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The formation of potassium titanate fibre with flux methods

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The formation of potassium titanate fibre was tried with fluxes such as PbO, Bi_2O_3, K_2CO_3–$K_4P_2O_7$, K_2CO_3–V_2O_5 and PbO–$K_4P_2O_7$. Also, the reaction was carried out with changing the cooling rate and the weight ratio of the flux to $K_2Ti_6O_{13}$ crystal powder. However, only needle-like crystals or a milky gel were formed and potassium titanate fibre was not formed under the experimental conditions.

1. Introduction

In general, potassium titanate has the chemical formula $K_2Ti \cdot nTiO_2$ (n = 1 to 6). In particular, the formula $K_2O \cdot 6TiO_2$ has the highest melting point (1370° C) and the best properties such as thermal insulation or heat stability. Potassium titanate fibre has been prepared by sintering [1–3], fusion [4], flux [5] and hydrothermal [6] methods. Industrially, potassium titanate fibre has been produced using fluxes such as K_2O–MoO_3 and K_2O–WO_3 by the Otsuka Chemical Co. in Japan; however, these are very expensive fluxes. The formation of potassium titanate fibre has now been investigated with fluxes such as PbO, Bi_2O_3, K_2CO_3–$K_4P_2O_7$, K_2CO_3–V_2O_5, and PbO–$K_4P_2O_7$, and the results are described in this paper.

2. Experimental procedure

$K_2O \cdot 6TiO_6$ was prepared by the reaction of TiO_2 (24 g) and K_2CO_3 (10.5 g); after TiO_2 and K_2CO_3 powders were mixed, the mixture was added to a platinum crucible having 30 ml capacity. The crucible was heated at 1450° C for 3 h, and then cooled by air to room temperature. To separate potassium titanate crystals, the reaction mixture in the crucible was washed with water. The residue insoluble in water was dried at 110° C.

To prepare potassium titanate fibre, the various fluxes used were one-component systems such as PbO and Bi_2O_3 or two-component systems such as K_2CO_3–$K_4P_2O_7$, K_2CO_3–V_2O_5 and PbO–$K_4P_2O_7$. In the case of two-component systems, a flux having a eutectic temperature is suitable for the preparation of potassium titanate fibre because of the low reaction temperature. The mole ratio in two-component systems and the eutectic temperature are given in Table I.

TABLE I The mole ratio and the eutectic temperature of two-component fluxes

Flux	Mole ratio	Eutectic temperature (° C)
K_2CO_3–$K_4P_2O_7$	6.9 : 93.1	690
K_2CO_3–V_2O_5	40 : 60	390
	53 : 47	500
	80 : 20	818
PbO–$K_4P_2O_7$	0.8 : 93.2	880

Varying the weight of the flux and potassium titanate crystal powder, they were mixed with an agate mortar and pestle for 30 min. The mixture was placed in the platinum crucible and was kept above the eutectic temperature of the flux for several hours, cooled to room temperature, and the solubility of potassium titanate in the flux was then observed by optical microscopy. After the new sample as judged by the observation was heated at the solubility temperature, the temperature was slowly decreased to the solidification temperature, and then cooled to room temperature. The flux contained in the crucible was dissolved in hot water and dilute hydrogen nitride. The residue was dried at 110° C for one night. The products prepared under the various experimental conditions were determined by X-ray diffraction analysis and by optical and electron microscopy.

3. Results and discussion

3.1. Synthesis of $K_2O \cdot 6TiO_2$ crystals

The product prepared by the reaction of K_2CO_3 and TiO_2 was determined by X-ray diffraction analysis, and the results are given in Fig. 1. It is found from Fig. 1 that the product is $K_2Ti_6O_{13}$ because the diffraction pattern is consistent with the appropriate ASTM card. Electron micrographs of $K_2Ti_6O_{13}$ before and

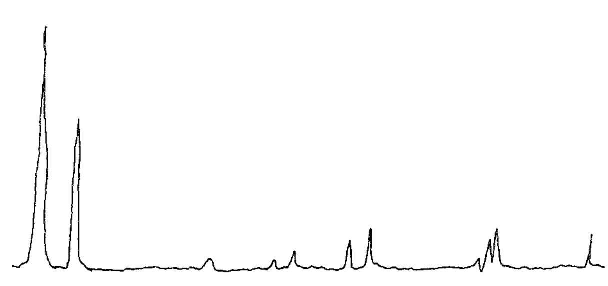

Figure 1 X-ray diffraction of the product with the reaction of K_2CO_3 and TiO_2.

