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# Methods of manufacturing of potassium titanate fibres and whiskers. A review

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Titanate fibres and whiskers are new materials with high heat resistance and good chemical stability. They have found numerous applications such as ion exchanger materials, thermal insulators, reinforcements, catalysts, photocatalysts and substitutes of asbestos. In this paper, the methods of fabricating potassium titanate fibres and whiskers have been discussed, e.g., calcination, hydrothermal reaction, flux growth, sol -gel technique, and others. Because asbestos fibres are known to cause fibrotic diseases in lungs we also refer to studies into the toxicity and carcinogenicity of potassium titanate fibres and whiskers.

Keywords: *potassium titanate; fibres; whiskers; production;*

## 1. Introduction

Two types of fibres are encountered into human society: natural fibres, which have existed for 4 000 years or more, and synthetic fibres developed 100 years ago, when Count Chardonnet invented artificial silk, an achievement that had been only a pipe-dream up to then [1].

A fibre can be defined as a thin and long substance which has both strength and the capacity to be elongated to a certain extent. Because it is by definition thin, the fibre is able to bend. To characterise the thinness and the length of fibres numerically, the ratio $L/D$ of their length $L$ to their diameter $D$ is commonly used to characterize the geometry of a fibre (this is known as the aspect ratio). A fibre can be then defined as a material that has an aspect ratio of 100 or more. Fibre diameters can be used to classify various fibre morphologies, which include whiskers (< 1 μm), staples (1–10 μm), continuous multifilament yarns (5–25 μm), and continuous monofilaments (> 100 μm). A whisker or microcrystalline fibre can be defined as a material having small diameters and minimal flaws or imperfections, which have very high strength and modulus values [1, 2].

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During the last thirty years important progress has been made on inorganic fibres and whiskers. This progress appertains to the synthesis of new fibres and whiskers which have a high tensile strength, tenacity, stiffness, modulus of elasticity and heat resistance. First of all, they have found application in production of metal, organic and ceramic matrix composites. Composite materials are fundamental materials for supporting the technologies required for the 21st century, as demanded by the automobile/aircraft industries, space technology and in the leisure field, such as golf, tennis, skiing and sailing. They may therefore have a great impact on many human activities [1, 3, 4].

Glass and asbestos fibres were initially inorganic fibres. The discovery that asbestos has carcinogenic properties has motivated the search for new kinds of fibres. The technical processes of fabricating fibres like aluminosilicate, alumina, boron and silicon carbide have been developed, some of these fibres in the shape of whiskers. Fibres and whiskers are now widely applied in the field of aerospace technology, automobile technology, marine technology, optical networks, the leisure industry, and for the production of materials such as safety/protective garments and friction materials. These applications are mainly to replace metal parts and to reduce the weight for the purpose of energy conservation [1, 3, 4].

In the last decade, a new generation of inorganic fibres and whiskers – titanates – has been discovered. A series of titanates having the chemical formula $M_2O \cdot nTiO_2$ (where M = alkali metal and $n = 2–8$) are well-known. All of them have tunnel or layered crystal structures constructed out of $TiO_6$ octahedra sharing edges with interlaying cations. Because of their excellent chemical and mechanical properties, they have been used in a wide range of applications in industry as ion exchange materials, reinforcements, heat insulators, friction materials, catalysts, photocatalysts and as substitutes of asbestos [5, 6]. The following titanates have been described:

$M_2O \cdot 2TiO_2$ – $M_2Ti_2O_5$ (M = Li, Na, K, Cs) [7], $M_2O \cdot 4TiO_2$ – $M_2Ti_4O_9$ (M = Li, Na, K, Rb, Cs) [8], $M_2O \cdot 6TiO_2$ – $M_2Ti_6O_{13}$ (M = Na, K, Rb, Cs) [9–11], $M_2O \cdot 8TiO_2$ – $M_2Ti_8O_{17}$ (M = K, Rb) [12], as well as $KTiO_2(OH)$ [12], $K_3Ti_8O_{17}$ [13], $K_4Ti_3O_8$ [7], $Na_2Ti_3O_7$ [14], $Na_2Ti_9O_{19}$ and others [15].

Among alkali titanates, potassium titanates such as $K_2Ti_2O_5$, $K_2Ti_4O_9$, $K_2Ti_6O_{13}$ and $K_2Ti_8O_{17}$ have attracted much attention, due to their specific photochemical properties or their artificial cage-type structure. They have been recognized as important functional materials with wide applications [5, 6].

Among whiskers, potassium titanate whisker has several advantages compared with other ceramic whiskers. One of its most desirable features is low production cost of the whisker itself, which is one of the critical factors for commercial applications of composites [16].

## 2. Potassium titanates

The crystal structure and properties of potassium titanates, $K_2O \cdot nTiO_2$ ($n = 2–8$), are dependent on the value of $n$. Characteristic feature of potassium titanates with a high potassium content ($n = 2, 4$) is the existence of a layer structure. They exhibit a distinctive intercalation capacity and catalytic activity. However, in the case of potassium titanates with a low potassium content ($n = 6, 8$), they have a tunnel structure and exhibit good thermo-insulation properties and good chemical stability [17].

Many methods have been developed to synthesize potassium titanate fibres and whiskers, including calcination, slow-cooling calcinations, hydrothermal reactions, flux growth (melting), flux evaporation and the combinative route of flux evaporation and the slow-cooling process. Among 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 [17, 18].

