

# Formation of Inorganic (TaC, TaN) Fibers by Thermal Decomposition of Cellulose Acetate–Tantalum Alkoxide Precursor Gel Fibers

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Received 20 April 2005; accepted 21 October 2005

DOI 10.1002/app.23833

Published online 8 March 2006 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Precursor gel fiber was formed by extruding cellulose acetate spinning solution into Tantalum (Ta) pentaethoxide acetone solution in a coagulation bath. Gel formation must be due to the coordination of Ta to OH and CO groups on the pyranose ring. The resultant precursor gel fiber was converted into carbide (TaC) or nitride (TaN) fibers by pyrolyzing them in Ar, N<sub>2</sub>, or NH<sub>3</sub> atmospheres.

TaC and TaN fibers can be obtained near theoretical temperatures calculated from thermodynamics data. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4320–4324, 2006

**Key words:** cellulose acetate; tantalum alkoxide; precursor gel fiber; tantalum carbide; tantalum nitride

## INTRODUCTION

SiC fiber is synthesized by pyrolyzing polycarbosilane precursor fiber and is obtained commercially.<sup>1</sup> With the progress in technology, higher performance inorganic fiber will be needed in the near future. Most transition metals of the fourth (Ti, Zr, Hf) and fifth (Nb, Ta) rows of the periodic table from carbides and nitrides in these groups with extremely high melting point (3000–4000°C), excellent high temperature strength, corrosion resistance and good hardness.<sup>2</sup> However, there are a few studies for these metal carbide and nitride fibers, because an appropriate precursor can not be easily obtained.

TiC/C composite fiber can be prepared by pyrolysis of metal Ti alkoxide-impregnated phenolic resin fiber (Kynol).<sup>3,4</sup> The sol–gel-derived oxide fibers have been prepared from spinnable viscous solutions obtained by controlling the hydrolysis and polycondensation of the alkoxide solutions.<sup>5</sup> TiC and TiN fibers have been prepared by heat-treatment the sol–gel-derived TiO<sub>2</sub> fiber.<sup>6</sup> However, continuous spinning is difficult because long periods are required for the sol–gel conversion. Thorne et al.<sup>7</sup> formed TiC fiber by pyrolysis of polymeric titanates formed by the reactions of various

esters with Ti isopropoxide, and Sugimoto et al.<sup>8</sup> formed TiN fiber from Ti alginate precursor fiber. These fibers are porous structured and brittle. Furthermore, Hasegawa et al.<sup>9</sup> synthesized ZrC fiber by heat-treatment of ZrO<sub>2</sub>-phenolic resin hybrid fiber spun from Zr tetrakis(2,4-pentanedionate)/phenolic resin viscous solution.

Kurokawa et al.<sup>10</sup> reported the formation of Ti and Nb nitride fibers by thermal decomposition of cellulose acetate (CA)-transition metal (Ti, Nb) alkoxide precursor gel fibers in NH<sub>3</sub> atmosphere. This precursor fiber could be easily formed and the nitride fiber could be produced at low temperature than for powder processing. In this study, we attempted to prepare tantalum (Ta) carbide and nitride fibers by the thermal decomposition of CA–Ta alkoxide gel fiber.

## EXPERIMENTAL

All chemicals were of the reagent-grade available commercially and used without further purification. Cellulose acetate (CA:  $M_w = 45,000$ ; acetyl content = 39.8%) was obtained from Wako Pure Chemicals Ind., Ltd. (Japan). Tantalum (Ta) pentaethoxide was obtained from Kojundo Chemical Lab. Co. Ltd. (Japan). Acetone was dehydrated using molecular sieves (Wako Pure Chemicals Ind.).

The CA–Ta alkoxide precursor gel fiber was formed by loading a CA (12.5 wt %) acetone solution (spinning solution) into a syringe, fitting a needle to the end of the syringe, and then using compressed N<sub>2</sub> gas (2

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Contract grant sponsor: The Society of Fiber Science and Technology, Japan.

