings by the CVD process and obtained very fine and adherent coatings on steel plates (1-4). We have obtained carbon microcoils by the metal-catalyzed pyrolysis of hydrocarbons at 700-850 ℃ with good reproducibility (5-7). The carbon microcoils have a double helix structure which is similar to that of deoxynucleic acid (DNA). Due to their unique and novel helical/spiral structure, carbon coils are potential candidates for many applications such as electromagnetic wave absorbers, tunable micro-devices, hydrogen storage materials, etc. It is necessary to control the morphology, microstructure and physical properties of carbon coils for these various applications.

The growth of carbon coils by the pyrolysis of hydrocarbons is a very complicated process. Carbon coils favorably grow on the substrate just under the source gas inlets and within the space of 5-15 mm, while no carbon coils grow beyond a distance of 20 mm. This result suggests that the source gas mixing is a very important factor for obtaining carbon coils. We have already reported the effect of the sonic (0.1-10 kHz) and ultrasonic (23-60 kHz) waves on the growth of carbon coils (8). It was found that the thickness of the coil layer, coil yield, coil diameter and some properties were affected by the sonic and ultrasonic wave irradiations.

In this study, the irradiation effect of the ultrasonic waves (23-400 kHz) in the reaction zone on the pyrolysis of acetylene, and the morphology and some properties of the carbon coils were examined.

2. Experimental

A horizontal quartz tube (700 mm long and 55mm i.d.), which has eight source gas inlets, was used as the reaction tube for the ultrasonic wave CVD process. Graphite plates, on which Ni fine powder catalyst (20-60nm diam.) were dispersed, was used as the substrate. The source gas mixture of C_2H_2, H_2, and H_2S was vertically introduced onto the substrate surface through eight upper gas inlets, and purged from a lower gas outlet. The gas flow rate of C_2H_2, H_2, and H_2S were fixed at 40 sccm (ml/min), 200 sccm, and 0.1 sccm, respectively. The reaction temperature and reaction time were fixed at 1043 K and 1 hr, respectively. The ultrasonic waves (23-400kHz) were horizontally irradiated onto the reaction zone through a window made of a thin vinyl sheet.

3. Results and discussion

3.1 Effect of the ultrasonic wave irradiation on the pyrolysis of acetylene

Without ultrasonic wave irradiation, the thickness of the coil layers was about 4 mm under the source gas inlets and about 2 mm in the intermediate part between the source gas inlets. On the other hand, uniform coil layer thickness of 3-4 mm were obtained with the ultrasonic wave irradiation of 23-400kHz. This result suggests that the chemical composition of the reactant gases is uniform through out the reaction tube. Fig. 1 shows the effect of the frequency of ultrasonic waves on the coils yield. It can be seen that maximum coil yield is obtained by 23kHz ultrasonic irradiation. We have reported that the coil yield was increased by the application of sonic and ultrasonic waves (8). It was found that, without ultrasonic wave irradiation, the source acetylene introduced into the

reaction zone was decomposed to mainly form four chemical species of CH_3^+(m/z=15), C_2^+(m/z=24), C_2H^+(m/z=25) and $C_2H_2^+$(m/z=26). The undecomposed acetylene ($C_2H_2^+$) was measured at the gas outlet tube using a Q-mass spectrometer when ultrasonic waves of 23 kHz were applied. The relationship between the amount of decomposed acetylene and the coil yield is shown in Fig. 2, in which the content of the decomposed acetylene in the reaction atmosphere is indicated as an ion current. It can be seen that when using the reaction tube with eight source gas inlets, the coil yield significantly increases with the decreasing amount of undecomposed acetylene, that is, increasing the amount of decomposed acetylene. On the other hand, using the reaction tube with a single source gas inlet as a reference, the coil yield only slightly increased by increasing the decomposed acetylene. These results indicate that the construction of the reaction tube strongly influences the irradiation effects of the ultrasonic waves for the growth of the carbon coils. The difference in the amount of decomposed acetylene with and without ultrasonic wave irradiation is shown in Fig. 3, in which the amount of decomposed acetylene is estimated by subtracting the content of the undecomposed acetylene in reaction atmosphere from the introduced acetylene, and is indicated as an ion current. The vertical axis indicates the difference in the amount of decomposed acetylene with and without ultrasonic wave irradiation. It can be seen that the amount of the decomposed acetylene was increased by the ultrasonic wave irradiation. This results indicate that ultrasonic waves promote the decomposition of acetylene, and thus increase the coil yield.

