FORMATION OF INORGANIC FIBERS BY THERMAL DECOMPOSITION OF CELLULOSE ACETATE-METAL ALKOXIDE PRECURSOR GEL FIBERS

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Introduction

SiC fiber is synthesized by pyrolyzing polycarbosilane precursor fiber and is obtained commercially. The higher performance inorganic fiber will be needed with progress of technology in near future. Most transition metals of the forth (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, good corrosion and good hardness. 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 fibers can be prepared by pyrolysis of metal Ti alkoxide-impregnated phenolic resin fibers (Kynol) [1]. TiC and TiN fibers have been prepared by heat-treatment the sol-gel derived TiO_2 fiber [2]. However, continuous spinning is difficult because long periods are required for the sol-gel conversion. Thorne *et al.* [3] formed TiC fiber by pyrolysis of polymeric titanates formed by the reactions of various esters with Ti isopropoxide, and Sugimoto *et al.* [4] formed TiN fiber from Ti alginate precursor fiber. These fibers are porous structure and brittle. Furthermore, Hasegawa *et al.* [5] synthesized ZrC fiber by heat-treatment of ZrO_2-phenolic resin hybrid fiber spun from Zr tetra-kis(2,4-pentanedionate)/phenolic resin viscous solution. Kurokawa *et al.* [6] reported that formation of Ti and Nb nitride fibers by thermal decomposition of cellulose acetate (CA)-transition metal (Ti, Nb) alkoxide precursor gel fibers in NH_3 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 [7].

Experimental

Materials

Cellulose acetate (CA: Mw = 45,000; acetyl content = 39.8%) was obtained from Wako Pure Chemicals Ind., Ltd., Japan. Tantalum (Ta) penta-ethoxide was obtained from Kojundo Chemical Lab. Co. Ltd., Japan. Acetone was dehydrated using molecular sieves (3A 1/16, Wako Pure Chemicals Ind., Ltd.)

Specimen preparation

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_2 gas (2 atm) to extrude the solution through the needle into a stirred Ta penta-ethoxide (7.5 wt%) acetone solution (coagulation solution bath) from a height of 2 cm above the surface of the bath. After standing for 1 hour, the resultant fiber was washed with flesh acetone and then was dried in air. The precursor fiber was heated up to a given temperature in alumina tube furnace at 800-1500°C in Ar or NH_3 atmospheres.

Apparatus and procedures

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

Results and discussion

Figure 1 shows photographs of the resulting fiber pyrolyzed in NH_3 gas flow at 1400°C. The fiber shows golden color above 1200°C heat treatment, but blue-argent color at 1100°C. On the other hand, the fibers pyrolyzed in Ar or N_2 gas flow showed ash color. The inner of the fibers is dense structure and the fibers have no pore and have smooth surface (Figure 2).

XRD patterns of pulverized fibers are shown in Figures 3 (under Ar) and 4 (under NH_3). In Fig.3, Ta_2O_5 and TaC are formed by heat treatment of precursor gel fiber until 1000°C and above 1100°C, respectively. Oxygen and carbon would be supplied from decomposition of CA. Similar tendency was

Figure 1 A view of CA-Ta fibers pyrolyzed under NH_3 at 1400°C.

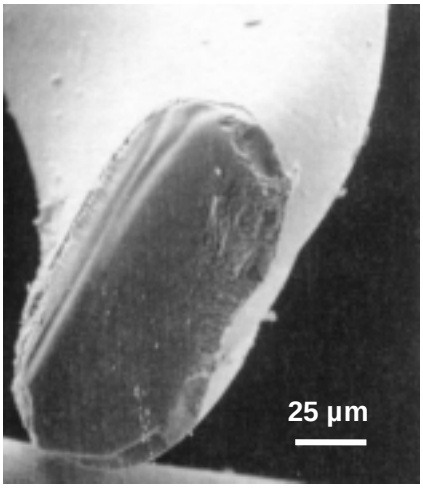

Figure 2 SEM image of CA-Ta fiber pyrolyzed under NH_3 at 1100°C.

observed in the case of N_2 atmosphere. In Fig.4, XRD peaks of Ta_3N_5 are observed from 900 to 1100 °C, and δ-TaN are formed at 1200°C. The peaks of TaN become sharp with increasing temperature. We can consider as the nitride because the fiber was golden color, which is special one for nitride.

