JOURNAL OF MATERIALS SCIENCE 39 (2004) 4561 – 4568

Synthesis of $K_2Ti_4O_9$ whiskers

T. ZAREMBA*, A. HADRYŚ
Department of Inorganic Chemistry and Technology, Faculty of Chemistry of Silesian University of Technology, ul. B. Krzywoustego 6, 44-100 Gliwice, Poland

Potassium tetratitanate ($K_2Ti_4O_9$) whiskers were synthesized by the calcination and slow-cooling method. Powder X-ray diffraction (XRD) analysis and differential thermal analysis (DTA) were used to study the formation of $K_2Ti_4O_9$. In the slow-cooling calcination process, the control of cooling rate was crucial to growth of $K_2Ti_4O_9$ whiskers. The characterization of the whiskers was carried out by means of scanning electron microscope (SEM). © *2004 Kluwer Academic Publishers*

1. Introduction

Fibrous crystals of potassium titanates with a high potassium content, were found to exhibit superior heat insulation, heat resistance and chemical resistance to corrosion properties, and numerous applications have been widely developed. Most of the ceramic composites which have high performance have been produced by the incorporation of inorganic fibres and whiskers into advanced ceramics. Whiskers are short, fibres-shaped single crystals, with high perfection and high aspect ratio (length to diameter). Potassium titanate whisker has also potential applications in whisker—reinforced plastics and metals [1–10]. In comparison to other ceramic whiskers, it has the advantages of lower cost. From this point of view, there is no competitive fibre to potassium titanate whisker. The price of potassium titanate whisker ranges from one-tenth to one-twentieth of the cost of silicon carbide whiskers. Even compared to alumina short fibres, the cost is about one-fifth [11, 12].

Many methods have been developed to synthesize potassium titanate fibres and whiskers, including calcination, slow-cooling calcination, hydrothermal reaction, flux growth (melting), flux evaporation and the combinative route of flux evaporation and slow-cooling process [2–5]. Among the many methods of synthesis, the slow-cooling calcination method has advantages in that it uses no flux; therefore, production costs could be reduced compared with other methods [2].

In the present study, $K_2Ti_4O_9$ whiskers were synthesized by the slow-cooling calcination process. The crystal shapes and the size of grown crystals were investigated.

2. Experimental procedure

Starting materials were dry reagent grade: K_2CO_3 (POCH-Gliwice, purity 99.8%) and TiO_2 ("Police Chemical Works", purity 99.5%). The mole ratio of K_2O to TiO_2 was 1:4. After being ground in an agate mortar under isopropyl alcohol and subsequent drying, platinum crucibles were filled with the powder mixture and heated at a rate of 300°C h^{-1} in a box furnace. $K_2Ti_4O_9$ compound synthesis was carried out by heating the samples of raw materials mixture up to temperatures of 900 and 1000°C (soaking time at those temperatures was 4 and 24 h) as well as up to 1150°C (soaking time at this temperature was 3 h) at which melting of $K_2Ti_4O_9$ took place. After calcining at 1150°C different methods and rates of samples cooling were applied, namely:

- rapid cooling by taking the sample out of the furnace at temperature 1150°C i.e. sample was quenched in air without slow cooling;
- natural cooling in the furnace down to the temperature of 950°C, 750°C and down to room temperature with decreasing rate of cooling; cooling from the temperature of 1150°C down to 950°C was carried out with an average rate of 300°C h^{-1}, and from the temperature of 950 to 750°C with the average rate of 180°C h^{-1};
- slow cooling with the controlled rate of 50°C h^{-1} to the temperature of 1000 and 950°C;
- slow cooling with the controlled rate of 35°C h^{-1} and 25°C h^{-1} to the temperature of 950°C.

The powder X-ray diffraction (XRD) analysis of the samples was carried out using DRON-2.0 diffractometer (Russia) operating at 36 kV and 20 mA with Cu K_α radiation. The various phases obtained in this study were identified using the JCPDS cards [13] or reference [14].

Differential thermal analysis (DTA) was used to investigate the thermal behaviour of the samples after thermal treatment in a box furnace. DTA was carried out using a F. Paulik–J. Paulik–L. Erdey (MOM, Hungary) type derivatograph in static air atmosphere. The 400 mg sample was placed in platinum crucible; α-Al_2O_3 powder was used as a reference material. The sample was

---

*Author to whom all correspondence should be addressed.