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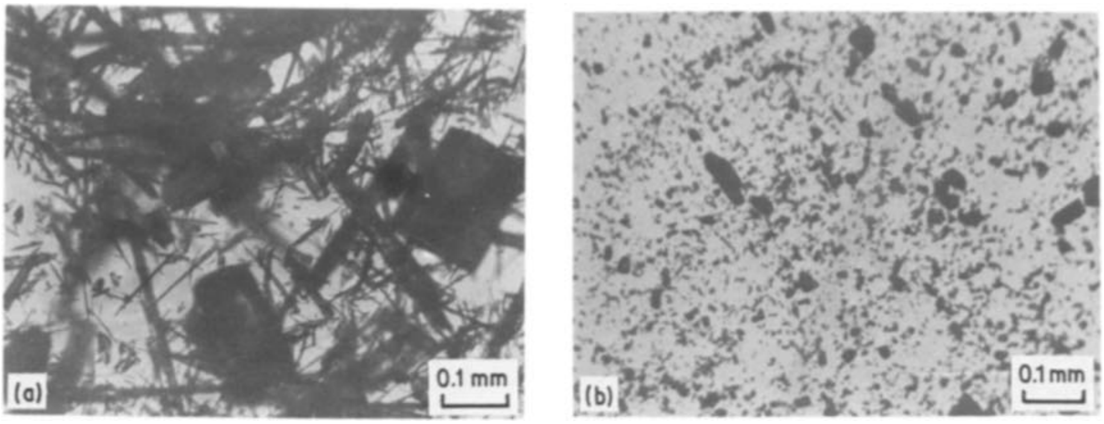

Figure 2 (a) $K_2Ti_6O_{13}$ crystals and (b) crystals crushed under 200 mesh.

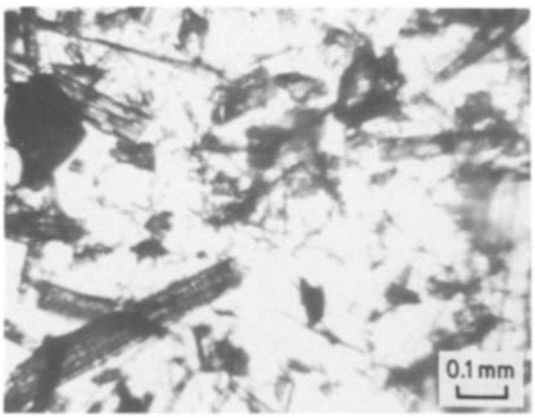

Figure 3 Electron micrograph of the crystals formed using Bi_2O_3 flux and the weight ratio flux/$K_2Ti_6O_{13}$ = 1.

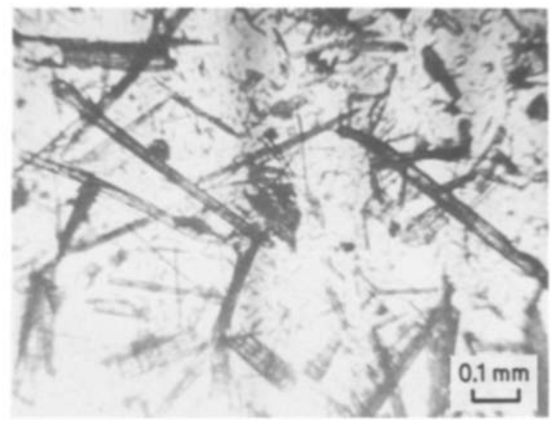

Figure 4 Electron micrograph of the crystals formed using PbO flux and the weight ratio flux/$K_2Ti_6O_{13}$ = 1.

after crushing under 200 mesh are shown in Fig. 2. Also, crushed $K_2Ti_6O_{13}$ was employed to prepare potassium titanate fibre.

3.2. PbO and Bi_2O_3 fluxes

The formation of potassium titanate fibre was carried out at 1300 to 1000° C using PbO and Bi_2O_3 fluxes while changing the weight ratio. Using a cooling rate of 3° C min^{-1}, the results obtained are given in Table II. It is found from Table II that microcrystals are formed with the weight ratio Bi_2O_3/potassium titanate = 3 and 2. When the weight ratio is less than 2, needle-like crystals are formed under these conditions. Also, the maximum length of the prepared crystals is 3 to 5 mm. An electron micrograph of the crystals prepared using the weight ratio Bi_2O_3/potassium titanate = 1 is shown in Fig. 3. On the other hand, using PbO flux, microcrystals were formed with the weight ratio PbO/potassium titanate = 3. Needle-like crystals having 0.05 to 0.1 mm average length were also prepared with the weight ratio PbO/potassium titanate = 0.7 to 2. An electron micrograph of the needle-like crystals prepared using the weight ratio PbO/potassium titanate = 1 is given in Fig. 4. Also, for a cooling rate of 3° C min^{-1}, the results are shown in Table III.

