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Preparation of micro-coiled carbon fibres by metal powder-activated pyrolysis of acetylene containing a small amount of sulphur compounds

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Micro-coiled carbon fibres were prepared by the transition metal-activated pyrolysis of acetylene containing a small amount of sulphur compounds, and the preparation conditions were examined in detail. The coiled carbon fibres grew at the reaction temperatures of 700–850 °C and thiophene gas flow rates of 0.14–0.45 standard $cm^3 min^{-1}$ (0.10–0.35 vol % reaction atmosphere). The optimum values depended on the type of metal catalysts used. Among the metal catalysts used, nickel, titanium and tungsten were the most effective for the growth of the coiled carbon fibres and a maximum yield of about 50%–55% was obtained. The bulk resistivity of the coiled carbon fibres decreased with increasing bulk density and was 10^0 S^{-1}cm at a bulk density of 1.

1. Introduction

Among currently available industrial raw materials, those with a micro-coiled or helical morphology are not available at present. Furthermore, research on the preparation and characterization of the coiled fibres or whiskers has rarely been carried out. However, coiled materials are very interesting in relation to their peculiar coiled morphology and novel applications as well as their growth mechanism.

We have reported that regularly coiled Si_3N_4 fibres were obtained from a gas mixture of $Si_2Cl_6 + NH_3 + H_2 + Ar$ at 1200 °C using iron metal as a catalyst [1, 2]. It has sometimes been observed that some of the vapour-grown carbon fibres were coiled helically [3–10]. We have recently produced coiled carbon fibres by the catalytic pyrolysis of acetylene at 750 °C using a nickel plate and powder as a catalyst [11–15]. However, detailed growth conditions, morphology and growth mechanism of the coiled carbon fibres have not been examined in detail.

In this work, the coiled carbon fibres were obtained on a graphite substrate on which various metal powders were dispersed as a catalyst by the catalytic pyrolysis of acetylene containing a small amount of sulphur compounds. The effect of the metal powder catalyst, reaction temperature, gas flow rate and ratio, and pre-sulphurization of the metals on the growth of the coiled carbon fibres, were examined in detail. The morphology and bulk electrical resistivity of the coiled carbon fibres obtained were also examined.

2. Experimental procedure

Commercial acetone-dissolved acetylene (97%–99%) was used without further purification as the carbon source. A gas mixture of the acetylene, sulphur compound, hydrogen and argon was introduced into the reaction tube (quartz, 40 mm i.d.) which was heated from the outside by a nichrome element. The reaction was carried out under atmospheric pressure. A graphite plate ($100 \times 20 \times 1$ mm^3) was used as the substrate on which a fine metal powder catalyst (about 5 μm diameter, 5 g) was dispensed by rubbing. The reaction was carried out using a nickel powder as a catalyst and thiophene as an impurity at the reaction temperature of 750 °C, unless otherwise noted.

Furthermore, the flow rates of acetylene, hydrogen and argon were fixed at 30, 70 and 40 standard cm^3 min^{-1}, respectively, unless otherwise described. The bulk electrical resistivity of the obtained coiled carbon fibres were measured using a 5mm diameter cylindrical cell.

3. Results and discussion

3.1. Growth conditions

Using nickel powder as a catalyst, the optimum reaction temperature and H_2S flow rate used as an impurity, at which the maximum coil yield relative to the introduced carbon source was obtained, was 750 °C and 0.05 standard $cm^3 min^1$, respectively. It was observed that those optimum conditions and the maximum coil yield were significantly different from the type of commercially available nickel powder. The

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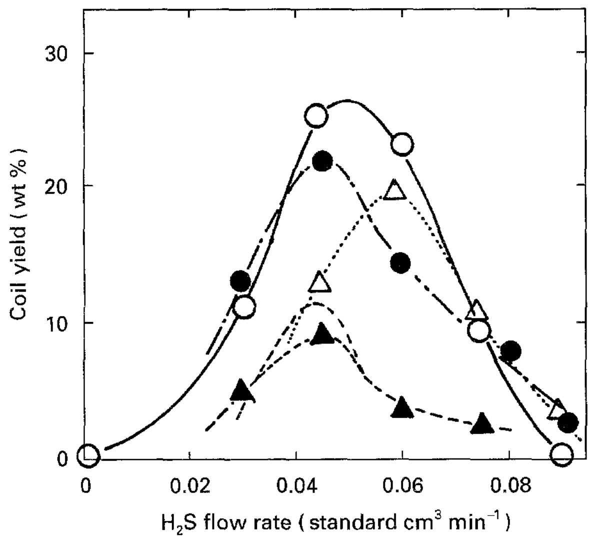

