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Preparation of micro-coiled SiC and TiC fibres by vapour phase metallizing of micro-coiled carbon fibres

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Micro-coiled fibres of SiC and TiC were prepared by the vapour phase metallizing of micro-coiled carbon fibres with full preservation of the coiling morphology of the source coiled carbon fibres, and their preparation conditions and bulk electrical resistivity were examined. The $SiC_{1.0}$ coils were obtained at 1400 °C for 2 h, and $TiC_{1.0}$ coils were obtained at 1100–1200 °C for 1.5 h. The bulk resistivity of the coiled TiC fibres sharply decreased with the bulk density and was $10^{-2}\ S^{-1}\ cm$ at $1.4\ g\ cm^{-3}$.

1. Introduction

Industrially available raw materials or functional materials with a micro-coiled or helical morphology are not currently available. Helical morphology of DNA or of some vine plants provides living bodies with essential functional roles. Accordingly, we could expect novel functional properties from such coiled materials.

The growth of micro-coiled carbon fibres by catalytic decomposition and the disproportionation of organic vapours or CO, have been reported by many researchers [1–7]. However, the obtained fibres were generally straight and/or tubular with a somewhat helical form.

We obtained regularly micro-coiled Si_3N_4 fibres by the metal impurity-activated chemical vapour deposition (CVD) process using Si_2Cl_6 [8–9], SiO_2 +C or SiO [10], as the Si source at 1200–1500 °C. Furthermore, we obtained regularly micro-coiled carbon fibres by the catalytic pyrolysis of acetylene [11–13]. The coiled fibres of SiC [14–16] or TiC [14, 17] were obtained by the CVD process or the metallizing of the coiled carbon fibres. However, their preparation conditions, morphology and characteristics have not been examined.

The coiled fibres of carbon or metal carbides are potential candidates for fillers in electromagnetic shielding materials, elastic packing or filter materials resistant to high temperatures and/or harsh or corrosive environments, micromechanical elements such as microsprings, microsensors, etc.

In this work, micro-coiled fibres of SiC and TiC were obtained by the vapour phase metallizing of the micro-coiled carbon fibres obtained by the catalytic pyrolysis of acetylene. The preparation conditions, morphology and electrical resistivity of the coiled fibres were examined.

2. Experimental procedure

Source micro-coiled carbon fibres (abbreviated to carbon coils hereafter) were prepared by the Ni metal catalysed pyrolysis of acetylene. The detailed preparation procedures and conditions are shown in ref. 12. The used carbon coils are 1–5 μm in coil diameter as shown in Fig. 1. The source carbon coils were placed in a mullite boat which was located in the central part of a horizontal mullite reaction tube (23 mm i.d.). The carbon coils were vapour phase siliconized under a $SiCl_4 + H_2$ atmosphere at 1100–1400 °C, and also titanized under a $TiCl_4 + H_2$ atmosphere at 900–1200 °C. Gas flow rates of $SiCl_4$, $TiCl_4$ and H_2 were fixed at 5 sccm (standard cubic centimetre per min), 9 sccm and 100 sccm, respectively.

3. Results and discussion

3.1. Preparation of micro-coiled SiC fibres

The source carbon coils were siliconized under a $SiCl_4 + H_2$ atmosphere, and the obtained siliconized fibres (abbreviated to SiC coils hereafter), after a 1 h siliconizing, are shown in Fig. 2. The coiling morphology of the source carbon coils was fully preserved, even after siliconizing under any of the siliconizing conditions, except for a slight diameter increase in the carbon fibres. Grain growth, or secondary crystal growth, on the surface of the SiC coils were not observed even after siliconizing the carbon coils at 1400 °C for 2 h. However, deposition of a small amount of thin and short whiskers were observed at

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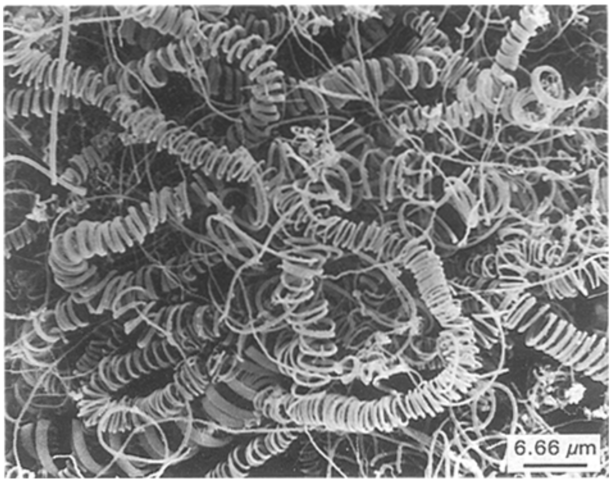

Figure 1 Source coiled carbon fibres.