It is found from Tables II and III that the maximum length of the needle-like crystals is about 5 mm, but many microcrystals are also formed with Bi_2O_3 as a flux. Consequently, it seems that PbO flux to prepare potassium titanate fibre is better than Bi_2O_3; however, the platinum crucible is corroded by PbO flux.

3.3. K_2CO_3–$K_4P_2O_7$ flux

After the reaction at 1100 to 900° C, the temperature was decreased with a cooling rate of 5° C min^{-1}. Also, the weight ratio of the flux to potassium titanate was changed from 1.5 to 15. The appearance of the product is given in Table IV.

TABLE II The appearance and length of the crystals formed using Bi_2O_3 flux

Weight ratio flux/$K_2Ti_6O_{13}$	Temperature (° C)	Appearance	Maximum length (mm)
3	1300 to 1000	Microcrystals	
2	1300 to 1000	Microcrystals	3
1.5	1300 to 1000	Needle-like crystals	4
1	1300 to 1000	Needle-like crystals	5
0.7	1300 to 1000	Needle-like crystals	3

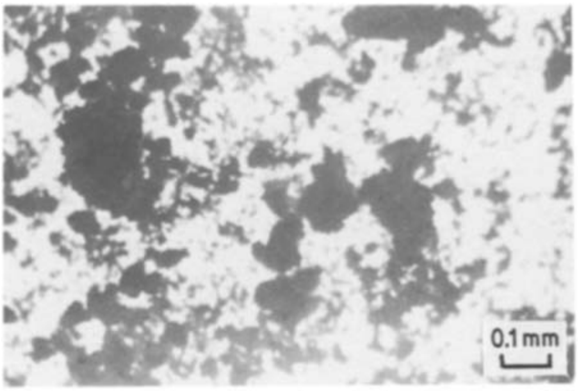

Figure 5 Electron micrographs of the milky gel formed using K_2CO_3–$K_4P_2O_7$ flux and flux/$K_2Ti_6O_{13}$ = 1.5.

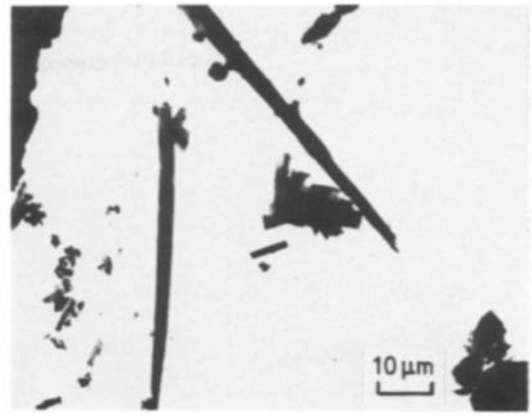

Figure 6 Electron micrograph of the crystals formed using as flux $K_2CO_3:K_4P_2O_7$ = 6.9 : 93.1 and the weight ratio flux/$K_2Ti_6O_{13}$ = 1.5.

It was found that a milky gel was formed under the experimental conditions. Then, a flux in the vicinity of the eutectic component of K_2CO_3–$K_4P_2O_7$, (mole ratio of K_2CO_3 and $K_4P_2O_7$ = 8 : 92) was selected. However, a milky gel was still formed under these conditions. The prepared milky gel was examined with optical and electron microscopy, and the result is shown in Fig. 5.

It seems that the very fine crystals appear as crystal growth is late. As it is possible to prepare potassium titanate fibre when the cooling rate is reduced, the formation of the fibre was carried out by cooling at $5^\circ C\,min^{-1}$. However, the needle-like crystals having 5 mm maximum length are prepared under these conditions as shown in Fig. 6. Also, according to X-ray diffraction analysis, the milky gel consists of $K_2Ti_6O_{13}$.

