Letter

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

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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 Ni3C 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 Si3N4 fibres by the metal impurity-activated chemical vapour deposition (CVD) process using SiCl4, SiO2+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 cm3 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.
Table 1
Optimum growth conditions of coiled carbon fibres

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Optimum reaction temperature (°C)</th>
<th>Optimum gas flow rate of thiophene (scm)</th>
<th>Maximum coil yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>775</td>
<td>0.47</td>
<td>54.0</td>
</tr>
<tr>
<td>Zr</td>
<td>750</td>
<td>0.34</td>
<td>4.8</td>
</tr>
<tr>
<td>Nb</td>
<td>750</td>
<td>0.42</td>
<td>25.8</td>
</tr>
<tr>
<td>Cr</td>
<td>700</td>
<td>0.24</td>
<td>22.7</td>
</tr>
<tr>
<td>Mo</td>
<td>850</td>
<td>0.14</td>
<td>18.1</td>
</tr>
<tr>
<td>W</td>
<td>750</td>
<td>0.45</td>
<td>55.4</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Co</td>
<td>850</td>
<td>0.14</td>
<td>11.2</td>
</tr>
<tr>
<td>Ni</td>
<td>750</td>
<td>0.34</td>
<td>48.8</td>
</tr>
<tr>
<td>NiS</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>MoSi₂</td>
<td>800</td>
<td>0</td>
<td>23.3</td>
</tr>
</tbody>
</table>

Using Ti powder as the catalyst and a small amount of thiophene gas (0.47 scm) 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 scm 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 pitch and coil diameter, and a brightened part was always observed on the tip of the coiled fibres.

Fig. 2. X-ray diffraction patterns of the coiled fibres shown in Fig. 1(a). (O) Ni₁₀C.

Fig. 3. (a) TEM dark image and (b) selected area electron diffraction patterns. (A) (1010); (B) (011); (C) (1107).
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 respective crystal planes of the Ni3C single crystal.

Acknowledgements

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

References