Growth Mechanisms and Properties of Coiled Whiskers of Silicon Nitride and Carbon*

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This paper reviews recent studies of regularly coiled whiskers of Si₃N₄ prepared by the chemical vapor deposition (CVD) method as well as those of carbon by the catalytic pyrolysis method. Coiled Si₃N₄ whiskers have been obtained from a gas mixture of SiCl₄ and NH₃ at 1200°C on substrates on which metal impurity was painted. The most effective impurity for the growth of the whiskers was Ni for the quartz substrate and Fe for the graphite. A vapor liquid solid (VLS) growth mechanism was suggested from morphology of the whiskers. Coiled carbon whiskers have been grown by the catalytic pyrolysis of acetylene at 300-750°C using Ni powder as a catalyst. A small amount of H₂S was indispensable for the growth of the coiled carbon whiskers. A Ni compound seed observed on the tip of the pair-coiled carbon whisker is a single crystal. It is suggested that each crystal plane of the Ni compound seed has a different catalytic ability for the growth of the coiled carbon whiskers. The growth mechanism for the coiled carbon whiskers involves the surface diffusion of carbon atoms on the Ni compound seed. Structure of the coiled whiskers of Si₃N₄ and carbon was investigated by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). Furthermore, extension characteristics of these whiskers were examined.

KEYWORDS: coiled Si₃N₄ whiskers, coiled carbon whiskers, coiled TiC whiskers, Ni compound seed, catalytic pyrolysis, spring characteristics

1. Introduction

Ceramics have many excellent characteristics, such as high refractoriness, hardness, compressive strength and chemical stability. However, ceramics have a definite defect, namely, catastrophic fracture, and this is the greatest drawback in such applications as high temperature engineering materials. Various ideas have been proposed to overcome this defect and to improve their fracture toughness and strength. One of the ideas is to use fine ceramics as whiskers. Research and development of whiskers and whisker-reinforced ceramic composites are carried out by many researchers.

Silicon nitride (Si₃N₄) can be used for high temperature engineering applications because of its great strength and toughness at high temperatures, compared to other fine ceramics.

Whisker growth of silicon nitride was observed by nitriding silicon,²,³ silicon dioxide⁴ and rice hulls.⁵,⁶ It is well known that filament-like carbon was obtained by catalytic disproportionation of carbon monoxide⁶,⁷ or by catalytic pyrolysis of hydrocarbons, such as acetylene.⁸-¹⁰ The whiskers thus obtained were generally tubular and helical to some extent.

Growth of coiled whiskers is very interesting in relation to their peculiar morphology, growth mechanism, as well as their application. With regard to this matter, a number of papers have been published by many authors,¹¹-¹⁴ including those for graphite having a hollow.¹³,¹⁴ However, their detailed morphology has not been examined, and the growth mechanism has not been discussed. Furthermore, their spring characteristics, such as extension or contraction ratio, have never been examined. Whiskers of coiled, helical or twisted shapes of GaAs,¹¹ MnAs¹² and 2H-SiC⁶ have also been reported, but coiled amorphous whiskers have never been observed.

In this work, we have obtained silicon nitride whiskers¹⁷ from a gas mixture of SiCl₄, NH₃ and H₂ at a temperature range between 1050 and 1200°C. We have found¹⁸ that very regularly coiled, springlike whiskers were obtained on a graphite substrate on which iron impurity was painted, at a temperature of 1200°C. Growth conditions, morphology of the coiled whiskers¹⁹,²⁰ and extension characteristics¹⁹-²³ were examined in some detail.

