JOURNAL OF MATERIALS SCIENCE 31 (1996) 5493–5498

Microstructural evolution of potassium titanate whiskers during the synthesis by the calcination and slow-cooling method

JONG-KOOK LEE
Department of Materials Engineering, Chosun University, Kwang-ju 501-759, Korea
KWANG-HO LEE, HWAN KIM
Department of Inorganic Materials Engineering, Seoul National University, Seoul, 151-742, Korea

$K_2Ti_6O_{13}$ whisker was synthesized by the calcination and slow-cooling method, and the microstructural evolution of whiskers, and the relations between the phase and the layer structure, were investigated. The amount of K_2O in the starting powder mixture played a key role in forming a layer structure, which can be obtained by addition of excess K_2O. During calcination, rod-like $K_2Ti_6O_{13}$ particles with a layer structure were formed by reactions between K_2O and TiO_2. During slow-cooling, the K_2O-rich liquid phase reacted with $K_2Ti_6O_{13}$ layers near the boundary and $K_2Ti_4O_9$ whiskers were produced by the splitting of layers within rod-like $K_2Ti_6O_{13}$ particles. $K_2Ti_4O_9$ whiskers were reformed into $K_2Ti_6O_{13}$ whiskers by treatment in boiling water and reheating. The synthesized $K_2Ti_6O_{13}$ whiskers had a clean surface and a length exceeding 100 μm.

1. Introduction

Most of the ceramic composites which have high performance have been produced by the incorporation of inorganic fibres or whiskers into advanced ceramics. Potassium titanate fibre or whisker has been used in a wide range of applications, as reinforcements, thermal insulators, ion replacements, friction materials and a substitute for asbestos [1–4].

The crystal structure and properties of potassium titanates, $K_2O \cdot nTiO_2$ ($n = 1$–9), are dependent on the value of n. Characteristic of potassium titanates with a high potassium content ($n = 2, 3, 4$) is the existence of a layer structure, and they show a distinctive intercalation ability and catalytic activity [1, 5–7]. However, in the case of potassium titanates with a low potassium content ($n = 6, 7, 8$), they have a tunnel structure and exhibit high thermal insulating ability and chemical stability [8–11].

Potassium titanate fibres and whiskers were fabricated by the methods of calcination [12, 13], hydrothermal reaction [14–17], flux growth [18–20], melt reaction [21], and slow-cooling calcination [22–24]. Among the many methods of synthesis, the slow-cooling calcination method has advantages in that it uses no flux and long whiskers can be obtained; therefore, production costs could be reduced compared with other methods.

Fujiki and co-workers [1, 9, 22, 23], reported that potassium titanate whiskers could be grown by an incongruent melt-association reaction and that their properties depend on the starting composition, calcination temperature and cooling rate [1, 9, 22, 23]. However, most of the previous reports concentrated on the phase relation of $K_2O \cdot nTiO_2$ whiskers and optimum conditions for whisker growth, and little attention was paid to the whisker-growth mechanism by the calcination and slow-cooling method. It is interesting to note that $K_2Ti_6O_{13}$ phase exhibits a rod-like shape at the calcination stage, each rod having a layer structure.

In the present study, $K_2Ti_6O_{13}$ whiskers were synthesized by the calcination and slow-cooling method under specific conditions, and the microstructural evolution of the whiskers, reactions of K_2O and TiO_2, and the relations between the phase and the layer structure of the specimen during the synthesis, were investigated. $K_2Ti_6O_{13}$ whiskers have found applications as automotive break linings, heat insulators and a reinforcement for various composite materials [1, 2].

2. Experimental procedure

As starting materials, K_2CO_3 (Shinyo Pure Chemicals Co.) and TiO_2 (Junsei Chemical Co.) were used. The mole ratio of K_2O and TiO_2 was basically fixed at 1/3, but powder mixtures were also prepared with the mole ratios of 1/2 and 1/5 in order to investigate the influence of excess K_2O at the same time. After milling for 24 h with ethanol and subsequent drying, a platinum crucible was filled with the powder mixture and heated to 1150 °C at a rate of 300 °C h^{-1} in a box furnace. After 6 h holding, the specimens were slowly cooled to 950 °C at a rate of 16 °C h^{-1} in furnace and quenched in water. The morphology of the specimens

0022-2461

during calcination and slow cooling was observed using scanning electron (Jeol; JSM-35) and transmission electron (Jeol; 2000FX) microscopes, and the particle and whisker phases were identified by X-ray diffraction.

To induce the transformation of the final $K_2Ti_6O_{13}$ whiskers from $K_2Ti_4O_9$, after the slow-cooling, $K_2Ti_4O_9$ whiskers were treated in distilled boiling water for 4 h, and dried at room temperature, then reheated at 1000 °C for 1 h. Phase transformation and surface morphology of the whiskers were also investigated by this process, using XRD and SEM.