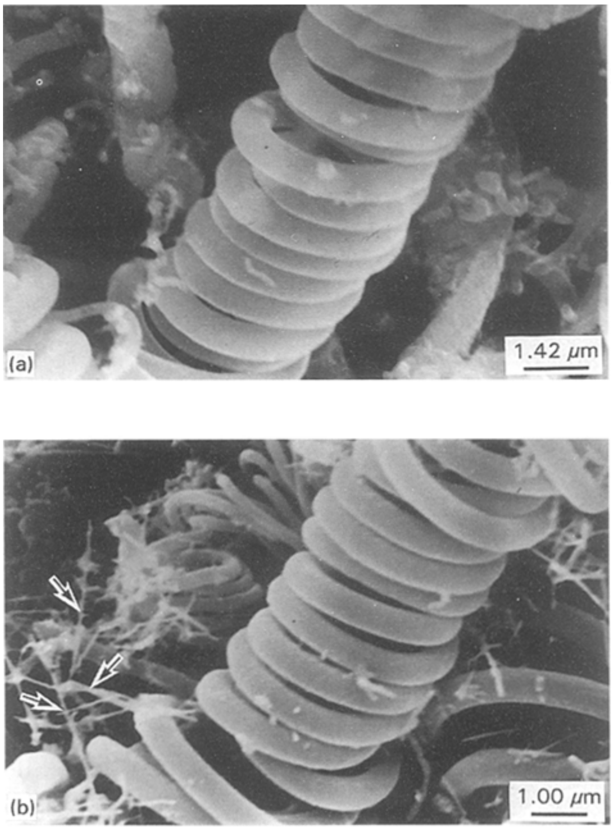

Figure 2 Siliconized coiled carbon fibres (SiC coils). Siliconizing conditions: temperature (a) 1100 °C, (b) 1400 °C; time 1 h; $SiCl_4$ gas flow rate is 5 sccm; H_2 flow rate is 100 sccm.

1100–1300 °C as shown by the arrow in Fig. 2. Fig. 3 shows the influence of siliconizing time and temperature on the Si/C ratio of the obtained SiC coils, in which the Si/C ratio was obtained from the weight gain due to the siliconizing. The Si/C ratio increased parabolically with increasing siliconizing times, irrespective of siliconizing temperatures. This suggests that the rate-determining step is diffusion of the Si or carbon through the deposited SiC layers. The fibres completely siliconized to the core (Si/C = 1) were obtained at 1300–1400 °C after 120 min. The X-ray diffraction patterns of the SiC coils are shown in Fig. 4, in which siliconizing time was fixed at 2 h.

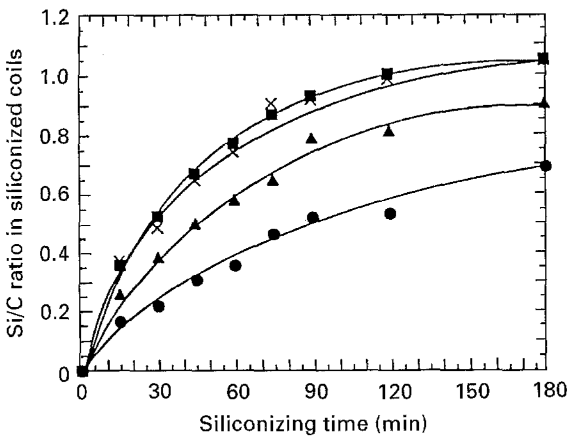

Figure 3 Influence of siliconizing time on the Si/C ratio of the SiC coils. Siliconizing conditions: temperature (●) 1100 °C, (▲) 1200 °C, (■) 1300 °C, (×) 1400 °C, $SiCl_4$ gas flow rate is 5 sccm; H_2 flow rate is 100 sccm.