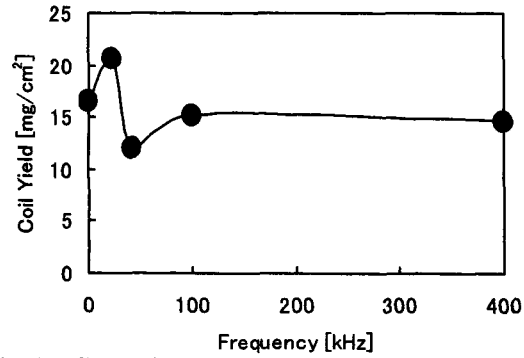

Fig. 1. Effects of the frequency on the coil yield. 0 kHz indicates without irradiation.

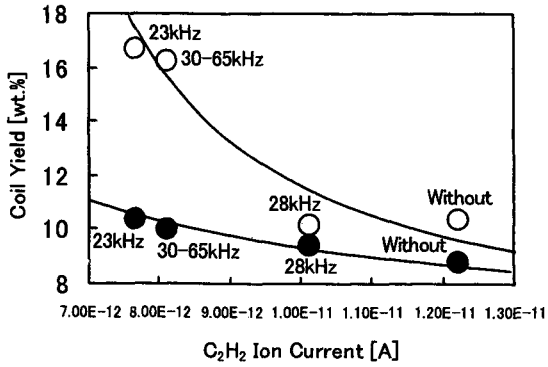

Fig. 2. Effects of the amount of undecomposed acetylene on the coil yield. (○) reaction tube with eight source gas inlets, (●) reaction tube with single source gas inlet.

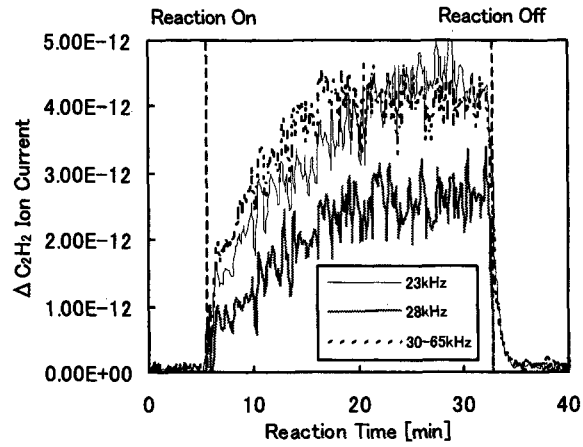

Fig. 3. Effects of the ultrasonic wave irradiation on the amount of decomposed acetylene.

3.2 Morphology and microstructure

Fig. 4 shows the representative carbon coils obtained with and without the application of the ultrasonic waves. The morphology of the double helical forms and the coiling direction were not influenced by the ultrasonic wave irradiation. On the other hand, the coil diameter was slightly increased by the application of the ultrasonic waves; 4-5 μ m for 23kHz, and 3-4 μ m for 400 kHz compared to 2.5-3 μ m without irradiation. The enlarged views of the surface of the carbon coils are shown in Fig. 5. It can be seen that the surface of the coils can be smoothened by the application of the ultrasonic waves as in the case of ceramic coatings on steels by CVD processes (1-4). Figs. 6 and 7 show the x-ray diffraction patterns and Raman spectra of the carbon coils, respectively. It can be seen that the carbon coils obtained with the application of the ultrasonic waves are more crystallized (graphitized) than that without application of ultrasonic waves.