3. Results and discussion

3.1. Formation of rod-like $K_2Ti_6O_{13}$ particles during calcination

Fig. 1 shows the morphology of particles produced by the reaction between K_2O and TiO_2 at 1000 °C. There is no remarkable growth of whiskers until heating to 1000 °C, but a rod-like particle with a length of 20–30 μm appeared on reaction of K_2O with TiO_2. Many needle-like particles grew on the surface of the rod-shaped particle with a diameter of 1–2 μm.

Fig. 2 shows the morphology of the rod-like particles calcined at 1150 °C. On heating to 1150 °C, the rod-like particles grew in length and diameter and the needle-like particles on it disappeared. However, in Fig. 2a equiaxed bulk, was also observed, which suggested unreacted particles. The rod-like particles were 100–200 μm long, had a diameter of 20–30 μm, and show a layer structure in the horizontal direction, as shown in Fig. 2a. On increasing the calcination time from 1 to 5 h, the number of rod-like particles increased, but their thickness decreased (Fig. 2b).

The growth of rod-like particles is due to the crystal structures of TiO_2 and $K_2Ti_6O_{13}$. It is easy to form a tunnel structure of $K_2Ti_6O_{13}$ by the reaction at the solid–liquid interface between solid TiO_2 and liquid K_2O as well as the chain structure of TiO_2 (rutile) composed of several TiO_6 octahedra [8–10].

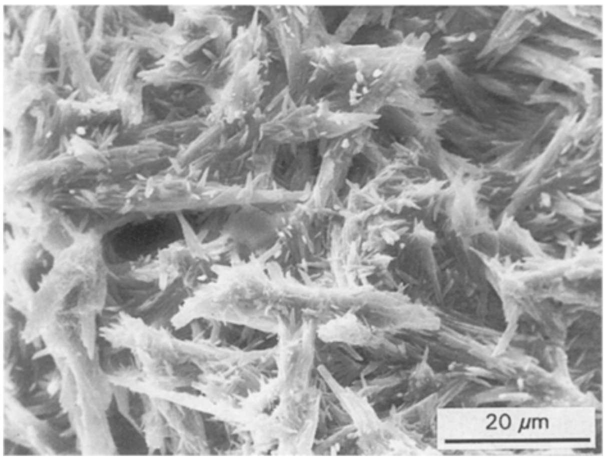

Figure 1 Scanning electron micrograph of particles formed by the reaction between K_2O and TiO_2 at 1000 °C.

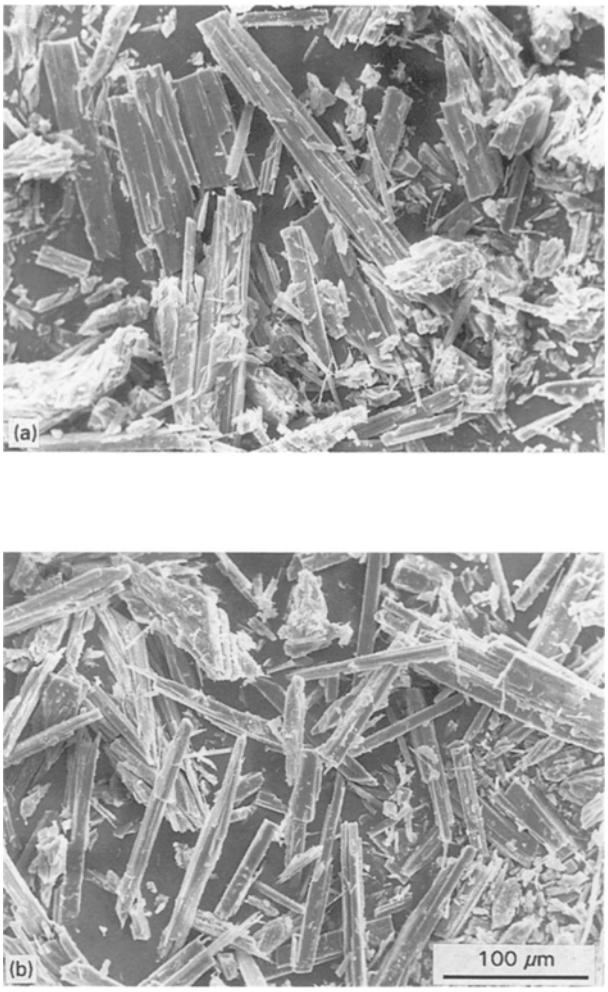

Figure 2 Scanning electron micrographs of rod-like particles calcined at 1150 °C for (a) 1 h and (b) 5 h.