Furthermore, we have obtained regularly coiled carbon whiskers²⁴,²⁵ by the catalytic pyrolysis of acetylene at 330-750°C using Ni plate or powders as a catalyst. We have examined the effect of gas impurities to the preparation conditions of the coiled carbon whiskers in the presence of a Ni catalyst. We have also examined the microstructure of the Ni compound seed held on the tip of the coiled carbon whiskers by means of a scanning electron microscope (SEM) and a transmission electron microscope (TEM) including electron diffraction. Based on these experiments, the growth mechanism of the coiled carbon whiskers is proposed.²⁶

2. Growth of Coiled Si₃N₄ Whiskers

2.1 Experimental procedure²⁶

A schematic drawing of the apparatus used in this work is shown in Fig. 1. A plate of quartz or graphite was used as a substrate, on which a metal chloride solution was painted and subsequently allowed to dry. The metal chloride was reduced to the corresponding metal particles (submicron in diameter) in a hydrogen atmosphere at an elevated temperature immediately before the beginning of the reaction. The substrate painted with the metal impurity was suspended vertically with a tungsten wire in the central part of the rec-
tion tube which was heated with SiC heaters. The substrate was set initially at the upper side of the reaction zone (dotted line) to avoid reaction of the metal impurity with the substrate and then was lowered to the reaction zone which was maintained at a constant reaction temperature and gas flow rate. Hydrogen carrier gas saturated with hexachlorodisilane (Si₃Cl₆, b.p. 144°C) using a circulation type saturator was introduced into the reaction zone immediately below the substrate through the lower vertical gas inlet tube. Ammonia was introduced directly into the reaction zone through the middle horizontal gas inlet.

2.2 Effect of the metal impurity and the reaction temperature on the Si₃N₄ whiskers

The effect of the metal impurity on the growth of the whiskers of silicon nitride on the quartz substrate is seen in Table 1. The whiskers obtained were in general similar in shape to wool or blanket fibers, and thus it was very difficult to measure the actual length of the individual whiskers. Accordingly, the average height of the bush or blanket of whiskers is used to indicate the length of the whiskers in this work. Therefore the actual average length of the whiskers should be 3–5 times the value indicated in this work.

For a quartz substrate, nickel impurity was found to be most effective in producing woollike white whiskers which reached a length of about 1 mm. Cobalt and iron impurities also showed some positive effect, but the yield was considerably lower than that of the nickel impurity. The thickness of the whiskers was about 1 μm, irrespective of the impurity used. For a graphite substrate, the most effective impurity was iron, as will be shown later.

The effect of the reaction temperature on the growth of the whiskers is shown in Fig. 2. In the case of nickel impurity, appreciable growth of the whiskers was observed at 1050°C, and the length increased markedly with temperatures above 1150°C, reaching about 1.2 mm at 1250°C. For cobalt or iron impurity, whisker growth was observed above 1150°C.

2.3 Morphology of the coiled Si₃N₄ whiskers on graphite substrates and their growth mechanism

When using a nickel impurity, the regularly coiled,

![Fig. 2. Effect of reaction temperature. Reaction time: 30 min, total gas flow rate: 9.1 ml/s, gas flow ratio (N/Si): 15, substrate: quartz plate, impurity: Ni (○ and ●), Fe (△), Co (□). (From ref. 19)](image)

![Fig. 3. Whiskers grown on graphite substrate. Reaction temperature: 1200°C, reaction time: 30 min, total gas flow rate: 9.1 ml/s, gas flow ratio (N/Si): 15, impurity: Ni. (From ref. 19)](image)

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Diameter (μm)</th>
<th>Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr powder</td>
<td>0.7–1.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Mn MnCl₂</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Fe powder</td>
<td>0.7–3.0</td>
<td>0.2–1.0</td>
</tr>
<tr>
<td>Co CoCl₂ powder</td>
<td>0.7–1.6</td>
<td>0.2–1.0</td>
</tr>
<tr>
<td>Ni NiCl₂ powder</td>
<td>1.3–1.9</td>
<td>&gt;1.0</td>
</tr>
<tr>
<td>Cu CuCl₂</td>
<td>—</td>
<td>—</td>
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springlike Si$_3$N$_4$ whiskers were observed (Fig. 3). The best regularly coiled whiskers have been obtained at 1200°C on a graphite substrate with iron impurity. Figure 4 shows an example of this. The coil pitch is 2–5 μm and the coil diameter is uniform of 10–15 μm, and the thickness of the whisker is 0.5–1 μm. The electron diffraction pattern from the whiskers, an example of which is given in the inset of Fig. 4(b), shows a halo characteristic of amorphous structure. An interesting feature is that after 20–30 turns, most of the whiskers stopped coiling for a while and then continued coiling again.