3.3 Mechanism

Using a Ni catalyst, a Ni_3C catalyst grain is present on the tip part of the carbon coils, and this is a growing point. It is considered that the Ni-C-S-O thin films of pseudo-liquid or a liquid-crystal-like phase is present on the surface of the catalyst grain. The driving force of the coiling pattern formation is the anisotropic characteristics in the catalytic activity between the catalyst crystal faces. The coil diameter is determined by the anisotropy between the catalyst crystal faces. It may be considered that the anisotropy is obtained by the difference in the chemical compositions of the Ni-C-S-O thin films present on the surface of the catalyst crystal (Ni_3C), and that the chemical composition is influenced by the chemical composition of the gas phases. It can be expected that the promotion of gas mixing and reduction of the thickness of the gas diffusion layers present on the surface of the catalyst crystals is effectively caused by the direct ultrasonic wave irradiation in the reaction zone and/or by the reflection of ultrasonic wave from the cylindrical reactor wall. That is, the uniform concentration of

chemical species can be obtained in the gas phase by the gas mixing effect of the ultrasonic waves. Furthermore, if the rate-determining step of the coil growth is the diffusion of the gas species through the boundary layers, the decreasing effect of the thickness of the boundary layers results in an increase in the coil yield. On the other hand, the cavitation effects of the ultrasonic waves in the pseudo-liquid or liquid-crystal-like phase of the Ni-C-S-O thin films results in the chemical composition uniformity between the respective crystal faces and the decrease in the anisotropy, and thus the coil diameter increases.

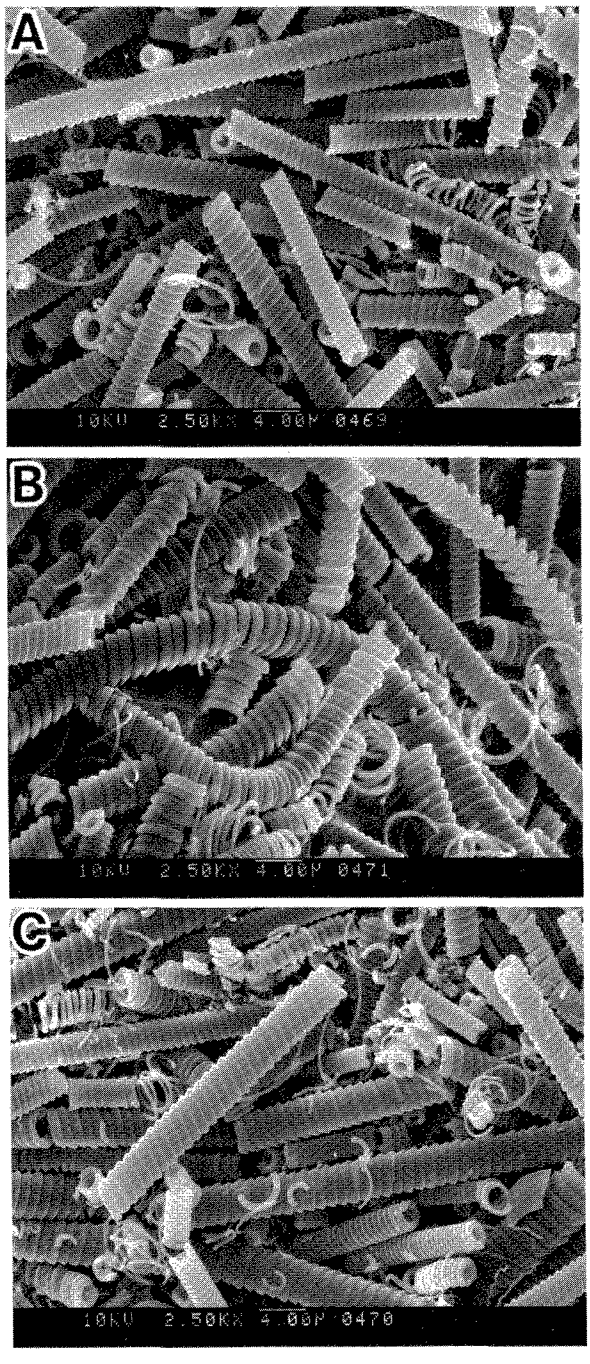

Fig. 4. Representative SEM image of the carbon coils. (a) Without irradiation of ultrasonic waves, (b) with irradiation (23kHz), (c) with irradiation (100 kHz).