3.2. Microstructural evolution of whiskers during slow-cooling

Fig. 3 shows the formation of whiskers from rod-like particles during slow cooling. As slow cooling proceeds, the aspect ratio of the whiskers gradually increases, but their length does not. In the initial stage of slow cooling, rod-like particles coexist with a small number of whiskers and unreacted particles (at 1000 °C, Fig. 3a). However, with decreasing cooling temperature, the number of rod-like particles decreased, but the number of whiskers increased (Fig. 3b). On slowly cooling to 950 °C, a bundle of whiskers was formed, as shown in Fig. 3c. It is observed that the powder mixture of K_2O and TiO_2 formed the rod-like $K_2Ti_6O_{13}$ particles with a layer structure during calcination at 1150 °C, and then $K_2Ti_4O_9$ whiskers formed by the splitting of layers in the rod-like particle during slow cooling.

Even though the slow cooling process was finished, the whiskers were still attached to each other by a K_2O-rich phase, and not separated completely, as shown in Fig. 3c. Therefore, to obtain completely separated whiskers after slow cooling, it was necessary to subject the bundle to a process for the scattering of whiskers.

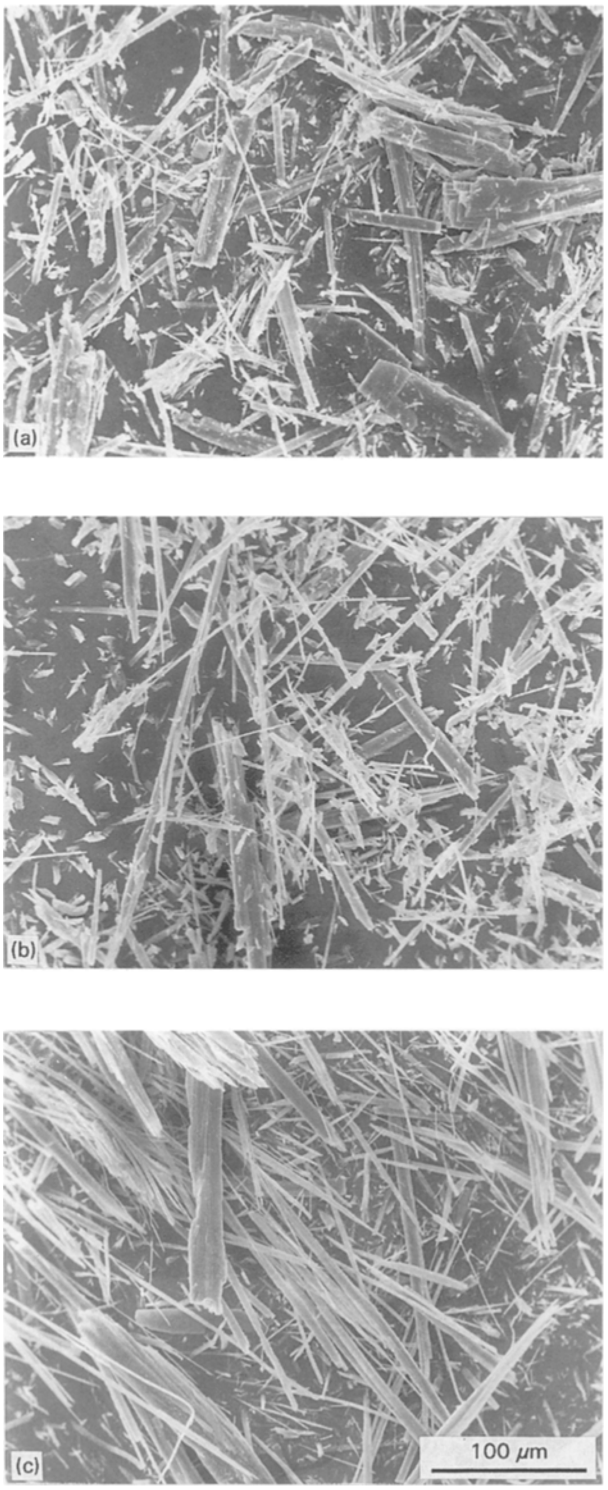

Figure 3 Microstructural evolution from rod-like particles to whiskers by slow cooling to a temperature of (a) 1000 °C, (b) 975 °C and (c) 950 °C.

