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Preparation of potassium hexatitanate long fibres by the flux evaporation method

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Potassium hexatitanate long fibres were successfully prepared by the flux evaporation method. The addition of a small amount of Li_2O to K_2MoO_4 flux was found to be very advantageous for growth of the long fibres. The crystal length was increased with the increase of the amount evaporated. The results of the experiment on the effects of flux to raw material ratio, filled amount and evaporation area on crystal growth are described.

1. Introduction

Because of its excellent thermal and chemical stability, potassium hexatitanate, $K_2Ti_6O_{13}$, is well known as the most promising artificial mineral fibre among the potassium titanates $K_2O \cdot nTiO_2$ ($n = 1$ to 6). Flux growth of fibrous potassium titanates has been widely investigated since the work of Gier [1] up to most recently by M. Kajiwara [2]. For use of K_2MoO_4 as a flux, Fujiki *et al.* [3] reported the growth of potassium titanates by a slow cooling method, and it has also been industrially produced by the Otsuka Chemical Co. The majority of potassium titanates synthesized to date, however, were short fibres less than 1 mm long. Long fibres of potassium hexatitanate have not been synthesized so far, except in vapour-phase growth reported by the present authors [4]. In this paper we report the growth of potassium hexatitanate long fibres using Li_2O–K_2MoO_4 flux.

2. Experimental details

Starting materials, Li_2CO_3, K_2CO_3, K_2MoO_4 and TiO_2 (anatase) were all of reagent grade. Raw material of non-fibrous potassium titanate was prepared by solid-phase reaction of K_2CO_3 and TiO_2. The mixture of K_2CO_3: TiO_2 = 1.5:6 (molar ratio) was put in a platinum crucible and heated at 1450° C for 5 h. The product was isolated using boiled water, followed by washing with water to remove excess potassium. X-ray diffraction (XRD) patterns showed that the product was $K_2Ti_6O_{13}$ contaminated with a small amount of $K_2Ti_4O_9$.

Flux and raw material were well mixed and were put into a platinum crucible (3.6 cm diameter × 4.5 cm high or 3.0 cm diameter × 3.2 cm high). The crucible was heated at a constant temperature for a predetermined time and rapidly cooled to room temperature in air. The products were separated by dissolving the flux with hot water, and dried at 110° C for 1 day. The crystals obtained were identified by X-ray diffraction analysis and observed by optical microscopy and scanning electron microscopy (SEM).

To investigate the composition change of the flux with reaction time, Li_2O concentration was analysed by spectrochemical analysis for the pure flux.

3. Results and discussion

3.1. Li_2O addition

The slow cooling method is normally used for crystal growth from the K_2MoO_4 flux because the vapour pressure of K_2MoO_4 is very low [3, 5]. We found that evaporation of K_2MoO_4 was enhanced by adding a small amount of Li_2O. Table I shows the results of crystal growth experiments using the flux of the system Li_2O–K_2MoO_4. Only short fibres were grown from Li_2O–K_2MoO_4 flux when the amount of Li_2O was 0.5 wt %. Crystal form was drastically changed by addition of 1.0 wt % Li_2O. The amount evaporated over 4 h was nearly doubled, and long fibres were grown. Further addition of Li_2O did not increase the evaporation rate. No short fibres were obtained in the run using 2.0 wt % Li_2O addition.

Ballman and Laudise [6] have investigated the solubility of basic oxide to alkali molybdates. They reported that the solvent ability of alkali molybdate was enhanced by alkali oxides in the order $K_2O < Na_2O < Li_2O$. It is thought that the increase in solubility of the raw material to K_2MoO_4 flux resulting from Li_2O addition reduced the nucleation rate in the initial stage in this experiment, and the long crystals of potassium titanate were grown.

TABLE I Effects of Li_2O addition to K_2MoO_4 flux on crystal growth of potassium titanate

Li_2O (wt %)	Evaporated amount (wt %)	Products
0	0.86	Particles and short fibres
0.5	0.84	Particles and prisms
1.0	1.68	Long fibres, max. 12 mm
2.0	1.54	Long fibres, max. 3 mm; short fibres were not grown

Temperature 1200° C; Time 4 h.

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TABLE II Effects of flux to raw material weight ratio (F/R) on crystal growth of potassium titanate

F/R	Evaporated amount (wt %)	Products
2.0	1.62	Fibres and needles
3.7	1.68	Long fibres, max. 12 mm
8.0	0.85	Needles or prisms of ragged surface
11.0	1.03	Prisms of ragged surface, 3–4 mm

Flux: 1.0 wt % $Li_2O \cdot K_2MoO_4$; temperature 1200° C; time 4 h.