### 2.1. Potassium dititanate $K_2Ti_2O_5$

Potassium dititanate $K_2Ti_2O_5$ has been the focus of intense research because of the interchangeable crystal structure that facilitates subsequent conversions into inorganic-organic/inorganic composites and new layered or three-dimensionally bonded compounds with a high photocatalytic activity [19, 20]. The crystal structure of $K_2Ti_2O_5$ consists of $(Ti_2O_5)^{2-}$ layers in which titanium atoms have fivefold coordination, separated by potassium ions (Fig. 1) [19, 21].

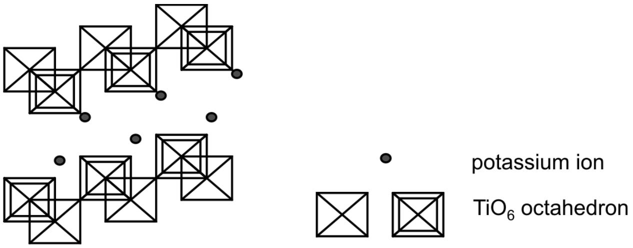

Fig. 1. Idealized crystal structure of $K_2Ti_2O_5$

According to Andersson and Wadsley [21], $K_2Ti_2O_5$ was obtained as colourless needles by melting $K_2CO_3$ and $TiO_2$ (anatase) in a platinum crucible. Whilst the crystals were kept for long periods in a desiccator, they decomposed on exposure to moist air. The layered structure of $K_2Ti_2O_5$ is not stable in water or acid solutions [20].

Bao et al. [22] synthesized $K_2Ti_2O_5$ single crystals using $K_2CO_3$ and nano $TiO_2$ (anatase) powders as starting materials with the $TiO_2/K_2CO_3$ molar ratio of 3.0. The precursors were mixed, and a small amount of water and surfactants was introduced to the mixture. The obtained paste was formed into 20 mm × 20 mm × 10 mm disks by mechanical pressing and dried in a oven at 100 °C for 10 h. The disks were then sintered in a muffle furnace at a calcination temperature of 830 °C for 10 h, and quickly removed at the end of the calcination for air-cooling. Monocrystals of $K_2Ti_2O_5$ obtained in the above way had the same size, morphology and surface; at 852 °C they transformed into $K_2Ti_4O_9$ whiskers. The following steps of their synthesis have been reported:

$$K_2CO_{3(solid)} \rightarrow K_2O_{(solid)} + CO_{2(gas)} \text{ at } T < 828\ °C$$

$$2TiO_{2(solid)} + K_2O_{(solid)} \rightarrow K_2Ti_2O_{5(solid)} \text{ at } T = 828\ °C$$

$$2K_2Ti_2O_{5(solid))} \rightarrow K_2Ti_4O_{9(solid)} + K_2O_{(liquid)} \text{ at } T = 952\ °C$$

Similarly as in the previous work, hydrous titanium dioxide $TiO_2{\cdot}nH_2O$ and $K_2CO_3$ were used to fabricate $K_2Ti_2O_5$ single crystals [18]. A reactant mixture with the $TiO_2/K_2CO_3$ molar ratio of 3.0 was dried in an oven at 90 °C for 10 h, calcination was performed in a muffle furnace at 820 °C for 30 min. Then the sintered mixture was removed from the furnace and cooled in air. The synthesized $K_2Ti_2O_5$ single crystals had the same properties as that fabricated by Bao et al. [22].

Masaki et al. [23] obtained potassium dititanate by the hydrothermal method, by oxidation of titanium metal powder in concentrated potassium hydroxide solution. 50 $cm^3$ of KOH aqueous solution and 10 g of Ti powder were placed in an autoclave with a magnetic stirrer. After being sealed, the autoclave was set into an electric furnace for 2 h at a desired temperature. Then it was taken out from the furnace and cooled immediately in air. The product was separated from the solution by the use of centrifuge, then rinsed with methanol, and finally dried at 105 °C for 12 h in an oven to remove the absorbed water. Well crystallized platelet crystals of hydrated $K_2Ti_2O_5$ were formed as single phases having KOH concentrations ranging from 20 to 25 mol/kg $H_2O$ at temperatures from 150 to 200 °C. Crystalline $K_2Ti_2O_5$ was also obtained from the amorphous compound synthesized at KOH concentration above 80 mol/kg $H_2O$ at 150 °C by heating at 800 °C.

### 2.2. Potassium tetratitanate $K_2Ti_4O_9$

Crystalline potassium tetratitanate ($K_2Ti_4O_9$), with a characteristic layered structure, consists of $TiO_6$ octahedra linked with K ions (Fig. 2) [24, 25]. Considering its strong ion exchange properties, $K_2Ti_4O_9$ can be widely used as an ion exchanger for alkali metal ions, alkali earth metal ions and divalent transition metal ions. Furthermore, $K_2Ti_4O_9$ shows good catalytic and photocatalytic activity which enables their application as catalysts and photocatalysts. Potassium tetratitanate fibres and whiskers have been prepared among others by calcination, slow cooling calcination and sol- gel technique [26].

Andersen et al. [26] synthesized potassium tetratitanate by a conventional solid state reaction. Potassium carbonate ($K_2CO_3$) and anatase ($TiO_2$) in the molar ratio of 1:4 were milled together in slurry with absolute ethanol saturated with potassium carbonate. The solid was separated, air dried, and 2 g tablets were formed by mechanical pressing. The tablets were then heated at 900 °C for 48 h.