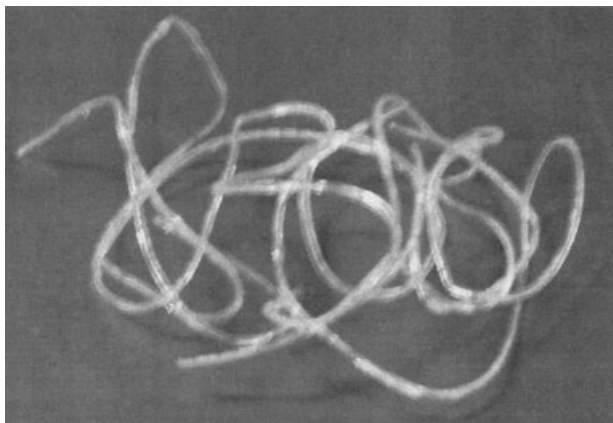


Figure 1 A view of CA-Ta alkoxide precursor gel fiber.

atm) to extrude the solution through the needle into a stirred Ta pentaethoxide (7.5 wt %) acetone solution (coagulation solution bath) from a height of 2 cm above the surface of the bath. After standing for 1 h, the resultant fiber was washed with fresh acetone and dried in air. The precursor fiber was heated up to a given temperature in alumina tube furnace at 800–1500°C in Ar, N<sub>2</sub>, or NH<sub>3</sub> atmospheres.

X-ray diffraction (XRD) measurements were taken using a CuK $\alpha$  with a Ni filter (40 kV, 30 mA). The microstructure of the surface and the cross section of the pyrolyzed fibers were observed by EPMA-8705 (Shimadzu, Japan). X-ray photoelectron (XP) and in-

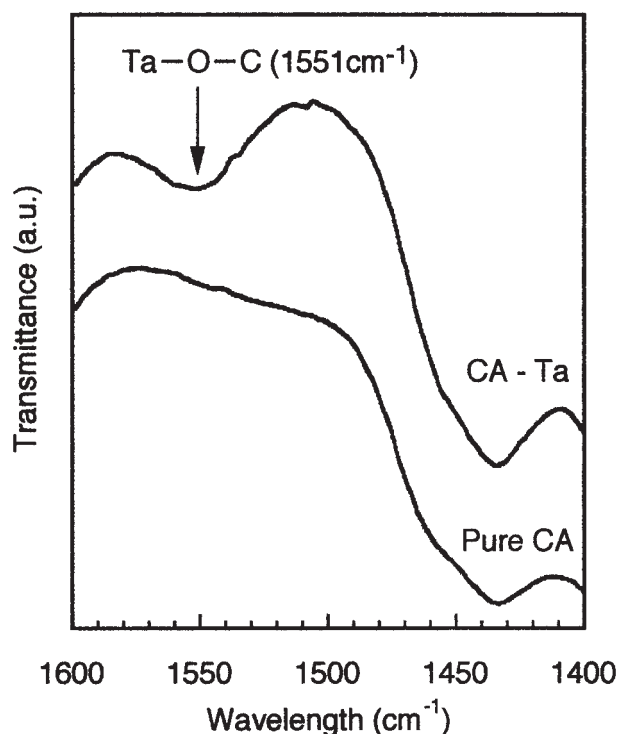


Figure 2 FTIR spectra of pure CA and CA-Ta alkoxide.

