

Vapor phase preparation of carbon nanocoils by noble metal catalysts

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The catalytic effect of various noble metals and the alloys on the growth of carbon nanocoils was examined. Pt/Pd mixed catalysts supported on Al₂O₃ powder was the most effective for the preparation of carbon nanocoils. The deposited carbon nanocoils was generally a twisted-form with a coil diameter of 100-600 nm and a coil length of 1-3 mm. The carbon nanocoils grew horizontally and adherently on the supporter (Al₂O₃ particle) surface.

Key words: carbon nanocoil, vapor grown carbon fiber, acetylene, catalyst, CVD

1. INTRODUCTION

Carbon microcoils/nanocoils with a 3D-helica/spiral structure, which is the fundamental structure of all objects, are very interesting in their peculiar morphology, coiling-chirality, growth mechanism, and applications. The carbon microcoils are key materials for nanoscience and nanotechnology, because they have various potential applications such as electromagnetic (EM) wave absorbers, tunable micro/nano-devices, microsensors, microactuators, chiral catalysts, hydrogen storage materials, microsprings, high elastic nanoelectronic elastic conductors, activators of metabolism, etc. We have found that carbon microcoils (CMC) could be obtained by the catalytic pyrolysis of acetylene at 750-800°C using different preparation processes [1-5]. We first focused on preparing carbon microcoils with the coil diameter of few microns in large-scale [6]. It is considered that using the CMC as effective EM wave absorbers of GHz band, the coil diameter is preferable to be smaller than that of the CMC reported by us previously. To obtaining the carbon coils with smaller coil diameter than that of the carbon microcoils; carbon nanocoils (CNC), the diameter of the carbon fiber, from which carbon coils is formed, must be as small as possible. The coil diameter of the grown carbon fiber is generally determined by the grain size of the used metal catalyst, and the smaller is the catalyst grain size, the smaller is fiber diameter (and thus carbon nanocoils) can be obtained. However, the fine-grained metal powders as the catalyst are easily sintered at reaction temperatures of 700-800°C. Accordingly, it is a key point to suppress the sintering of fine catalyst grain for obtaining carbon nanocoils. We have reported the preparation of carbon nanocoils using sputtered thin films as the catalysts [7] and continued to find that the carbon nanocoils with a coil diameter of a few hundreds to few tens nanometers were obtained by using various catalysts supported on fine ceramic powders. F. Cesar et al.[9] studied on the synthesis and characterization of helical carbon filaments grown from Pd₃P colloids, in the atmosphere of propane, 200 sccm (ml/min) N₂, at 600 °C. M. Zhang et al. [10] prepared carbon tubule nanocoils in high yield using iron-coated indium tin oxide as catalyst. H. Takikawa, et al. [11] prepared amorphous carbon fibril-form carbon nano-materials using catalytic thin films of Fe, Ni, Cr, Ti, Zn and their oxides, coated on silicon and copper substrates.

In this study, we obtained carbon nanocoils with the coil diameter of 50-450 nm and the coil length of 1-3 mm. The preparation conditions and morphology of the carbon nanocoils were examined.

2. EXPERIMENTAL

Fig. 1 shows a schematic apparatus. A horizontal quartz tube (30 mm i.d., 700 mm length), on the central part of which a vertical gas inlet and outlet are attached, was used as the reaction tube. Various noble metal catalysts, such as Au, Ag, Pt, or Pd, were sputter-coated using an ion coater on the graphite plate substrate, or deposited on the substrate from metal solution. Fine

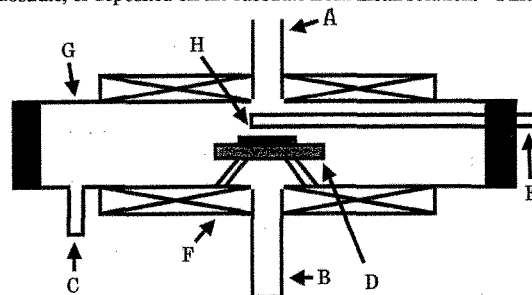


Fig.1. Schematic diagram of the reaction tube for the preparation of the carbon nanocoils. (A) source gas inlet (C₂H₂ + H₂ + H₂S), (B) gas outlet, (C) sealing gas inlet, (D) susceptor, (E) thermocouple, (F) nichrome heater, (G) reaction tube (quartz, length 700mm, i.d. 26mm), (H) substrate

colloid particles (Au, Pt) and Al₂O₃ powder supported metals (Pt, Pd) were also used as the catalysts. The source gas mixture of C₂H₂, N₂, and H₂S were vertically introduced onto the substrate surface from the upper gas inlet, and purged from the lower gas outlet. The gas flow rate of C₂H₂, N₂ and H₂S was 10-80 sccm, 50-300 sccm, and 0.1-20 sccm, respectively. The reaction temperature was 740-770°C.