0022–2461 © *2004 Kluwer Academic Publishers*

TABLE I Results of phase composition examination of selected samples depending on heat treatment and cooling conditions

Thermal treatment			
Temperature (°C)	Soaking time (h)	Cooling	Phase composition
900	4	In furnace up to the room temperature	$K_2Ti_4O_9$
1150	3	Without slow cooling (taken out of the furnace at 1150°C)	$K_2Ti_2O_5$ $K_2Ti_6O_{13}$ $K_2Ti_4O_9$
1150	3	In furnace down to room temperature	$K_2Ti_4O_9$
1150	3	To 950°C at a rate of 300°C h^{-1} in furnace	$K_2Ti_4O_9$ $K_2Ti_6O_{13}$ $K_2Ti_2O_5$
1150	3	To 750°C at a rate of 180°C h^{-1} in furnace	$K_2Ti_4O_9$
1150	3	To 1000°C at a rate of 50°C h^{-1} in furnace	$K_2Ti_4O_9$ $K_2Ti_6O_{13}$ $K_2Ti_2O_5$
1150	3	To 950°C at a rate of 50°C h^{-1} in furnace	$K_2Ti_4O_9$
1150	3	To 950°C at a rate of 35°C h^{-1} in furnace	$K_2Ti_4O_9$
1150	3	To 950°C at a rate of 25°C h^{-1} in furnace	$K_2Ti_4O_9$

heated with a rate of ca. 10°C min^{-1} within the range of temperatures 20–1000°C. Natural cooling of sample was carried out in an oven of thermal analyzer.

The morphology of the starting materials and samples after calcination and cooling was examined by scanning electron microscopy, SEM (Tesla BS 340, Czech Republic). Microscope observations were made after coating the samples surface with a thin layer of gold.

3. Results and discussion

Research results of phase composition of samples after thermal treatment are presented in Table I. X-ray diffraction patterns of selected samples are presented in Figs 1 and 2, and the heating up and cooling DTA curves in Fig. 3. Information used to identify phases detected on XRD patterns are shown in Table II. Raw materials and selected samples microstructures are shown in Figs 4–7.

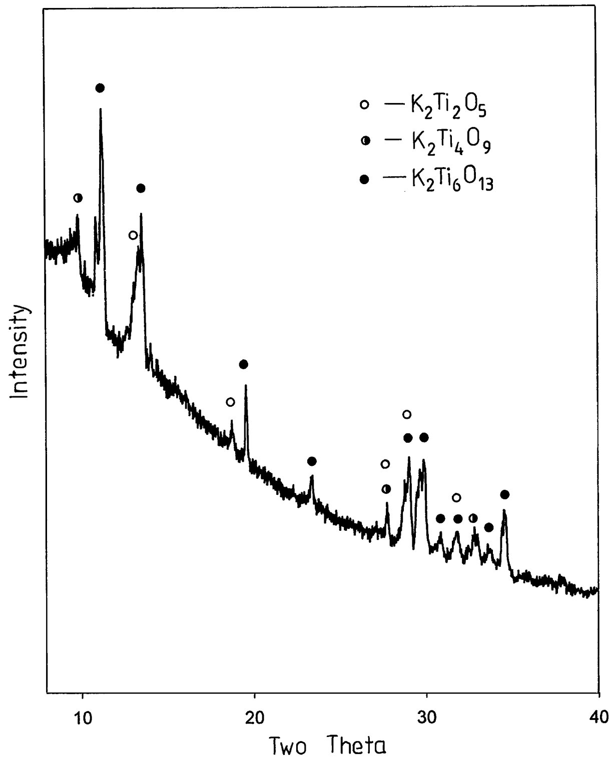


Figure 1 XRD pattern of a sample calcined at 1150°C for 3 h and taken out of the furnace at this temperature.