TABLE III Effects of filled amount and evaporation area on crystal growth

Filled amount (g)	Evaporation area (cm^2)	Evaporated amount (wt %)	Crystal length (mm)
5.0	7.1	0.76	8–10
15.1	7.1	0.71	8–10
23.0	7.1	0.61	8–10
7.3	10.2	1.68	max. 12

Flux: 1.0 wt % $Li_2O \cdot K_2MoO_4$; temperature 1200° C, time 4 h.

3.2. Flux to raw material ratio, filled amount and evaporation area

The effects of flux to raw material weight ratio (F/R), filled amount of mixture of flux and raw material and evaporation area on crystal growth were investigated. The results are shown in Tables II and III. $F/R = 3.7$ gave a favourable supersaturation for growth of long fibres. Crystal length was reduced by increasing the fraction of flux. The shape of crystals obtained in the run of $F/R = 8$ or 11 was prismatic with ragged surfaces (Table II). Although the filled amount, which is associated with the height of the melt surface from the bottom of the crucible, varied from 5 to 23 g, little effect was seen on evaporation and crystal growth. It was considered that the viscosity of the melt was sufficiently low or that a reasonably good convection was realized. On the other hand, evaporation was apparently enhanced, and crystal length along the fibre axis increased, with evaporation area (Table III). Consequently, it can be concluded that the evaporation rate is determined not by diffusion of solute but by the evaporation area; therefore, evaporation and crystal growth can be controlled by this.

The evaporation rate was decreased after a certain extended time. This is thought to be due to a composition change of the flux with reaction time. Fig. 1 shows the variation in evaporated amount and Li_2O concentration with reaction time for a flux containing no raw material. The evaporation rate at 1200° C approaches 0 after more than 6 h, whereas Li_2O concentration is constant even if after 10 h. A major component volatilized may be K_2O. The addition of Li_2O, which has stronger affinity for molybdate, caused an exchange reaction of $Li_2O + K_2MoO_4 \rightarrow K_2O + Li_2MoO_4$, and excess K_2O volatilized. The weight loss calculated from the exchange reaction is (Li_2O wt % added) × Li_2O/K_2O (molar ratio) = 3.2 wt %,which is roughly in agreement with the evaporated amount of 2.8 wt % after 10 h in our experiment.

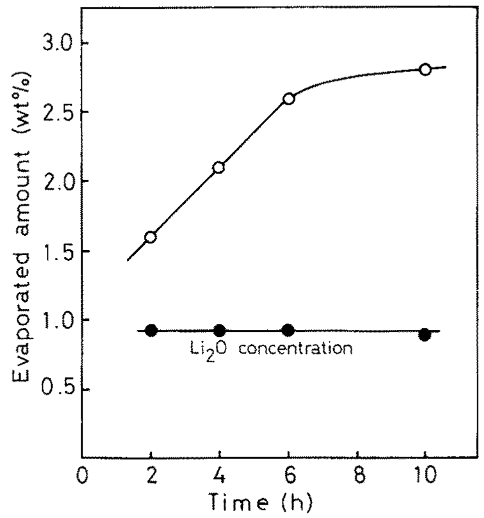

Figure 1 Time dependence of evaporated amount and Li_2O concentration of 1.0 wt % $Li_2O \cdot K_2MoO_4$ flux containing no raw material.

3.3. Temperature and time

The temperature and time dependence of crystal growth of potassium hexatitanate are summarized in Tables IV and V. The amount evaporated over 4 h increased linearly with temperature between 1100 and 1300° C. In the run below 1150° C, products were particles about 0.1 mm in size, which were similar to the raw material of non-fibrous potassium titanate. Above 1250° C, the majority of the product was short fibres less than 1 mm long. At higher temperatures, the nucleation rate was supposed to be higher, because the increase in evaporation rate is greater than the increase in solubility, so short fibres are liable to grow.