Andersen et al. [26] also synthesized $K_2Ti_4O_9$ by the sol-gel method. The solution of titanium isopropoxide in dry *n*-propanol was added slowly to a solution of potassium *t*-butoxide in dry methanol. The molar ratio of $KOC_4H_9$ to $Ti(OC_3H_7)_4$ was 1:2. This clear solution was hydrolyzed with a solution of water in *n*-propanol. The amount of water for hydrolysis was 4 mol $H_2O$ per mol $Ti(OC_3H_7)_4$ plus 1 mol $H_2O$ per 1 mol $KOC_4H_9$. The obtained gel was stirred for three days. Most of the liquid phase was then removed by centrifugation and decantation. The gel was dried in air at room temperature on a glass plate. The resulting white powder was heated for 1 h at 100 °C and then at 900 °C for 60 h. $K_2Ti_4O_9$ fabricated by Andersen et al. [26] was hydrolyzed to obtain hydrous titanium(IV) oxide ($H_2Ti_4O_9{\cdot}nH_2O$) which is an ionic conductor like other hydrous metal oxides ($Sb_2O_5{\cdot}nH_2O$, $ZrO_2{\cdot}nH_2O$, $SnO_2{\cdot}nH_2O$).

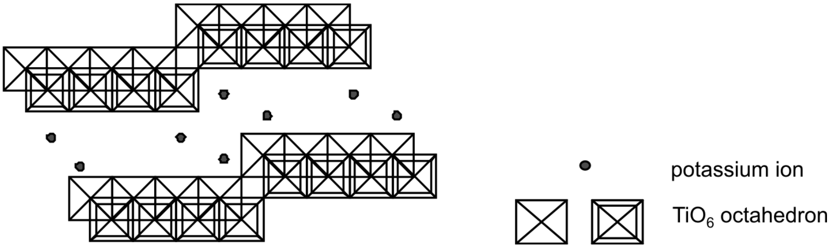

Fig. 2. Idealized crystal structure of $K_2Ti_4O_9$

Bao et al. [18] obtained $K_2Ti_4O_9$ whiskers by the calcination process. Hydrous titanium dioxide was mixed with $K_2CO_3$, and then the reactant mixture was dried in an oven at 90 °C for 10 h. Also, a mixture of anatase–$K_2CO_3$ was applied. Calcination was carried out in a muffle furnace at 920 °C for 30 min. The stirred mixtures were then removed at the corresponding calcination temperature, cooled in air and leached in boiling water for 2 h. $K_2Ti_4O_9$ whiskers had a uniform size and good morphology. Compared with anatase, amorphous hydrous titanate lowered the phase change temperature.

Another method to synthesize $K_2Ti_4O_9$ fibres is based on ion exchange and gelation of sodium alginate $(C_5H_7O_4COONa)_x{\cdot}yH_2O$, which is well known as an ion exchangeable organic polymer. This method does not require expensive reagents. In addition, viscous solutions of sodium alginate have an advantage in that it gel in any shape, such as fibre, film, and bead, by ion exchange with protons or multivalent metal ions. 5 g of sodium alginate was added slowly to 100 g of vigorously stirred deionized water. Stirring was continued for 5 h, and then the solution was degassed with a vacuum pump, after which it was left for 24 h to remove air bubbles. An aqueous solution of 5% sodium alginate was extruded from a nozzle into 1 M HCl. The extruded sodium alginate sol turns into alginic acid gel fibre through the ion exchange of its sodium ions with protons in the HCl solution. The alginic acid (H-alginate) fibre was rinsed in deionized water three times, dried in air for 24 h, and then immersed into a mixture of titanium sulfate ($Ti(SO_4)_2$) and potassium nitrate ($KNO_3$) for more than

10 h. The obtained K-Ti alginate fibre was rinsed in deionized water, dried at ambient temperature and then heated at 800 °C for 3 h in air. The average length and thickness of the potassium tetratitanate fibres were about 2.5 cm and 150 μm, respectively [27].

According to Fujiki and Yoshinori [28], $K_2Ti_4O_9$ fibres can be produced at low cost without using any flux or catalyst. Starting materials, $TiO_2$ and $K_2CO_3$, are mixed at the ratio satisfying the general formula $K_2O{\cdot}n TiO_2$ with $n$ ranging from 3 to 5. The mixtures of powders were then heated in the temperature range from 950 °C to 1300 °C and then cooled slowly to 900–950 °C and left for decomposition for 3 to 5 h. Afterwards the crucibles were taken out of the furnace into open air, and allowed to cool to room temperature. The products were washed with cold or warm distilled water and dried at 100 °C. The production process is strongly dependent on the molar ratio of $TiO_2/K_2O$, the starting materials and the cooling rate. In order to obtain potassium tetratitanate fibres on an industrial scale, it is advisable to apply the decomposition temperature in the range 1100–1150 °C. The product must be held at this temperature for at least 4 h and then cooled at a low rate of 15–35 °C per h for satisfactory growth rate of fibres.

Recently, fibrous potassium tetratitanate was obtained at the Silesian University of Technology in the following way: The substrates, $K_2CO_3$ and $TiO_2$, were first ground in an agate mortar in isopropyl alcohol and dried. A powdered stoichiometric mixture was then placed into platinum crucibles and heated to 900–1000 °C in a box furnace. Obtained $K_2Ti_4O_9$ formed short and tightly packed rod-like crystals. Further $K_2Ti_4O_9$ syntheses were carried out by heating the mixture of raw materials to 1150 °C for 3 h thus, causing $K_2Ti_4O_9$ to melt incongruently. $K_2Ti_4O_9$ melts at 1114 ± 15 °C decomposing to $K_2Ti_6O_{13}$ stable solid phases and $K_2O$-rich liquid phases, which creates $K_2Ti_2O_5$. Then the samples were cooled to 950 °C in a furnace at the cooling rate within the range 50–25 $°C{\cdot}h^{-1}$. On cooling, $K_2Ti_4O_9$ whiskers were formed and the association reaction occurred as follows:

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

Fig. 3. SEM of $K_2Ti_4O_9$ whiskers synthesized by the calcination at 1150 °C for 3 h and cooled to 950°C at the rate of 35$°C{\cdot}h^{-1}$ [29]

Fig. 4. SEM of $K_2Ti_4O_9$ whiskers synthesized by the calcination at 1150 °C for 3 h and cooled to 950 °C at the rate of 25$°C{\cdot}h^{-1}$ [29]

The cooling rate was found to be a determining factor of the size of $K_2Ti_4O_9$ whiskers. At the cooling rate of 50 °C·h$^{-1}$, the whisker length was up to 60 μm. The cooling at 35 °C·h$^{-1}$ caused $K_2Ti_4O_9$ to decompose more quickly (Fig. 3). At the lowest cooling rate (25 °C·h$^{-1}$), whiskers of a high aspect ratio, exceeding the minimum value required for whiskers, were obtained (Fig. 4) [29–32].

### 2.3. Potassium hexatitanate $K_2Ti_6O_{13}$

Potassium hexatitanate belongs to materials attracting a growing interest, due to its potential economic importance. This relatively cheap, fibrous material has good thermal durability, chemical resistivity and dispersibility and has been found to be useful as a reinforcement material for plastic and ceramics, heat-insulating paints and automotive brake linings [17, 25, 33–37]. The structure of this material is one in which the structural unit of three $TiO_6$ octahedra forms the tunnels with sharing edges and joining through the corners as shown in Fig. 5 [25]. Because potassium ions in $K_2Ti_6O_{13}$ are enclosed by the tunnelling structure and isolated from the environment, potassium ions can not escape from the tunnelling structure in the solution [35]. This tunnel structure has also attracted additional interest because of its possible application as a photocatalytic material [25, 33, 38].

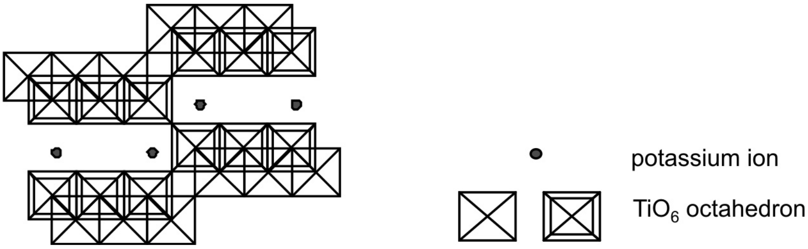

Fig. 5. Idealized crystal structure of $K_2Ti_6O_{13}$

$K_2Ti_6O_{13}$ whiskers may be synthesized by the calcination and slow cooling method. As starting materials, $K_2CO_3$ and $TiO_2$ were used in the molar ratio $K_2O/TiO_2$ 1:3. The powder mixture was milled for 24 h with ethanol and subsequently dried. Then a platinum crucible was filled with the mixture and heated to 1150 °C for 6 h. After having been stored for a specified time at an assigned temperature, the specimens were slowly cooled to 950 °C at the rate of 16 °C·h$^{-1}$ in a furnace and quenched in water. During calcination at 1150 °C, rod-like $K_2Ti_6O_{13}$ particles were formed, and $K_2Ti_4O_9$ whiskers were formed from $K_2O$-rich phase and $K_2Ti_6O_{13}$ during slow cooling (by the splitting of $K_2Ti_6O_{13}$ layers). The final $K_2Ti_6O_{13}$ whiskers were obtained from $K_2Ti_4O_9$ after treatment with boiling distilled water for 4 h and subsequent reheating to 1000 °C for 1 h. The $K_2Ti_6O_{13}$ whiskers had a clean surface and the length exceeding 100 μm [17].

Potassium hexatitanate fibres were fabricated by the combinative route of flux evaporation and slow cooling. 1 wt. % of $Li_2CO_3$ was added to $K_2MoO_4$ flux to enhance evaporation of the flux, then the flux ($Li_2O–K_2MoO_4$) and raw materials ($K_2O:TiO_2 = 1:6$) were mixed in an agate mortar. The molar ratio of flux to raw materials was kept at 7:3, which was found to lead to the optimum growth condition. After calcining at 1150 °C for 4 h, the sample was slowly cooled to 900 °C in a furnace at the rate of 10 $°C·h^{-1}$, and then quenched in air. The product was washed with distilled hot water and dried at 110 °C. The $K_2Ti_6O_{13}$ fibres grown by this process had a columnar type shape with very smooth and clean surface. They had a very uniform size, 1.5 mm in length and 2–3 μm in diameter [36].

Yokoyama et al. [37] synthesized $K_2Ti_6O_{13}$ long fibres by the flux evaporation method using $Na_2O–K_2O–B_2O_3$ flux fabricated from $Na_2CO_3$, $K_2CO_3$ and $B_2O_3$ in various molar ratios. Non-fibrous $K_2Ti_6O_{13}$ was prepared by solid-state reaction of $K_2CO_3$ and anatase ($TiO_2$) at 1450 °C. The mixture of $K_2Ti_6O_{13}$ and flux was put into a platinum crucible, heated at 1050 °C for 1–15 h, and then rapidly cooled to room temperature in air. The products were separated by dissolving the flux with HCl. It was found that the addition of $Na_2O$ to $3K_2O·5B_2O_3$ flux was highly conducive to the growth of long $K_2Ti_6O_{13}$ fibres.

