JOURNAL OF MATERIALS SCIENCE **35** (2000) 3307–3311

Hydrothermal synthesis of potassium titanates in Ti-KOH-H_2O system

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The hydrothermal oxidation of titanium metal powder was performed in concentrated potassium hydroxide solutions above 150 °C. $K_2Ti_2O_5$, $K_4Ti_3O_8$ and a new compound $KTiO_2(OH)$ were formed as single phase and fibrous amorphous products which transformed to $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$ and $K_2Ti_2O_5$ by calcination were also obtained depending on the reaction conditions. A formation diagram of products in the Ti-KOH-H_2O system has been constructed at the region of KOH concentration from 0 to 90 mol·kg^{-1}-H_2O and the temperature from 150 to 350 °C. © *2000 Kluwer Academic Publishers*

1. Introduction

Many kinds of potassium titanates with unique crystal structures containing layered and tunnel structures have been synthesized over the past years [1, 2] and their various physico-chemical properties such as ferroelectric property, optical property, ionic and electronic conductivity, have been investigated well for their wide applications in industry as ion exchanger, filter, reinforcement of ceramics, heat insulator, catalyst, etc.

Among the various potassium titanates [$K_2O \cdot nTiO_2$] ($1 \le n \le 8$), $K_2Ti_2O_5$ and $K_2Ti_4O_9$ are one of the most interesting compound for their specific photochemical property. They showed photoluminescence [3] and photovoltaic activities for H_2 evolution by the water cleavage reaction even without Pt co-catalysts [4, 5]. The structure consists of layered sheets made of TiO_5 pentahedra or TiO_6 octahedra and linked with the K atoms [6–8]. Potassium hexatitanate $K_2Ti_6O_{13}$ is also well known for artificial material with cage type structure [9]. The hydrous titanium dioxide which can be represented as $(H_3O)Ti_6O_{12}(OH)$ has a large cation exchange capacity [10–14].

In spite of variety of wide application of these potassium titanates, the synthesis way of them are few to name, viz. conventional solid state and flux method. These methods employ TiO_2 and K_2CO_3 or K_2O as raw materials and are not suitable to control the particle size and morphology of products. In this point of view hydrothermal synthesis is a promising method. In this study, therefore, a series of experiments was carried out to investigate the formation of various potassium titanates under hydrothermal conditions using metal Ti powder as the raw material with the intention of high reactivity and no second phase products.

2. Experimental procedure

All chemicals used were reagent grade and used directly without any further purification. Ti powder (Wako Pure Chemical Industries, Ltd.) used as the starting material was min. 95% purity with $<45\ \mu$m diameter. The chemical analysis of the potassium hydroxide was as follows: Potassium carbonate (K_2CO_3) <1.5%, Chloride (Cl) <0.002%, Phosphate (PO_4) <0.001%, Sulfate (SO_4) <0.001% and that of the sodium hydroxide was: Sodium carbonate (Na_2CO_3) <1.5%, Chloride (Cl) <0.005%, Phosphate (PO_4) <0.001%, Sulfate (SO_4) <0.001%. Water was deionized by the ion exchanger after the distillation.

A typical experimental procedures can be described as follows. Initially 50 mL of KOH aqueous solution and 1.0 g Ti powder were put into an autoclave of 200 cm^3 internal volume with a magnet driving stirrer made by SUS 316 type stainless steel. Except for the experiments above 300 °C, the polytetrafluoroethylene (Teflon®) cup was placed inside the autoclave to prevent further corrosion. After sealing the autoclave, the autoclave was set into an electric furnace at the desired temperature. During the reaction period, the autoclave was kept at an autogeneous saturation vapor pressure of the solution with stirring at 300 rpm. After

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maintaining at the desired temperature for 2 h, the autoclave was taken out from the furnace, cooled immediately by forced air. The product was separated from the solution by centrifuge, then rinsed with methanol, and finally dried in an oven to remove the absorbed water at 105 °C for 12 h.