The evaporation rate remained constant up to 6 h at 1200° C (Fig. 2). Crystal length increased with time, and a maximum length of 12 mm was obtained after 4 h. In runs longer than 4 h, the crystal length appeared to be limited by the crucible size. Longer fibres will be able to grow if larger crucibles than that employed in this experiment are used. At 1300° C, the evaporation rate began to decrease after 4 h (Fig. 2). Evaporation was affected by the evaporation surface area as described above. Potassium titanate crystals are grown at the bottom of a crucible because the specific gravity is greater than the flux, thus the evaporation surface area is not decreased by grown crystals. A decrease in evaporation rate is, therefore, thought to be caused by a composition change of the melt. Long fibres were not grown, but the yield of short fibres increased with reaction time at 1300° C. The

TABLE IV Effects of reaction temperature on crystal growth

Temp. (° C)	Evaporated amount (wt %)	Products
1100	0.76	Particles, 0.1 mm
1150	1.31	Particles, 0.1 mm
1200	1.68	Fibres, max. 12 mm
1250	1.86	Fibre 2–3 mm and flexible short fibres < 1 mm
1300	2.62	Fibres of 2 mm, and flexible short fibres in good yield

Flux: 1.0 wt % $Li_2O \cdot K_2MoO_4$; time 4 h.

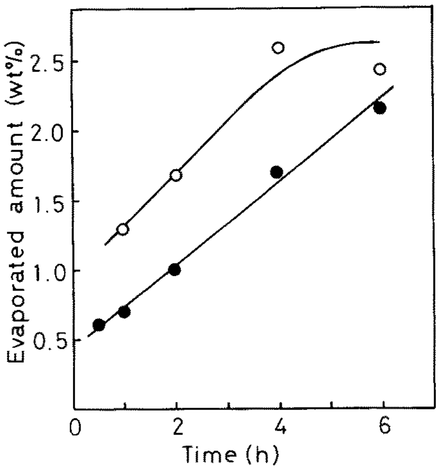

Figure 2 Time dependence of evaporated amount of 1.0 wt % $Li_2O \cdot K_2MoO_4$ flux saturated with potassium titanates, at (○) 1300° C, (●) 1200° C.

TABLE V Effects of reaction time on crystal growth

Temp. (° C)	Time (h)	Evaporated amount (wt %)	Products
1200	0.5	0.61	Prisms, 1 mm
1200	1	0.71	Needles, 5–8 mm
1200	2	0.99	Fibres, 7–10 mm
1200	4	1.68	Fibres, max. 12 mm
1200	6	2.15	Fibres, max. 0.5 × 12 mm
1300	1	1.31	No long fibres were grown Yield of short fibres was increased with time
1300	2	1.70	
1300	4	2.62	
1300	6	2.40	

Flux: 1.0 wt % $Li_2O \cdot K_2MoO_4$

nucleation rate is thought to be greater than the growth rate because of the higher supersaturation at this temperature.

3.4. Observation of grown crystals

SEM observation shows that potassium titanate fibre appeared to grow by the following process: (1) nucleation takes place at particles or needles which were undissolved raw material of potassium titanate (Fig. 3a); (2) parallel growth occurs (Fig. 3b); (3) parallel growth is divided (Fig. 3c); and (4) the divided individual crystal grows along the fibre axis (Fig. 3d).

Representative short and long fibres obtained in this experiment are shown in Figs 4a and b. Fine and flexible fibres less than 1 mm long were grown in good yield at 1300° C (Fig. 4a). Long fibres (maximum size 0.2 mm × 12 mm) were grown at the growth rate of 3 mm h^{-1} at 1200° C. Crystal length limitation by crucible size indicates the possibility of the growth of longer fibres. Using XRD analysis, all the crystals obtained in this experiment were determined to be $K_2Ti_6O_{13}$, and contamination with other potassium titanates or lithium compounds was not detected.

4. Conclusion

Potassium hexatitanate long fibres were grown by the flux evaporation method using $Li_2O–K_2MoO_4$ flux. Favourable Li_2O concentration and flux to raw material weight ratio for growth of long fibres were found to be 1.0 wt % Li_2O and F/R = 3.7. Li_2O concentration was kept constant for at least 10 h at 1200° C. The evaporation rate could be controlled by the evaporation surface area. The length of fibrous crystal increased with evaporated amount which, in turn, increased linearly with time up to 6 h at 1200° C. The maximum growth rate of 3 mm h^{-1} along the fibre axis was observed. Flexible fine fibres less than 1 mm long were grown in good yield at 1300° C.