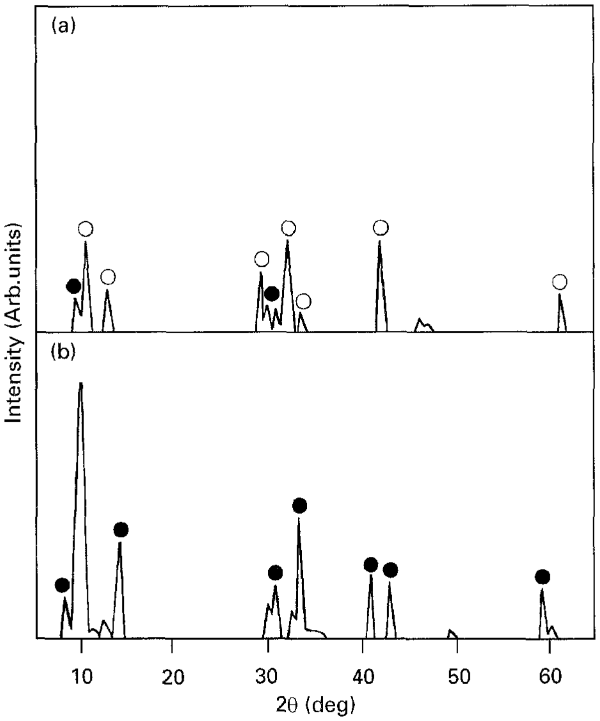

Figure 4 XRD patterns of the specimens (a) calcined at 1150 °C for 5 h and (b) slowly cooled to 950 °C after being calcinated at 1150 °C for 6 h. (●) $K_2Ti_4O_9$ (○) $K_2Ti_6O_{13}$.

3.3. Phase change during calcination and slow cooling

The phases of rod-like particles and whiskers formed at each stage were measured by the XRD method. Fig. 4 shows the XRD patterns of the specimen calcined at 1150 °C for 5 h and subsequently cooled to 950 °C. From the analysis of XRD patterns, the rod-like particles formed by calcination were confirmed to be $K_2Ti_6O_{13}$ phase, and the whiskers formed by slow cooling to 950 °C were $K_2Ti_4O_9$ phase. The formation of rod-like $K_2Ti_6O_{13}$ particles during calcination at 1150 °C and phase transformation of $K_2Ti_6O_{13}$ from $K_2Ti_4O_9$ during slow cooling could be explained in the K_2O–TiO_2 phase diagram. From the phase diagram of the K_2O–TiO_2 system [22–23], the composition of $K_2O \cdot 3TiO_2$ is expected to decompose to a K_2O-rich liquid phase and a solid phase of $K_2Ti_6O_{13}$ above 1114 °C. Therefore, the phase formed by calcination at 1150 °C might be shown to be a mixture of $K_2Ti_6O_{13}$ rod-like particles (major phase) and K_2O-rich liquid phase (minor phase). On cooling below 1114 °C, which is the incongruent melting temperature of $K_2Ti_4O_9$, the mixture of $K_2Ti_6O_{13}$ and K_2O-rich liquid phase reacts to form $K_2Ti_4O_9$, as shown in Fig. 4.

3.4. The formation mechanism of the layer structure during slow cooling

Fig. 5 shows the layer structure of the rod-like particles calcined at 1150 °C for 5 h and the particles attached to their surface. Both rod-like particles and whiskers which were formed by calcination and slow cooling exhibited the layer structure, and small particles were observed near the boundary between the layers and the surface of the whiskers, as indicated by arrows in Fig. 5. TEM analysis of the ring patterns confirmed the small particles between the two layers to be amorphous phase [25]. It is suggested that the small particles are a K_2O-rich phase formed from solidification of K_2O-rich liquid phase during quenching. In this study, K_2O existed within the particles, compared with the atomic ratio of $K_2Ti_6O_{13}$, because the ratio of K_2O to TiO_2 is 1/3 in the starting mixture powder. So, it is expected that the K_2O-rich liquid phase

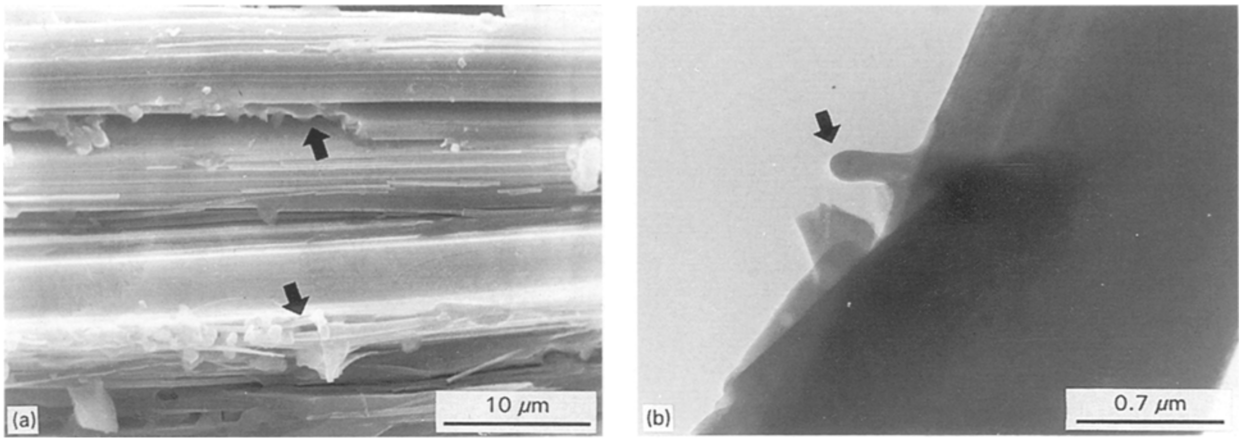

Figure 5 Layer structure of the rod-like particles calcined at 1150 °C, 5 h and the particles attached to their surface observed by (a) scanning electron microscopy and (b) transmission electron microscopy.