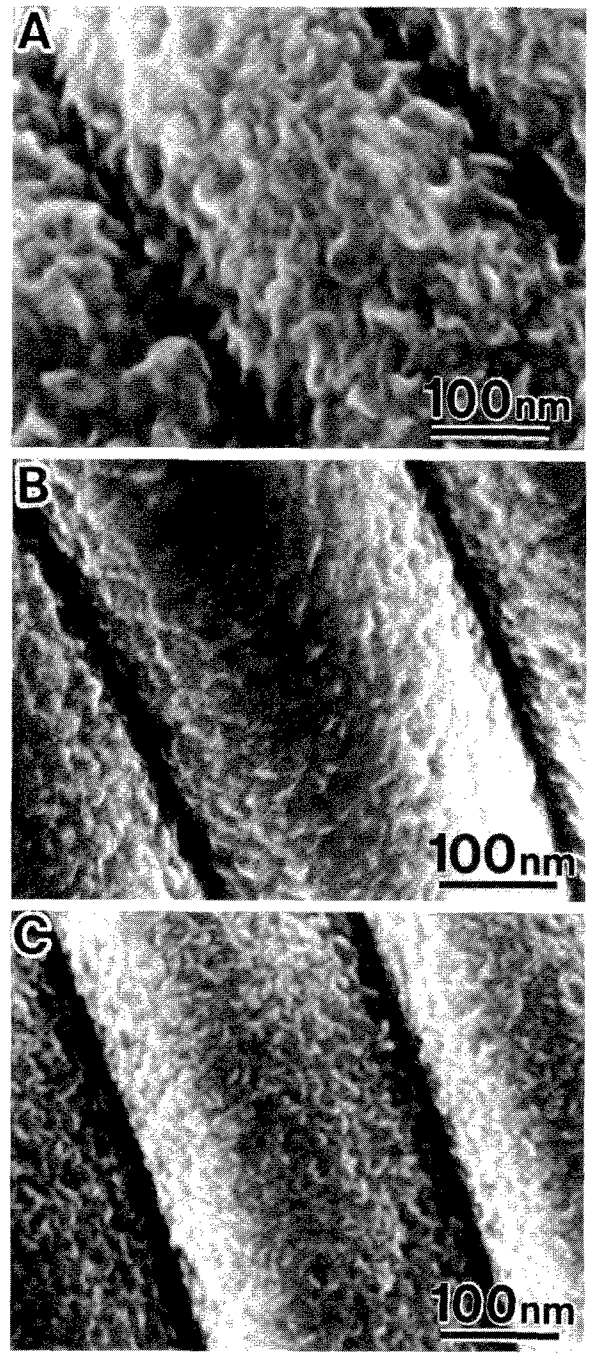

Fig. 5. Enlarged view of the surface of the carbon coils. (a) Without irradiation, (b) with irradiation (23kHz), (c) with irradiation (100kHz).

3.4. Properties

The density of the carbon micro-coils obtained without ultrasonic wave irradiation was 1.80 g/cm^3. The density was increased to 1.96-2.00 g/cm^3 with irradiation at 23-65 kHz, while it was not increased by the application of 100-400kHz (0.83 g/cm^3) (Table 1). This tendency is the same as the irradiation effect on the coil yield shown in Fig. 1. On the other hand, the specific surface area decreased after ultrasonic wave irradiation.