At several positions in a whisker, spherical droplet-like nodules are observed as indicated by Q in Fig. 4(b). Although iron impurity was not detected in such nodules by an electron probe microanalyzer (EPMA), these rounded nodules seem to be related to a vapor-liquid-solid (VLS) mechanism in the growth process of the coiled whiskers. Sometimes, another whisker grew into a coiled whisker as shown in Fig. 5(a). The fact that the threading whisker also has a uniform diameter strongly suggests a VLS mechanism; in the case of the direct vapor growth process, the diameter should be sensitive to the surrounding situation. In Fig. 5(a), branching of the whisker is seen as indicated by X. This branching occurs also with similar diameter. Such a branching phenomenon is again difficult to understand if this happened as a result of impingement of two vapor-growing whiskers, but can be understood if we assume that the branchings took place by a VLS mechanism at the droplet-like nodules as seen in Fig. 4(b). Figure 5(b) is a special case where the coil diameter decreases gradually and the coil ends with a rounded tip Q, which also suggests a VLS growth mechanism.

We find both right-handedly winding coils and left-handedly winding ones with the same probability. We often find whiskers whose winding direction changes several times during their growth, as shown in Fig. 6.

![Fig. 5. (a) Branching and interpenetrating complex growth of whiskers. (b) A special shape of coiled whisker with decreasing coil diameter. Note the round tip Q at the end of the whisker. (From ref. 20)](image)

2.4 Spring characteristics of the coiled Si$_3$N$_4$ whiskers

In order to clarify the spring characteristics of the coiled Si$_3$N$_4$ whiskers, we performed two kinds of tensile experiments using special devices: one involves the observation of great elongation of the coils by SEM and
the other involves the tensile tests under an optical microscope.

In the first experiment, we first cut a typical parallel-grid metal mesh for TEM observation into the shape shown in Fig. 7(a), where the mesh was cut in half leaving two long filaments of the grid. To points P and Q on the two long filaments we glued a coil specimen as shown in Fig. 7(b), and to the other ends of the filaments A and B we glued thin metal wires. These metal wires were then supported at X and Y with adhesive. Points P and Q are separated step by step and the stretched coiled whisker was observed by SEM at each step.

Figure 8 shows some examples of the results. The values of X given in the micrographs indicate the coil length with respect to the initial length. In this particular case, the coil fractured at X=2.2. Figure 8(e) shows the coil after the fracture. By comparison of the distance of the two nodules, A and B, on the coil between the initial state (a) and the final fracture state (e), it is found that no plastic deformation took place during stretching until fracture. Figure 9 shows an enlarged view of the fracture point. We see nodule B near the fracture point, meaning that the fracture was initiated at the stress concentration site at the nodule. It is found that the fracture surface is oblique to the growth direction. When a coil is elongated, a torsion stress is exerted on each part of the specimen. In the torsion stress of a wire, the maximum tensile stress component is at $45^\circ$ to the torsion axis. Thus, Fig. 9 indicates that the fracture took place almost along the maximum tensile stress plane, which is typical for brittle materials.

According to the elasticity theory, the ratio of the maximum shear stress acting at the surface of the whisker, $\tau_{max}$, to the shear modulus $G$ of the material is given by

Fig. 6. (a) A SEM micrograph showing changes of winding direction in a coiled whisker. (b) An enlarged view showing a joining region at the turning point indicated by an arrow. R and L indicate the direction of winding. (From ref. 20)

Fig. 7. (a) A special tensile device for stretching coiled whiskers. (b) An enlarged view of the specimen of which the two ends are glued at P and Q. (From ref. 20)

Fig. 8. A series of SEM micrographs showing elongation of a coiled whisker. (From ref. 20)
$$\tau_{\text{max}}/G = \delta/(4\pi nr^2)$$

where, $d$ is the whisker diameter, $r$ the coil radius, $\delta$ the amount of elongation and $n$ the number of turns. In the case of Fig. 8, the value of $\tau_{\text{max}}/G$ at the fracture stress is calculated to be 0.023. In thinner whiskers, the value of $\tau_{\text{max}}/G$ was as large as 0.035.

