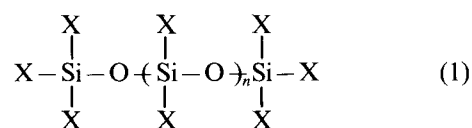


Preparation of TiO₂ fibres by hydrolysis and polycondensation of Ti(O-*i*-C₃H₇)₄

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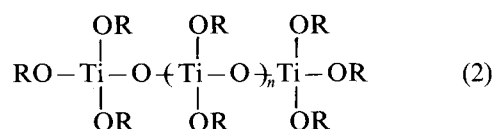
The present authors have been studying the sol-gel method for making oxide glasses using metal alkoxides as starting materials [1, 2]. In the sol-gel method, metal alkoxides (M(OR)_n, where R represents alkyl groups) are hydrolysed to form gels consisting of metaloxane polymers, which are converted to oxide glasses by heating to temperatures much lower than the conventional melting method required. In order to obtain fibres by the sol-gel method, it is required that the alkoxides form primarily chain-like or linear metaloxane polymers in solutions through hydrolysis and polycondensation reactions. It has been found in the case of Si(OC₂H₅)₄ solutions that the formation of chain-like polymers is achieved when the molar ratio of the added water to the alkoxide is relatively small [3]. That is, if the molar ratio of the water added to Si(OC₂H₅)₄ is less than four to five, this alkoxide gives linear siloxane polymers



(where X represents the R of OH group) or linear polymers having some branches. From that solution, gel fibres can be drawn; then they are converted to SiO₂ glass fibres by heating to ~1000°C. In a similar manner, silicate glass fibres of the TiO₂-SiO₂, Al₂O₃-SiO₂ and ZrO₂-SiO₂ systems have been obtained by drawing gel fibres from the corresponding mixed alkoxide solutions in the course of hydrolysis, followed by heating to temperatures below 1000°C [1].

As for TiO₂, the following methods have been used to produce fibres. In one method, the colloidal solution containing very small TiO₂ particles is made by hydrolysing titanium alkoxides Ti(OR)₄ or titanium tetrachloride TiCl₄; then that TiO₂ hydrosol is gelled and frozen unidirectionally [4]. Thus, fibres with the polygonal cross-section for TiO₂ composition are formed in the columnar interstices between columns of ice. In the other method, a viscosity-increasing agent is added to the TiO₂ hydrosol and spinning of the sol is performed. These processes for making fibres may be conveniently called "colloidal methods".

On the other hand, it has been postulated by Boyd [5] that linear titanoxane polymers



are essentially produced from a titanium alkoxide through hydrolysis and polycondensation when the molar ratio of the added water to the alkoxide is less than unity. This fact suggests that fibrous gels can be drawn from the solution containing those linear titanoxane polymers, just as in the case of Si(OC₂H₅)₄ solutions. However, so far, the direct production of TiO₂ fibres from Ti(OR)₄, exploiting its hydrolysis and polycondensation (here, we call this process the "chemical polymerization method"), has not been published yet.

The present letter describes the preparation of TiO₂ fibres by the chemical polymerization method from titanium tetra-*iso*-propoxide (Ti(O-*i*-C₃H₇)₄).

Ti(O-*i*-C₃H₇)₄ (hereafter abbreviated as Ti(O-*i*Pr)₄) of Wako Chemicals was used as a starting material. The 25.6 g (0.09 mol) of Ti(O-*i*Pr)₄ was mixed with the prescribed amounts of water, anhydrous ethyl alcohol (EtOH) and hydrogen chloride (HCl). The 32 solutions, whose compositions (in molar ratio) are listed in Table I, were prepared. EtOH is used as a mutual solvent and HCl acts as a deflocculating agent. For preparing Ti(O-*i*Pr)₄-H₂O-EtOH-HCl solutions having the required compositions, Ti(O-*i*Pr)₄ was first mixed with half the prescribed amount of EtOH, then water and HCl dissolved in the remaining EtOH was added dropwise to the Ti(O-*i*Pr)₄-EtOH solution while stirring. The addition of the alcoholic solution of water and HCl was made so slowly that turbidity did not occur in the mixed solution. In general, 0.5 to 1.0 h was needed to complete the preparation of a solution, depending on the solution composition. The solution was cooled by water during the above procedures.