The products were identified by X-ray powder diffraction (Shimadzu diffract meter XD-D1). The thermal property of products was examined by TG-DTA analysis (Rigaku TAS-200). Chemical analysis was carried out by ICP-AES (SEIKO SPS-1200A) and AAS (Shimadzu AA-6500S) after dissolving the sample by aqua regia.

3. Results and discussion

3.1. Formation diagram of Ti-KOH-H_2O system

A formation diagram of products synthesized in Ti-KOH-H_2O system at the region of KOH concentration from 0 to 90 mol·kg^{-1}-H_2O and the temperature from 150 to 350 °C has been constructed. The result is shown in Fig. 1. Typical XRD patterns of products at 200 °C are also shown in Fig. 2.

Amorphous potassium titanate, amorphous A and amorphous B were found at 1–35 mol·kg^{-1}-H_2O KOH above 250 °C and 80–90 mol·kg^{-1}-H_2O KOH at 150 °C, respectively. Single phase $K_4Ti_3O_8$ was formed mainly at KOH concentrations above 35 mol·kg^{-1}-H_2O and the temperatures above 200 °C. Well crystallized hydrated $K_2Ti_2O_5$ was formed as single phase at KOH concentrations from 20 to 25 mol·kg^{-1}-H_2O and the temperatures from 150 to 200 °C, while amorphous $K_2Ti_2O_5$ precursor was formed at KOH concentrations above 80 mol·kg^{-1}-H_2O and the temperature 150 °C. It is notable that a new compound $KTiO_2(OH)$ has been successfully obtained as single phase at KOH concentrations from 30 to 40 mol·kg^{-1}-H_2O and 200 °C. Chemical formula of this compound was determined by ICP-AES, AAS and TG-DTA analyses. Existence of hydroxyl group was confirmed by IR spectroscopy. The lattice parameters of this compound were refined by X-ray powder diffraction patterns at 293 K using graphite monochromatized CuK_α radiation. The crystallographic parameters are as follows: hexagonal $P6_122$ (or $P6_3/mmc$), $a = 9.8935(2)$, $c = 28.6845(6)$ Å.

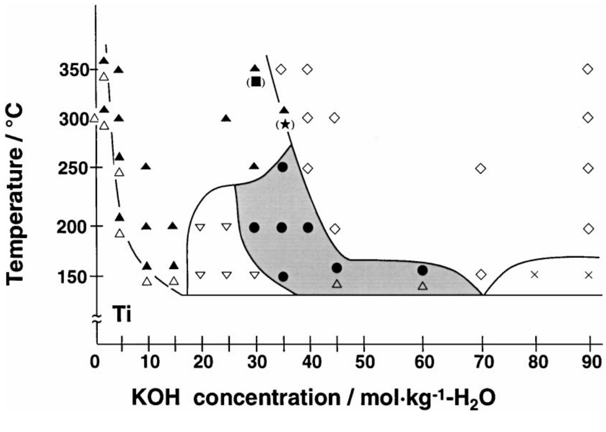


Figure 1 Formation diagram of products in Ti-KOH-H_2O system after hydrothermal treatment of Ti powder for 2 h at various KOH concentrations and temperatures. △: Ti, ▲: amorphous A (fibrous), ▽: $K_2Ti_2O_5 \cdot nH_2O$, ★: $K_2Ti_4O_9$, ■: $K_2Ti_6O_{13}$, ●: $KTiO_2(OH)$, ×: amorphous B and ◇: $K_4Ti_3O_8$.