Figure 1 Effect of H_2S flow rate on the coil yield in relation to the nickel powder source. Catalyst: nickel powder. Nickel powder source and the average grain diameter: (○) company A, 2.47 μm; (●) company B, 4.97 μm; (△) company C, 1.36 μm; (▲) company D, 2.61 μm. Reaction temperature 750 °C, reaction time 15 min, C_2H_2 flow rate 30 standard cm^3 min^{-1}, H_2 flow rate 70 standard cm^3 min^{-1}, Ar flow rate 40 standard cm^3 min^{-1}.

effect of H_2S flow rate on the coil yield in relation to the nickel powder source is shown in Fig. 1. Among the nickel powders used, nickel powder A shows the highest coil yield of about 26% at the H_2S flow rate of 0.05 standard cm^3 min^{-1}, while nickel powder D showed only a maximum coil yield below 10%. Furthermore, the optimum H_2S flow rate was different based on the kind of nickel powder used. The average grain size of nickel powder D was the same as that of A which was 2.47–2.61 μm. Fig. 2 shows the SEM images of the nickel powders A and D. No apparent difference between A and D could be observed except that nickel powder A was more crystalline than D. Hereafter, nickel powder A was used unless otherwise noted. The most significant factors affecting coil growth between the various nickel powder sources are still unknown.

The effect of metal and metal sulphide powders other than nickel powder on the growth of the coiled carbon fibres was examined. The effects of reaction temperature on the coil yield are shown in Fig. 3, in which thiophene (0.34 standard cm^3 min^{-1}) was used as the impurity in the case of metal powder but not with MoS_2. It was observed that MoS_2 as well as cobalt, molybdenum and tungsten were also effective catalysts without the addition of thiophene, and a maximum yield of about 23% was obtained at 800 °C. The optimum reaction temperature was different based on the kind of metal or metal sulphide. Table I shows the optimum reaction conditions and maximum coil yield for the growth of the coiled carbon fibres using thiophene as an impurity for various metal and metal sulphide catalysts. It can be seen that almost all of the metal powders used except for the iron powder showed a catalytic effect on the growth of the coiled carbon fibres. The optimum reaction temperature was generally within 700–850 °C. On the other hand, the optimum thiophene flow rate was within 0.14–0.48 standard cm^3 min^{-1} (0.10%–0.35% in the reaction atmosphere). It can be seen that the most effective metal catalysts were nickel, titanium and tungsten, and the maximum coil yield of 50%–55% was obtained at their

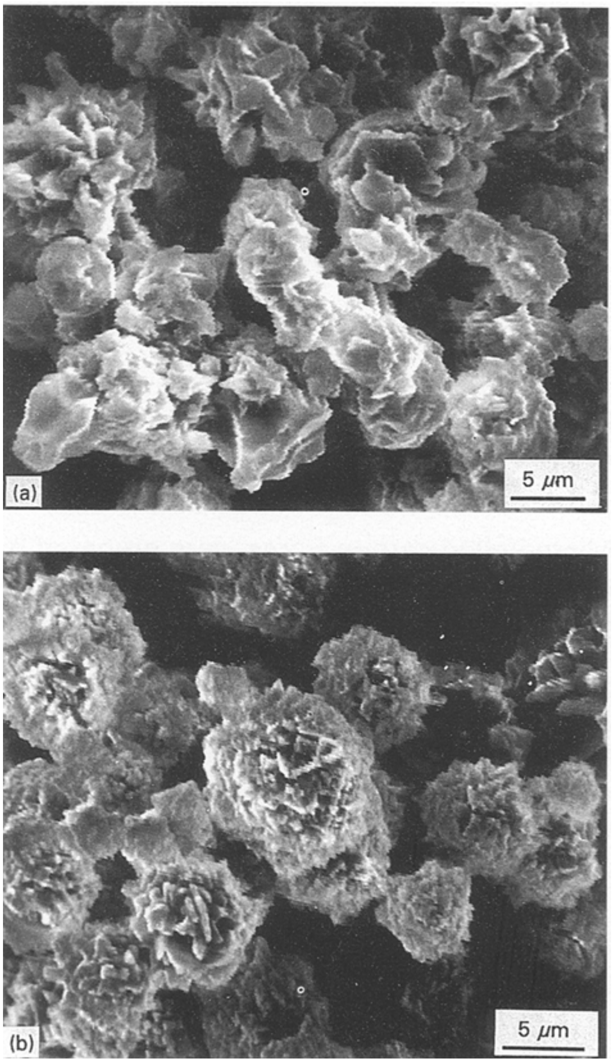

Figure 2 SEM images of the nickel powder. Source of nickel powder: (a) company A, (b) company D.

