ELSEVIER

Materials Science and Engineering B34 (1995) L9–L11

MATERIALS SCIENCE & ENGINEERING B

Letter

Effect of metal impurities on the growth of micro-coiled carbon fibres by pyrolysis of acetylene

S. Motojima[a], S. Asakura[a], M. Hirata[a], H. Iwanaga[b]

[a]*Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu 501-11, Japan*
[b]*Faculty of Liberal Arts, Nagasaki University, Nagasaki 852, Japan*

Received 17 December 1994; in revised form 11 May 1995

Abstract

Micro-coiled carbon fibres were prepared by the impurity metal-activated pyrolysis of acetylene containing a small amount of thiophene. The growth conditions and catalytic effect of the metal impurities were examined. Of the various metals, Ni, Ti and W were the most effective for the growth of the coils. In the case of Ni metal impurity, it was considered that Ni_3C single crystallites present in the tip part of the coils have a catalytic effect on the coiling of the carbon fibres.

Keywords: Carbon; Fibres; Chemical vapour deposition; Acetylene

The peculiar morphology and growth mechanisms of the coiled inorganic fibre or helical structure of organic polymers are very interesting. The growth of coiled carbon fibres by catalytic decomposition, disproportionation of organic vapours or CO has been widely reported [1–7]. The fibres obtained were generally straight and/or tubular with an irregular helical form.

We obtained regularly coiled Si_3N_4 fibres by the metal impurity-activated chemical vapour deposition (CVD) process using Si_2Cl_6, $SiO_2 + C$ or SiO as the Si source at 1200–1500 °C [8–10]. Furthermore, we obtained regularly coiled carbon fibres by the catalytic pyrolysis of acetylene at 550–750 °C using Ni plate and powder as the catalyst [11–13]. The coiled carbon fibre could be vapour-phase metallized to form coiled fibres of SiC, TiC, etc. [14]. The coiled fibres of carbon or metal carbides are potential candidates for fillers in electromagnetic shielding materials, elastic packings or filter materials resistant to high temperatures and/or harsh or corrosive environments and micromechanical elements such as microsprings and microsensors, etc.

In this work, coiled carbon fibres were obtained on a graphite or metal plate substrate by the catalytic pyrolysis of acetylene containing a small amount of thiophene as the impurity gas. Fine metal powder (about 5 μm in diameter) was used as the catalyst and 10–50 mg cm^{-2} powder was dispersed by rubbing on a graphite substrate. A metal plate substrate was also used as a catalyst.

The effects of the kind of metal impurity and reaction conditions on the yield of the coiled carbon fibres were examined. The impurity metal particle observed on the tip of the coiled carbon fibres was examined by energy dispersive X-ray microanalysis, scanning electron microscopy and transmission electron microscopy (TEM) in order to elucidate the growth mechanism. Commercial acetone-dissolved acetylene was used as the carbon source without further purification. Acetylene (97%–99%), hydrogen and argon were introduced into a horizontal reaction tube (quartz, 40 mm i.d.) which was heated from the outside by a Nichrome heater element. The flow rates of acetylene, hydrogen and argon were fixed at 30, 70 and 40 standard $cm^3\,min^{-1}$ (sccm), respectively.

Coiled carbon fibres grew exclusively on the upper region of the source gas steam, and the maximum yield was obtained on the substrate separated 0.7 cm from the gas inlet. No coiled carbon fibres were observed at 2.5 cm separation.

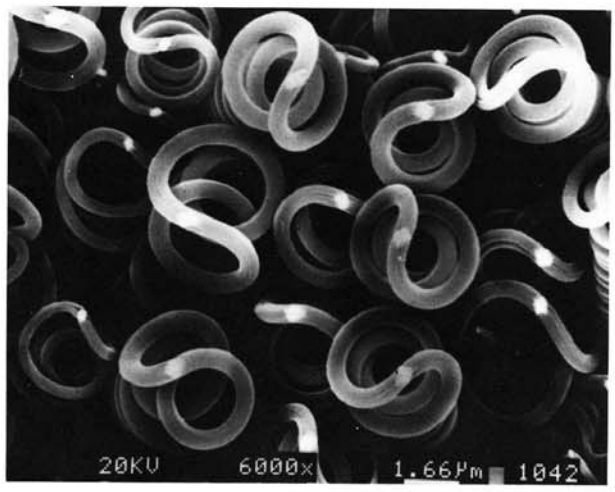
SSDI 0921-5107(95)01233-8

Table 1
Optimum growth conditions of coiled carbon fibres

Catalyst	Optimum reaction temperature (°C)	Optimum gas flow rate of thiophene (sccm)	Maximum coil yield (%)
Ti	775	0.47	54.0
Zr	750	0.34	4.8
Nb	750	0.42	25.8
Cr	700	0.24	22.7
Mo	850	0.14	18.1
W	750	0.45	55.4
Fe	–	–	0
Co	850	0.14	11.2
Ni	750	0.34	48.8
NiS	–	–	0
$MoSi_2$	800	0	23.3