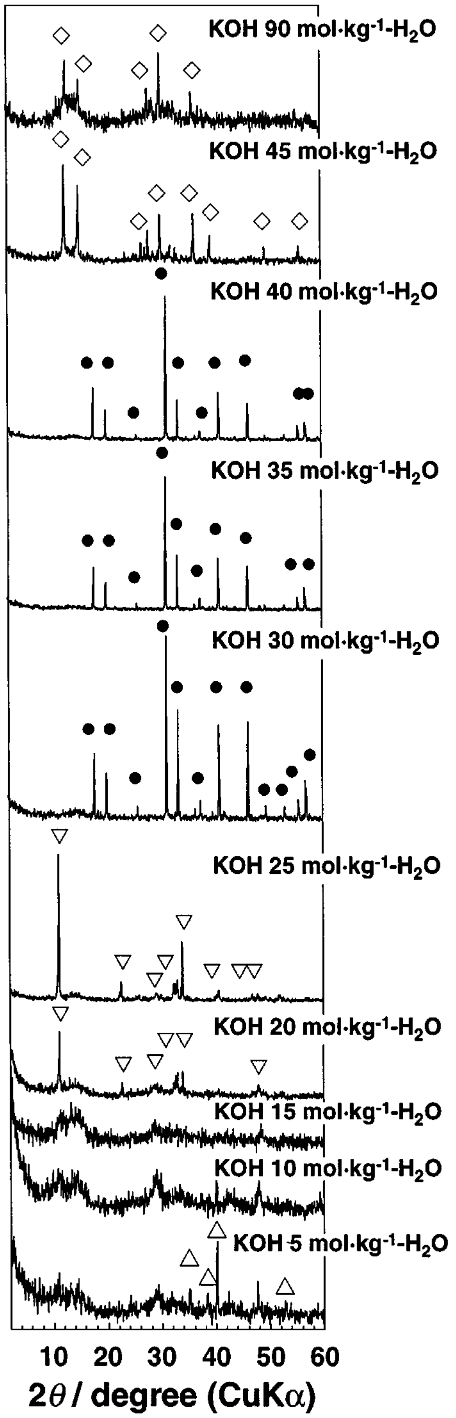


Figure 2 XRD patterns of products synthesized at 200 °C.

The K/Ti atomic ratio diagram of products is shown in Fig. 3.

It was seen that K/Ti ratio increase with increasing KOH concentration. The K/Ti ratio of amorphous A was 0.33 or 0.5. The K/Ti ratio of $K_2Ti_2O_5 \cdot nH_2O$, and $KTiO_2(OH)$ and amorphous B was 1.0. Here, the atomic valence of Ti in all products was 4.0 and the maximum K/Ti ratio was 1.33 in $K_4Ti_3O_8$. While more basic titanates such as $K_6Ti_2O_7$ [15] and K_4TiO_4 [16] are described in the literature, these compounds could not be found within the reaction conditions at KOH concentrations 90 mol·kg^{-1}-H_2O and the temperature 350 °C.

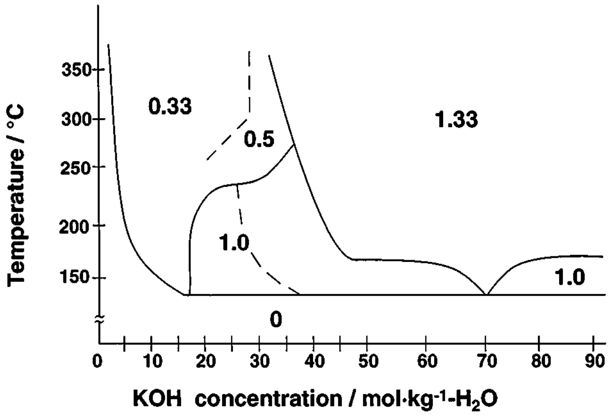
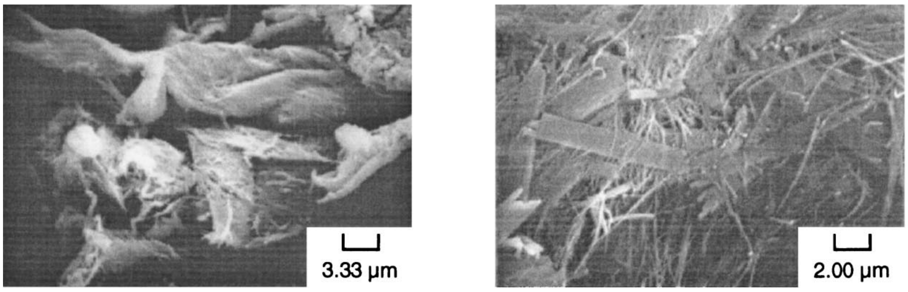


Figure 3 K/Ti molar ratio of products in Ti-KOH-H_2O system after hydrothermal treatment of Ti powder for 2 h at various KOH concentrations and temperatures.