3. RESULTS AND DISCUSSION

3.1 Au metal Fig. 2 shows the carbon nanocoils obtained using Au sputtered films as a catalyst. The carbon nanocoils were generally a single-helix and twisted-form coil with a coil diameter of 100-800 nm (600 nm av.) and coil length of 1-3 mm. The small amount of spring-like carbon coils were also observed. The coil yield against introduced acetylene was 2.0 mg/cm²-substrate, and coil content in deposits was about 90 %. The enlarged view of carbon nanocoils with a twisted form and without inner coil diameter is shown in Fig. 3. This morphology is considerably different from that of the carbon microcoils with spring-like form and with an inner coil diameter. The carbon nanocoils were amorphous and there is no fine pore was observed in the central part of the carbon fibers by which coils were formed while carbon nanotubes have a fine pore. Using an Au colloid of

5 nm diam., no carbon coil was obtained, probably mainly caused by too small Au particle. For obtaining carbon nanocoils, carbon fiber, from which carbon coils were formed, must be as small as possible. For obtaining carbon fibers with small fiber diameter,

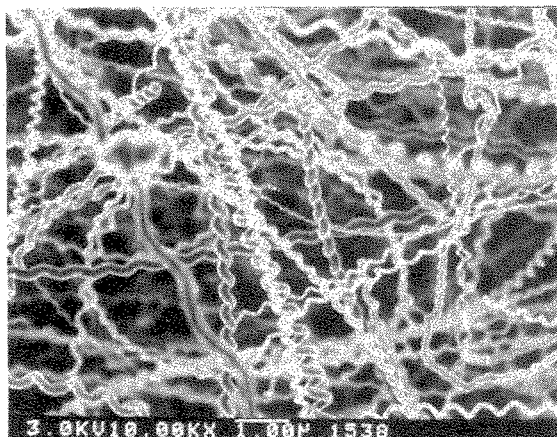


Fig. 2. SEM images of the deposits obtained using catalyst : Au sputter-coated film.

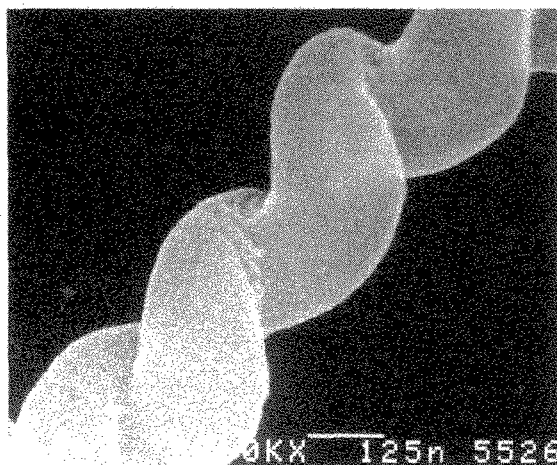


Fig. 3. Enlarged view of the carbon nanocoils obtained with Au catalyst.

catalyst grain must be as small as possible. However, too small catalyst grain has generally poor crystallinity, and thus may result in small or zero catalytic anisotropy between respective crystal faces of the catalyst grain and result in no coil growth. Another reason may be the contamination of Au colloid particle by organic dispersion medium.

3.2 Ag metal Using Ag-sputtered films, the carbon nanocoils could not be obtained and irregular-bent nanofibers with about 50 nm thick were deposited as shown in Fig. 4.

3.3 Pt metal Using sputter-coated Pt thin films, carbon nanocoils with twisted-form and coil diameter of 100-300 nm (200 nm av.) were obtained. However, the coil contents in the deposits was as low as 30-40%. The deposited nanocoils was adhered on the substrate surface and could not be separated. Pt fine particles supported on Al_2O_3 powder was used as the catalyst, in which H_2PtCl_4 solution (0.1M) was mixed with Al_2O_3 fine powder (5 μm diam), evaporated the water, and dried. However carbon nanocoils was not obtained, and large amount of twisted fibers or straight fibers were deposited. Using Pt cluster, a small amount

of carbon nanocoils as well as straight nanofibers were obtained as shown in Fig. 5. Using fine Pt metal colloid particles (av. 5 nm diam.), carbon nanocoils could not be obtained, and irregularly bent carbon nanofibers were obtained (Fig. 6).