If no HCl was added, the flocculation or precipitation of colloidal particles was encountered on adding the ethanolic solution of water to the alkoxide solution, and it was not possible to prepare any clear solutions. The HCl content of the respective solutions shown in Table I is the minimum needed to avoid the flocculation of the solutions. For compositions with very small amounts of EtOH (solutions 5 and 12), the components were not miscible. The compositions with a relatively large amount of water, whose molar ratio to the alkoxide was greater than five, showed turbidity while standing in the room, even if a relatively large amount of HCl was added.

The mixed alkoxide solutions, thus prepared, were kept standing in the air at 30° and 60°C. The solutions increased in viscosity with increase in standing time and were gelled into elastic masses at the times shown

TABLE I Compositions, gelation time t_g and spinnability of the $Ti(O-iPr)_4-H_2O-EtOH-HCl$ solutions

Solution	Composition (mol ratio)				Gelation time, t_g (h)		Spinnability*	
	$Ti(O-iPr)_4$	H_2O	$EtOH$	HCl	30° C	60° C	30° C	60° C
1	1	0	2	0.0	144.5		×	
2	1	0.2	0.5	0.02	77.3		×	
3	1	0.5	0.5	0.07	82.4		△	
4	1	0.5	2	0.05	77.9		○	
5	1	1	0.1	0.21	Immiscible			
6	1	1	0.5	0.18	35.0	5.1	○	×
7	1	1	1	0.15	74.8	4.5	○	×
8	1	1	2	0.12	24.1	7.1	○	△
9	1	1	5	0.01	78.0	6.1	×	△
10	1	1.5	0.5	0.27		3.6		○
11	1	1.5	2	0.23		4.6		○
12	1	2	0.1	0.42	Immiscible			
13	1	2	0.5	0.40	50.8	2.7	○	○
14	1	2	1	0.37	51.3	3.8	○	○
15	1	2	5	0.30		4.4		○
16	1	2	2	0.32	28.0		○	
17	1	3	0.1	0.64	35.3	2.2	○	○
18	1	3	0.5	0.60	56.2	3.3	○	○
19	1	3	1	0.55	70.0	3.6	○	○
20	1	3	2	0.53	95.8	2.6	○	○
21	1	3	5	0.50	116.1	3.6	○	○
22	1	3	10	0.30	8.6	6.5	×	×
23	1	4	0.5	0.80	79.3	3.6	○	△
24	1	4	2	0.70	124.3	4.3	○	△
25	1	4	5	0.55	126.8	3.3	○	△
26	1	5	2	0.90	84.1		×	
27	1	7	0.5	1.1	65.5		×	
28	1	7	2	0.95	77.8		×	
29	1	7	5	0.80	126.3		×	
30	1	7	10	0.70		7.3		×
31	1	10	1	1.2	102.0		×	
32	1	10	2	1.0	138.5		×	

*Spinnability: ○, yes; ×, no; △, yes, but drawn fibres are broken into pieces on drying.

in Table I. The gelation time t_g was defined as the standing time for which no more fluidity was observed on tilting the solution container. It is noticed that the gelation time at 60° C is considerably shorter than at 30° C. Many solutions exhibited spinnability just before gelling as in the case of $Si(OC_2H_5)_4-H_2O-EtOH-HCl$ solutions. The whole result on the spinnability of the $Ti(O-iPr)_4-H_2O-EtOH-HCl$ solutions is shown in Fig. 1a and b, as well as in Table I. Fibres could be drawn from the solutions marked by circles in the figures by dipping a glass rod and pulling it up by hand. Triangles in those figures indicate that the corresponding solutions showed spinnability, but

the drawn fibres were broken into numerous small pieces during drying in the room.