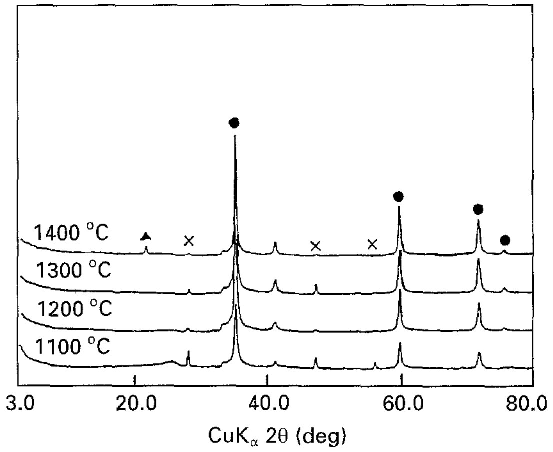

Figure 4 X-ray diffraction profiles of the SiC coils. Siliconizing temperature: (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C; (●) β-SiC, (×) Si, (▲) SiO_2.

Small peaks of free Si as well as the apparent large peaks of β-SiC were observed at 1100–1300 °C. These Si peaks are probably caused by the codeposited Si whiskers. Single peaks of β-SiC were observed at 1400 °C, for siliconizing times greater than 15 min.

3.2. Preparation of micro-coiled TiC fibres

The carbon coils were titanized to form coiled TiC fibres (abbreviated TiC coils hereafter) with full preservation of the coiling morphology of the source carbon coils. A representative example of the obtained TiC coils is shown in Fig. 5. Secondary grown crystals were frequently observed on the surface at 1200 °C as shown in Fig. 5(b) and (c). The transmission electron microscope (TEM) image of the TiC coils and selected area electron diffraction patterns of the secondary grown crystals on the surface, are shown in Fig. 6. The electron diffraction pattern shows that the secondary grown crystals are also TiC crystals. Fig. 7 shows the influence of titanizing time and temperature on the Ti/C ratio in the TiC coils. The Ti/C ratio in the TiC coils increased parabolically with increasing titanizing time and attained a Ti/C = 1.0 at 1100–1200 °C