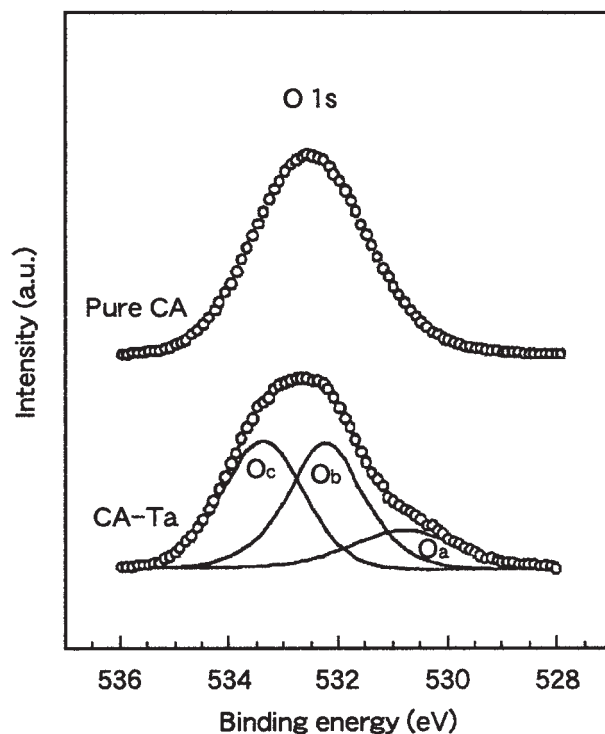


Figure 3 XP spectra (oxygen 1s) of pure CA and CA-Ta alkoxide.

frared (IR) spectra were measured using a PHI 5600 ESCA System (Perkin-Elmer, MgK $\alpha$ , Japan) and a FTIR-8100 (Shimadzu, Japan) (KBr disk method), respectively.

## RESULTS AND DISCUSSION

### Formation of CA-Ta alkoxide precursor gel fibers

Figure 1 shows a view of the precursor gel fiber. The diameter was about 0.3 mm. The size of the fiber was possible to be changed from 0.3 to 1.0 mm by changing the nozzle diameter. The CA-Ta alkoxide gel fiber was semitransparent and slightly elastic in acetone and water. The surface of the fiber was smooth, and large pores were not observed by scanning electron microscopy (SEM). Approximately 20 wt % Ta<sub>2</sub>O<sub>5</sub> per gram of fiber remained by a thermogravimetric analysis up to 1000°C in air.

The IR spectra of pure CA and CA-Ta alkoxide are given in Figure 2. The peak in the vicinity of 1430 cm<sup>-1</sup> was assigned to the acetyl group. A new, weak peak at 1551 cm<sup>-1</sup> was observed for CA-Ta alkoxide. This would be due to Ta—O—C bond.<sup>11,12</sup>

The XP spectra of oxygen 1s for pure CA and CA-Ta alkoxide are given in Figure 3. A bisymmetric peak is observed for pure CA. In the XP spectrum of CA-Ta alkoxide fiber, the peak shifted slightly to the left, and a shoulder appeared to the right side. This spectrum was separated into three peaks.<sup>12,13</sup> Peak O<sub>a</sub> is due to



**Figure 4** A view of CA-Ta fiber pyrolyzed under  $\text{NH}_3$  at  $1400^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$\text{Ta}_2\text{O}_5$  itself, and  $\text{O}_b$  is due to noncoordinate oxygen on CA. Peak  $\text{O}_c$  may be due to the coordination of the CO (acetyl) and OH groups on a pyranose ring to tantalum.

#### Formation of inorganic fibers by thermal decomposition of precursor fibers

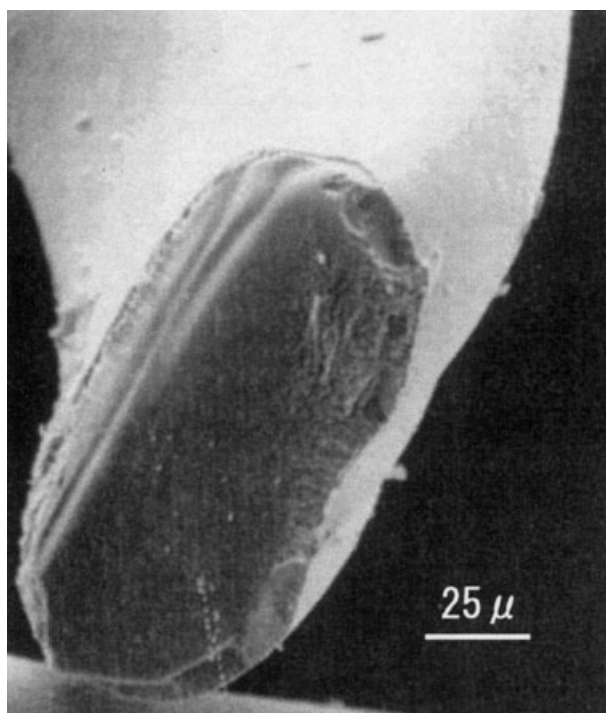
The precursor gel fibers were heated to given temperatures under Ar,  $\text{N}_2$ , or  $\text{NH}_3$  flow atmospheres for 1 h. The fibers remained after each heating condition. Figure 4 shows photographs of the resulting fiber pyrolyzed in  $\text{NH}_3$  gas flow at  $1400^\circ\text{C}$  (1 h). The fiber shows golden color above  $1200^\circ\text{C}$  heat treatment, but blue-argent color at  $1100^\circ\text{C}$ . On the other hand, the fibers pyrolyzed in Ar or  $\text{N}_2$  gas flow showed ash color. Figure 5 shows SEM image of the fiber pyrolyzed in  $\text{NH}_3$  gas flow at  $1100^\circ\text{C}$  (1 h). The inner of the fiber is dense structured, and the fiber had no pore but had smooth surface.