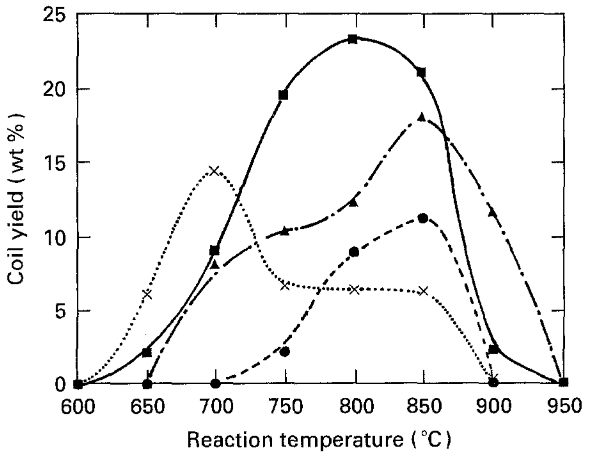

Figure 3 Effect of reaction temperature on the coil yield in relation to the kind of catalyst. Impurity: thiophene, flow rate 0.34 standard cm^3 min^{-1}. Other gas flow rates were the same as that of Fig. 1. Catalyst: (●) Co, (▲) Mo, (■) MoS_2, (×) Cr.

TABLE I Optimum reaction conditions

Metal catalyst	Optimum reaction temperature (°C)	Optimum thiophene flow (standard $cm^3 min^{-1}$)	Maximum coil yield (%)
Ti	775	0.47	54.0
Zr	750	0.34	4.8
Hf	800	0.48	7.2
V	725	0.24	9.3
Nb	750	0.42	25.8
Ta	850	0.34	17.6
Cr	700	0.24	22.7
Mo	850	0.14	18.1
W	750	0.45	55.4
Mn	700	0.34	2.4
Fe	–	–	0
Co	850	0.14	11.2
Ni	750	0.34	48.8
MoS_2	800	0	23.3
NiS	–	–	0

respective optimum reaction conditions. It is very interesting that iron powder, which is currently used as a catalyst for the growth of vapour-grown straight carbon fibres (VGCF), is exceptionally non-catalytic for the growth of the coiled carbon fibres.

The presence of an optimum amount of sulphur compounds as well as a metal catalyst in the reaction atmosphere was indispensable for the growth of the coiled carbon fibres. Furthermore, metal sulphides such as MoS_2 also showed some catalytic effects as already described. Accordingly, it may be reasonably considered that the metal powder was sulphidized in the reaction atmosphere to form a metal sulphide, and this metal sulphide then has actual catalytic effects on the growth of the coiled carbon fibres. Accordingly, nickel powder was pre-sulphidized in an H_2S atmosphere at 1000 °C before the reaction. The effect of the pre-sulphidizing time of the nickel powder on the coil yield is shown in Fig. 4, in which the H_2S flow rate was fixed at 0.06 standard $cm^3 min^{-1}$. It was observed that the coil yield slightly decreased when pre-sulphidizing the nickel powder. This result suggests that there is an optimum sulphidizing degree for the metal powder.

The effect of reaction atmosphere (H_2 + Ar) on the coil yield is shown in Fig. 5. Without the addition of hydrogen, only a small number of coils grew. The maximum coil yield was obtained at a hydrogen concentration of about 60% but decreased above or below this value. The effect of H_2S flow rate on the coil diameter is shown in Fig. 6. The coiled carbon fibres have a considerably wide range of coil diameters from 5–15 μm. The averaged coil diameters were not affected by the H_2S flow rate and were about 8–10 μm, except for the H_2S flow rate above 0.09 standard $cm^3 min^{-1}$ at which only a small number of the coiled fibres grew.