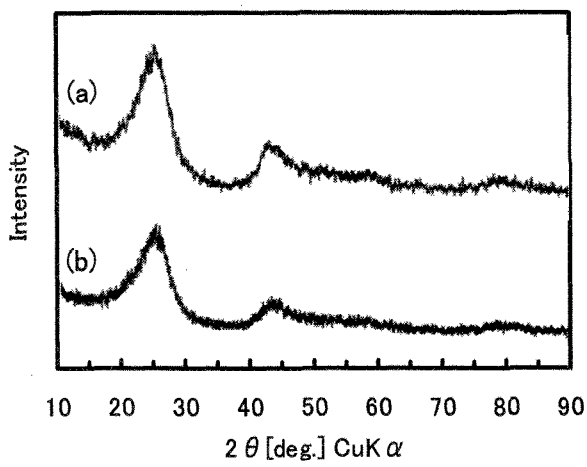

Fig. 6. X-ray diffraction patterns.
(a) With irradiation (23kHz), (b) without irradiation.

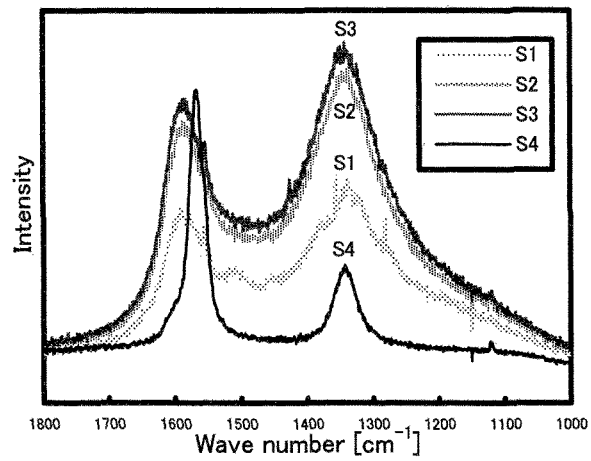

Fig. 7. Raman Spectra.
(S1) Without irradiation, (S2) with irradiation (23kHz) (S3) with irradiation (28kHz), (S4) heat-treated carbon coils at 2500℃.

Table 1 Density and specific surface area of carbon microcoils

Samples	Supersonic Frequency (kHz)	Density (g/cm^3)	Specific surface area (m^2/g)
As-grown Carbon coils	—	1.80	120
	0.1	1.88	79
	2.5	1.90	71
	5	1.83	62
	10	1.83	72
	23	2.00	69
	30-65	1.96	79
	100	1.83	75
	400	1.83	44
Graphite coils*)	—	2.19	16
VGCF	—	2.12	12
Carbon fibers (PAN)	—	1.81	2
Graphite powder	—	2.30	21

*) 3000℃, 6hrs, in $CO+CO_2$

4. Conclusions

Carbon coils were obtained by the Ni-catalyzed pyrolysis of acetylene at 1043K. The irradiation of the ultrasonic waves in the reaction zone influenced the promotion of the pyrolysis of acetylene, and the morphology and some properties of the carbon coils were examined. By ultrasonic wave irradiation, the decomposition of the acetylene was promoted and the coil yield increased. The coil diameter increased from 2.5-3 μm without irradiation to 3-5 μm with irradiation. It is considered that these ultrasonic wave irradiation effects are attributed to the promotion effect of the gas mixing and diffusion through boundary layers and also the cavitation effect in the Ni-C-S-O thin films present on the surface of the Ni_3C catalyst grain.

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References

[1] T. Takahashi and H. Itoh, J. Electrochem. Soc., 14, 797-802(1977).

[2] T. Takahashi and H. Itoh, J. Mater. Sci., 14, 1285-1290(1979)

[3] T. Takahashi and H. Itoh, J. Cryst. Growth, 49, 445-450(1980)

[4] K. Sugiyama, K. Kinbara, and H. Itoh, Thin Solid Films, 112, 257-266(1984)

[5] X. Chen, S. Motojima, W. In-Hwang, M. Kohda, Y. Hishikawa and H. Iwanaga, Trans. Mater. Res. Soc. Jpn., 25(2), 565-568(2000).

[6] X.Chen, W-In Hwang, and S. Motojima, Mater. Technol., 18(6), 229-237(2000).

[7] W-In Hwang, X. Chen and S. Motojima, Mater. Technol., 18(7), 263-270(2000).

[8] C. Kuzuya, Y. Hishiikawa and S. Motojima, J. Chem. Eng. Jpn., (accepted).

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