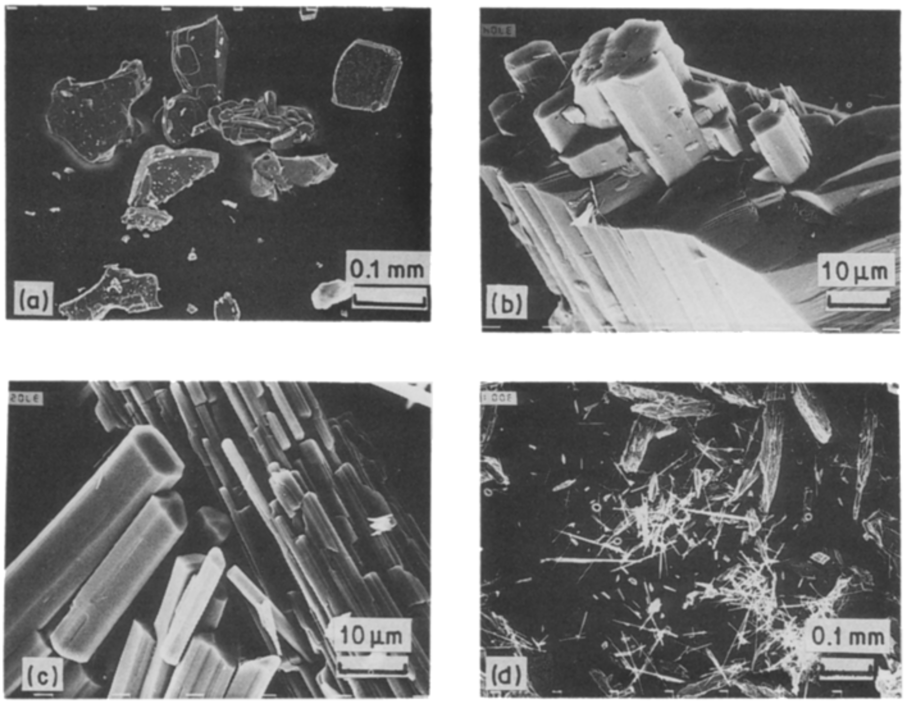

Figure 3 Growth process of potassium hexatitanate crystal; (a) un-dissolved raw material of potassium titanates, (b) beginning of parallel growth, (c) parallel growth division, and (d) fibrous crystals.

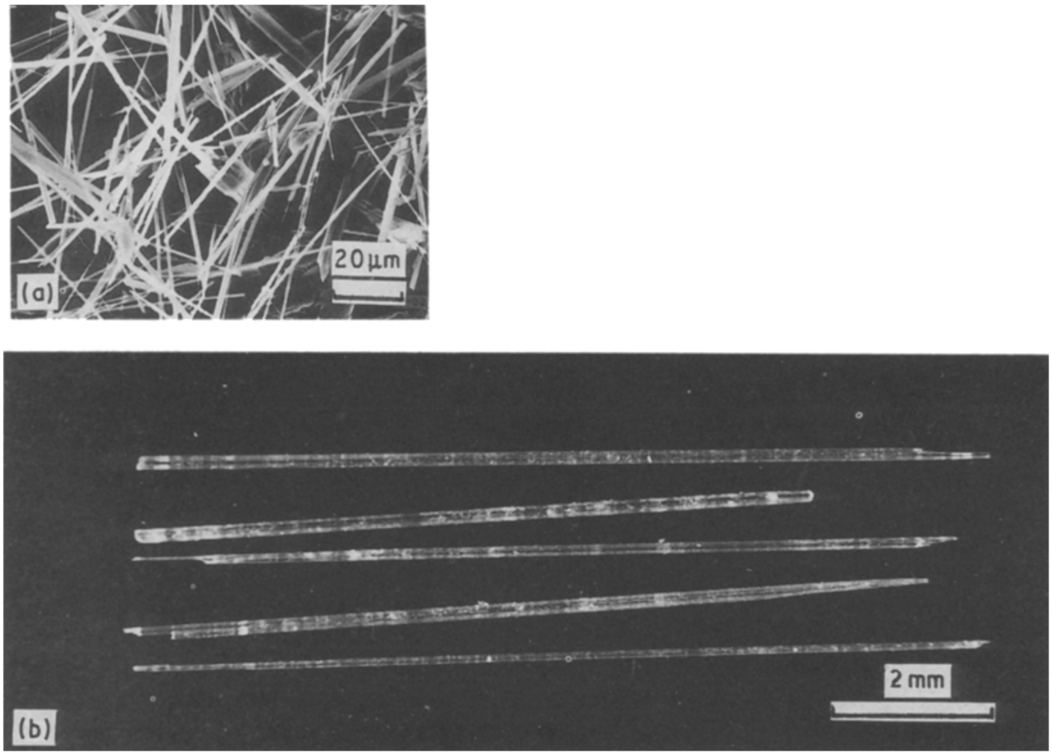

Figure 4 Representative crystals grown in this experiment; (a) flexible short fibres grown at 1300° C, and (b) long fibres of potassium hexatitanate grown at 1200° C.

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