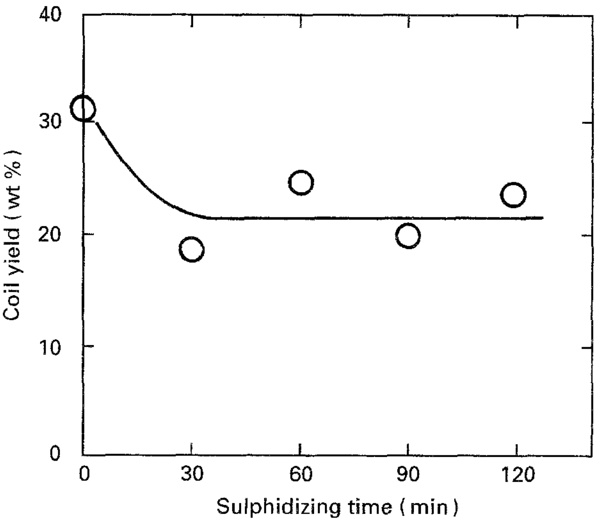

Figure 4 Effect of pre-sulphidizing time of the nickel powder using H_2S on the coil yield. Pre-sulphidizing conditions: temperature 1000 °C, H_2S flow rate 0.66 standard $cm^3 min^{-1}$. Reaction conditions: H_2S flow rate 0.06 standard $cm^3 min^{-1}$, other conditions were the same as those of Fig. 1.

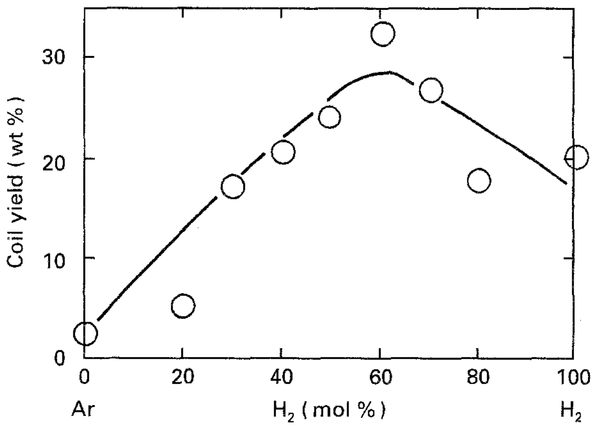

Figure 5 Effect of gas atmosphere (H_2 + Ar) on the coil yield. H_2S flow rate 0.06 standard $cm^3 min^{-1}$, total flow rate of H_2 + Ar 110 standard $cm^3 min^{-1}$, other conditions were the same as those of Fig. 1.

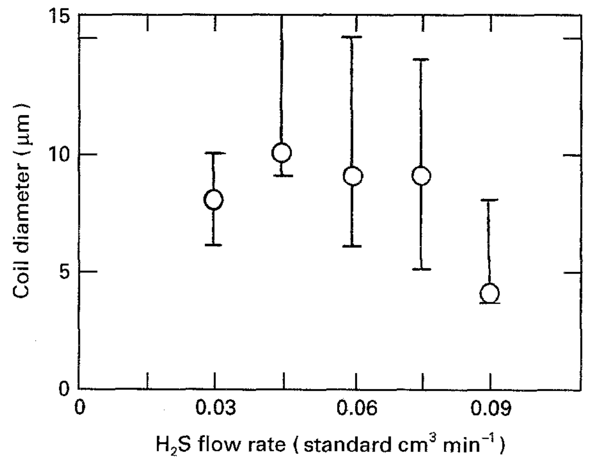

Figure 6 Effect of H_2S flow rate on the coil diameters. Reaction conditions were the same as those of Fig. 1.

3.2. Morphology

Fig. 7 shows representative coiled carbon fibres obtained using a nickel metal catalyst and thiophene impurity at 750 °C. It can be seen that many of the carbon fibres coiled with a relatively constant coil diameter within a coil. The coil length of about 1–2 mm was obtained after 1h reaction time. The coiled carbon fibres were generally double coils,