In the tensile experiments (Fig. 10) using an optical microscope, load was applied by a weight, which was actually a piece of cover glass in our experiments. The weight was connected to one end of a coil specimen, of which the other end was fixed. By inclining the optical microscope gradually together with the microscope stage on which the specimen with the weight was placed, we observed that the weight slid on the slide glass due to gravity to apply a load on the specimen. The threshold inclination angle of the microscope for initiation of sliding of the weight is 20°-25°, which corresponds to the static friction coefficient of 0.35-0.5.

Figure 11 shows optical micrographs of a coil during a tensile test on the microscope stage. The coil specimen in this experiment is the same as that used in Fig. 8(e). Figure 11(a) shows the specimen with natural length attached to a platinum wire $R$, which was connected to the weight, with a droplet of adhesive. Figure 11(b) shows the state after adhesion of the wire to the specimen. Figures 11(c) and 11(d) show the specimen elongations at inclination angles of 40° and 50°, respectively. The specimen finally fractured at nodule A (see also Fig. 8) at an inclination angle of 55°. The elongation at the fracture point was $X=3.2$, which is considerably larger than that in the first extension experiment of Fig. 8, where $X=2.2$. This finding indicates that the fracture strength of a specimen increases toward the ideal value as the stress concentration decreases.

In Fig. 12, we plot the load-elongation relationship for the case of Fig. 11. Here the load was estimated by assuming the constant friction coefficient of 0.35 or 0.5. The calculated shear modulus of the material from the slope of the load-elongation relationship is $G=130$-160 GPa. Further details of the tensile tests of the whiskers will be reported in the future.

2.5 Auger electron spectrum

An Auger electron spectrum of the whiskers, which were sputtered with argon for 3 min, is shown in Fig. 13. Two very strong peaks of silicon (97 eV) and nitro-
gen (400 eV), as well as small peaks of carbon (280 eV) and oxygen (530 eV) were observed. The peak patterns of silicon and nitrogen observed are nearly the same as that of the pure silicon nitride. These results show that the coiled whiskers obtained in this work are composed of amorphous silicon nitride containing small amounts of carbon and oxygen. The carbon may have originated from the carbon substrate.

2.6 Amorphous $\text{Si}_3\text{N}_4$ whiskers containing a crystalline core

Figure 14(a) shows a dark-field electron micrograph of a straight whisker taken with a strong spot in the spotty electron diffraction pattern given in Fig. 14(b). It is found that the whisker consists of two regions, the outer region with a dark contrast and the inner core region with a bright contrast having contour lines, indicating that the core region is crystalline. An enlarged view of the tip of the whisker is shown in Fig. 14(c). The crystalline core is found to terminate on the inside of the whisker and contain some defects. The diffraction pattern shows (00.1) of $\beta$-$\text{Si}_3\text{N}_4$ and the growth direction is parallel to the [11.0] direction.

Figure 15 shows a dark-field electron micrograph of a zigzag whisker, composed of segments of straight portions, taken with diffraction spots given in the figure. It is found that the zigzag whisker also contains a crystalline core and that every part of the zigzag crystal has the same crystal orientation, indicating that the zigzag core is a single crystal as a whole. Furthermore, the growth direction of the zigzag crystal appeared to be nearly parallel to one of the three $\langle 11.0 \rangle$ directions.

On the other hand, a close examination of the coiled whiskers, grown together with straight or zigzag whiskers, did not reveal any sign of a crystalline core at any portion. Both in the micrographs and in the diffraction patterns, as shown in Fig. 4(b), we see no indication of the existence of a crystalline phase. Figure 16 shows an interesting branched whisker with two straight branches forming an angle of about 120° and one bent branch. The micrograph clearly indicates that there is a thin crystalline core in the two straight branches, but no core in the bent branch, consistent with the above-described results of straight and coiled whiskers. The diameter of the crystalline core ranges from 100 to 1000 nm and the ratio of the core diameter to the whisker diameter ranges from 0.05 to 0.25.