Chemical analyses were carried out for some representative compounds. The results were summarized in Table I. In general, K and Ti contents and K/Ti ratio agreed almost with calculated one. Nevertheless, K contents in the amorphous A (fibrous) tended to be higher. This might be due to the incomplete rinse of products from the KOH solution or mixture state of chemical formula in the products $K_2O{\cdot}n TiO_2$. It was found that the higher KOH concentration led the higher K content in the amorphous A (fibrous).

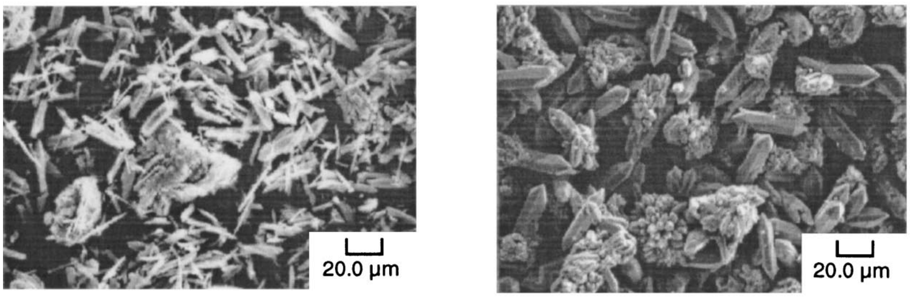
3.2. Morphology of products

The particle size and morphology of products were investigated by SEM. Scanning electron micrographs of each product are shown in Fig. 4.



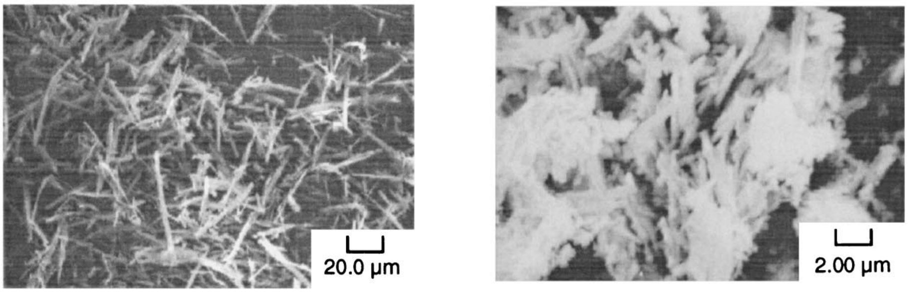
(a) fibrous amorphous A
(KOH 10 mol·kg^{-1}-H_2O, 200 °C)

(b) fibrous amorphous A
(KOH 30 mol·kg^{-1}-H_2O, 250 °C)



(c) $K_2Ti_2O_5 \cdot n H_2O$
(KOH 25 mol·kg^{-1}-H_2O, 200 °C)

(d) $KTiO_2(OH)$
(KOH 40 mol·kg^{-1}-H_2O 200 °C)



(e) $K_4Ti_3O_8$
(KOH 40 mol·kg^{-1}-H_2O, 250 °C)

(f) amorphous B
(KOH 90 mol·kg^{-1}-H_2O, 150 °C)

Figure 4 SEM photographs of products.

TABLE I Chemical analyses of products by AES and AAS

Compound		Ti/wt%	K/wt%	K/Ti molar ratio
Amorphous A (fibrous)	Obs.	43.7	17.1	0.48
($K_2Ti_6O_{13}$ precursor)	Calc.	50.1	13.6	0.33
KOH 10 mol·kg^{-1}-H_2O, 200 °C				
Amorphous A (fibrous)	Obs.	42.7	22.9	0.66
($K_2Ti_4O_9$ precursor)	Calc.	46.3	18.9	0.50
KOH 30 mol·kg^{-1}-H_2O, 250 °C				
$KTiO_2(OH)$	Obs.	37.3	34.4	1.1
KOH 40 mol·kg^{-1}-H_2O, 200 °C	Calc.	35.2	28.8	1.0
$K_4Ti_3O_8$	Obs.	29.9	32.1	1.3
KOH 40 mol·kg^{-1}-H_2O, 250 °C	Calc.	33.6	36.5	1.3