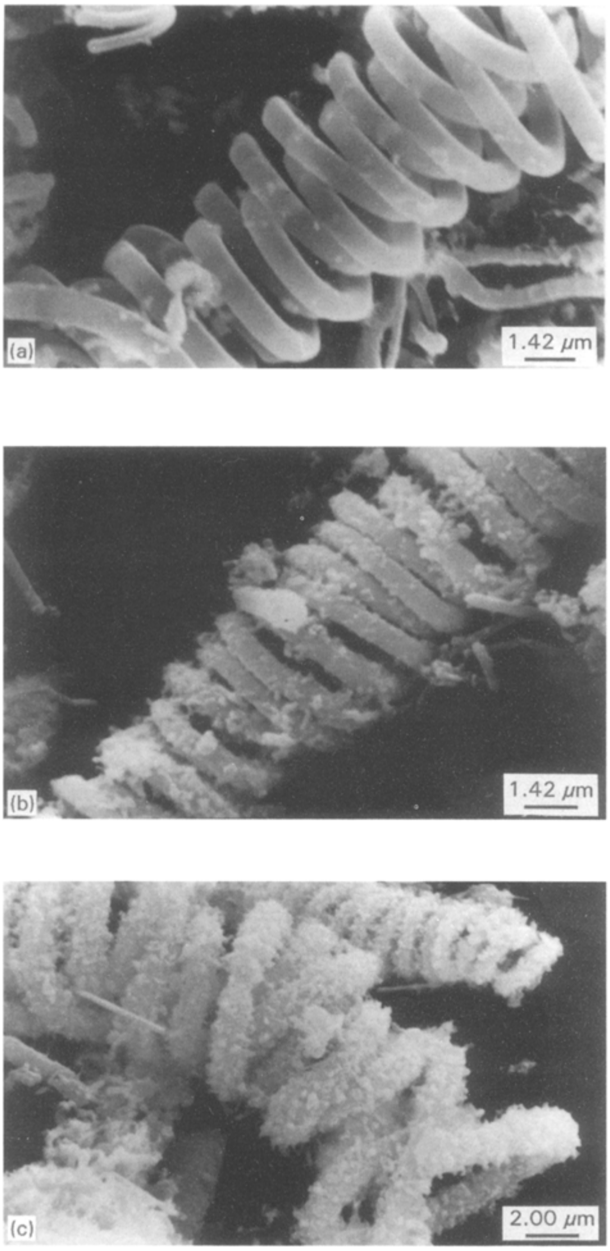

Figure 5 Titanized coiled carbon fibres (TiC coils). Titanizing conditions: temperature (a) 1100 °C, (b) and (c) 1200 °C; time (a) and (c) 2 h, (b) 1 h; $TiCl_4$ gas flow rate is 9 sccm; H_2 flow rate is 100 sccm.

for 90 min followed by a gradual increase to Ti/C = 1.1–1.2 for times above 120 min, probably caused by the secondary grown TiC crystals on the surface.

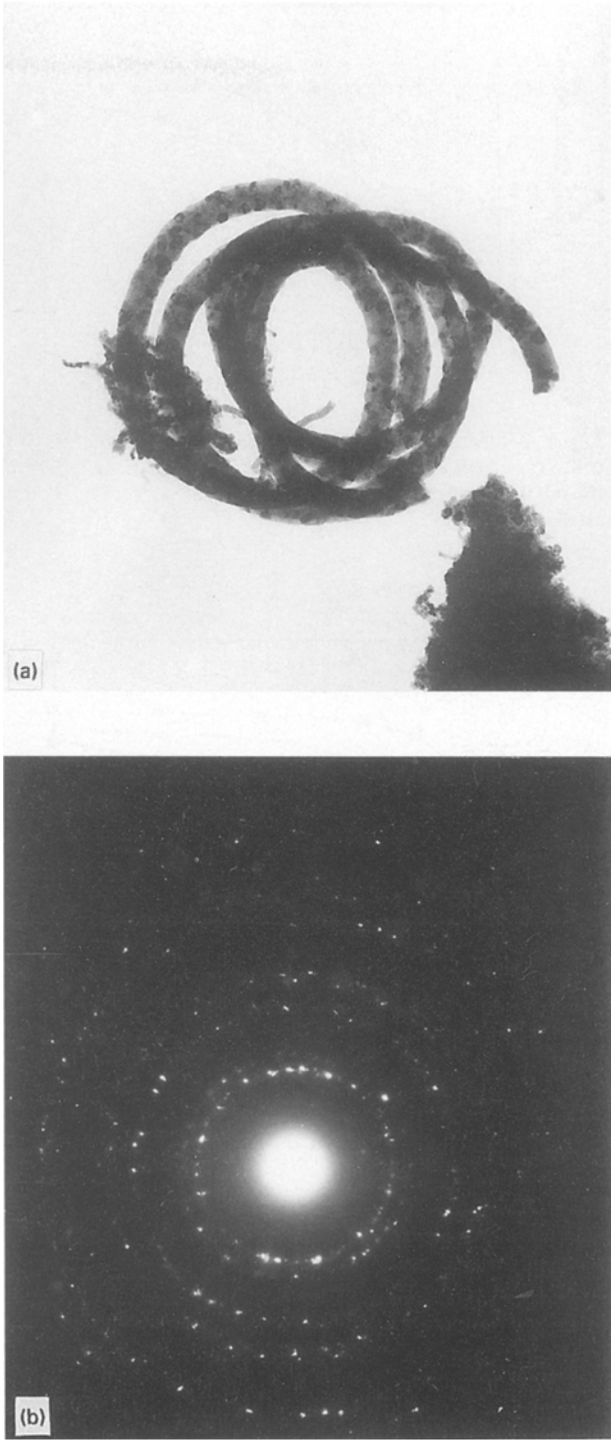

Figure 6 TEM image of the TiC coils (a) and selected area electron diffraction pattern of secondary grown crystals on the surface (b).