XRD patterns of pulverized fibers are shown in Figures 6 (under Ar) and 7 (under  $\text{NH}_3$ ). In Figure 6,  $\text{Ta}_2\text{O}_5$  and TaC are formed by heat treatment of precursor gel fiber up to  $1000^\circ\text{C}$  and above  $1100^\circ\text{C}$ , respectively. Oxygen and carbon would be supplied from decomposition of CA. Similar tendency was observed in the case of  $\text{N}_2$  atmosphere. In Figure 7, XRD peaks of  $\text{Ta}_3\text{N}_5$  are observed from  $900$  to  $1100^\circ\text{C}$ , and  $\delta$ -TaN are formed at  $1200^\circ\text{C}$ . The peaks of TaN become sharp with increasing temperature. We cannot distinguish between carbide and nitride in XRD peaks, because the XRD peaks of TaC and TaN appear at the same position. But, it was confirmed from XP spectra that the nitride was formed by pyrolyzing in  $\text{NH}_3$  atmosphere.

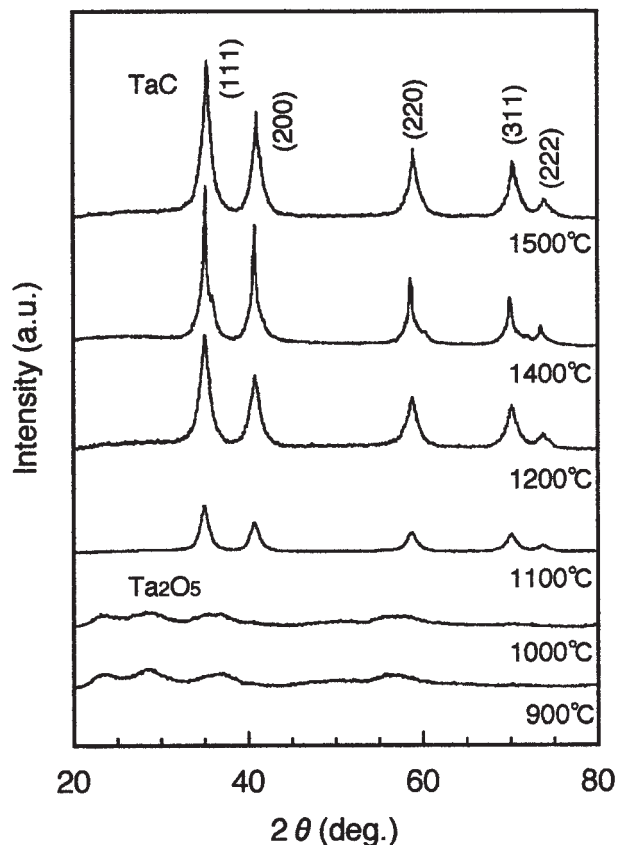
We considered that the carbonization and the nitridation proceed as follows<sup>2</sup>:



