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Vapour Growth of Micro-Coiled Ceramic Fibers and their Properties

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Abstract: Micro-coiled fibers of carbon, SiC, Si₃N₄, TiC, ZrC and HfC were prepared by a metal-impurity activated chemical vapor deposition or vapour phase metallizing of the coiled carbon fibers. The growth conditions, morphology, growth mechanism and some properties were examined. The double-coiled carbon fibers were prepared using acetylene as a carbon source and various powders or plates of transition metals, metal carbides, MoS₂, Ti₂O₃, and Ni single crystal plate as a catalyst at 650–850°C. The triple-coiled SiC fibers were prepared using coked rice husks and/or SiO as a Si-source and Ni, Cr or Fe as a catalyst at 1400–1500°C. The double-coiled TiC fibers were prepared by the PCl₃ activated CVD process on a graphite substrate using a Pt+Si or Pd+Si mixed catalyst at 1050–1250°C.

1. Introduction

Industrially available raw materials or functional materials with a micro-coiled or helical morphology are not currently available. However, we can expect novel functional properties from such coiled materials. For example, the coiled fibers of carbon or metal carbides are potential candidates for fillers in electromagnetic shielding materials, micro-elastic packing or filter materials resistant to high temperatures and/or harsh or corrosive environments, micromechanical elements such as microsprings, micro sensors, etc.

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

We obtained micro-coiled carbon fibers (abbreviated "carbon coils" hereafter) by the catalytic pyrolysis of acetylene [8–10]. Furthermore, we obtained regularly micro-coiled Si₃N₄ fibers by the metal impurity-activated CVD process using Si₂Cl₆ [11–12], SiO₂+C or SiO [13] as the Si source at 1200–1500°C. The coiled fibers of SiC [14–16] or TiC [14, 17] were obtained by the CVD process or the metallizing of the coiled carbon fibers. However, their preparation conditions, morphology and properties have not been examined.

In this work, micro-coiled fibers of carbon, SiC, Si₃N₄, and metal carbides were obtained from vapour phase using the metal-impurity catalyzed chemical vapor deposition process or by the vapour phase metallizing of the coiled carbon fibers. The growth conditions, morphology, growth mechanism and some properties were examined.

2. Experimental

A graphite plate substrat, on which metal powder as a catalyst was uniformly dispersed, was placed in the central part of a horizontal reaction tube (quartz or mullite, 30 mm i.d.) which was heated from the outside. A metal plate was also used as the substrate and catalyst for preparation of the carbon coils. The source gas system used for the preparation of respective fibers were as follows.

3) Results and discussion

3.1) Coiled carbon fibers: Commercial acetone-dissolved acetylene (97-99% purity), in which a small amount of thiophene gas was added, was used without further purification. The gas flow rates were fixed as follows; C₂H₂ 30 sccm, H₂ 70 sccm and Ar 40 sccm. The effect of reaction temperature on the coil yield is shown in Fig.1, in which Ti powder was used as the catalyst and thiophene gas flow rate was fixed at 0.34 sccm. It was observed that the maximum coil yield (about 30%) was obtained at 775°C and the coil yield outstandingly decreased above or below this temperature. The effect of thiophene gas flow rate on the coil yield was shown in Fig.2, in which reaction temperature was fixed at 775°C. It was observed that the maximum coil yield (about 54%) was obtained at 0.47 sccm and the yield outstandingly decreased above or below this value. These results indicate that the growth conditions of the carbon coils were restricted within very narrow ranges. We examined the optimum growth conditions for growing carbon coils, at which maximum coil yield was obtained, using various metal powder catalysts, and the results are shown in Table 1. It can be seen that among used metal catalysts, Ti, Ni and W were the most effective for obtaining carbon coils with higher yield. The optimum reaction temperatures and thiophene gas flow rates were 700-850°C and 0.14-0.47 sccm (0.1-0.3 vol% in total gas), respectively. We have observed that, using oxygen free Ti plate which was etching-treated by conc. HCl solution, the coil yield was very low or nearly zero. On the other hand, Ti powder which was pre-oxidation treated at 850°C for 30 min in air have some catalytic effects for growing carbon coils and the maximum coil yield of about 27% was obtained. Furthermore, we have found that Ti₂O₃ powder was also effective for growing carbon coils and the maximum coil yield of 13 % was obtained. However, the carbon coils could not obtained using TiO₂ or TiO powders. These results suggest that surface oxide layers formed on the metal catalyst have some important

role for growing carbon coils as like as strong catalytic effect of iron suboxide for growing straight carbon fibers from a vapor phase [18].

Figure 3 shows the morphology of representative carbon coils obtained using a Ni powder as the catalyst. The coiling morphology of the carbon coils obtained using metal catalysts other than Ni were also similar to that of Fig.3. A Ni grain usually observed on the tip of carbon coils obtained using the Ni catalyst was identified to be a Ni_3C phase by a XRD and electron diffraction. The presence of metal carbide phase corresponding to the used metal as the catalyst were also observed on the tip of the carbon coils. That is, it may be reasonably considered that metal carbide acts as an actual catalyst for growing carbon coils. We examined the catalytic effect of various metal carbide powder on the growth of the carbon coils. Among metal carbides used, only TiC powder was effective for obtaining carbon coils. However, the maximum coil yield was only 14%, which is very low value compared to that obtained using the Ti metal catalyst of 54%.

