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Nitridation of TiO_2 fibres prepared by the sol–gel method

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Preparation of TiN fibres by ammonolysis of the sol–gel derived TiO_2 fibres has been performed in the present study. TiO_2 gel fibres were prepared from $Ti(O\text{-}i\text{-}C_3H_7)_4$ by hydrolysis and polycondensation. As a result, TiN is found to form above 900° C. A thermodynamic interpretation of the nitridation reaction of TiO_2 was considered. Moreover, from the kinetic treatment, it is found that the nitridation reaction of TiO_2 is controlled by diffusion of either reactant (NH_3) or one of the products (H_2O) through the reaction layer.

1. Introduction

In recent years, much attention has been paid to the sol–gel method for preparing various kinds of oxide-based glasses and ceramics in the forms of bulk body, thin film and fibre [1] in addition to powder. The authors have reported the preparation of pure TiO_2 fibres [2] and thin films [3] only via hydrolysis-polycondensation of titanium–iso–propoxide, $Ti(O\text{-}i\text{-}C_3H_7)_4$, without adding a viscosity-increasing agent such as hydroxypropylcellulose.

On the other hand, there has been increasing interest in non-oxide ceramics such as silicon nitride and silicon carbide which possess high temperature strength and corrosion-resistance. Among these, titanium nitride is currently of great technological importance because of its extreme hardness and abrasion-resistance comparable to diamond, its high melting temperature (2950° C), high chemical durability, gold colour and metallic conduction. So far, many studies have been conducted, especially on the TiN coating on the substrate using a variety of methods such as CVD (chemical vapour deposition) [4], sputtering and ion implantation [5].

In the present study, preparation of TiN fibres has been performed by ammonolysis of the sol–gel derived TiO_2 in the flow of NH_3 gas. At the same time, the mechanisms of nitridation of TiO_2 gel fibres have also been investigated.

2. Experimental procedure

2.1. Preparation of TiO_2 gel fibres

The preparation method of TiO_2 gel fibres has been reported previously [2] and will be described briefly here. $Ti(O\text{-}i\text{-}C_3H_7)_4$ (Wako Chemical Co. Osaka) was used as a starting material. It was diluted with half the prescribed amount of anhydrous C_2H_5OH. The mixture was then hydrolysed by adding drops of water mixed with C_2H_5OH and HCl as a catalyst. The amount of each chemical in the present study was $Ti(O\text{-}i\text{-}C_3H_7)_4 : H_2O : C_2H_5OH : HCl = 1:3:2:0.55$ in molar ratio. After being well mixed for 1 h, the sol solution was placed in an oven maintained at 40° C, until it became viscous for fibre drawing. After the sol solution was cooled down to room temperature, fibres were drawn from the solution by dipping a glass rod and pulling it up. The drawn fibres were dried in air for more than 2 days prior to nitridation treatment. The whole process is summarized in Fig. 1.

2.2. Nitridation of TiO_2 gel fibres

The TiO_2 gel fibres thus obtained were subjected to nitridation treatment in the flow of NH_3 gas using a SiC furnace shown in Fig. 2. A heating schedule shown in Fig. 3 was adopted in the present study. After a reaction tube of silica glass was filled with flowing N_2 gas, the TiO_2 gel fibres were heated up to a given temperature at a heating rate of $5° \mathrm{C\,min^{-1}}$ in the flow of NH_3 gas. The flow rate of NH_3 gas was $160\,\mathrm{ml\,min^{-1}}$. Nitridation time varied from 0 to 10 h, where the starting time was termed as the time just when a temperature of the sample reached the prescribed one ranging from 300 to 1100° C. The sample was then cooled in the flow of N_2 gas.

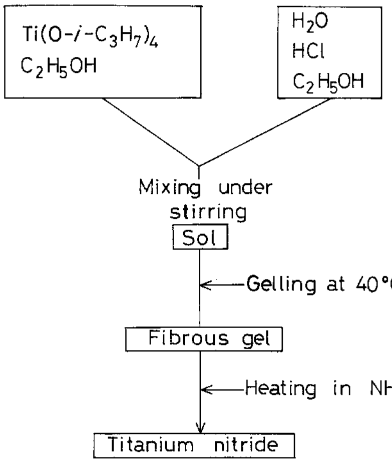

Figure 1 Flow chart for preparing TiN fibres via TiO_2 gel fibres made by the sol–gel method.