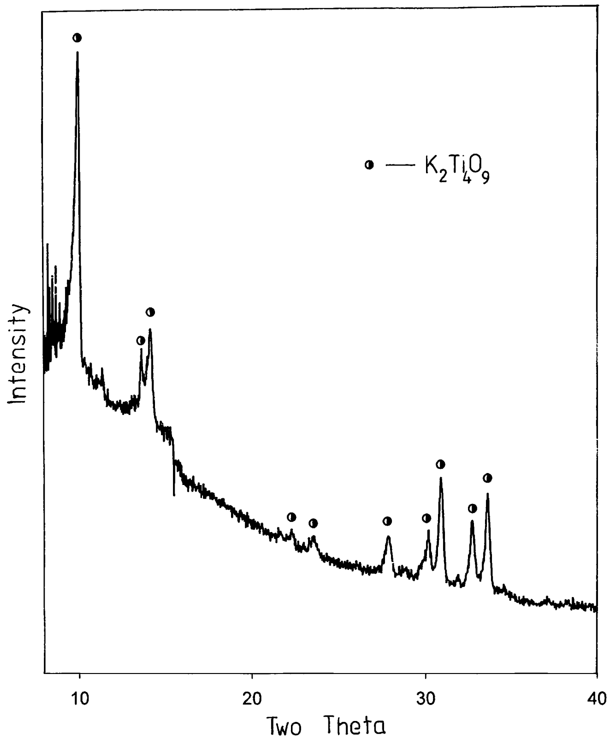


Figure 2 XRD pattern of a sample calcined at 1150°C for 3 h and taken out of the furnace after cooling down to room temperature.

As a result of heating up of starting powder mixture to the temperature of 900 and 1000°C (4 h holding) the raw materials reacted completely i.e. sam-

TABLE II Information used to identify phases detected in this study

Phase	Card number or reference
$K_2Ti_2O_5$	13-448
$K_2Ti_4O_9$	Andersen *et al.* [14]
$K_2Ti_6O_{13}$	13-574; Andersen *et al.* [14]

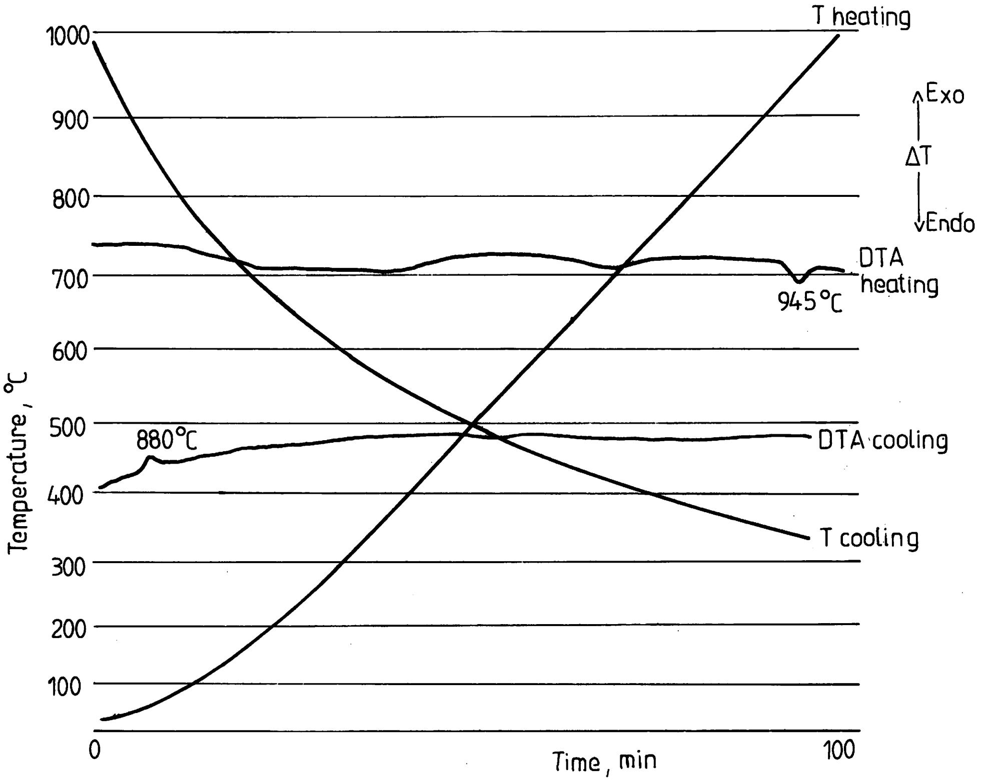


Figure 3 DTA curves of a sample included $K_2Ti_2O_5$.

ples after heat treatment included $K_2Ti_4O_9$ only, but received a rod-like particles were short and packed. 24-hour samples holding at the temperature of 900 and 1000°C did not practically change their microstructure. That is why the consecutive $K_2Ti_4O_9$ syntheses were carried out by heating up the raw materials mixture up to the temperature of 1150°C and then $K_2Ti_4O_9$ was melted. Incongruent melting temperature of $K_2Ti_4O_9$ is 1114 ± 15°C [15]. According to [2], $K_2Ti_4O_9$ melts with decomposition to $K_2Ti_6O_{13}$ stable solid phase and to K_2O-rich liquid phase.