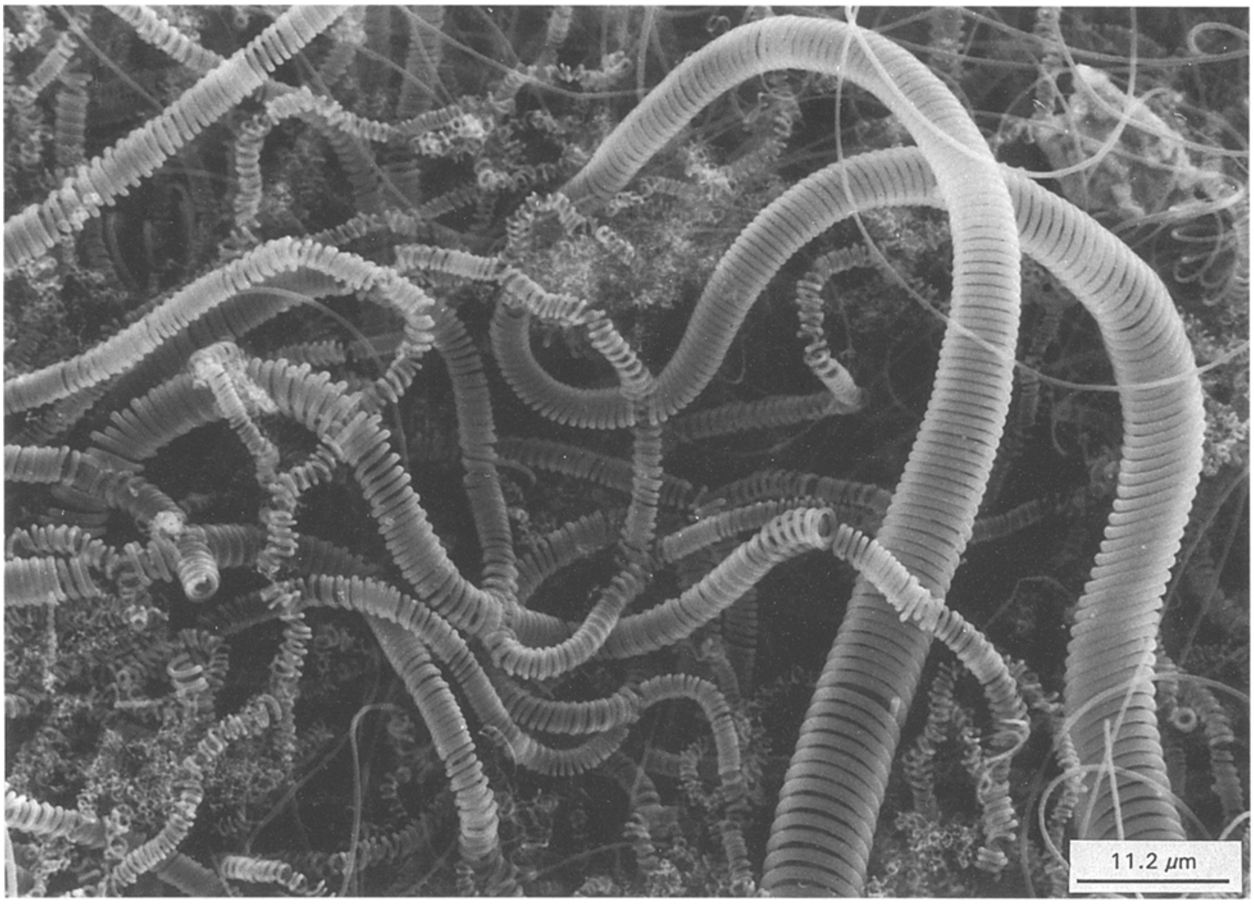

Figure 7 Representative coiled carbon fibres. Impurity: thiophene, flow rate 0.34 standard $cm^3 min^{-1}$, other reaction conditions were the same as those of Fig. 1.

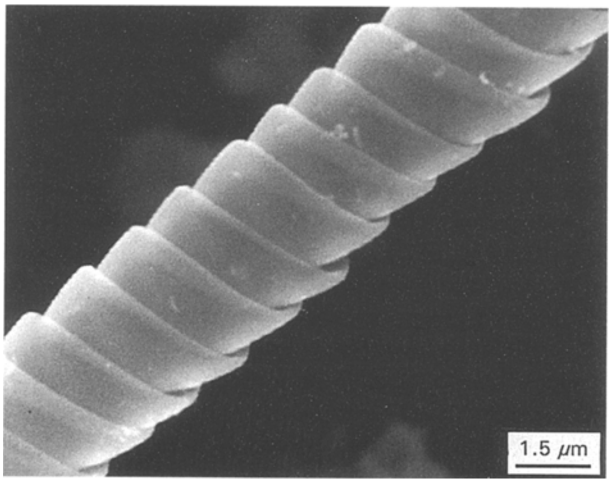

Figure 8 Regularly coiled ribbon-like flat carbon fibres.

similar to DNA. Fig. 8 shows the regularly coiled carbon fibres in which ribbon-like flat fibres were involved. These regularly coiled carbon fibres were also double coils. Other types of coiled carbon fibres with an interesting coiling morphology were also sometimes observed. Fig. 9 shows triple coils in which a single coil overlap-coiled the double coils. Fig. 10 shows the very regularly coiled double coils in which a single coil, having a large coil pitch, coiled on a single coil having a dense coil pitch. Fig. 11 shows a single coil in which a ribbon-like flat fibre coiled along the coil axis followed by a concentric coiling. These concentric coiling patterns were observed only on the ribbon-like flat fibres. Sometimes a straight carbon fibre suddenly branched (arrow in Fig. 12) when forming two fibres, immediately followed by their entwining to form double coils. Fig. 13 shows the tip part of the coils. A nickel catalyst grain was usually present on the tip part of the coiled carbon fibres. The brightened part depicted by the arrow in Fig. 13a is a nickel particle from which two fibres or apparently four fibres grew to form double coils. A striation was observed in the coils as shown in Fig. 13b. These observations support the growth mechanism proposed by Kawaguchi *et al.* [13].