3.3. Bulk electrical resistivity of the SiC and TiC coils

The bulk electrical resistivity of the SiC and TiC coils were measured using a 10 mm i.d. cylindrical measurement cell. Fig. 8 shows the effect of siliconizing time and temperature on the bulk electrical resistivity of the SiC coils. The resistivity of the SiC coils increased steeply with increasing siliconizing time followed by a reduction in rate after 10–30 min. Fig. 9 shows the effect of titanizing time on the resistivity of the TiC coils. The resistivity of the TiC coils decreased steeply with increasing titanizing time, and a low resistivity of $10^{-2}\ \mathrm{S^{-1}\,cm}$ was obtained for the sample obtained after heating at 1000–1200 °C for 1.5–2 h. Fig. 10 shows the relationships between bulk resistivity and bulk density of the SiC and TiC coils, together with that of the source carbon coils and straight carbon fibres as a reference. The bulk resistivity of the TiC coils decreased steeply with increasing bulk density following a decrease in the rate above $0.7\ \mathrm{g\,cm^{-3}}$, and attained a value of about $10^{-2}\ \mathrm{S^{-1}\,cm}$ at $1.0\text{–}1.5\ \mathrm{g\,cm^{-3}}$.

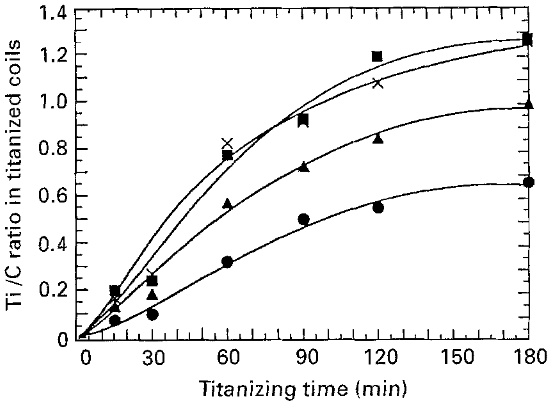

Figure 7 Influence of titanizing time on the Ti/C ratio of the TiC coils. Titanizing conditions: temperature (●) 900 °C, (▲) 1000 °C, (■) 1100 °C, (×) 1200 °C; $TiCl_4$ gas flow rate is 9 sccm; H_2 flow rate is 100 sccm.

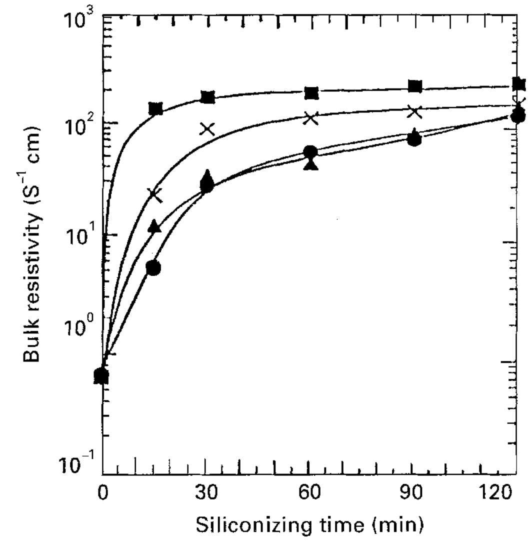

Figure 8 Influence of siliconizing time on the bulk resistivity of the SiC coils. Siliconizing temperature: (●) 1100 °C, (▲) 1200 °C, (×) 1300 °C, (■) 1400 °C. Bulk density is 0.7 $g\,cm^{-3}$.

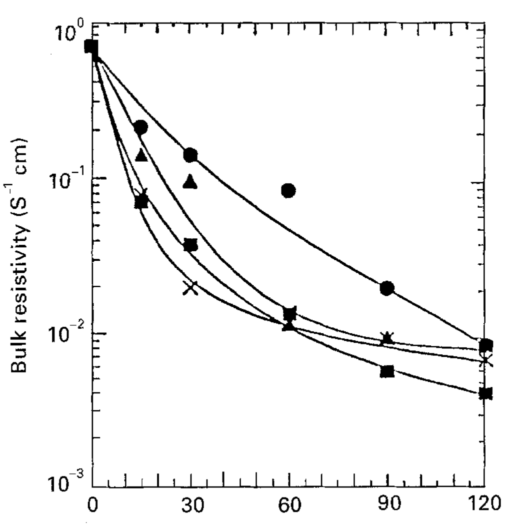

Figure 9 Influence of titanizing time on the bulk resistivity of the TiC coils. Titanizing time (●) 900 °C, (▲) 100 °C, (×) 1100 °C, (■) 1200 °C. Bulk density is 1.0 $g\,cm^{-3}$.