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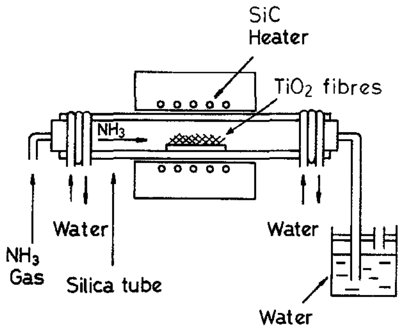

Figure 2 Silica tube furnace for nitridation.

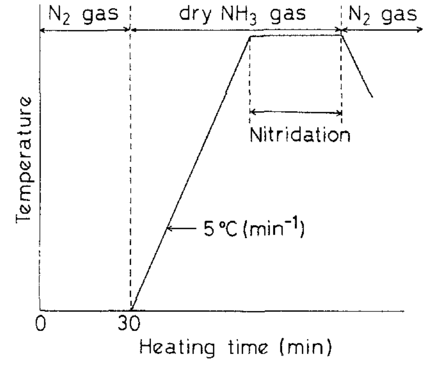

Figure 3 Heating schedule of gels.

2.3. Identification and quantitative analysis of the precipitated crystals by X-ray diffraction

An X-ray powder diffraction technique was used for identifying the crystals precipitated during heat treatment. The amount of TiN formed was also determined using the same method. For the purpose, a calibration curve relating peak ratio $TiN_{(200)}$: $Si_{(220)}$ to TiN content (wt %) was predetermined by using pure TiN (99.9%), TiO_2 (rutile, > 99%) and Si (> 99.9%), where the last was added as an internal standard in the ratio 1 : 10 by weight to the TiN–TiO_2 mixture.

3. Results

The fibres obtained by heating in the flow of NH_3 gas at several temperatures and for various time intervals are summarized in Table I. The fibres obtained above 900° C were golden in colour and electrically conductive, while those below 700° C were creamy white or silver grey in colour and non-conductive (see Fig. 4).

X-ray diffraction patterns of the pulverized fibre samples are shown in Figs 5 and 6. From the figures, distinct peaks assigned to TiN are seen above 900° C, corresponding to the results shown in Table I. Although the sample heated at 900° C for 1 h was golden in colour, no peaks other than those due to TiO_2 (rutile) are seen, indicating that the TiN formed on the surface is too thin to be detected. Only the peaks due to TiN are seen for the sample heated at 1100° C for 5 h. On the other hand, TiN is found not to form at temperatures below 700° C, TiO_2 (rutile) and TiO_2 (anatase) are coprecipitated and the former replaces the latter with increasing heating time. At temperatures below 500° C, only TiO_2 (anatase) is precipitated irrespective of the heating time.

The relation between the TiN content and the heating time at various temperatures above 900° C is shown in Fig. 7. The TiN content seems to increase with square root of heating time at each temperature. It is also obvious that the higher the heating temperature, the more the TiN content. It should be mentioned here that a certain amount of TiN above 1000° C is formed at zero heating time. This is due to

TABLE I Ammonolysis conditions and properties of the products

Sample	Heating temperature (° C)	Heating time (h)	Colour of fibre	Electric conduction
T3 · 1	300	1	creamy	×
T5 · 1	500	1	creamy	×
T5 · 5	500	5	creamy	×
T6 · 5	600	5	white	×
T7 · 1	700	1	white	×
T9 · 1	900	1	golden	○
T9 · 3	900	3	golden	○
T9 · 5	900	5	golden	○
T9 · 7	900	7	golden	○
T9 · 10	900	10	golden	○
T9.5 · 3	950	3	golden	○
T9.5 · 5	950	5	golden	○
T9.5 · 10	950	10	golden	○
T10 · 0	1000	0	golden	○
T10 · 1	1000	1	golden	○
T10 · 3	1000	3	golden	○
T10 · 5	1000	5	golden	○
T10 · 7	1000	7	golden	○
T10 · 10	1000	10	golden	○
T10.5 · 0	1050	0	golden	○
T10.5 · 5	1050	5	golden	○
T10.5 · 10	1050	10	golden	○
T11 · 0	1100	0	golden	○
T11 · 1	1100	1	golden	○
T11 · 3	1100	3	golden	○
T11 · 5	1100	5	golden	○
T11 · 10	1100	10	golden	○