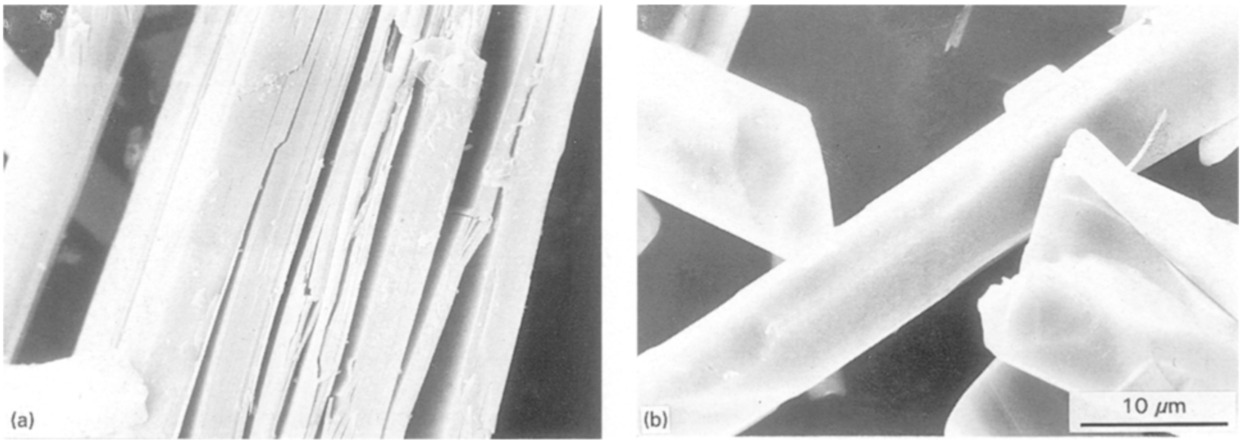

Figure 6 Variation of the morphology of whiskers with the mole ratio of K_2O and TiO_2 (a) 1/2 and (b) 1/5, in the starting powder mixture, and the whiskers obtained by calcination at 1150 °C for 6 h and slow cooling to 950 °C.

was formed from excess K_2O during heating, and accumulated between the two $K_2Ti_6O_{13}$ layers during calcination. On slow cooling, a portion of the K_2O-rich liquid phase reacted with $K_2Ti_6O_{13}$ near the boundary and produced the $K_2Ti_4O_9$ phase. Consequently, splitting of the two $K_2Ti_4O_9$ layers was induced owing to the peritectic reaction mentioned above and the demand for continual consumption of K_2O-rich liquid phase at the layer boundary. Of course, the contraction of K_2O-rich liquid phase on cooling could be a factor causing the splitting between the two layers of $K_2Ti_4O_9$.

3.5. Effect of the ratio of K_2O and TiO_2 on the formation of the layer structure

Fig. 6 shows the variation in the morphology of whiskers with the mole ratio of K_2O and TiO_2. In the case of a higher K_2O content ($K_2O/TiO_2 = 1/2$), compared with the initial case ($K_2O/TiO_2 = 1/3$), the same layer structure and split edge as in initial case is found (Fig. 6a). With lower K_2O content ($K_2O/TiO_2 = 1/5$), however, a smooth surface (Fig. 6b), but no layer structure and split edges were found. It is suggested that the amount of K_2O plays a key role in the formation of the layer structure, which resulted from the distribution of excess K_2O-rich liquid phase between the whiskers.

To obtain $K_2Ti_4O_9$ whiskers, two reactions are known to occur [22]. Firstly, TiO_2 particles and liquid K_2O react to give $K_2Ti_6O_{13}$, and then $K_2Ti_6O_{13}$ and liquid K_2O react to produce $K_2Ti_4O_9$ at 1114 ± 15 °C by a peritectic reaction. According to the phase diagram [23], $K_2Ti_4O_9$ is formed in the region where the mole ratio of K_2O and TiO_2 is 1/2–1/6. However, the growth of $K_2Ti_4O_9$ whiskers is optimized around the ratio of 1/3 experimentally [22]. Thus the K_2O-rich composition has a significant effect on the growth of whiskers. K_2O-rich liquid phase exists excessively between two layers of rod-like particles or whiskers, and it is induced to form a layer structure of $K_2Ti_6O_{13}$. This implies that $K_2Ti_6O_{13}$ grows to over 100 μm in length with a rod-like shape and a layer structure during calcination, and its aspect ratio increases by reaction between $K_2Ti_6O_{13}$ and K_2O-rich phase during slow cooling, which induces splitting between the two layers and the phase transformation of $K_2Ti_6O_{13}$ to $K_2Ti_4O_9$ by a peritectic reaction.