Researches carried out in this paper of phase composition of samples heated up the temperature of 1150°C (Table I) confirmed the incongruent melting of $K_2Ti_4O_9$ and showed that $K_2Ti_2O_5$ creates the liquid phase. Reid and Watts [16] reported that potassium dititanate melts congruently at the temperature of 942°C.

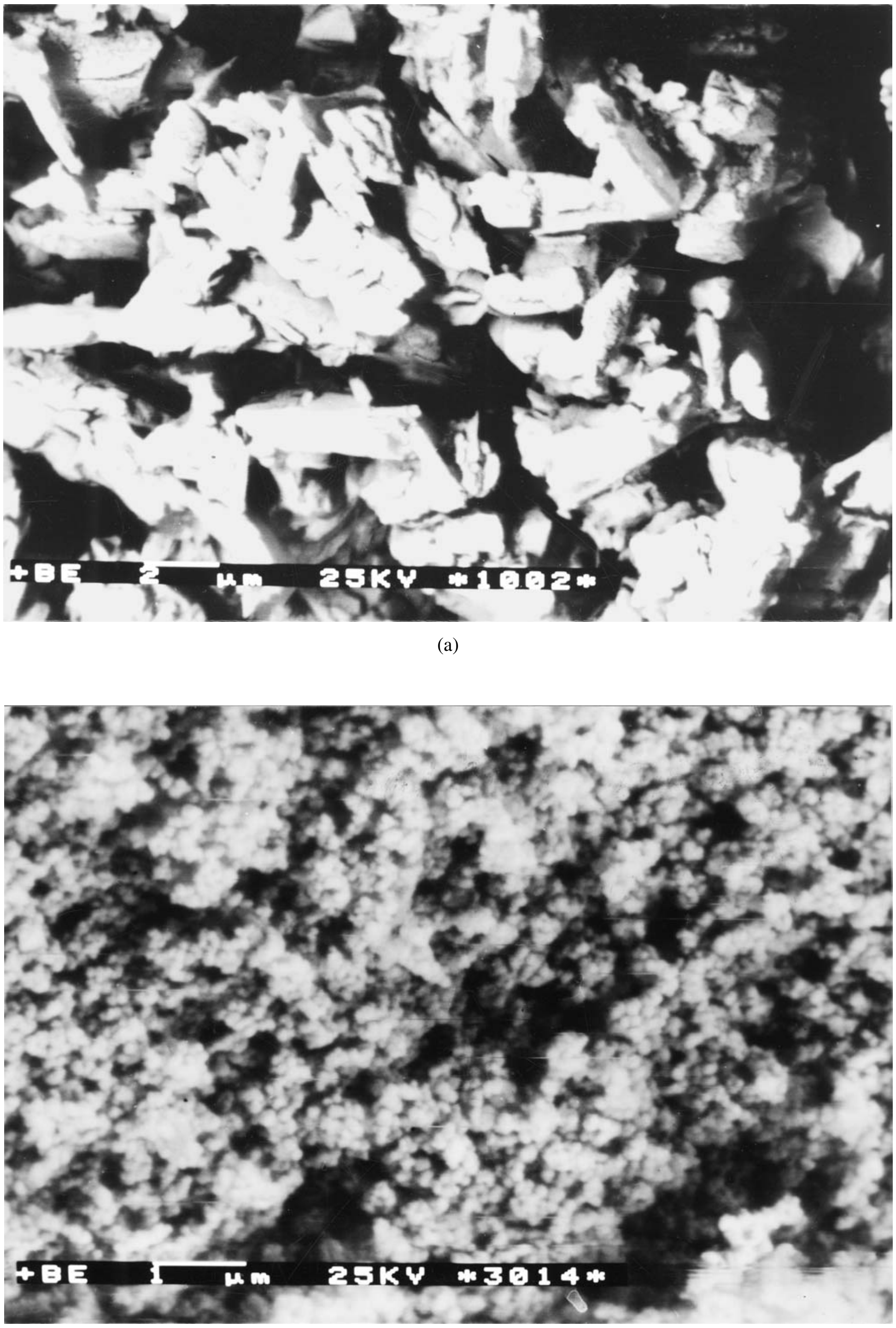
While cooling the samples the products formed as a result of $K_2Ti_4O_9$ decomposition react with each other, i.e. the association reaction occurs as follows:

$$K_2Ti_6O_{13(s)} + K_2Ti_2O_{5(l)} \rightarrow 2\ K_2Ti_4O_{9(s)}$$

Cooling conditions affect significantly the course of the association reaction. Sample heated up to the temperature of 1150°C and then taken out of the furnace at this temperature constituted the mixture of $K_2Ti_6O_{13}$, $K_2Ti_2O_5$ and $K_2Ti_4O_9$ (Table I, Fig. 1), because under conditions of rapid cooling the association reaction could only proceed to an insignificant extent. In the consecutive test, calcined sample at the temperature of 1150°C was cooled to 950°C at an average rate of 300°C h^{-1} in the furnace. Examination of phase composition showed that the sample cooled by means of such method, the association reaction ran in significantly higher rate than previously, but not completely, because, besides $K_2Ti_4O_9$, there were trace quantities of $K_2Ti_6O_{13}$ and $K_2Ti_2O_5$ in the sample. Association reaction ran completely in the samples that were cooled to lower temperatures (for instance 750°C) as well as in the sample cooled together in the furnace down to room temperature (Table I, Fig. 2).

In the calcination method, the control of cooling rate was crucial to phase composition of examined samples. It was found that in case samples cooled to 950°C at the cooling rate of 50°C h^{-1}, 35°C h^{-1} and 25°C h^{-1}, association reaction ran completely, i.e. samples included $K_2Ti_4O_9$ only (Table I). Except cooling rate the significant factor that had influence on the phase composition of samples was temperature up to which the samples were cooled. There were three titanates: $K_2Ti_4O_9$, $K_2Ti_6O_{13}$ and $K_2Ti_2O_5$ in samples cooled to 1000°C at the rate of 50°C h^{-1} (Table I).

In case of samples that did not include the final product only, X-ray diffraction patterns identification was made difficult by the fact that $K_2Ti_2O_5$ diffraction lines are partially supressed by the lines of $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$. Differential thermal analysis of materials after heat treatment in furnace allowed the assertion in which samples $K_2Ti_2O_5$ compound is present. If the sample included $K_2Ti_2O_5$ endothermic effect with $T_{\max} \sim 940°C$ on the heating DTA curve was present (without loss in weight) that resulted from



(a)

(b)

Figure 4 Scanning electron micrographs of the starting materials (a) K_2CO_3 and (b) TiO_2.

$K_2Ti_2O_5$ melting, and on the DTA curve recorded while cooling crystallisation exothermic effect, respectively (Fig. 3).

Samples microstructure examination calcined at 1150°C in order to melt $K_2Ti_4O_9$ shown that cooling conditions have the decisive influence on $K_2Ti_4O_9$ crystals habit and size. The sample being rapid cooled, i.e. taken out of the furnace of the temperature of 1150°C consisted of non-splitted, longitudinal crystals of prismatic shape and the width within the range of 10–25 μm (Fig. 5a). The sample cooled to 950°C at the average rate about 300°C h^{-1} was partly splitted (Fig. 5b). Cooling the sample in the consecutive test together with the furnace up to room temperature caused the progress in splitting the $K_2Ti_4O_9$ (Fig. 5c).