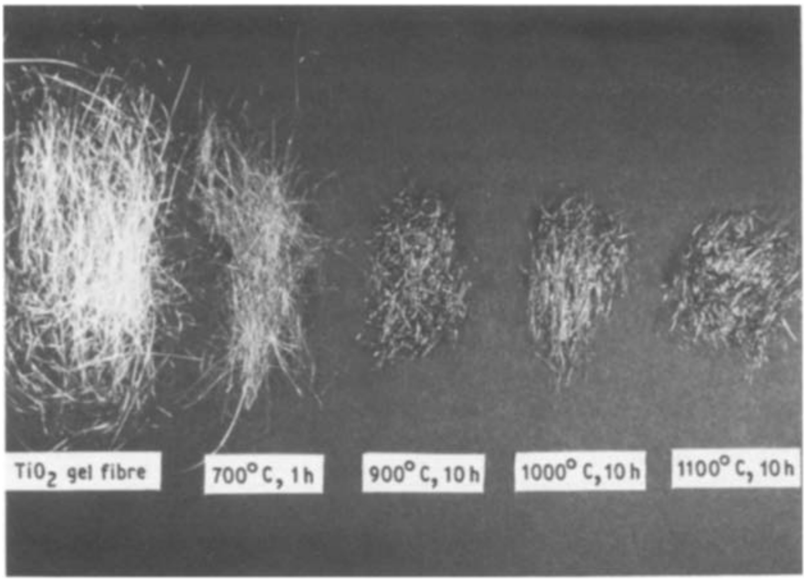

Figure 4 Picture of TiO_2 fibres heated at various temperatures in the flow of NH_3 gas.

the nitridation reaction which occurred before the temperature becomes constant. However, this will cause no problems on analysing the mechanisms of nitridation reaction as will be seen later.

The precise lattice parameters of TiN prepared in the present study and commercially available were determined by X-ray powder diffraction using silicon powder as an internal standard. The present result is in excellent agreement with the values for pure TiN (99.9%) and cited from the ASTM card as shown in Table II, indicating that the TiN prepared in the present study is stoichiometric.

4. Discussion

4.1. Thermodynamics of nitridation of TiO_2

Conversion of TiO_2 gel fibres into TiN fibres has been found to take place above 900° C in the flow of NH_3 gas. The total reaction of TiO_2 with NH_3 to form TiN is represented as follows,

$$6TiO_2 + 8NH_3 \rightarrow 6TiN + 12H_2O + N_2 \quad (1)$$

The Gibbs' free energy change ΔG for the reaction is given using the available thermodynamic data [6],

$$\Delta G = 914.79 - 0.7267T\,(\mathrm{kJ\,mol^{-1}}) \quad (2)$$

Reaction 1 will proceed, if the $\Delta G < 0$, i.e., $T >$ 1259 K (986° C). This corresponds well with the

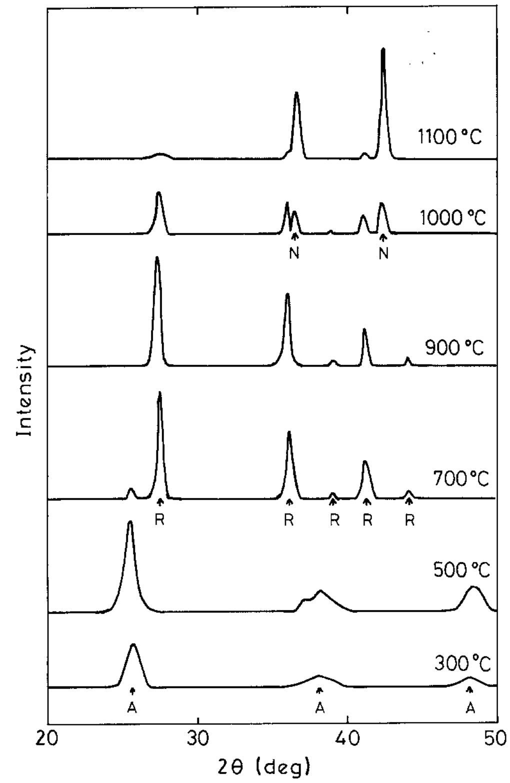

Figure 5 X-ray diffraction patterns of the TiO_2 fibres heated at various temperatures in NH_3 for 1 h. N, TiN; R, TiO_2 (rutile); A, TiO_2 (anatase).