At 30° C, the spinnability is found in the solutions with the water content ranging from 0.5 to 4.0 in the molar ratio to $Ti(O-iPr)_4$. It is also seen that too high a degree of dilution with EtOH is not suitable for spinning. The compositional area for spinnability becomes narrower when the reaction temperature is raised to 60° C. Fibres were obtained within several hours at 60° C (much shorter than at 30° C). The narrowing of the spinnability area and shortening of the time required for drawing fibres upon raising the reaction temperature have also been observed in the

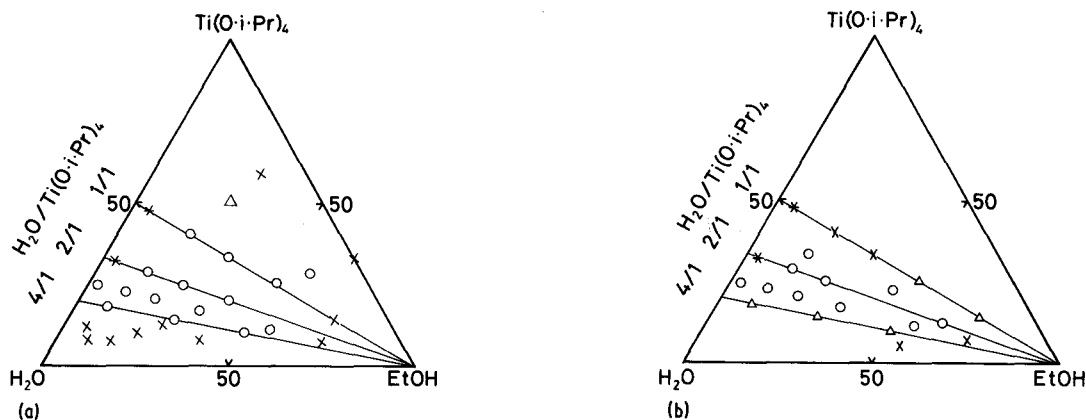


Figure 1 Fibre-drawing behaviour of $Ti(O-iPr)_4-H_2O-EtOH-HCl$ solutions (a) at 30° C and (b) at 60° C: ○ spinnable; △ spinnable, but drawn fibres are broken into pieces on drying; × not spinnable; * immiscible.

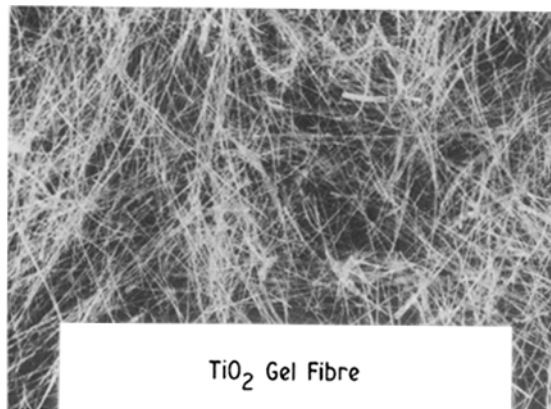


Figure 2 Photograph of TiO_2 gel fibres.

$\text{Si}(\text{OC}_2\text{H}_5)_4\text{-H}_2\text{O-H}_2\text{O-EtOH-HCl}$ solutions [2]. In Fig. 2, the drawn gel fibres for TiO_2 composition are shown. Those were drawn by hand, so the fibre diameter is not uniform, ranging from $\sim 10\ \mu\text{m}$ to $\sim 100\ \mu\text{m}$. The cross-section of fibres was circular or dumbbell shaped, in contrast to fibres made by the unidirectional freezing of TiO_2 hydrogel [4]. Fig. 3 shows X-ray diffraction patterns of fibres drawn from solution 20 at 60°C and heated to different temperatures up to 750°C in air for 1 h. Fibres heated at 100°C are amorphous. It is seen that anatase crystal precipitates at 150°C , increasing in crystallinity as the heating temperature is increased. At 700°C , a part of the anatase crystal transforms to rutile. Fibres heated to 750°C are mainly composed of rutile. Microphotographs of fibres are shown in Fig. 4a and b. The fibres heated to 700°C are transparent and a lower fibre can be seen through the upper one in Fig. 4a; they become opaque at 750°C as can be seen in Fig. 4b. The transparency of fibres heated to 700°C may be due to the