KOH concentration and temperature were as follows; (a) amorphous A: 10 mol·kg^{-1}-H_2O, 200 °C (b) amorphous A: 30 mol·kg^{-1}-H_2O, 250 °C (c) $K_2Ti_2O_5 \cdot nH_2O$: 25 mol·kg^{-1}-H_2O, 200 °C (d) $KTiO_2(OH)$: 40 mol·kg^{-1}-H_2O, 200 °C (e) $K_4Ti_3O_8$: 40 mol·kg^{-1}-H_2O, 250 °C and (f) amorphous B: 90 mol·kg^{-1}-H_2O, 150 °C.

Amorphous A consisted of fibrous and/or plate like materials. Namely, the product (a) consisted of large fibers reaching a few cm. The large fibers are the aggregates of fibers of less than 0.2 μm in diameter. On the other hand, sample (b) synthesized at relatively higher KOH concentration around 30 mol·kg^{-1}-H_2O and 250 °C contained plate like compounds together with fibrousones. $K_2Ti_2O_5 \cdot nH_2O$ (c) consisted of platelet crystals with average length of 27μm and as pectratio of 5.5. The new compound $KTiO_2$ (OH) (d) showed hexagonal columnar representation which has 5.4 μm in average length. The longest crystal was ca. 20 μm. $K_4Ti_3O_8$ (e) consisted of rod like crystals with mean particle length of 40 μm and aspect ratio of 14. The amorphous B (f), which exists at lower temperature than $K_4Ti_3O_8$ showed also rod like style. The mean particle length and aspect ratio were 3.6 μm and 14, respectively.

3.3. Effect of heat treatment of products

The samples synthesized by hydrothermal oxidation of Ti were heated at different temperatures to understand the thermal stability and crystallographic phase transition of them. The heating rate was 10 °C/min and the temperature range was from 600 to 1200 °C. The samples were heated in air by electric furnace for 1 h, then identified by XRD analysis. The results are shown in Fig. 5.

It can be seen that crystalline phase shifts from $K_2Ti_6O_{13}$ to $K_2Ti_2O_5$ via $K_2Ti_4O_9$ along with KOH concentration in any temperatures. It was found that $K_4Ti_3O_8$, the only compound which has the K/Ti ratio above 1 in Fig. 1, transformed to $K_2Ti_2O_5$ over 600 °C.

In spite of the narrow range of formation conditions single phase $K_2Ti_4O_9$ was obtained from the amorphous A synthesized at 35 mol·kg^{-1}-H_2O KOH and 300 °C and at 30 mol·kg^{-1}-H_2O KOH and 250 °C by heating at 600–1200 °C. Single phase $K_2Ti_6O_{13}$ was obtained from the amorphous A synthesized at 10–15 mol·kg^{-1}-H_2O KOH and 200–250 °C by heating at 800 °C. Single phase $K_2Ti_2O_5$ was obtained from the amorphous B synthesized at 80–90 mol·kg^{-1}-H_2O KOH and 150 °C by heating at 800 °C.