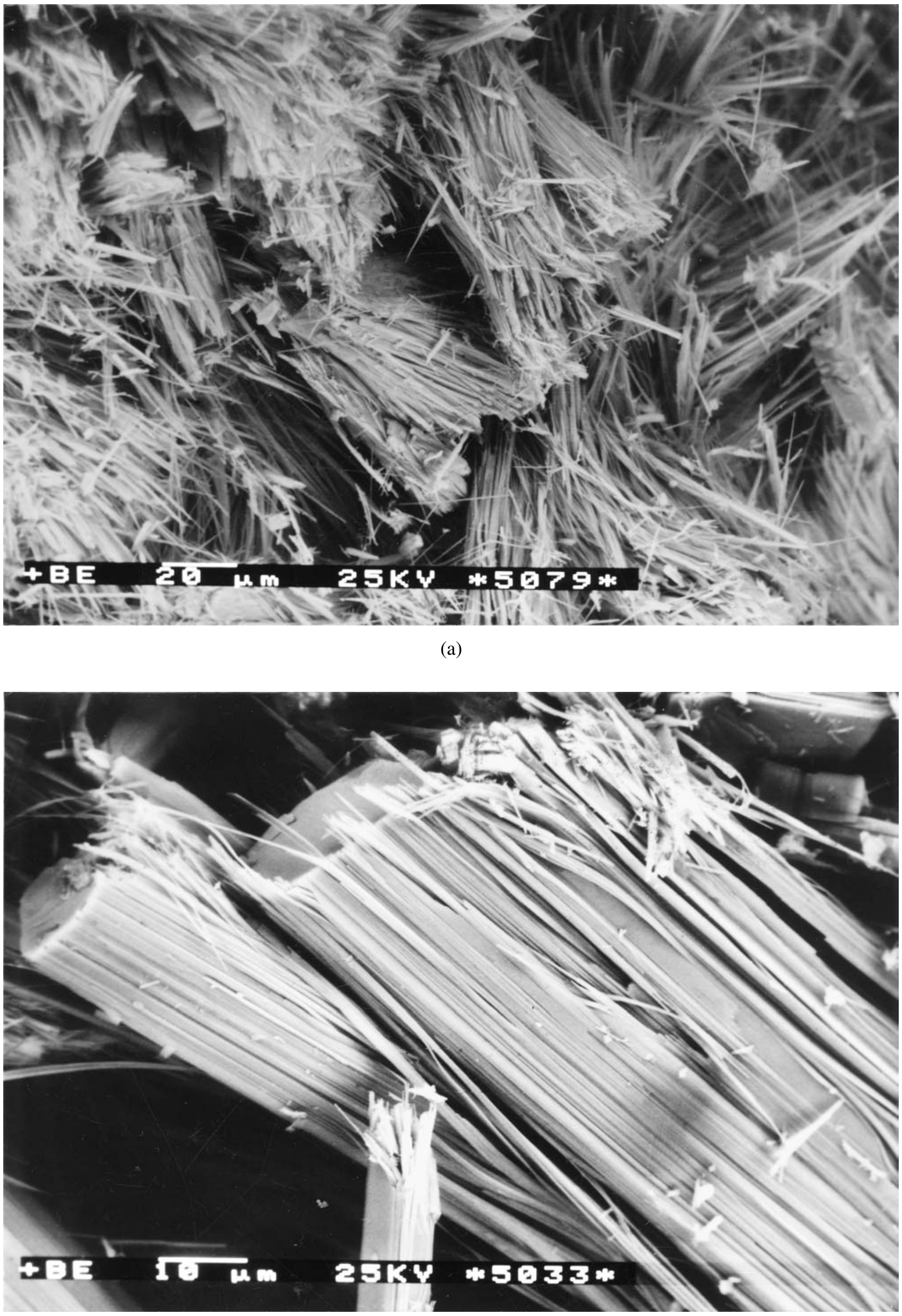
The best results were obtained while cooling the samples down to the temperature of 950°C and decreasing the rate of cooling according to examination results presented in [2, 3]. At the cooling rate of 50°C h^{-1} whiskers length were up to 60 μm (Fig. 6a), sporadically up to 80–90 μm, but the sample was not completely splitted and crystals in the form of packed prismatics were presented sporadically

(a)

(b)

(c)

Figure 5 Scanning electron micrographs of samples calcined at 1150°C for 3 h and taken out of the furnace at the temperature of (a) 1150°C, (b) 950°C and (c) 20°C.