A phenomenological interpretation for the fact that crystalline core exists only in straight whiskers is that
the core crystal, once formed, appears to be destined to grow only in the \( \langle 110 \rangle \) directions, and hence the growth direction of the core whisker is guided by the orientation of the crystal. Although it is difficult to form conjectures as to the mechanism of the coiled growth without a core, the above observations may provide us with some hints for the mechanism.

As previously stated regarding Fig. 5(b), the growth process of the whiskers is considered to be due to a VLS mechanism. At the whisker tip, the solid phase precipitates from a liquid droplet containing a metallic impurity, which lowers the melting point, and the precipitated substance is supplied in turn from the vapor. For solidification from the melt into an amorphous solid, rather than a crystalline one, some impurity with a concentration higher than the critical value may be required to stabilize the amorphous structure. Such an impurity must also be supplied from the vapor phase and hence the concentration of the impurity in the liquid droplet will have a negative gradient toward the center. The crystalline core is assumed to be formed as the result of the concentration of the impurity in the central part of the growth front of the whisker being insufficient for solidification into the amorphous state.

3. Growth of Coiled Carbon Whiskers

3.1 Experimental procedure

Representative profiles of reaction temperature and deposition region in the experimental apparatus are schematically shown in Fig. 17. Fine Ni powder (about 5 \( \mu \)m diameter, 5 g weight) was dispersed on a quartz boat in the central part of a horizontal reaction tube.

Both high-purity acetylene gas (99.999%) and commercial acetylene were used as a source gas. Small amounts of other gases, such as \((\text{CH}_3)_2\text{CO}, \text{O}_2, \text{H}_2\text{O}, \text{CO}, \text{NH}_3, \text{SiH}_4, \text{Ar} \) and \( \text{H}_2\text{S} \), were added to the source acetylene to examine their influence on the growth of the coiled carbon whiskers.

3.2 Influence of impurity on the growth of the coiled carbon whiskers

The coiled carbon whiskers were rarely obtained using high-purity acetylene, but were obtained in high yield using commercial acetylene. Commercial acetylene contains small amounts of \((\text{CH}_3)_2\text{CO}, \text{H}_2\text{S}, \text{PH}_3 \) etc. as impurities. This suggests that some of these impurities play an important role in the growth of the coiled carbon whiskers. Among these impurities, only hydrogen sulfide (\( \text{H}_2\text{S} \)) showed a strong positive effect for the growth of the coiled carbon whiskers, and the optimum concentration of hydrogen sulfide in acetylene was 0.06\textendash}0.08 vol%. Excessive amounts of hydrogen sulfide, however, acted as a poison. It is concluded that a small amount of sulfur impurity acts as an activation agent for the growth of the coiled carbon whiskers with a Ni catalyst.

3.3 Morphology of the coiled carbon whiskers

When Ni powder was used as a catalyst and a small amount of \( \text{H}_2\text{S} \) was added to pure acetylene gas, carbonaceous deposits obtained from a 1-h reaction time were mostly composed of coiled carbon whiskers as shown in Fig. 18. The average coil length was 2\textendash}5 mm, and the coil pitch was generally so narrow that the coil gap was sometimes nearly zero.

It was observed in many coiled whiskers that two primary coils were crossed or entwisted to form the regular combination coils as can be seen in Fig. 19, in which

![Fig. 17. Schematic drawing of apparatus, representative temperature profile and deposition region. (a) Reaction tube, (b) Ni plate or quartz boat, (c) electric furnace, (d) \( \text{C}_2\text{H}_2 +=\text{Ar} \) or/and \( \text{H}_2 \), (e) gas outlet, (f) growth region of the coiled whiskers, (g) deposition region of carbonaceous films or powder. (From ref. 25)](image1)

![Fig. 18. Representative coiled whiskers obtained using fine Ni powder as a catalyst. (From ref. 25)](image2)

![Fig. 19. Regularly coiled whiskers showing crossing or entwisting of two primary coils (combination coils) (using Ni powder). (From ref. 25)](image3)
the coiled whiskers were slightly extended. Figure 20 shows the double coils in which coils with a narrow coil pitch "a" were coiled with those with a very wide coil pitch "b", where the coils with a narrow coil pitch should be combination coils. Appearance of the combination coil made of two primary coils (A and B) is shown in Fig. 21.