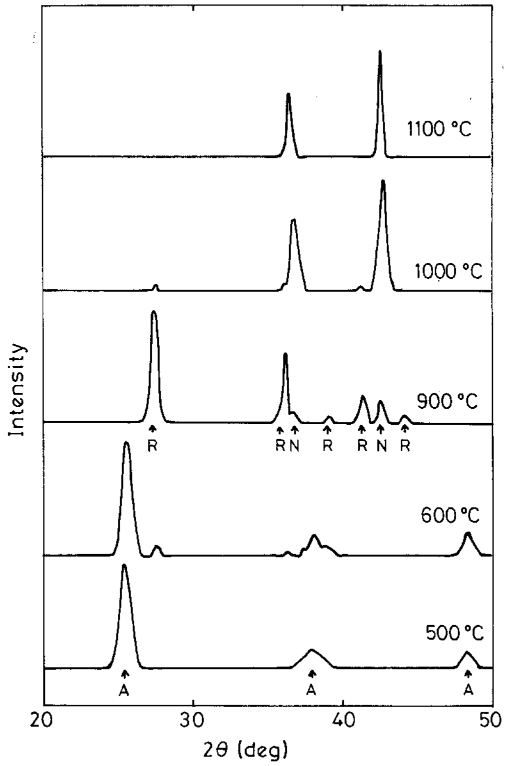

Figure 6 X-ray diffraction patterns of the TiO_2 fibres heated at various temperatures in NH_3 for 5 h. N, TiN; R, TiO_2 (rutile); A, TiO_2 (anatase).

TABLE II Lattice parameter of TiN (fcc)

Sample	a_0/A
Present study	4.236 ± 0.004
Pure TiN (99.9%)	4.237 ± 0.001
ASTM card	4.240

present result. It is found in the present study that TiN formation occurs at temperatures as low as 900° C. This is probably due to the porous structure and surface activity of the TiO_2 gel fibres.

The total Reaction 1 is considered to consist of the following three elementary processes,

$$NH_3 \xrightarrow{\Delta} 1/2N_2 + 3/2H_2 \quad (3)$$

$$2TiO_2 + H_2 \longrightarrow Ti_2O_3 + H_2O \quad (4)$$

$$Ti_2O_3 + 2NH_3 \longrightarrow 2TiN + 3H_2O \quad (5)$$

Reaction 3 occurs thermodynamically above 181° C. In order for TiN to be produced from TiO_2, TiO_2 must be reduced to Ti_2O_3, in the present case, by hydrogen resulting from the thermal decomposition of NH_3. The resultant Ti_2O_3 undergoes a nitridation reaction by NH_3 as shown by Reaction 5, not by N_2 gas. This is revealed by the experimental fact that TiO_2 does not react directly with N_2 below 1000° C even in the presence of a reducing agent such as carbon [7]. Since Reactions 4 and 5 have a positive Gibbs' free energy around 1000° C, the total Reaction 1 can be concluded to take place as a result of coupling phenomenon of Reactions 4 and 5 with Reaction 3.

4.2. Nitridation kinetics

To know what kind of mechanism controls nitridation of TiO_2 fibre is of practical importance. In the present case, two kinds of mechanism, diffusion and chemical reaction, will be considered, because they seem most probable.

When a reaction proceeds from the surface to the interior of fibrous specimen in a cylindrical form, the rate equations for diffusion- and chemical reaction-controlled processes, respectively, are given below [8]

diffusion control

$$k_d r^{-2} t = x + (1 - x) \ln (1 - x) \quad (6)$$

chemical reaction control

$$k_r r^{-1} t = 1 - (1 - x)^{1/2} \quad (7)$$

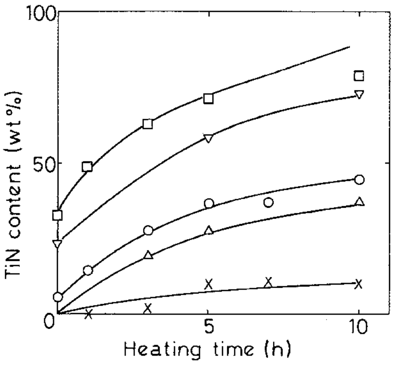

Figure 7 Plot of TiN content (wt %) against heating time at various temperatures. □, 1100° C; ○, 1000° C; △, 950° C; x, 900° C.