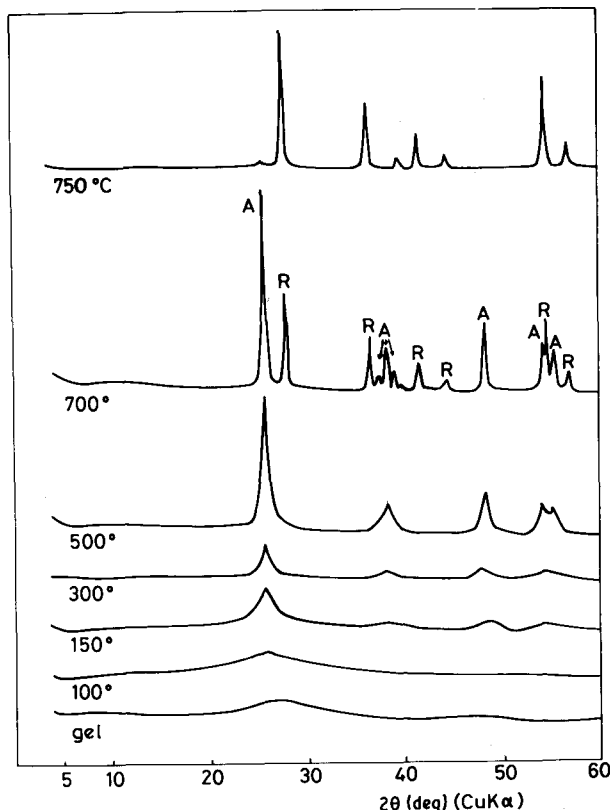


Figure 3 X-ray diffraction patterns of TiO_2 fibres heated to the indicated temperatures: A, anatase; R, rutile

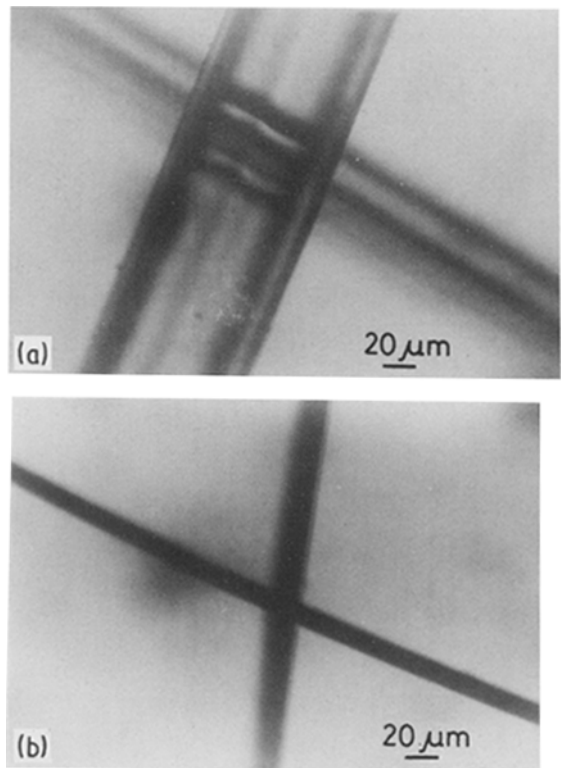


Figure 4 Micrographs of TiO_2 fibres taken by the transmitted light heated to (a) 700°C and (b) 750°C .

small crystallite size of precipitated anatase or rutile (less than 25 nm).

As has been pointed out previously and described above, the spinnability of the $\text{Ti}(\text{O-}i\text{Pr})_4\text{-H}_2\text{O-EtOH-HCl}$ solutions should be a reflection of the formation of chain-like or linear polymers in the solutions. Therefore, the present result may support Boyd's assumption described above. In the actual case, however, spinnability in the $\text{Ti}(\text{O-}i\text{Pr})_4$ solutions, with molar ratios of water to the alkoxide larger than unity, was also observed. This suggests that some degree of branching of the chain-like polymers does not severely limit drawing fibres, as indicated in the case of preparing SiO_2 glass fibres by the sol-gel method. Studies on the type of titanoxane polymers formed in the alkoxide solutions used in the present work, the microstructure and properties of TiO_2 fibres obtained are proposed for the future.

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