3.2) TiC coils: We obtained micro-coiled TiC fibers (abbreviated "TiC coils" hereafter) from a gas mixture of $\text{TiCl}_4 + \text{H}_2 + \text{PCl}_3 + \text{Ar}$ at 1050°C on a graphite substrate using the mixed impurities of Si+Pd on a graphite substrate. Figure 4 shows the representative TiC coils obtained among TiP whiskers. The TiC coils were in a polycrystalline state with a $1\text{--}5\text{ }\mu\text{m}$ coil diameter and $20\text{--}150\text{ }\mu\text{m}$ coil length. The TiC coils were generally double coils similar to the carbon coils. The carbon source of TiC coils is considered to be graphite substrate. The effect of PCl_3 or HCl by-produced by the hydrogen reduction of PCl_3 on the vapourization of carbon and/or growth of the TiC coils are not yet known.

3.3) Si_3N_4 coils: Micro-coiled Si_3N_4 fibers (abbreviated " Si_3N_4 coils" hereafter) was obtained from a gas mixture of $\text{SiO}-\text{HN}_3-\text{H}_2-\text{Ar}$ using a Co or Fe metal catalyst. Representative Si_3N_4 coils obtained is shown in Fig.5. The Si_3N_4 coils were a single coil of an amorphous state having a $10\text{--}20\text{ }\mu\text{m}$ coil diameter and $100\text{--}1500\text{ }\mu\text{m}$ coil length. The Si_3N_4 coils showed a maximum shear stress of about 12 GPa and the rigidity of 110 GPa.

3.4) SiC coils: Micro-coiled SiC fibers (abbreviated "SiC coils" hereafter) were sometimes observed among amorphous straight SiC fibers. The SiC coiled fibers were generally triple-coiled or three-braided fibers in which three fibers were entwisted each other. The coil diameter was $0.3\text{--}1\text{ }\mu\text{m}$ and coil length was $5\text{--}50\text{ }\mu\text{m}$. Some of the triple-coiled SiC fibers are shown in Figs. 6 and 7. Two kind of coiling patterns were generally observed. One pattern is that of very regularly and densely coiled fibers as shown in Fig.6. The coil diameter was about $0.5\text{ }\mu\text{m}$ and length was $5\text{--}30\text{ }\mu\text{m}$. Three fibers (A, B and C) grew from a bulk deposit (arrow in Fig.6b) and entwisted each other to form triple-coiled SiC fibers. Another type is a relatively loosely coiled fibers with a wide coil pitch such as three braids (Fig.7). Some of closing parts were coalesced each other as shown in Fig.7b. This observation suggests that in the first place thin triple coils grew to the fiber growth axis with very high speed, and then the coils grew to the radial direction

with very low speed to form coalesced part. Single-coiled SiC fibers were rarely observed, even though sine-curved fibers which were coiled with very large coil pitch of 5–20 μm were frequently observed. Growth mechanism of these triple-coiled SiC fibers are not yet known.

3.5) HfC coils: The HfC coils grew sometimes among HfP whiskers from a gas mixture of $\text{HfCl}_4 + \text{C}(\text{graphite substrate}) + \text{H}_2 + \text{PCl}_3 + \text{Ar}$ on a graphite substrate. Representative micrograph of the HfC coils obtained is shown in Fig. 8.

3.6) ZrC coils: Micro-coiled ZrC fibers were obtained by the vapour phase zirconizing of the carbon coils at 1100–1250°C using $\text{ZrCl}_4 + \text{H}_2 + \text{Ar}$ gas mixtures. Representative ZrC coils obtained is shown in Fig. 9. The coiling morphology of the source carbon coils were perfectly preserved after zirconizing at high temperatures.

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Fig.1. Effect of reaction temperature on the yield of carbon coils.
Catalyst: Ti powder, C_4H_4S
flow rate: 0.34 sccm.

Fig.2. Effect of thiophene gas flow rate on the yield of carbon coils.
Catalyst: Ti powder, Reaction temperature: 750°C.

Catalyst	Fs/10 ² ml/min	RT/°C	Yield/%
Ti	47	775	54
V	24	725	9.3
Cr	24	700	23
Mn	34	700	2.4
Fe	—	—	0
Co	14	850	11
Ni	34	750	49
Zr	34	750	4.8
Nb	42	750	26
Mo	14	850	18
Hf	48	800	7.2
Ta	34	850	18
W	45	750	55

Fs:Flow rate of thiophene
RT:Reaction temperature

Table 1. Optimum growth conditions of the carbon coils using various metal powders as a catalyst.

Fig.3. Micro-coiled carbon fibers.

Fig.4. Micro-coiled TiC fibers.

Fig.5. Micro-coiled Si_3N_4 fibers.

Fig.6. Regularly micro-coiled SiC fibers (a) and the enlarged view of the tip (b).

Fig.7. Three-braided micro-coiled SiC fibers (a) and the enlarged view of the crossing part (b).

Fig.7. Three-braided micro-coiled SiC fibers (a) and the enlarged view of the crossing part (b).

Fig.8. Micro-coiled HfC fibers.

Fig.9. Micro-coiled ZrC fibers obtained by the vapour phase zirconizing of the micro-coiled carbon fibers.