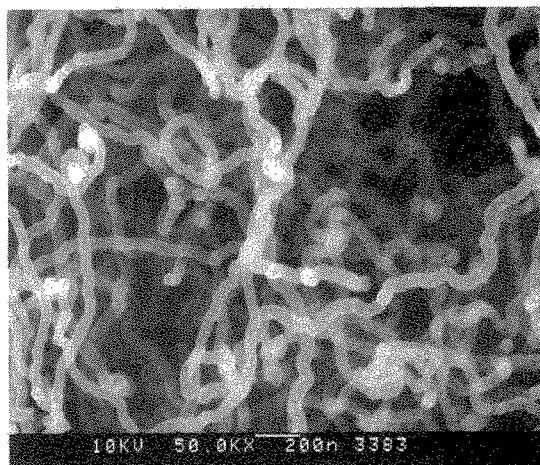


Fig. 4. SEM images of the deposits obtained using rare metal catalysts. catalysts : Ag sputter-coated film.

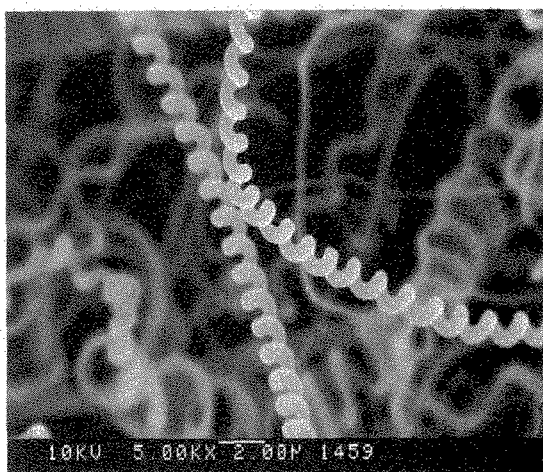


Fig. 5. SEM images of the deposits obtained using catalyst: Pt cluster.

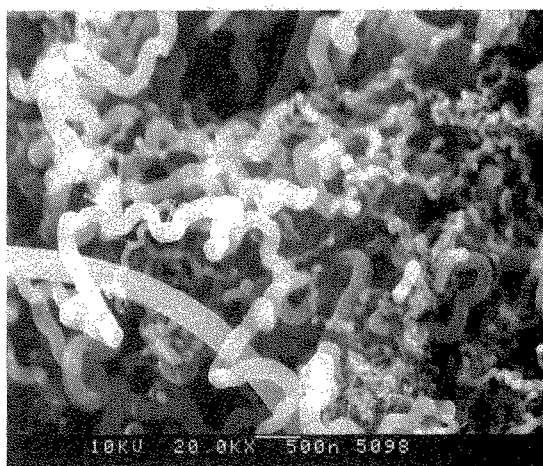


Fig. 6. SEM images of the deposits obtained using catalysts : Pt colloid.

3. 4 Pd metal Using Pd/Al₂O₃ fine powder as the catalyst, small amount of twisted carbon nanocoils were obtained as shown in Fig. 7. The coil contents in deposits were as small as 10-15 %.

3. 5 Pt/Pd mixed metal Using a sputter-coated Pt/Pd thin films of the graphite substrate, carbon nanocoils with twisted-form of a coil diameter of 250-500 nm (300 nm av.) were obtained (Fig. 8). The coil content in the deposits was 70-80%. In this case too, the deposited coils were tightly adhered to the substrate surface, and could not be separated. Pt/Al₂O₃ particle was mixed with PdCl₂ solution (0.1M), evaporated the water, and dried. This Pt/Pd metal supported on Al₂O₃ powder was used as the catalyst. Using this catalyst, a large amount of carbon nanocoils with twisted-form was obtained and the coil contents in the deposits was as high as above 90%. The representative carbon nanocoils is shown in Fig. 9. The well formed and twisted carbon nanocoils with the coil diameter of 100-300 nm was obtained. The coil yield was as high as 2.7 mg/cm²- substrate. This value is the highest one among the catalyst used in this work.