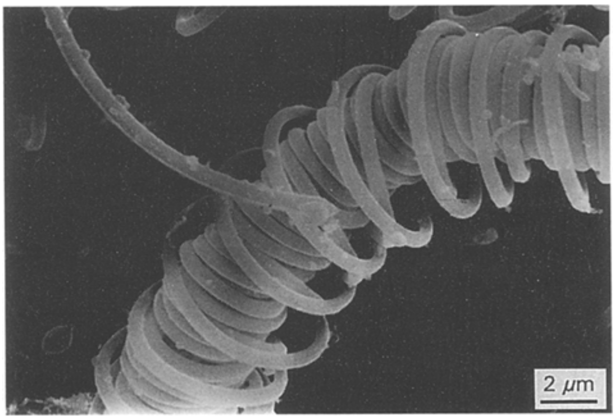

Figure 9 Triple coils.

Sometimes, a large number of very thin carbon fibres grew in a ball-like form from the nickel particle present at the tip of the coils, as shown in Fig. 14.

These thin fibres may grow by the sudden fluctuation in growth conditions at one particular site.

3.3. Bulk electrical resistivity

Fig. 15 shows the relationship between the bulk electrical resistivity and bulk density of the coiled carbon fibres in relation to that of the commercial acetylene black and Ketjen black. The bulk resistivity of the coiled carbon fibres decreased steeply with increasing bulk density and had a value of $10^{0}\ \mathrm{S^{-1}cm}$ for a bulk density of 1. This value is one to two orders of magnitude larger than that of the acetylene black or Ketjen black. This may probably be caused by a small contact area between each coiled carbon fibres.

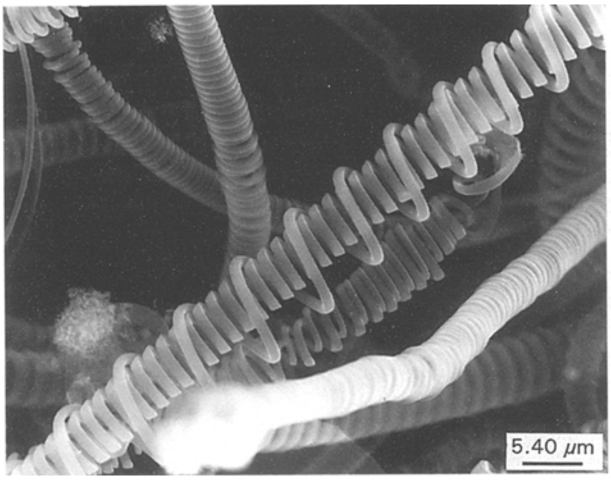

Figure 10 Regular combination coils.

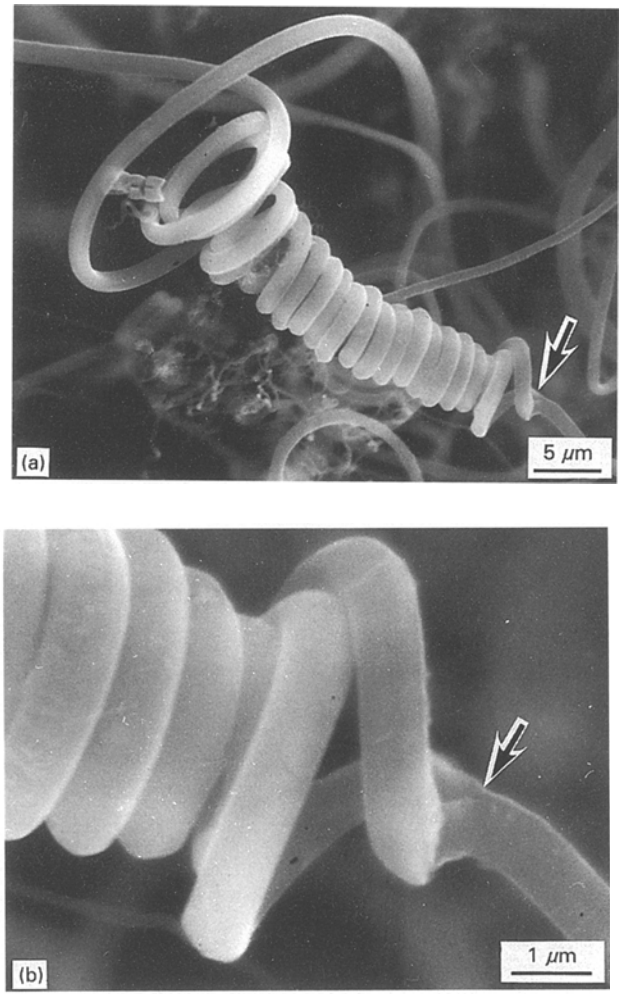

Figure 12 (a) Branched coils and (b) enlarged view.