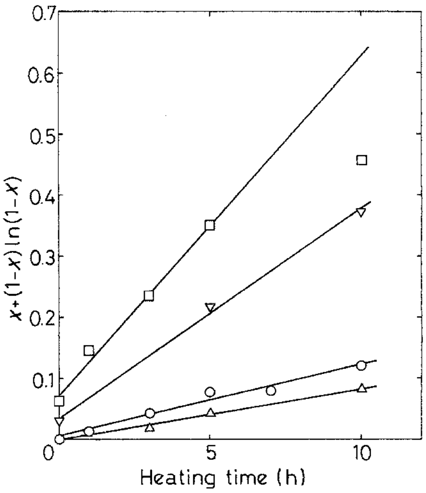

Figure 8 Plot of $x + (1 - x) \ln (1 - x)$ against heating time at various temperatures. □, 1100° C; ▽, 1050° C; ○, 1000° C; △, 950° C.

where k_d and k_r are the rate constant, r is the fibre radius, t the time and x the fraction of product in wt %.

Based on the results shown in Fig. 7, $x + (1 - x) \ln (1 - x)$ and $1 - (1 - x)^{1/2}$ are calculated and plotted against the heating time as shown in Figs 8 and 9, respectively. It is obviously seen from these figures that the plot of $x + (1 - x) \ln (1 - x)$ against t gives an excellent straight line but that of $1 - (1 - x)^{1/2}$ against t does not, indicating that the nitridation reaction of TiO_2 fibre is governed by the diffusion process of either reactant (NH_3) or one of the products (H_2O) through the nitrided layer.

Fig. 10 shows the Arrhenius plot of the rate parameter $k_d r^{-2}$. As TiO_2 gel fibres were drawn one by one, by hand, the fibre diameters ranged from 10 to 180 μm. For the present purpose, therefore, the fibres of about 100 μm in diameter on the average were used, but because of its uncertainty the rate parameter was taken as $k_d r^{-2}$ not as k_d itself in the present case. Regardless of this, the activation energy E_d can be estimated to be 177.65 kJ mol^{-1} from the slope in Fig. 10.

In order to elucidate which diffusion process is

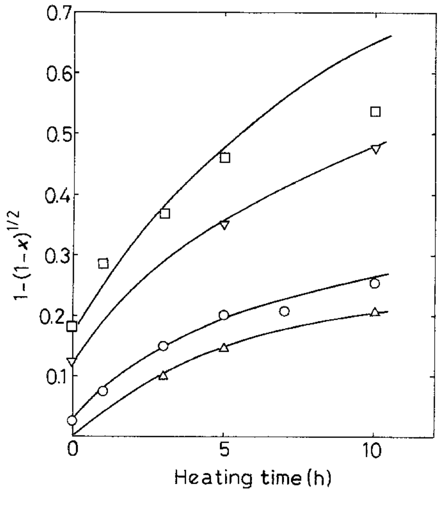

Figure 9 Plot of $1 - (1 - x)^{1/2}$ against heating time at various temperatures. □, 1100° C; ▽, 1050° C; ○, 1000° C; △, 950° C.

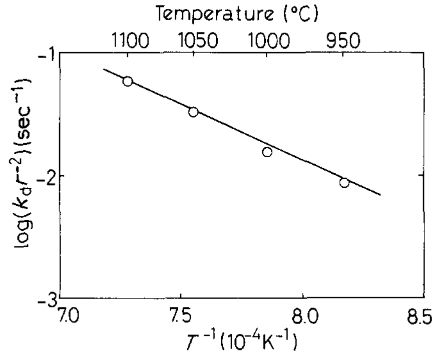

Figure 10 Arrhenius plot of the rate parameter. $E_d = 177.65$ kJ mol^{-1}.

responsible for the rate determining step, a flow rate of NH_3 was changed from 160 to 40 ml min^{-1}. As a result, the flow rate in the range has no effect on the nitridation rate. This may suggest that diffusion of NH_3 gas into the fibre is not rate-controlling. A more detailed study is required.

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