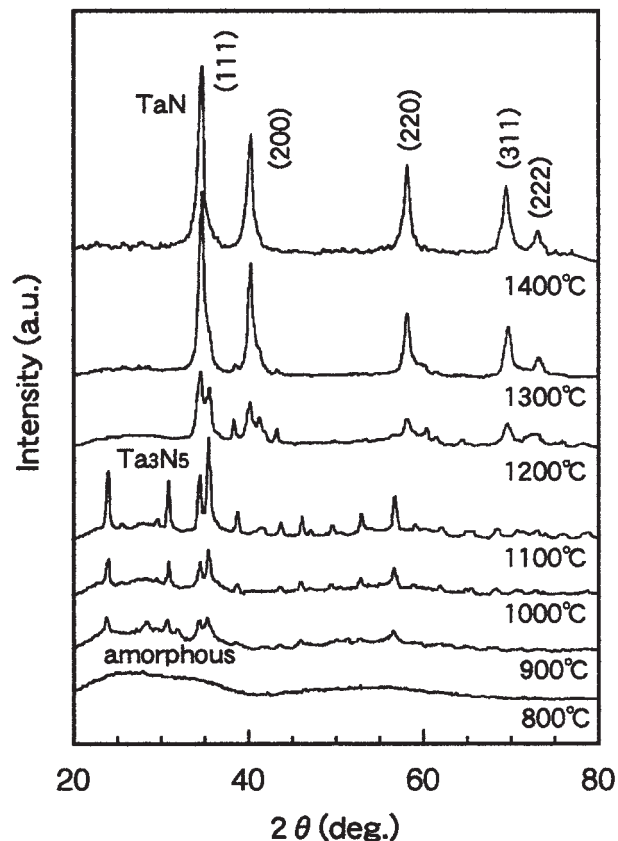
The Gibbs free energy change  $\Delta G^\circ$  for the reaction is given using the available thermodynamic data.<sup>14</sup> If the  $\Delta G^\circ < 0$ , reaction will proceed. Initial carbonization (TaC) and nitridation (TaN) temperatures calculated from thermodynamics data are  $1115$  and  $1052^\circ\text{C}$ , respectively. The temperature for TaC is higher than the observed temperature of  $1100^\circ\text{C}$  (as shown in Fig. 6). This denotes that the precursor gel fiber is a molecular scale mixture of Ta and carbon



**Figure 5** SEM image of CA-Ta fiber pyrolyzed under  $\text{NH}_3$  at  $1100^\circ\text{C}$ .



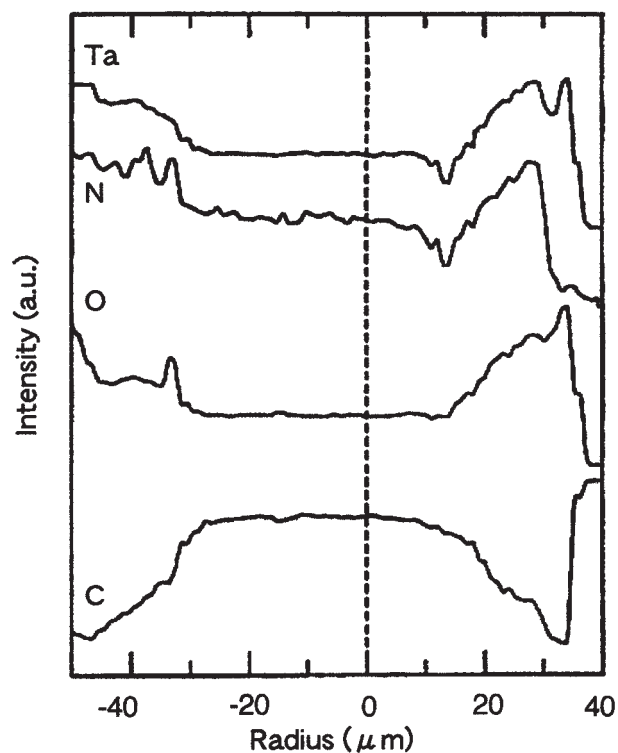
**Figure 6** XRD of CA-Ta fibers pyrolyzed at various temperatures in Ar gas flow.