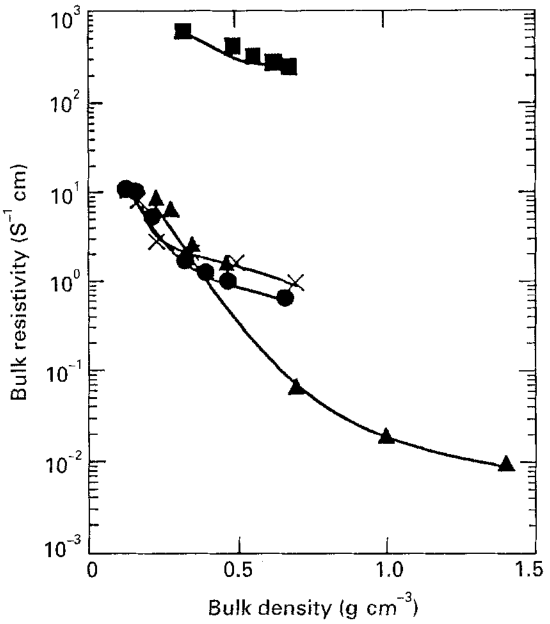

Figure 10 Influence of bulk density on the bulk resistivity of fibres. (■) SiC coils (Si/C = 1.0), (▲) TiC coils (Ti/C = 1.0), (●) source carbon coils, (×) vapour grown straight carbon fibres.

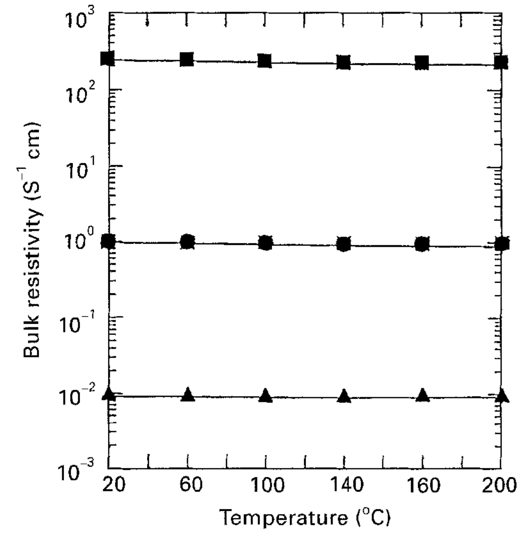

Figure 11 Dependence of bulk resistivity on temperature. (■) SiC coils, bulk density is 0.7 $g\,cm^{-3}$, (▲) TiC coils, bulk density is 1.4 $g\,cm^{-3}$, (●) source carbon coils, bulk density is 0.2 $g\,cm^{-3}$.

The dependence of the bulk resistivity of the fibres on temperature is shown in Fig. 11, together with that of the source carbon coils as a reference. The resistivity of the SiC and TiC coils as well as the carbon coils shows a constant value, depending on the type of fibres, between 20–200 °C.

4. Conclusions

Micro-coiled fibres of SiC and TiC were prepared by vapour phase siliconizing and titanizing, respectively, and their preparation conditions, morphology and electrical resistivity were examined. The coiling morphology of the source carbon coils were fully preserved even after siliconizing or titanizing under any conditions. The $SiC_{1.0}$ coils were obtained at

1400 °C for 2 h, and $TiC_{1.0}$ coils were obtained at 1100–1200 °C for 1.5 h. The bulk resistivity of the coiled TiC fibres decreased steeply with the bulk density and was 10^{-2} S^{-1} cm at 1.4 g cm^{-3}.

Acknowledgement

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