Synthesis of potassium hexatitanate fibres was also carried out by hydrothermal reactions by using potassium hydroxide solution and titanium tetraisopropoxide as raw materials in a K:Ti molar ratio of 1:2. Both reactants were thoroughly stirred for 30 min to 1 h before heating in the autoclave using a nickel tube. Heating temperatures of 350 °C, 400 °C and 450 °C and heating durations of 2.5 and 25 h were employed. The products were allowed to cool slowly in an autoclave followed by filtering, washing with distilled water and ethanol, and finally drying at 50 °C for about 24 h. $K_2Ti_6O_{13}$ fibres synthesized hydrothermally were stable, long, felt-like, thin, of large surface area as compared with the fibres obtained from the solid state method. The heating temperature and duration employed in the hydrothermal synthesis do not seem to have much effect on the crystal morphology and structure of the fibres, but do have an effect on their size [38].

$K_2Ti_6O_{13}$ fibres were fabricated by ion exchange reaction from potassium tetratitanate fibres ($K_2Ti_4O_9$) based on the thermodynamic model. $K_2CO_3$ and hydrous titania ($TiO_2·nH_2O$) at the molar ratio of 3.0 were mixed and then dried in an oven at 90 °C for 10 h. To prepare $K_2Ti_4O_9$ fibres (initial material), the mixture was sintered in a muffle furnace at 960 °C for 10 h. The sample was then removed from the furnace and cooled in air. Fibrous $K_2Ti_4O_9$ was suspended in vigorously stirred water, simultaneously while adding 1 M HCl continuously, the pH value and the concentration of potassium ions were controlled, to obtain the hydration intermediates which were separated by filtration and washed with distilled water, followed by drying at room temperature in a desiccator. The final product, $K_2Ti_6O_{13}$ fibres, were synthesized by heat treatment of intermediate ($K_{1.33}H_{0.67}Ti_4O_9·H_2O$) at 850 °C in a muffle furnace for 2 h. Fibres had a structure similar to that of $K_2Ti_4O_9$ which was used as a precursor [39].

Liu et al. [40] also obtained potassium hexatitanate fibres by the ion exchange approach using fibrous potassium titanate ($K_4Ti_3O_8$) as an initial material. Synthesis of $K_4Ti_3O_8$ was carried out by mixing $TiO_2$ with 80 wt. % concentrated KOH solution at 220 °C for 2 h under atmospheric pressure. The hydrolytic process was carried out, while controlling the pH value from 10.9 to 12.00, to obtain the hydrolytic intermediates from $K_4Ti_3O_8$ fibres, which next were heated at 610 °C in a muffle furnace for 2 h and then fibrous $K_2Ti_6O_{13}$ was formed. Fibres had an average length of 10–30 µm and the mean diameter of 0.3–1.0 µm.

Potassium hexatitanate ($K_2Ti_6O_{13}$) whiskers were also synthesized by the calcination and slow cooling method in the Department of Chemistry, Inorganic Technology and Fuels at the Silesian University of Technology. Starting materials were dry $K_2CO_3$ and $TiO_2$ reagent grade. The molar ratio of $K_2O$ to $TiO_2$ was 1:6. After being ground in an agate mortar under isopropyl alcohol and subsequent drying, platinum crucibles were filled with the powder mixture and heated to 1150 °C at the rate of 300 $°C·h^{-1}$ in a box furnace. After calcination at 1150 °C for 3 h various methods and rates of cooling were applied. The mixture containing an excessive amount of $K_2CO_3$ was also examined (molar ratio $K_2O:TiO_2 = 1:2$). The samples of such mixture were also heated to 1150 °C. After 3 h of calcinations, these samples were slowly cooled to 950 °C at an adjusted rate and quenched in water or treated in distilled boiling water (for 1 or 4 h). Then it was decanted, dried at 50 °C and reheated at 1000 °C for 1 h. The residual water after decantation was checked for the presence of potassium ions, by conducting conventional reactions, characteristic of $K^+$ ions. The samples ($K_2O:TiO_2 = 1:6$) calcined at 1150°C proved that $K_2Ti_6O_{13}$ final product was created regardless of the cooling conditions. A slow cooling rate resulted in more crystalline $K_2Ti_6O_{13}$ in comparison with samples cooled rapidly.

Fig. 6. SEM of $K_2Ti_6O_{13}$ whiskers synthesized by the calcination and slow cooling [31]

The samples of the mixture with an excess of $K_2CO_3$ after heat treatment at 1150 °C, cooling and quenching in water and drying, were not homogeneous, they were partially compact and X-ray amorphous. Secondary heat treatment at 1000 °C caused crystallization of $K_2Ti_6O_{13}$, but the crystals had the shape of weakly split prisms. The applied treatment of the samples in boiling water, before secondary heating, contributed to splitting of the prisms into single whiskers. The longest $K_2Ti_6O_{13}$ crystals, up to 550 µm long (Fig. 6), were obtained using initial heat treatment of the mixture with excess of $K_2CO_3$ at 1150 °C, followed by cooling to 950 °C at the rate of $25°C\cdot h^{-1}$, treatment of the sample in boiling water for 4 h and subsequent reheating to 1000°C for 1 h [31, 33, 34, 43].

## 2.4. Potassium octatitanate $K_2Ti_8O_{17}$

Potassium octatitanate $K_2Ti_8O_{17}$ possesses a stable tunnel-like structure, i.e. it has a framework enclosing tunnel structures formed by edge- and corner-shared $TiO_2$ octahedra (Fig. 7) [12]. $K_2Ti_8O_{17}$ exhibits characteristic properties such as a high thermal insulating ability, chemical stability and, compared with potassium hexatitanate ($K_2Ti_6O_{13}$), high ion conductivity. $K_2Ti_8O_{17}$, difficult to obtain, may be used as a novel functional material, also as an advanced reinforcement material, for example as a composite or friction material for braking systems.