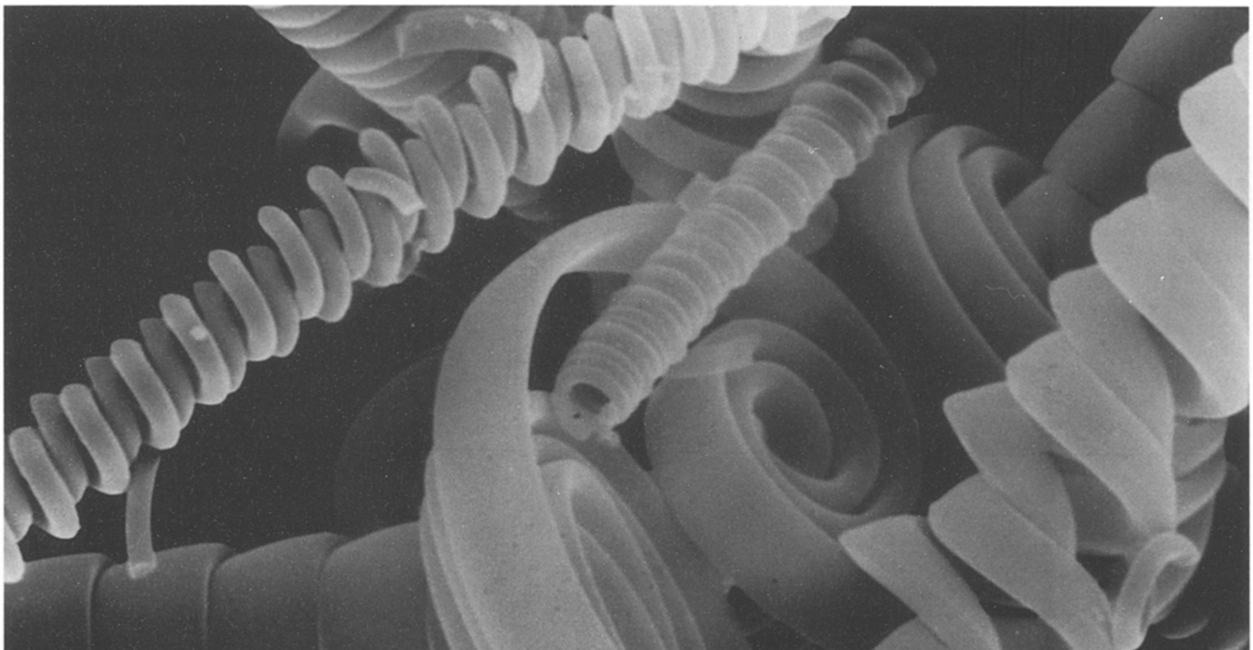

Figure 11 Single coil grown along the coil axis followed by concentric growth.

3.4. Miscellaneous

The composition and surface area of the bulk coiled carbon fibres were examined, and the results are shown in Table II. The coiled carbon fibres contained a small amount of sulphur, oxygen and hydrogen, and the carbon content was 97%–98%.

It was observed that the coiled carbon fibres had a high surface area of 293–352 $m^2 g^{-1}$.