Using Ti powder as the catalyst and a small amount of thiophene gas (0.47 sccm) as the impurity, the optimum reaction temperature was 775 °C, at which a maximum coil yield of 54% was obtained. The coil yield decreased steeply above or below this temperature. However, the optimum thiophene gas flow rate was about 0.47 sccm at the optimum reaction temperature of 775 °C. The yield of coil decreased steeply above or below this flow rate. These results indicate that the optimum reaction temperature and flow rate of thiophene for the growth of coiled fibres are restricted to very narrow ranges. Table 1 shows the optimum reaction temperature and gas flow rate of thiophene and the maximum coil yield. Of the various metal catalysts used, Ti, W and Ni showed the highest coil yield of about 50%. Other metal powders are also effective for the growth of coiled carbon fibres. It is very interesting that Fe powder, which is the most effective catalyst for obtaining straight vapour-grown carbon fibres, was not effective and hardly any coiled fibres were obtained.

Fig. 1 shows the early stage of growing coiled carbon fibres using an Ni plate (catalyst and substrate). The coiled fibres grew perpendicularly on the substrate with a constant coil patch and coil diameter, and a brightened part was always observed on the tip of the coiled fibres.



(a)

(b)

Fig. 1. Tip part of the coiled carbon fibres. Reaction time: (a) 30 s; (b) 5 min.

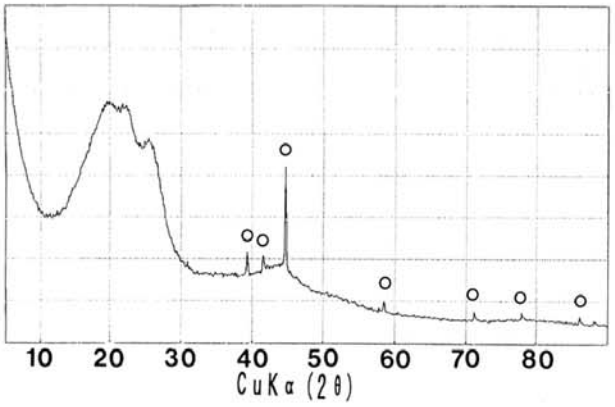


Fig. 2. X-ray diffraction patterns of the coiled fibres shown in Fig. 1(a). (○) Ni_3C.

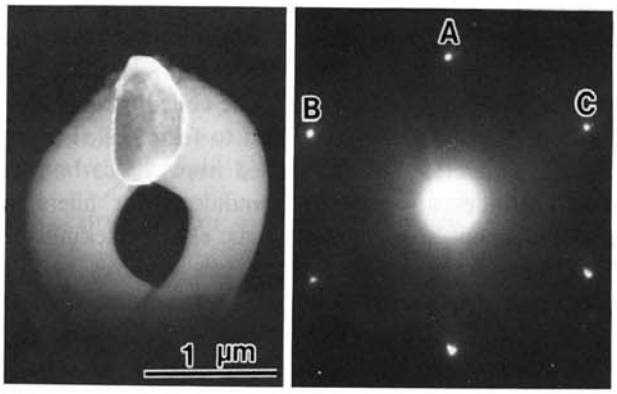
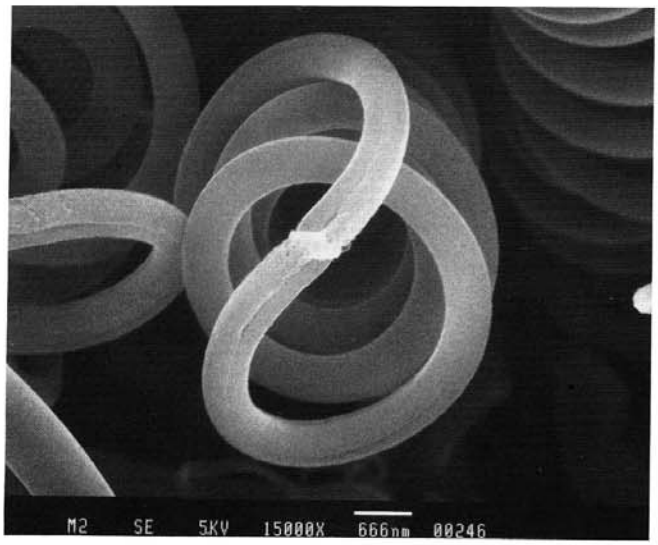
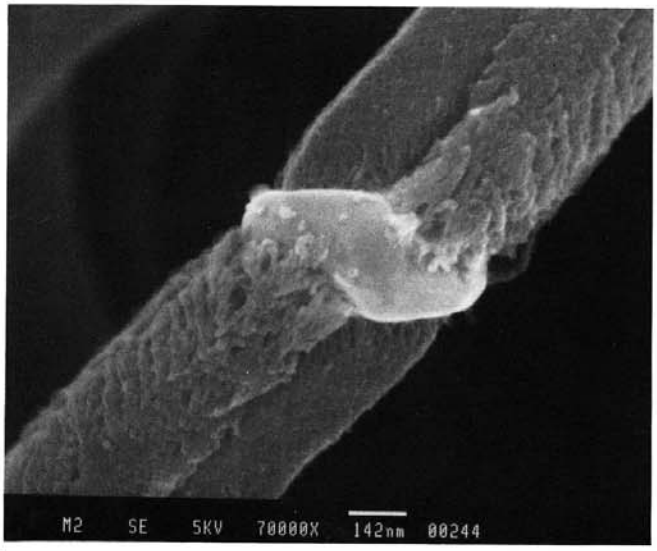