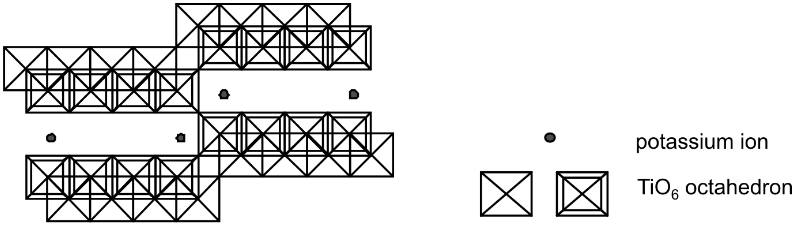

Fig. 7. Idealized crystal structure of $K_2Ti_8O_{17}$

One of the methods to synthesize $K_2Ti_8O_{17}$ is the hydrolysis of $K_2Ti_4O_9$. The starting material, $K_2Ti_4O_9$, was obtained by heating a mixture of $KNO_3$ and $TiO_2$ (anatase) in the molar ratio 1:2 at 1000 °C for two days. Then the hydrolysis of potassium tetratitanate was carried out by heating it with $H_2O$ at 100 °C for three days. After thermal treatment of $KH_3OTi_4O_9$ previously obtained at 500 °C, potassium octatitanate was formed [12].

Fibrous octatitanate ($K_2Ti_8O_{17}$) was obtained from fibres of $K_2Ti_4O_9$, which were fabricated by melting of a mixture of $TiO_2$ and KCl (molar ratio 3:1) with addition of flux $K_2MoO_4$ at 1100 °C. Then the mixture was cooled slowly at the rate of $4\ °C\cdot min^{-1}$. Next fibrous $K_2Ti_4O_9$ was converted into a protonated form by treatment with HCl aqueous solution. The resulting product, $H_2Ti_4O_9\cdot nH_2O$, was dried and shaken with a mixed solution of KCl and KOH to obtain $KHTi_4O_9\cdot 0.5H_2O$, which next was dehydrated by heating at 500 °C. The final product was fibrous $K_2Ti_8O_{17}$ with fibres 0.5–1.0 mm long and 0.01–0.03 mm thick [42].

Whiskers of potassium octatitanate were fabricated by thermal treatment of $KHTi_4O_9\cdot nH_2O$, which was prepared by exchanging one-half of the $K^+$ ions in fibrous $K_2Ti_4O_9$ with $H^+$ ions using aqueous HCl. Pure $KHTi_4O_9$ was obtained by treating of $K_2Ti_4O_9$ with 0.005 M HCl for 30 min. The thermal treatment at temperatures ranging from 250 °C to 500 °C for 3h, however, enables obtaining only $K_2Ti_8O_{17}$. This compound was decomposed above 600 °C to $K_2Ti_6O_{13}$ and $TiO_2$. The average length and diameter of the $K_2Ti_8O_{17}$ whiskers were 125 and 1 μm, respectively [41].

In a similar way, He et al. [39] synthesized $K_2Ti_8O_{17}$ fibres by ion exchange, starting from potassium tetratitanate ($K_2Ti_4O_9$) fibres. To obtain $K_2Ti_4O_9$, dried mixture of $K_2CO_3$ and hydrous titania ($TiO_2 \cdot nH_2O$), in a molar ratio $TiO_2/K_2O$ of 3.0, was sintered in a muffle furnace at 960 °C for 10 h. The so-produced, fibrous $K_2Ti_4O_9$ was vigorously stirred under water while 1 M HCl was introduced continuously. pH value of the resulting solution was 0.5. The hydration intermediate was then filtered, washed with distilled water and dried at room temperature in a desiccator. The further thermal treatment at 500 °C for 2 h produced fibres of $K_2Ti_8O_{17}$ of the diameter of 0.2–1 μm and 10–30 μm long.

In the Department of Chemistry, Inorganic Technology and Fuels, Silesian University of Technology, a research aimed at identifying possible routes of synthesis of potassium octatitanate was conducted [43]. It was carried out by two methods: solid state reaction (conventional) and ion-exchange reaction. In the former case, a mixture of starting materials ($K_2CO_3$ and $TiO_2$) was subject to thermal treatment in two separate ways: one method was based on gradual linear heating of the precursors right up to the target temperature, at which calcinations were promptly aborted, and the other was based on isothermal processing of the precursors for a specified time period. Next, the samples were dried and heated at 400–700 °C. Obtaining of $K_2Ti_8O_{17}$ by a conventional method was not possible, pure $K_2Ti_8O_{17}$ could be synthesized, however, using the method based on ion-exchange reaction. Samples of $K_2Ti_4O_9$ were treated with hydrochloric acid to remove potassium ions from the structure. Next, the samples were heated in the temperature range 400–500 °C. The shape of the obtained $K_2Ti_8O_{17}$ crystals was the same as the primary shape of $K_2Ti_4O_9$ crystals. The experiment confirmed that $K_2Ti_8O_{17}$ decomposes above 600 °C.

## 3. Nano potassium titanate

In the past decade, the design and fabrication of nanostructures (structures with one of the characteristic sizes not exceeding 100 nm) based on metal oxides has attracted much attention because of their unique physical, mechanical and chemical properties and their potential applications in nanodevices. Nanofibres, nanorods, nanotubes and nanowires based on alkali metal titanates have been widely used as semiconductors in dye-sensitized solar cells, water treatment materials, catalysts, photocatalysts, gas sensors, nanoelectronic and optoelectronic nanodevices [44, 45].