**Figure 7** XRD of CA-Ta fibers pyrolyzed at various temperatures in  $\text{NH}_3$  gas flow.

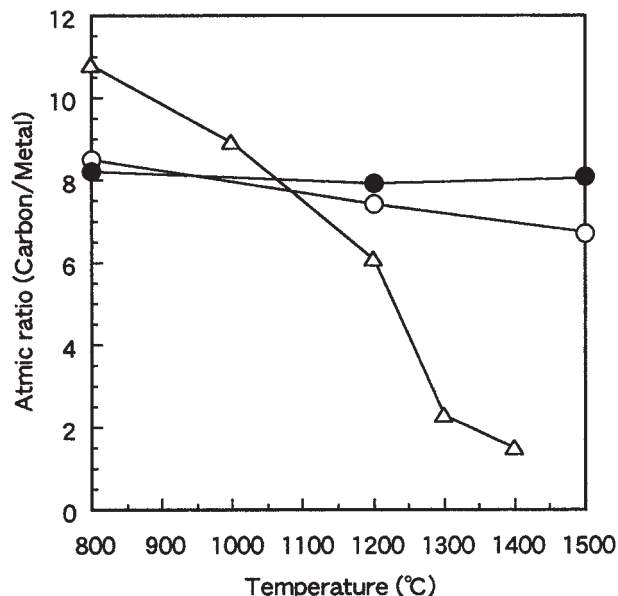
sources. On the other hand, the observed temperature (1200°C, in Fig. 7) for the production of TaN is higher than the calculated one. This may be due to the production of  $\text{Ta}_3\text{N}_5$ , which is stable in structure, at 900°C. On the heat treatment of CA-Niobium (Nb) alkoxide gel fiber in  $\text{NH}_3$  atmosphere, we confirmed that the nitridation (NbN) temperature becomes lower with increasing heating time [observed temperature: 900°C (heating, 1 h)  $\rightarrow$  800°C (5 h)].<sup>10</sup> Thus, TaN fiber will also be obtained at the vicinity of the calculated temperature by increasing the heating time.

Figure 8 shows the elemental distributions of CA-Ta alkoxide fiber (cross-section) pyrolyzed at 1100°C in  $\text{NH}_3$  gas flow. The dotted line in this figure means the center of the fiber. Ta, N, and O exist in large numbers at the vicinity of fiber surface, but C has an opposite tendency. C will be in amorphous state because there is no peak of graphite crystal from Figure 7. O remained because the heating condition would be not completely oxygen-free atmosphere. Consequently, the fiber after heat treatment has a skin-core structure; the skin is TaN layer, and the core is the mixture of amorphous carbon, TaN, and TaC microparticles.



**Figure 8** EPMA of CA-Ta fiber pyrolyzed under  $\text{NH}_3$  at 1100°C.





**Figure 9** Atomic ratio (C/Ta) of CA-Ta fibers pyrolyzed at various temperatures: (○) in Ar, (●) in N<sub>2</sub>, and (△) in NH<sub>3</sub>.

Figure 9 shows the atomic ratio (Carbon/Ta) of CA-Ta alkoxide gel fiber pyrolyzed under various conditions. The ratios are almost constant values when the fiber was pyrolyzed in Ar or N<sub>2</sub>. This is due to the carbonization (TaC) using carbon in CA molecules. On the other hand, the ratio at NH<sub>3</sub> atmosphere gradually decreased with increasing temperature. The nitridation (TaN) proceed and carbon will be removed from the fiber. Amorphous carbon still remained in pyrolyzed fiber even at 1400°C for 1 h (C/Ta = 1.5). It will be completely removed by longer heating.

## CONCLUSIONS

Tantalum carbide and nitride fibers have been formed by thermal decomposition of CA-Ta alkoxide gel fiber obtained by spinning of CA solution in alkoxide solution. This method gives the formation of ceramic fibers that are difficult to form by conventional organic polymer and sol-gel derived precursors. By the optimization of heating conditions, high-grade ceramic fibers will be obtained using CA-metal alkoxide precursor gel fibers.

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