3.6. Transformation of $K_2Ti_4O_9$ to $K_2Ti_6O_{13}$ whiskers by treatment in boiling water and reheating

To transform $K_2Ti_6O_{13}$ whiskers from $K_2Ti_4O_9$ and to obtain completely scattered whiskers after slow

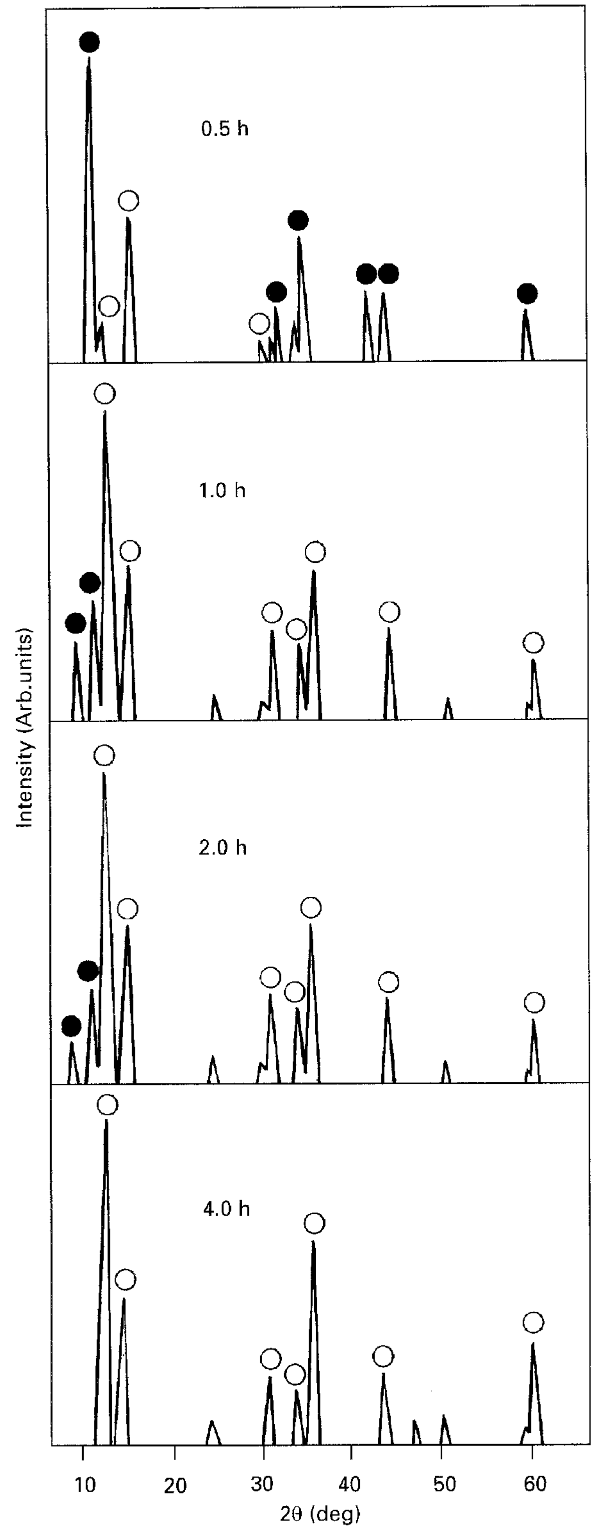

Figure 7 XRD patterns of the whiskers treated in boiling water for (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 4 h, and subsequently reheated at 1000 °C for 1 h. (●) $K_2Ti_4O_9$, (○) $K_2Ti_6O_{13}$.

cooling, it is necessary to extract the excess K^+ ions and the dissolved K_2O-rich phase simultaneously. A bundle of $K_2Ti_4O_9$ whiskers was treated in boiling water for 4 h to achieve these two aims. Fig. 7 shows the XRD patterns of the whisker treated in boiling water for 0.5, 1, 2 and 4 h. It is seen that the whisker phase was transformed to $K_2Ti_6O_{13}$ from $K_2Ti_4O_9$ by treatment in boiling water. With increasing treatment time, the main peak of $K_2Ti_6O_{13}$ ($2\theta = 10°$) increased, but the main peak of $K_2Ti_4O_9$ ($2\theta = 11.4°$) reversely decreased. All whiskers were completely transformed back to $K_2Ti_6O_{13}$ phase by treatment in boiling water for 4 h, as shown in Fig. 7c.