Fig. 3. (a) TEM dark image and (b) selected area electron diffraction patterns. (A) $(10\bar{1}0)$; (B) $(01\bar{1}1)$; (C) $(1\bar{1}0\bar{1})$.



(a)



(b)

Fig. 4. Enlarged view of the tip part of the coiled fibres shown in Fig. 1(a).

Raman spectra, X-ray diffraction and selected area electron diffraction patterns shows that the coiled fibres are in an amorphous state. The X-ray diffraction pattern of the structure in Fig. 1(a) is shown in Fig. 2. Some peaks of Ni_3C (rhombohedral) can be seen, in addition to that of amorphous carbon. This result suggests that the brightened part located at the tip of the coiled fibres is the Ni_3C phase. A TEM image and selected area electron diffraction pattern of the tip part (Ni_3C crystallite) of the coiled fibres indicated by the arrow in Fig. 1(b) are shown in Fig. 3. Six spots can be seen in Fig. 3(b), and spots A, B and C can be assigned to $(10\bar{1}0)$, $(01\bar{1}1)$ and $(1\bar{1}0\bar{1})$ of the Ni_3C phase, respectively. That is, the Ni_3C particle is a single crystal.

We have proposed a growth mechanism of coiled carbon fibres based on the anisotropic deposition rate of carbon of crystal planes of the catalytic particles [15]. Amelinckx et al. [16] proposed a formation mechanism for a catalytically grown helix-shaped graphite nanotube. Fig. 4 is an enlarged view of the tip part of the coiled carbon fibres shown in Fig. 1(a). The surface of the outer part of the coiled fibres is more roughened than the inner surface, suggesting that the growth rate of the outer part is faster than that of the inner part. Carbon deposition from some crystal facets was not observed. These observations suggest that these crystal facets are not catalytic for the deposition of carbon, that is, of the coiled carbon fibres. Accordingly, it is reasonably considered that the driving force of curling of the carbon fibres to form coiled fibres is the anisotropic deposition rate of carbon of the repective crystal planes of the Ni_3C single crystal.

Acknowledgements

This work was supported by the Iketani Science and Technology Foundation and Kazuchika Okura Memorial Foundation.

References

[1] W.R. Davis, R.J. Slawson and G.R. Rigby, *Nature (London), 171* (1953) 756.
[2] W.R. Davis, R.J. Slawson and G.R. Rigby, *Trans. Br. Ceram. Soc., 56* (1957) 67.
[3] R.T.K. Baker, M.A. Barber, P.S. Harris, F.S. Feates and R.J. Waite, *J. Catal., 26* (1972) 51.
[4] L.S. Lobo and D.L. Trimm, *J. Catal., 29* (1973) 15.
[5] R.T.K. Baker and R.J. Waite, *J. Catal., 37* (1975) 101.
[6] M. Hillert and N. Lange, *Z. Kristallogr., 111* (1958) 24.
[7] J. Caluszka and M.H. Back, *Carbon, 22* (1984) 141.
[8] S. Motojima, S. Ueno, T. Hattori and K. Goto, *Appl. Phys. Lett., 54* (1989) 1001.
[9] S. Motojima, S. Ueno, T. Hattori and H. Iwanaga, *J. Cryst. Growth, 96* (1989) 383.
[10] S. Motojima et al., unpublished results.
[11] S. Motojima, M. Kawaguchi, K. Nozaki and H. Iwanaga, *Appl. Phys. Lett., 56* (1990) 321.
[12] S. Motojima, M. Kawaguchi, K. Nozaki and H. Iwanaga, *Carbon, 29* (1991) 379.
[13] S. Motojima, I. Hasegawa, S. Kagiya, M. Momiyama, M. Kawaguchi and H. Iwanaga, *Appl. Phys. Lett., 62* (1993) 2322.
[14] S. Motojima, I. Hasegawa, M. Kawaguchi, K. Nozaki and H. Iwanaga, *J. Chem. Vapor Depos., 1* (1992) 136.
[15] M. Kawaguchi, K. Nozaki, S. Motojima and H. Iwanaga, *J. Cryst. Growth, 118* (1992) 309.
[16] S. Amelinckx, X.B. Zhang, D. Bernaerts, X.F. Zhang, V. Ivanov and J.B. Nagy, *Science, 265* (1994) 635.