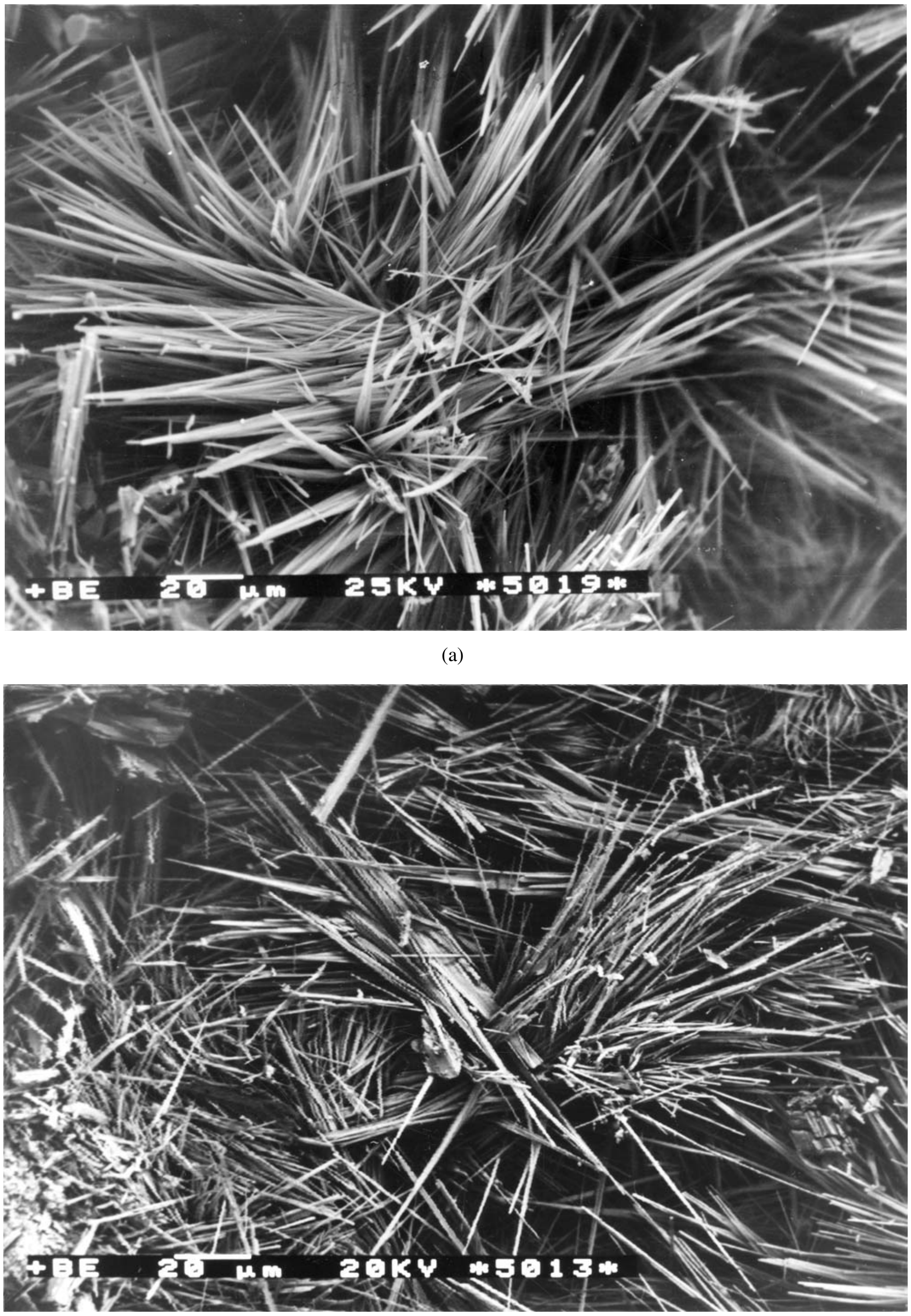
(a)

(b)

Figure 6 Scanning electron micrographs of sample calcined at 1150°C for 3 h and cooled to 950°C at a rate of 50°C h^{-1} (a) sample had the many places that were better splitted and (b) sample had sporadically places that were worse splitted.

(Fig. 6b). Cooling at the rate of 35°C h^{-1} caused the progress in splitting the $K_2Ti_4O_9$ (Fig. 7a). While applying the slowest cooling of melted sample during carried out examinations (25°C h^{-1}) whiskers of high aspect ratio c/a (c and a denote the length and diameter of whiskers), exceeding the minimum value required for whiskers, i.e. 20–25 were obtained (Fig. 7b).