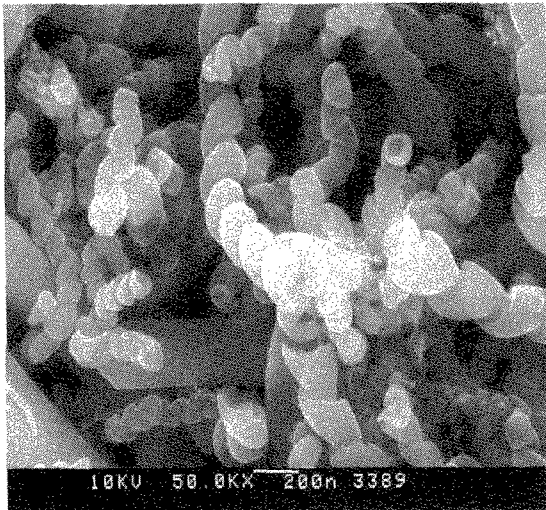


Fig. 7. SEM images of the deposits obtained using catalyst: PdCl₂(aq).

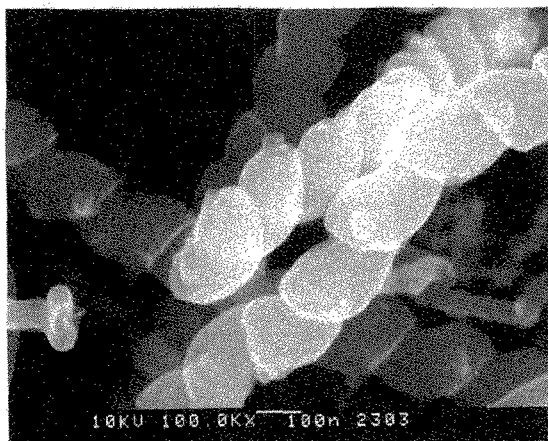


Fig. 8. SEM images of the deposits obtained using catalysts:Pt/Pd sputter-coated film.

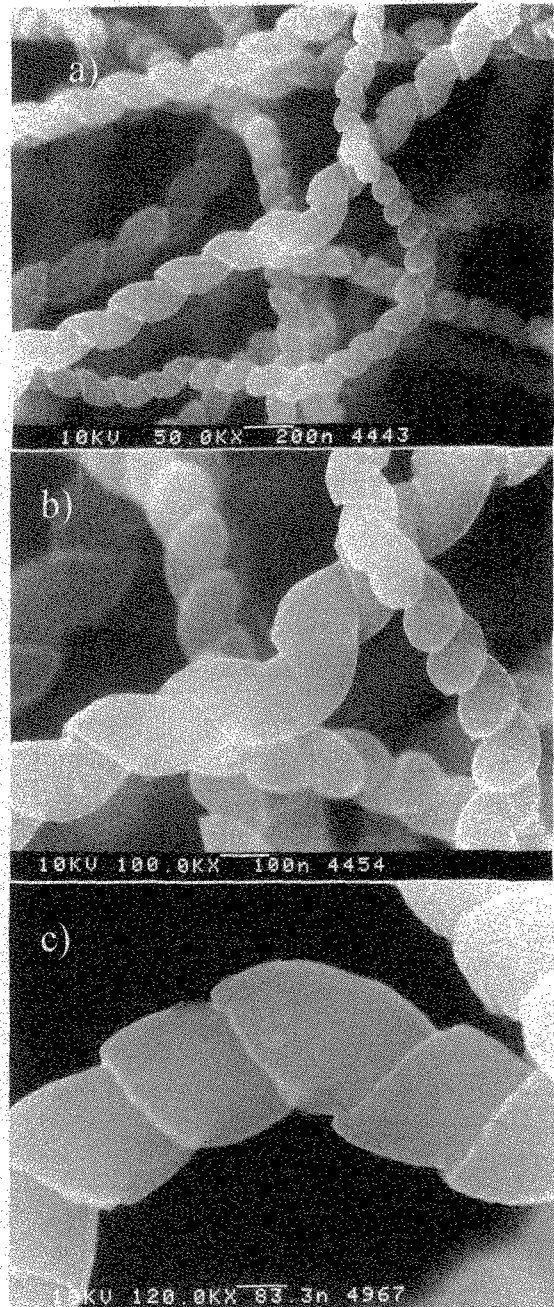


Fig. 9. Carbon nanocoils with changing coil chirality using catalysts:Pt/Al₂O₃-Pd.