We considered that the carbonisation and the nitridation proceed as follows:

$$Ta_2O_5 + 7C \rightarrow 2TaC + 5CO$$
$$Ta_2O_5 + 2C + 2NH_3 \rightarrow 2TaN + 3H_2O + 2CO$$

The Gibbs free energy change (ΔG°) for the reaction is given using the available thermodynamic data [8]. If the ΔG° < 0, the reaction will proceed. Initial carbonization (TaC) and nitridation (TaN) temperatures calculated from thermodynamics data are 1115°C and 1052°C, respectively. The temperature for TaC is higher than observed temperature, 1100°C (as shown in Fig.3). This denotes that the precursor gel fiber is a molecular scale mixture of Ta and carbon sources. On the other hand, the observed temperature (1200°C, in Fig.4) for the production of TaN is higher than the calculated one. This may be due to the production of Ta_3N_5, which is stable structure, at 900°C. On the heat treatment of CA-Niobium (Nb) alkoxide gel fiber in NH_3 atmosphere, Kurokawa *et al.* confirmed that the nitridation (NbN) temperature becomes lower with increasing the heating time [observed temperature: 900°C (heating, 1h) → 800°C (5h)] [6]. Thus, TaN fiber will be also obtained at the vicinity of the calculated temperature with increasing the heating temperature.

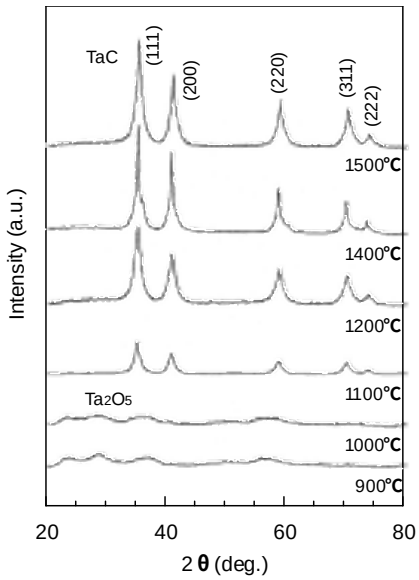

Figure 3 XRD of CA-Ta fibers pyrolyzed at various temperatures in Ar gas flow.

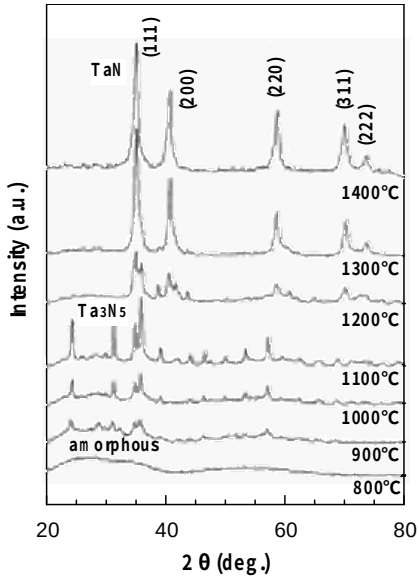

Figure 4 XRD of CA-Ta fibers pyrolyzed at various temperatures in NH_3 gas flow.

References

1. Hasegawa, I.; Nakamura, T.; Motojima, S.; Kajiwara, M. *J Mater Chem* 1995, 5, 193.
2. Nomura, K.; Takasuka, Y.; Kamiya, K.; Nasu, H. *J Mater Sci Mater Elec* 1994, 5, 53.
3. Thorne, K.; Ting, S. J.; Chu, C. J.; Mackenzie, J. D.; Getman, T. D.; Hawthorne, M. F. *J Mater Sci* 1992, 27, 4406.
4. Sugimoto, A.; Sano, T.; Kaneko, Y. *Nippon Kagaku Kaishi (Journal of the Chemical Society of Japan)* 1994, No.2, 126. (in Japanese)
5. Hasegawa, I.; Fukuda, Y.; Kajiwara, M. *Ceramics International* 1999, 25, 523.
6. Kurokawa, Y.; Ishizaka, Y.; Suzuki, M. *J Mater Sci* 2001, 36, 301.
7. Nakane, K.; Ogata, N.; Kurokawa, Y. *J Appl Polym Sci* 2006, 100, 4320.
8. Barin, I. "*Thermochemical Data of Pure Substances*" (VCH, Weinheim, Germany) 1993.