3.4 Microstructure of the coiled carbon whiskers and shape of Ni compound catalyst

It is very interesting to find that bright, diamond-shaped deposits were formed on the top of the coil (arrow in Fig. 22). These deposits were frequently observed at the inflection point of curls of the not-coiled whiskers (precursorlike whiskers of the coils, as shown in Fig. 23), as well as on the top of the coiled whiskers. These deposits were identified to be Ni compound by an electron probe microanalysis.

Figure 24 shows the spotty electron diffraction patterns of this Ni compound seed. The interplanar spacing \( \text{d} \) corresponding to points p, q and r in Fig. 24(a) was estimated to be 3.71, 3.31 and 3.60 Å, respectively. The interplanar spacing \( \text{d} \) corresponding to point s in Fig. 24(b) was 5.88 Å, which should be one of three lattice constants of the Ni seed. However, these \( \text{d} \) values do not agree with those of Ni metal, Ni, C or other Ni compounds reported thus far.

The Ni seed became unstable and decomposed completely after heat treatment at 2000°C for 1 h in Ar atmosphere as shown in Fig. 25. Since ordinary Ni-C compounds are unstable above 1000°C, the Ni seed should be a single crystal which consists of particular Ni-C compounds not reported thus far.

3.5 Growth mechanism of the coiled carbon whiskers

The growth mechanism of coiled carbon whiskers can be deduced from previously described experimental results. The exclusive growing point is considered to be the Ni compound seed (Fig. 26(a)) which is on top of each coiled carbon whisker. In Fig. 26(a), the opposite planes (X-X), (Y-Y) in the Ni compound seed are crystallographically similar, whereas adjacent planes (X-Y) are dissimilar. It is likely that different crystal planes have different catalytic ability for the growth of the coiled carbon whiskers.

One possible growth mechanism for the coiled carbon whiskers is as follows (see Figs. 26(b) and 27). First, a Ni compound seed is formed by the reaction of a Ni particle with acetylene and the impurity gas (H₂S). The Ni compound seed then catalyzes the decomposition of acetylene, and two carbon whiskers begin to grow in two directions opposite to each pair of planes (X-Y) of the Ni compound seed (Fig. 26(a)). If the growth rate on the Y-plane is greater than that on the X-plane, the whisker should be bent as shown in Fig. 26(b). The coil diameter may depend not only on the difference in the growth rate, but also on the flexibility of the carbon whiskers.

The growth of the inorganic whiskers in CVD with a metal impurity is generally related to the VLS mechanism, in which a liquid phase including a metal impurity must be present at the growth temperature. For example, the straight carbon whiskers obtained by Fe catalytic pyrolysis of hydrocarbon (\( \text{C}_6\text{H}_6 \)) at high temperatures (about 1000°C) are reported to grow by the VLS mechanism. There is no liquid phase for the Ni-C phase within the reaction temperature range of 600-800°C at which coiled carbon whiskers grow. However, it is reasonable to consider that during the growth of the coiled carbon, a Ni compound seed should, at least in the vicinity of the surface, be in a liquidlike state (quasi-liquid), so that the carbon atoms on the surface
Fig. 23. Diamond-shaped deposits (using Ni powder). (From ref. 25)

Fig. 24. Spotty electron diffraction patterns of a diamond-shaped Ni compound seed shown in Fig. 23. (From ref. 26)

Fig. 25. Tip of a carbon whisker heat treated in Ar at 2000°C for 1 h. (From ref. 27)

Fig. 26. Simplified scheme for growth mechanism of coiled carbon whisker. (a) Ni compound seed (single crystal) on tip of coiled carbon whiskers. (b) Growth mechanism of coiled carbon whisker. (From ref. 26)

Fig. 27. Growth process of coiled carbon whisker. (From ref. 26)

can diffuse rapidly enough to maintain the growth rate of the carbon whiskers. It is therefore concluded that the coiled carbon whisker grows by a "quasi-VLS mechanism" activated by a Ni compound seed.