3.4. K_2CO_3–V_2O_5 flux

The formation of potassium titanate fibre was carried out using five kinds of eutectic component ($K_2CO_3:V_2O_5$ = 40 : 60, 48 : 52, 53 : 47, 80 : 20) and changing the weight ratio of the flux to potassium titanate. The results given by X-ray diffraction analysis, the observations by optical microscopy and the maximum length of the crystals are summarized in Table V. From Table V, rutile with the needle-like crystals having 4 mm maximum length is prepared using a flux with the mole ratio $K_2CO_3:V_2O_5$ = 40 : 60. In the case of other fluxes, products such as needle-like crystals having the composition $K_2Ti_6O_{13}$ are formed under these experimental conditions. However, microcrystals are formed using the flux of mole ratio 80 : 20 because it has a high viscosity. Also, crystals having 6 to 9 mm maximum length and 1 μm diameter are prepared with a cooling rate of $5^\circ C\,min^{-1}$. Electron micrographs of the crystals prepared various experimental conditions are shown in Fig. 7. On the other hand, fibrous crystals having

TABLE III The appearance and length of the crystals formed using PbO flux

Weight ratio flux/$K_2Ti_6O_{13}$	Temperature (°C)	Appearance	Length (mm)	
			Maximum	Average
3	1250 to 900	Microcrystals		
2	1250 to 900	Needle-like crystals	3	0.05
1.5	1250 to 900	Needle-like crystals	4	0.1
1	1250 to 900	Needle-like crystals	5	0.2
0.7	1250 to 900	Needle-like crystals	4	0.1

TABLE IV The appearance and length of the crystals formed using K_2CO_3–$K_4P_2O_7$ flux

$K_2CO_3:K_4P_2O_7$	Weight ratio flux/$K_2Ti_6O_{13}$	Temperature (°C)	Appearance	Maximum length (mm)
6.9 : 93.1	15	1100 to 900	Milky gel	
	7.5	1100 to 900	Milky gel	
	5	1100 to 900	Milky gel	
	3	1100 to 900	Milky gel	
	2	1100 to 900	Milky gel	
	1.5	1100 to 900	Milky gel	
	1.5*	1200 to 900	Needle-like crystals	5
8 : 92	3	1100 to 900	Milky gel	
	2	1200 to 900	Milky gel	
	1.5	1200 to 900	Milky gel	
	1.5*	1200 to 900	Needle-like crystals	4

*Cooling rate $5^\circ C\,min^{-1}$.

TABLE V The appearance and length of the crystals formed using K_2CO_3–V_2O_5 flux

$K_2CO_3:V_2O_5$	Weight ratio flux/$K_2Ti_6O_{13}$	Temperature (°C)	Appearance	Maximum length (mm)
40:60	1.5	1200 to 900	Rutile, needle-like	4
80:20	3	1250 to 900	Microcrystals	
	2	1250 to 900	Microcrystals	
	1.5	1250 to 900	Microcrystals	
	1	1250 to 900	Microcrystals	
58:42	2	1250 to 700	Needle-like crystals	2
	1.5	1250 to 700	Needle-like crystals	3
	1	1250 to 700	Needle-like crystals	4
	1*	1250 to 700	Needle-like crystals	6
53:47	10	1200 to 800	Microcrystals	2
	8	1200 to 800	Needle-like crystals	2
	5	1200 to 800	Needle-like crystals	2
	3	1200 to 800	Needle-like crystals	2
	2	1200 to 900	Needle-like crystals	5
	1.5	1200 to 900	Needle-like crystals	5
	1	1200 to 900	Needle-like crystals	4
	1.5*	1250 to 900	Needle-like crystals	8
48:52	2	1250 to 700	Needle-like crystals	4
	1.5	1250 to 700	Needle-like crystals	5
	1	1250 to 700	Needle-like crystals	4
	1.5*	1250 to 700	Needle-like crystals	9

*Cooling rate 5° C min^{-1}; the product formed under these conditions was needle-like fibrous crystals.

TABLE VI The appearance and length of the crystals formed using PbO–$K_4P_2O_7$ flux

$PbO:K_4P_2O_7$	Weight ratio flux/$K_2Ti_6O_{13}$	Temperature (°C)	Appearance	Maximum length (mm)
12:88	28	1100 to 800	Microcrystals	
	14	1100 to 800	Microcrystals	
	7	1100 to 800	Microcrystals	
	3.5	1100 to 800	Microcrystals	
	3	1200 to 800	Needle-like crystals	2
	2	1200 to 800	Needle-like crystals	2
	1.5	1200 to 800	Needle-like crystals	3
	1	1200 to 800	Needle-like crystals	5
	0.7	1200 to 800	Needle-like crystals	3
	1*	1200 to 800	Needle-like crystals	7
18:82	1.5	1200 to 800	Needle-like crystals	3
	1	1200 to 800	Needle-like crystals	4
	0.7	1200 to 800	Microcrystals	2
	1*	1200 to 800	Needle-like crystals	7

*Cooling rate 5° C min^{-1}.