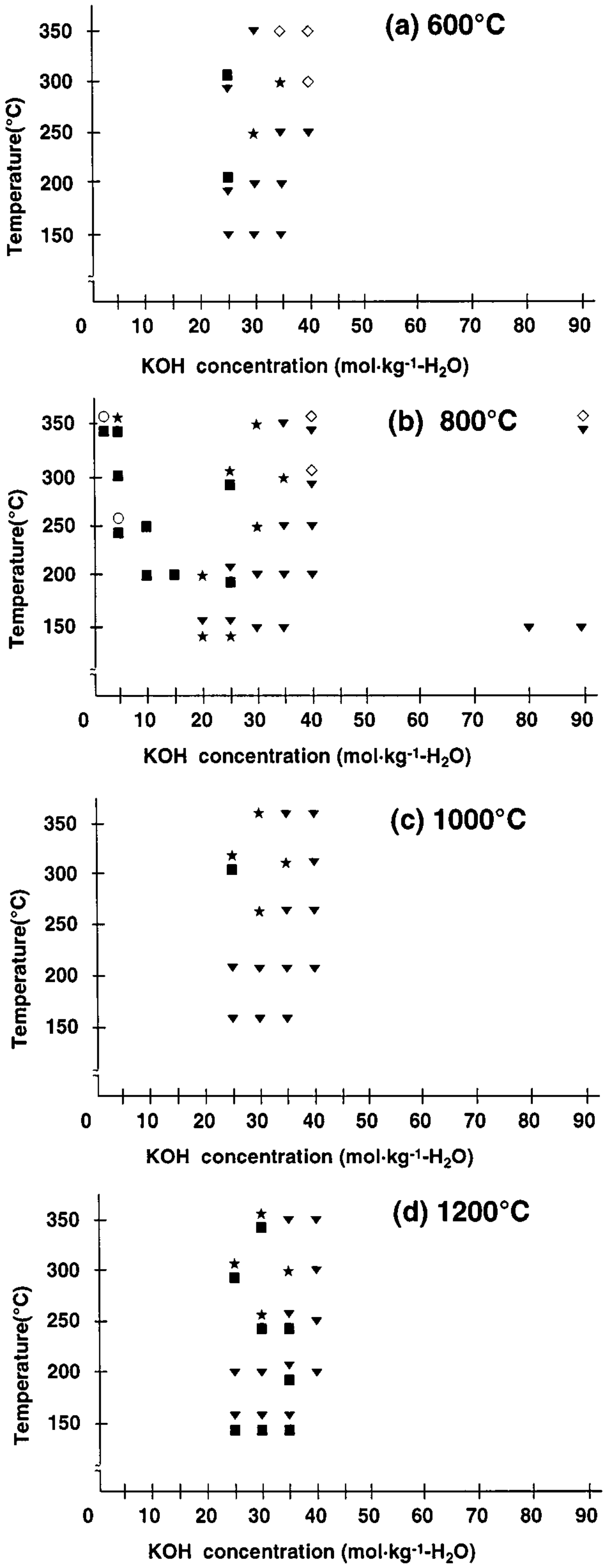


Figure 5 Formation diagram of heated products synthesized by hydrothermal reactions of Ti powder in KOH solutions. ■: $K_2Ti_6O_{13}$, ★: $K_2Ti_4O_9$, ▼: $K_2Ti_2O_5$, ○: TiO_2 and ◇: $K_4Ti_3O_8$.

4. Conclusions

From the results of tests described, the following conclusions may be drawn:

1. A formation diagram of products in Ti-KOH-H_2O system has been constructed at the region of KOH

concentration from 0 to 90 mol·kg^{-1}-H_2O and the temperature from 150 to 350 °C. Among the various potassium titanates, a new compound $KTiO_2(OH)$ was obtained as single phase.

2. Single phase hydrated $K_2Ti_2O_5$ was formed at KOH concentrations from 20 to 25 mol·kg^{-1}-H_2O and the temperatures from 150 to 200 °C, while amorphous $K_2Ti_2O_5$ precursor was formed at KOH concentrations above 80 mol·kg^{-1}-H_2O and 150 °C. Single phase $KTiO_2(OH)$ was obtained at KOH concentrations from 30 to 40 mol·kg^{-1}-H_2O and 200 °C. Single phase $K_4Ti_3O_8$ was obtained mainly at KOH concentrations above 35 mol·kg^{-1}-H_2O and the temperatures above 200 °C.

3. Single phase $K_2Ti_4O_9$ was obtained from the amorphous sample synthesized at 35 mol·kg^{-1}-H_2O KOH and 300 °C and at 30 mol·kg^{-1}-H_2O KOH and 250 °C by heating at 600–1200 °C. Single phase $K_2Ti_6O_{13}$ was obtained from the amorphous sample synthesized at 10 to 15 mol·kg^{-1}-H_2O KOH and 200–250 °C by heating at 800 °C.

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Received 25 May
and accepted 28 December 1999