Figure 28(a) shows a transmission electron micrograph of a part of the coiled carbon whiskers which was heat treated in Ar at 2800°C for 1 h. A dark-field electron micrograph of the squared area in Fig. 28(a) is shown in Fig. 28(b). A diffraction pattern is shown in the upper right region of the figure. In Fig. 28(b),
3.6 Preparation of the coiled TiC whiskers

Titanium carbide (TiC) layer is easily deposited on a graphite substrate by vapor phase titanizing using a gas mixture of TiCl₄+H₂ at 1100–1300°C. We prepared coiled TiC whiskers by a vapor phase titanizing of the coiled carbon whiskers, where the flow rates of TiCl₄ and H₂ were fixed at 3.0 and 4.0 sccm, respectively.

Apparent peaks of TiC were observed on the X-ray diffraction profiles at a titanizing temperature of 1200°C for 1 h. The representative morphology and polished cross sections of the coiled carbon whiskers titanized at 1200°C are shown in Figs. 29 and 30, respectively. It can be seen that the coiled morphology of the titanized carbon whiskers is the same as that of the source coiled carbon whiskers except for slight thickening (Fig. 29). Furthermore, the cross section shown in Fig. 30(a) indicates that after 2h of titanizing the coiled carbon whisker was titanized partly to form tubular TiC, while the whole whisker was titanized completely up to the center as seen in Fig. 30 after 5 h.

The coiled carbon whiskers are easily prepared, and easily titanized to form the coiled TiC whiskers as described above. No other process for obtaining coiled TiC whiskers has been reported thus far. Accordingly, this process is very useful for preparing coiled TiC whiskers.

3.7 Extension characteristics of the coiled carbon whiskers

Extension characteristics of the coiled carbon whiskers were examined, and the results are shown in Fig. 31. The coiled whiskers having about 0.5 μm coil diameter, 100 μm coil length and 5 μm coil pitch were used in this experiment. Furthermore, the coiled whiskers used were those that were crossed or entwist-
ed with the two primary coils, as shown in Fig. 31. One end of the coil was fixed with an adhesive on a parallel copper mesh for TEM, and the other end was pulled to extend the coil. The values of $X$ denote the extension ratio based on the original coil length ($X=1$ in Fig. 31(a)). When the coils were released after stepwise extension up to 2.8 times their original coil length, they recovered their original state. These results show that the coiled carbon whiskers could be extended elastically up to about three times their free length. This extension ratio is larger than that of the present coiled whiskers of amorphous Si$_3$N$_4$. The coiled whiskers were further extended up to about 4.5 times at which the coils were nearly straight. In this case, the coils did not recover their original state and the coil length after release was about 1.5 times the original length (Fig. 31(e)).

4. Application and Prospects

Regularly coiled whiskers of extremely small size were fabricated from Si$_3$N$_4$ and carbon, both of which are known to be stable and corrosion-resistant under high temperatures. The coils obtained were of 2–20 $\mu$m in diameter, and consisted of the element whiskers having thickness of 0.1–1 $\mu$m. They were prepared by means of the CVD method using a small amount of Ni powder and the catalytic pyrolysis method using small amounts of Ni and H$_2$S.

Stretching experiments for both coiled whiskers have demonstrated their excellent spring characteristics which indicate potential for use of the material as the smallest helical spring in the world.

Both coiled whiskers can be applied not only as micro-springs but also as excellent reinforcing elements for composite materials, because they are more resistant to pulling out from the matrix than straight whiskers due to their form.

The coiled TiC whiskers, which are more stable than carbon whiskers, can be prepared easily by the vapor phase titanizing of the coiled carbon whiskers, which maintains the shape of the original carbon coils.

Very small carbon coils are expected to be used in various fields as filters, cushions, reactance elements of electric circuits, etc.