$K_2Ti_6O_{13}$ nanowires were synthesized by a simple hydrothermal reaction between $Na_2Ti_3O_7$ and KOH. Sodium trititanate was made by solid state reaction at 1000 °C using $Na_2CO_3$ and $TiO_2$ (anatase) as raw materials. Then aqueous solution of KOH or KCl (concentrations from 3 to 10 M) was introduced to the $Na_2Ti_3O_7$ and the obtained paste was heated in a furnace at 150–250 °C for 24–72 h. A large quantity of nanowires, with the uniform diameter around 10 nm and the length ranging from several hundred to several thousand nanometers, were obtained by using 10 M KOH and heating the mixture at 200 °C for 72 h. A lower heating temperature (150 °C) resulted in low quantity of nanowires, while at a higher temperature (250 °C) the nanowires were shorter. For comparison, 3 M KOH or KCl solutions were used for the reaction and the results obtained were similar [46].

Potassium hexatitanate nanowires were fabricated by the hydrothermal synthesis under supercritical conditions using a plug-flow reactor. The starting materials, sols of titanium hydroxide and potassium hydroxide, were prepared by mixing these materials into distilled water. Concentration of titanium ion was 0.02 M and concentration of potassium hydroxide was varied in the range of 0.002–0.4 M. Reactants and the preheated distilled water were supplied to the reactor and mixed, and then heated rapidly (to 350, 400 and 420 °C). Residence time was 2–3 s under the pressure of 30 MPa. The resulting product was dried in an oven at 60 °C for 24 h. Well crystallized nanowires 10 nm in diameter and the length ranging from 500 to 1000 nm were obtained at 400 °C under 30 MPa. In comparison with the conventional hydrothermal method which proceeds for several hours, this method enables fabrication of nanoscaled potassium hexatitanate particles, even at nearly the same temperature and pressure, since the reaction time is limited to the order of several seconds [47].

Titanate nanowires of $K_2Ti_8O_{17}$were synthesized hydrothermally via a reaction of titania particles and KOH solution (the concentration of KOH solution was in the range of 4–25 M). Hydrothermal treatment was carried out in a teflon-lined autoclave for one or two days in the temperature range of 130–240 °C. The nanowires were almost uniform with the diameter of 5–10 nm and the length in the range from several micrometers to several tens micrometers. During calcination in a conventional muffle above 600 °C, $K_2Ti_8O_{17}$ nanowires tend to decompose to $K_2Ti_6O_{13}$ and $TiO_2$ [48, 49].

$K_2Ti_8O_{17}$ nanowires have also been prepared in a one-step hydrothermal reaction between pure Ti and KOH solution. In a typical experiment, commercially available $TiO_2$ powder was added to 20 ml of ca. 1 M aqueous solution of KOH. Then the mixture was heated in a sealed autoclave at 200 °C for 3 days. After heating, the products were filtered and washed with deionized water. Nanowires were the final product. In another experiment, instead of Ti powder, Ti plates were used. During the process the whole Ti plate was consumed. The product was a brown coloured block composed of layered structures with a lot of open pores. The layers consisted of nanowires. The length of the nanowires ranged from several hundred nanometres to more than 8 μm and the diameter was around 40 nm [50].

Alkali titanate nanorods ($K_2Ti_8O_{17}$ and $Na_2Ti_3O_7$) were fabricated by the hydrothermal synthesis. 1.5 M HCl was used to adjust pH of distilled water to 2. Titanium tetrachloride ($TiCl_4$) was then dissolved in 30 ml of acid solution to get a concentration of 0.04 M, to which 10 ml, 25 M AOH (A = Na and K) aqueous solution was added. The mixture was stirred for 10 min and then transferred into a Teflon-lined stainless autoclave, sealed and maintained at 180 °C for 48 h. The product obtained was thoroughly washed with distilled water until all the chloride was removed, and finally dried at 60 °C for 3 h. Sodium and potassium titanate nanorods had average diameters of 50 nm and 30 nm, respectively, with the lengths of up to several micrometers [51].

# 4. Influence of inorganic fibres on living organisms

Pulmonary fibrosis (asbestosis), lung cancer and mesothelioma are known to occur after exposure to asbestos in both humans and animals. Therefore, inorganic (man-made) and natural fibres have been often substituted for asbestos. Although numerous inhalation studies demonstrated no significant increase in tumour incidence in animals exposed to such substitutes, several mineral fibres (refractory ceramic fibres and fibre glass) were carcinogenic in rodent chronic inhalation studies. Moreover, in animal intraperitoneal studies, the fibre length of asbestos and other mineral fibres has been found to be one of the major descriptors of tumorigenicity.

Fibre dimension, durability, chemical composition and surface properties are thought to be important factors in the evaluation of potential fibre toxicity. Fibre diameter is a critical determinant of respirability. Respirable fibres have a mass median aerodynamic diameter not higher than 3.5 µm, the length over 5 µm and the ratio of the length to diameter of over 3 [52].

A variety of inorganic fibres such as mineral wool, continuous filament, superfine and refractory or ceramic MMMF are known as man-made mineral fibres (MMMF). The names of these classes of materials have different origins and are not necessarily mutually exclusive.