In accordance with [17], toxicity of fibrous particle depends both on its chemical composition and its dimensions. On the other hand, results of selected laboratory examinations suggest that all mineral fibres of similar dimensions, shape and stability can lead to the same health effect and even to the same risk level. One cannot exclude that fibres of the same physical properties shall cause similar health effect, regardless of their chemical composition. However this hypothesis requires to be confirmed by clinical and epidemiological examinations. Bearing in mind the potential health problems with inorganic fibres such examinations over effect of potassium titanates whiskers of specified size on health are indispensable ones. The research programme presented in paper did not include this issue.



(a)

(b)

Figure 7 Scanning electron micrographs of samples calcined at 1150°C for 3 h and cooled to 950°C at a rate of (a) 35°C h^{-1} and (b) 25°C h^{-1}.

4. Conclusion

There were examinations on obtaining the $K_2Ti_4O_9$ potassium titanate carried out using the K_2CO_3 and TiO_2 mixture calcination method at the temperature of 900 and 1000°C and the combinative route of the $K_2Ti_4O_9$ melting method at the temperature of 1150°C and slow cooling process. $K_2Ti_4O_9$ compound obtained as a result of heating up the raw materials mixture to 900 and 1000°C formed short a rod-like crystals. Relatively thin and long $K_2Ti_4O_9$ crystals were obtained by melting $K_2Ti_4O_9$ at the temperature of 1150°C for 3 h, and then cooling to the temperature 950°C. It was confirmed that $K_2Ti_4O_9$ melts incogruently i.e. with the decomposition to $K_2Ti_6O_{13}$ (solid phase) and $K_2Ti_2O_5$ (liquid phase), however while cooling association reactions runs together with forming the $K_2Ti_4O_9$ final product whiskers. While cooling to the temperature of 950°C at the rate within the range of 50–25°C h^{-1} the association reaction runs completely. Cooling rate is a decisive factor of $K_2Ti_4O_9$ whiskers size. Applying the cooling rate of 25°C h^{-1}, $K_2Ti_4O_9$ whiskers of high length to diameter ratio significantly exceeding the minimum value required for whiskers, i.e. 20–25 can be obtained.

Acknowledgements

The authors are indebted to Dr Teresa Buczek for SEM work.

References

1. T. ENDO, H. NAGAYAMA, T. SATO and M. SHIMADA, *J. Mater. Sci.* **23** (1988) 694.
2. J.-K. LEE, K.-H. LEE and H. KIM, *ibid.* **31** (1996) 5493.
3. J.-H. CHOY and Y.-S. HAN, *Mater. Lett.* **34** (1998) 111.
4. G. L. LI, G. H. WANG and J. M. HONG, *J. Mater. Sci. Lett.* **18** (1999) 1865.
5. N. BAO, X. FENG, X. LU and Z. YANG, *J. Mater. Sci.* **37** (2002) 3035.
6. Q.-J. XUE, Z.-Z. ZHANG, W.-M. LIU and W.-CH. SHEN, *J. Appl. Polym. Sci.* **69** (1998) 1393.
7. J. LU and X. LU, *ibid.* **82** (2001) 368.
8. S. C. TJONG and Y. Z. MENG, *Polymer* **39** (1998) 5461.
9. *Idem., ibid.* **40** (1999) 7275.
10. D. YU, J. WU, L. ZHOU, D. XIE and S. WU, *Compos. Sci. Technol.* **60** (2000) 499.
11. K. SUGANUMA, T. FUJITA, K. NIHARA and N. SUZUKI, *J. Mater. Sci. Lett.* **8** (1989) 808.
12. J. H. LI, X. G. NING, H. Q. YE, J. PAN and H. FUKUNAGA, *J. Mater. Sci.* **32** (1997) 543.
13. JCPDS—ICDD, PDF2 data base (1995).
14. E. KROGH ANDERSEN, J. G. KROGH ANDERSEN and E. SKOU, *Solid State Ionics* **27** (1988) 181.
15. Y. HASEGAWA, H. TANAKA and Y. FUJIKI, *J. Ceram. Soc. Jpn.* **91** (1983) 565.
16. A. F. REID and J. A. WATTS, *J. Solid. State Chem.* **1** (1970) 310.
17. A. KABAŁA-DZIK and J. S. PASTUSZKA, *Ceramika-Materialy Ogniotrwale* No 3 (1998) 97 (in Polish).

Received 5 May 2003
and accepted 6 April 2004