The optimum reaction conditions were as follows; gas flow rate of $C_2H_2=60$ sccm, $H_2S=0.09$ sccm, $N_2=275$ sccm, reaction temperature= $720^\circ C$, reaction time= 1 hr. The coiling direction; coiling-chirality, are usually the same, and are right-clockwise or left clockwise within a piece of the coil. Using the Pt/Pd catalyst supported on Al_2O_3 powder, it was frequently observed that the coiling direction was changed within a piece of coil. An arrow showing in Figs. 9b and c shows the changed part of the coiling direction. These phenomena was also observed in the case of Fe-Cr-Ni or WS_2 catalyst [8]. It was proposed that the changing coiling-chirality might be caused by changing chemical composition of the thin quasi-liquid-like layers present on the surface of the catalyst grain. However, another reasons, such as inner stress accumulation and the release or changing (or fluctuation) of reaction conditions may be considered, and further research is necessary. Table 1 shows the summary of the deposits obtained by various catalysts. Fig. 10 shows the coil diameter of the carbon nanocoils obtained by various catalysts. The most small coil diameter was obtained by Pt/Pd mixed catalyst.

3. 6 Properties The carbon nanocoils obtained by Pt/Pd mix catalyst were amorphous, and an averaged density and specific surface area was about $1.85-2.00$ (av. 1.95) g/cm^3 and 152 m^2/g , respectively. The electrical resistivity of a piece of carbon nanocoil with about 200 nm coil diameter was 1000 $M\Omega cm$. These values are comparable to that of the carbon microcoils.

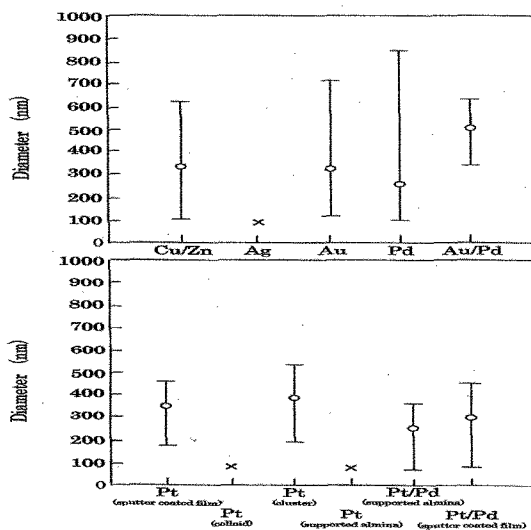


Fig.10. Relationship between coil diameter and metal catalysts, ×: no deposit.

Table 1. Kind of deposit by different catalysts

Catalysts	majority deposits	minority deposits
Ag	fibers	no
Au	nanocoils(m)	fiber
Pd	nanocoils(S)	fibers
Au/Pd	nanocoils(S)	fiber
Pt (sputtered p.)	nanocoils(S)	fiber
Pt (colloid p.)	fiber	no
Pt (cluster p.)	fiber	no
Pt/ Al_2O_3	fiber	no
Pt-Pd (sputtered)	nanocoils (S)	fibers
Pt/ Al_2O_3 -Pd	nanocoils (L)	fibers

S: small amount, M: midium amount, L: large amount

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REFERENCES

- [1] S. Motojima, M. Kawaguch, K. Nozaki, and H. Iwanaga, Appl. Phys. Lett., 56, 321-323 (1990).
- [2] S. Motojima, M. Hirata, and H. Iwanaga, J. Chem. Vapor Deposition, 3, 87-99 (1994).
- [3] S. Motojima, Y. Itoh, S. Asakura, and H. Iwanaga, J. Mater. Sci., 30, 5049-5055 (1995).
- [4] S. Motojima and X. Chen, J. Appl. Phys., 85, 3919-3921 (1999).
- [5] X. Chen and S. Motojima, Carbon, 37, 1817-1823 (1999).
- [6] X. Chen, W.-In Hwang, S. Motojima, Mater. Technol., 18, 229-237 (2000).
- [7] C. Kuzuya, W.-In Hwang, S. Hirako, Y. Hishikawa, and S. Motojima, Adv. Mater., Chem. Vapor Deposition, 8, 57-62 (2002).
- [8] S. Yang, X. Chen, and S. Motojima, Appl. Phys. Lett., 81, 3567-3569 (2002).
- [9] F. Cesar, J.-O. Bovin, and L.R. Wallenberg, J. Mater. Res., 15, 1857-1859 (2000).
- [10] M. Zhang, Y. Nakayama, and L. Pan, Jpn. J. Appl. Phys., 39, 1242-1244 (2000).
- [11] H. Takikawa, M. Yatsuki, R. Miyano, M. Nagayama, T. Sakakibara, Jpn. J. Appl. Phys., 39, 5177-5179 (2000).

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