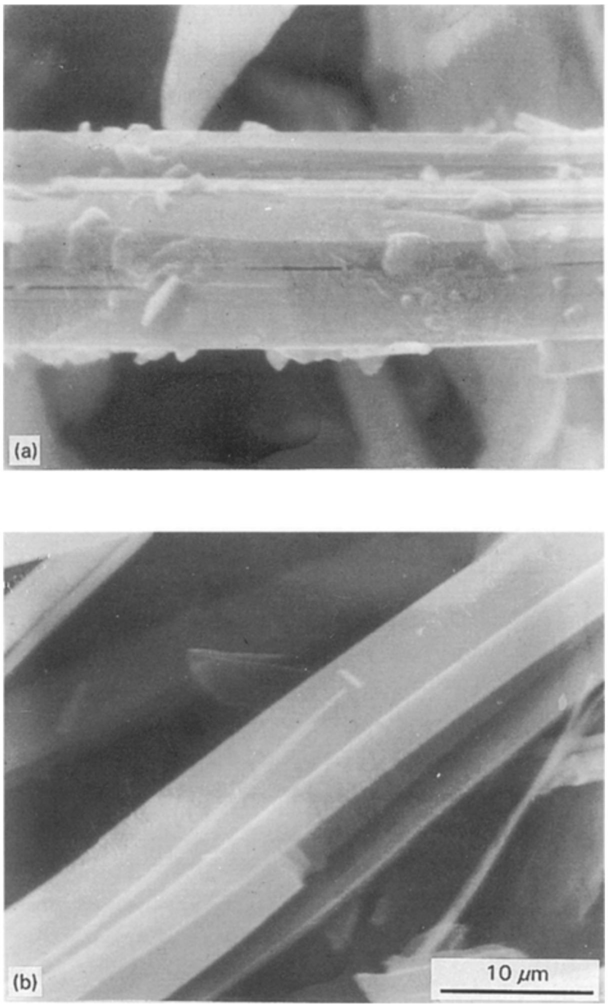

Figure 8 Morphology of the whiskers treated in boiling water for (a) 0.5 h and (b) 1 h, and subsequently reheated at 1000 °C for 1 h.

Fig. 8 shows the morphology of whiskers treated in boiling water for 0.5 and 1 h. The whisker treated in boiling water for 0.5 h (Fig. 8a) was found to have a rough surface due to the attachment of K_2O-rich phase and partially mutual adhesion. But, in case of 1 h treatment (Fig. 8b), whiskers had a clean surface and completely scattered morphology. The mechanism of phase transformation and scattering of whiskers by treatment in boiling water could be explained by the crystal structures of $K_2Ti_6O_{13}$ and $K_2Ti_4O_9$ [5–10]. In $K_2Ti_4O_9$ crystal, the titanium atom exists in the centre of an oxygen octahedron, and TiO_6 octahedra, which are linked to each other by a corner and an edge, consist of a layer structure. On treatment in boiling water, some of the K^+ ions, which existed between the two TiO_6 layers, might be easily extracted from the layer because their radius is very small. By extracting K^+ ions from the layer, the crystal structure is changed to a more open structure, which might be easily transformed to tunnel structure. On reheating, one of the TiO_6 octahedra which are linked by an edge in a layer structure, was rotated by absorption of energy, and then the $K_2Ti_4O_9$ with layer structure was transformed to $K_2Ti_6O_{13}$ with

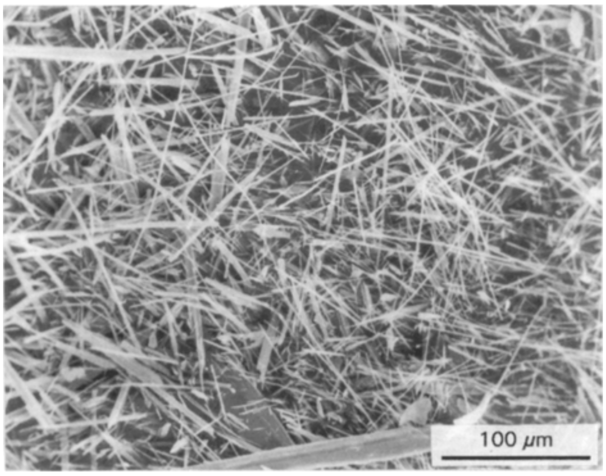

Figure 9 Morphology of $K_2Ti_6O_{13}$ whiskers synthesized by the calcination and slow cooling process.

tunnel structure which contained trapped K^+ ions among the TiO_6 octahedra. ICP analysis of residual water after treatment in boiling water [26], detected more K^+ ions than Ti^{4+} ions. Thus the dissolution of K^+ ions from K_2O-rich phase and $K_2Ti_4O_9$ is easier than that of Ti^{4+} ions.