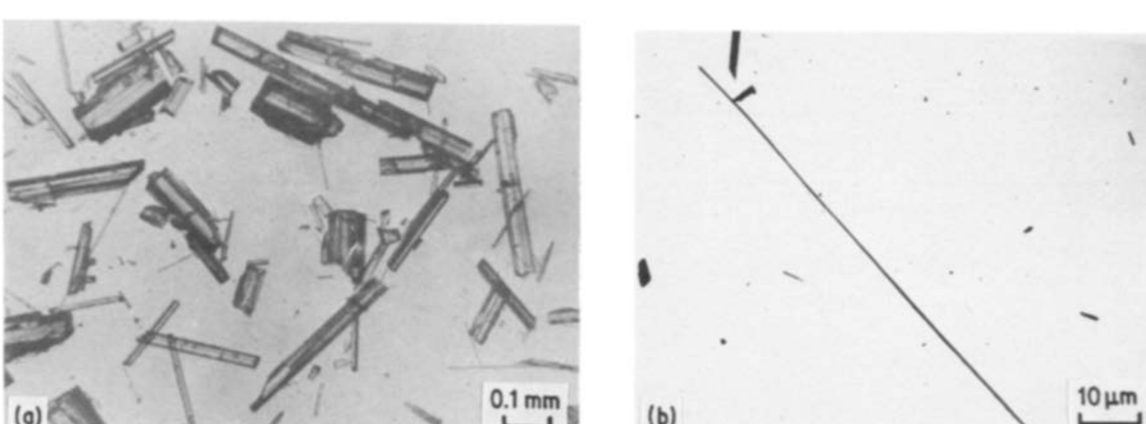

Figure 7 Electron micrographs of the crystals formed using as flux $K_2CO_3:V_2O_5$ = (a) 53:47 and (b) 48:52 and the weight ratio flux/$K_2Ti_6O_{13}$ = 1.5.

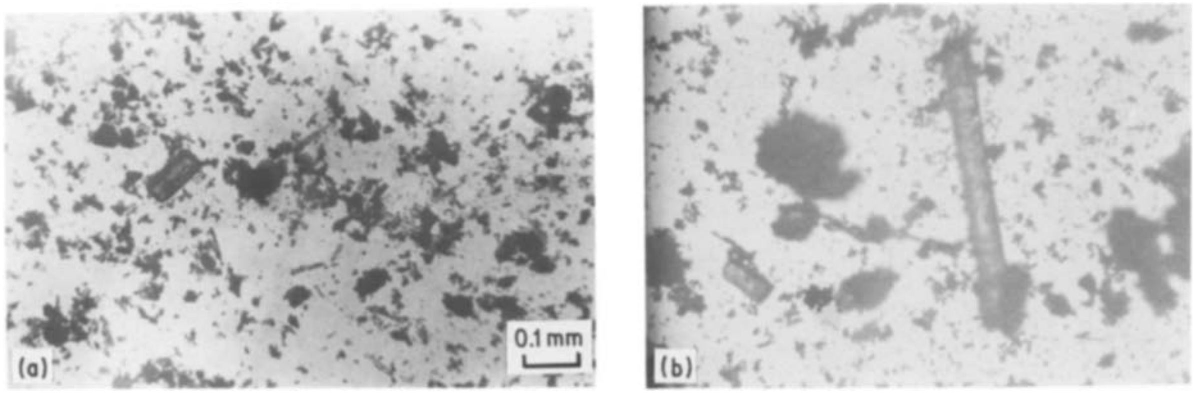

Figure 8 Electron micrographs of the crystals formed using as flux $PbO:K_4P_2O_7 = 12:88$ and the weight ratio flux/$K_2Ti_6O_{13}$ = (a) 3.5 and (b) 0.7.

9 mm maximum length appeared by cooling at $5°C\,min^{-1}$.

3.5. $PbO-K_4P_2O_7$ flux

The relation between the weight ratio of the flux to potassium titanate and the length of the product is given in Table VI. It is found from Table VI that the main crystals are $K_2Ti_6O_{13}$. Also, potassium titanate fibre is not formed since $K_2Ti_6O_{13}$ does not have enough solubility in the flux when the weight ratio of the flux to potassium titanate is 28 to 3.5. On the other hand, decreasing the mole ratio of the flux to potassium titanate, needle-like crystals are precipitated from the flux. However, long needle-like crystals are not prepared since much $K_2Ti_6O_{13}$ is dissolved in the flux and the rate of the supersaturation is very high. The formation of potassium titanate fibre was attempted using the flux $PbO-K_4P_2O_7$ at a ratio of 1.5 and cooling at $5°C\,min^{-1}$. The results show that needle-like crystals having 7 mm maximum length (Fig. 8) are prepared under these conditions. However, it is impossible to obtain potassium titanate fibre even if the cooling rate is slowed down.

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