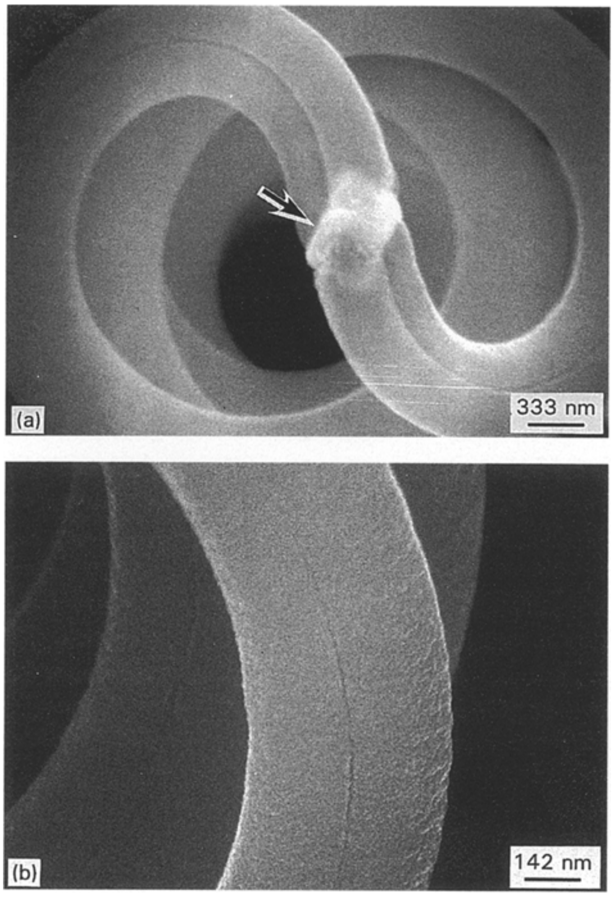

Figure 13 (a) The tip of the coils and (b) enlarged view of the surface of the coils.

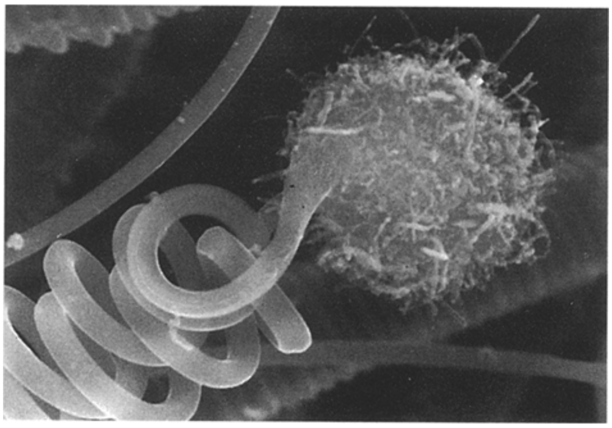

Figure 14 Ball-like tips.

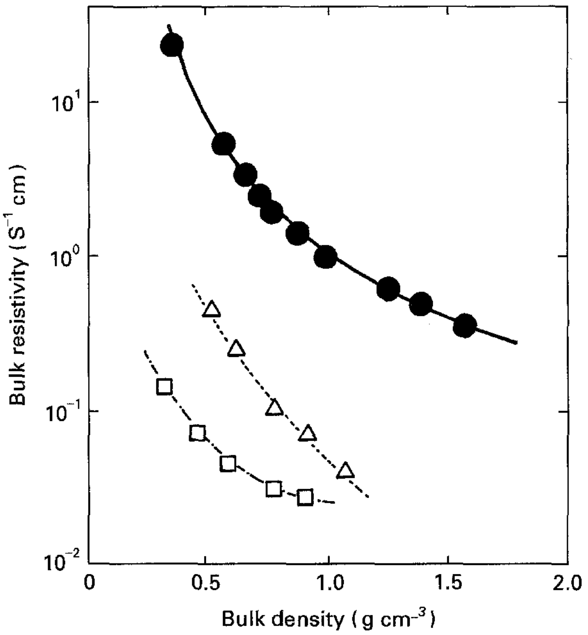

Figure 15 Relationship between bulk density of the coils and the bulk electrical resistivity. (●) Coiled carbon fibres (△) commercial acetylene black, (□) commercial Ketjen black.

4. Conclusion

The coiled carbon fibres were prepared by the metal-catalysed pyrolysis of acetylene, and the growth conditions and morphology were examined in detail. Among the metal powders used, nickel, titanium and tungsten were the most effective for the growth of the coiled carbon fibres, and the maximum coil yield of 50%–55% was obtained. The coiled carbon fibres grew at the reaction temperature of 700–850 °C and a thiophene gas flow rate of 0.14–0.45 standard $cm^3 min^{-1}$. The optimum values depended on the metal powder used. Various kinds of coiling patterns, such as a single coil, concentric coils, triple coils, combination coils, branched coils as well as double coils, were observed. The bulk resistivity of the coils having a bulk density of 1 was 10^0 S^{-1} cm.

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TABLE II Composition and surface area of the coiled carbon fibres

Sample	Impurity	Composition (wt %)					Surface area (BET, $m^2 g^{-1}$)
		Ni	S	H	O	C	
Carbon	H_2S	0.25	0.09	1.4	1.0	97.26	352
Coils	Thiophene	0.25	0.03	1.0	0.6	98.12	293
Carbon Powder	H_2S	–	0.10	0.33	0.5	–	–

(–) Not measured.

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