Fig. 9 shows the final $K_2Ti_6O_{13}$ whiskers obtained from $K_2Ti_4O_9$ after treatment with boiling water for 4 h and subsequent reheating to 1000 °C for 1 h. The synthesized $K_2Ti_6O_{13}$ whiskers had a considerable aspect ratio, a clean surface and a length exceeding 100 μm.

4. Conclusion

From a powder mixture of K_2O and TiO_2, $K_2Ti_6O_{13}$ whiskers were synthesized by the calcination and slow cooling method. During calcination at 1150 °C, rod-like $K_2Ti_6O_{13}$ particles with a layer structure were formed by reactions between K_2O and TiO_2, and $K_2Ti_4O_9$ whiskers formed from these particles during slow cooling. The amount of K_2O in the starting powder mixture played a key role in forming a layer structure, which can be obtained by the addition of excess K_2O powder. K_2O-rich liquid phase formed and accumulated on the boundary between two $K_2Ti_6O_{13}$ layers during heating and calcination. On slow cooling, the K_2O-rich liquid phase reacted with $K_2Ti_6O_{13}$ layers near the boundary by a peritectic reaction, and induced the production of $K_2Ti_4O_9$ whiskers by the splitting layers due to the peritectic reaction. $K_2Ti_4O_9$ whiskers were transformed back to $K_2Ti_6O_{13}$ whiskers by treatment in boiling water for the dissolution of K_2O and reheating. Synthesized $K_2Ti_6O_{13}$ whiskers had a clean surface and a length exceeding 100 μm.

References

1. Y. FUJIKI, Y. KOMASTSU and T. SASAKI, *Ceram. Jpn* **19** (1984) 126.
2. M. TAKENAKA, *Kino Zairyo* **3** (1983) 31.
3. M. SANDO, A. TOWATA and A. TSUGE, in "Ceramic Transactions", Vol. 22 edited by S. Hirano, G. L. Messing and H. Hausner (American Ceramic Society, Westerville, OH, 1991) p. 101.
4. H. HUKUNAKA and J. PAN, in "Advanced Structural Materials" (Elsevier Science, North-Holland, 1991) p. 45.
5. S. ANDERSSON and A. D. WADSLEY, *Acta Crystallogr.* **14** (1961) 1245.
6. M. DION, Y. PIFFARD and M. TOURNOUX, *J. Inorg. Nucl. Chem.* **40** (1978) 917.
7. H. IZAWA, S. KIKKAWA and M. KOIZUMI, *J. Solid State Chem.* **69** (1987) 336.
8. S. ANDERSSON and A. D. WADSLEY, *Acta Crystallogr.* **15** (1962) 194.
9. Y. FUJIKI and T. MITSUHASHI, *Ceram. Jpn* **19** (1984) 200.
10. T. SASAKI and Y. FUJIKI, *J. Solid State Chem.* **83** (1989) 45.
11. T. SASAKI, M. WATANABE, Y. FUJIKI and Y. KITAMI, *ibid.* **105** (1993) 481.
12. T. SHIMIZU, H. YANAGIDA and K. HASHIMOTO, *Yogyo Kyokaishi* **86** (1978) 339.
13. T. SHIMIZU, H. YANAGIDA, K. HASHIMOTO and Y. NISHIGAWA, *ibid.* **88** (1980) 84.
14. F. MUTO and M. KUNITOMI, *Kogyo Kagaku Zasshi* **65** (1962) 1775.
15. S. TAKI and K. TANAKA, *ibid.* **66** (1963) 417.
16. T. SHIMIZU, K. HASHIMOTO and H. YANAGIDA, *Yogyo Kyokaishi* **83** (1975) 305.
17. *Idem, ibid.* **84** (1976) 36.
18. Y. FUJIKI and N. OHTA, *ibid.* **88** (1980) 111.
19. H. SAITO and N. TAGUSAGAWA, *Kogyo Kagaku Zasshi* **67** (1964) 297.
20. Y. FUJIKI and F. IZUMI, *Yogyo Kyokaishi* **85** (1977) 155.
21. T. SHIMIZU, H. YANAGIDA and K. HASHIMOTO, *ibid.* **85** (1977) 567.
22. Y. FUJIKI, *ibid.* **91** (1983) 189.
23. *Idem, ibid.* **90** (1982) 624.
24. A. WATANABE, Y. TAKEUCHI and G. SAEKI, *J. Am. Ceram. Soc.* **68** (1985) C-308.
25. K. H. LEE, MS thesis, Seoul National University (1995).
26. K. H. LEE, J. K. LEE and H. KIM, *J. Kor. Assoc. Cryst. Growth* **5** (1995) 261.

*Received 8 January
and accepted 18 March 1996*