## 4.1. Influence of ceramic fibres on living organisms

Ceramic fibres comprise a wide range of amorphous or crystalline synthetic mineral fibres characterized by their refractory properties (i.e., stability at high temperatures). They are typically made of alumina, silica and other metal oxides, or less commonly of nonoxide materials such as silicon carbide. Since there are several types of ceramic fibres there is also a range of chemical and physical properties [53]. Their trade names are Zirlane, Kerlane, Pyronap, Keronap, Kaowoll, Fibrefrax, Pyroblok, Cartolane, Fibremax, Mattec, Saffil, Rubill, Nextel, aluminosilicate, aluminium oxide silicate, aluminium silicom polder, DOT, ceramic fibre, cyanite, Disthene, Kaopolite, Kyanite, Mullite, Oil-Dri, SafeN-Dri, Silicotic, Acid Aluminium Salt, Snow Tex, UN 1389, Valfor, Fybex, MAN, PKT, Langfaster, Thermowool [53].

The primary route of potential human exposure to ceramic fibres is by inhalation, mainly during manufacture and formation, especially in the workplace. The workplace population is exposed to potential contact with ceramic fibres mainly in the manufacturing environment, during installation, and during removal. Epidemiological research on relatively large populations exposed to ceramic fibres strongly suggests that these fibres can act as skin irritants as well as eye irritants, affecting the conjunctiva and possibly causing focal pleura fibrosis. At present, such research has not provided convincing proof which indicates that there is a growing risk of tumour illness associated with these fibres. This viewpoint is based upon consideration of a relatively short period of exposure, as well as from the fact that a significant proportion of employees working in this industry was exposed to asbestos previously [53–57].

Results of experimental research carried out on laboratory animals (rats and hamsters) exposed via inhalation to ceramic fibres or on animals that had been given ceramic fibres via surgical implantation in trachea indicate that some ceramic fibres can induce tumours of lungs (adenomas and cancers) and pleura (mesotheliomas). Tumours of lungs and pleura occurred principally in single animals, the number of diseased animals was linked to the concentration (or dose) of fibres relative to the duration of exposure. Also, some kinds of fibres that had been inserted directly into body cavities (pleural or abdominal) did induce tumours – mesotheliomas. Research on the solubility of the fibres has not provided convincing data that those fibres of low solubility are strongly carcinogenic influence [53–57].

Results from numerous studies lead to the conclusion that basically all types of elongated dust particles can induce tumours if they are sufficiently long, thin and durable in the tissue [54].

Experts at the International Agency for Research on Cancer (IARC) maintain that a documentary evidence of the results of experimental research on animals does exist, showing that ceramic fibres do have a carcinogenic influence. However, there is no information about the carcinogenic influence of ceramic fibres on humans. Thus, according to the IARC, they have been classified to group 2B, this is possibly carcinogenic to humans [58]. However, experts at the European Union have classified refractory ceramic fibres for special purposes, for substances of category 2, this is for substances investigated as carcinogenic for humans with attributed expression R49 which can cause cancer in repercussion of exposing respiratory tract [58].

### 4.2. Influence of titanate fibres and whiskers on living organisms

It is well known that the inhalation of asbestos in the working environment leads to pulmonary fibrosis, lung cancer and mesothelioma. Various kinds of asbestos substitutes are now being produced, but the fibrous nature of these substances similar to asbestos, and their health effects, are still being investigated. One of these substitutes are fibres and whiskers of potassium octatitanate. These materials have a wide range of industrial applications due to their high tensile strength, weight advantage over metals, and stability at high temperatures [59–61].

Animal studies, which were carried out in 1981, show that whiskers of potassium octatitanate which are used in filters, separators and catalyst carriers, cause fibrosis, suggesting fibrogenic potential similar to that of asbestos [59].

Chronic inhalation toxicity/carcinogenicity studies on fibres of potassium octatitante (TISMO) have been carried out in the last few years on rats. Fibre dimension was mostly lower than 50 μm in length and lower than 2 μm in width. Rats were exposed via whole-body inhalation of fibres in concentrations of 0, 20, 60, or 200 fibres/cm$^3$ 6 h/day, 5 day/week for 24 months. Some rats were killed after 3, 6, 12, 18 and 24 months of exposure for lung damage evaluations. Other rats were removed from the exposure after 6 months and then from this group 6 rats were killed at 3, 6, 9, 12 and 18 months later to study lung clearance. Results of studies have shown that there were no abnormalities in the fibre retention and the lung clearance rate. There was only negligible macrophage response to TISMO at 20 fibres/cm$^3$ exposure. Also, sometimes minimal collagenized pulmonary fibrosis was found at 60 or 200 fibres/cm$^3$for 24 month inhalation exposure, but neither pulmonary neoplasm nor pleural mesotheliomas were present [62].

Also a study was carried out of airborne concentration and the exposure-related potential hazard of potassium octatitanate fibres (TISMO). The airborne fibres were measured at 14 designated production workplaces once a year for a period of 2 days from 1994 to 1999. A health hazard evaluation was carried out on 27 current employees and 18 former employees. The average employment of the current employees was 7.6 years while that of the former was 5.9 years. In 1994, the fibre concentrations ranged from 0.2 to 1.6 fibres/cm$^3$ and decreased to 0.10–0.14 fibres/cm$^3$ in 1999. There were no exposure-related abnormalities in both pulmonary function and radiographic screening in the fibres found in production workers. Based on the animal experiments and medical surveys on workers, exposure to fibre concentrations not higher than 1 fibre/cm$^3$ would not constitute a significant health hazard to humans in the workplace [62].

In 2005, the WHO Workshop on Mechanism of Fibre Carcinogenesis and Assessment of Chrysotile Asbestos Substitutes considered that respirable potassium octatitanate fibres are likely to pose a great hazard to humans after inhalation exposure [63].

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