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Synthesis of potassium polytitanate precursors by treatment of TiO_2 with molten mixtures of KNO_3 and KOH

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Abstract

The synthesis of potassium titanate by treatment of TiO_2 with molten mixtures of KNO_3 and KOH was investigated. The stage of TiO_2 transformation into potassium titanate depends on the temperature of treatment, contents of KOH in the molten salt mixture and admixtures of K_2CO_3. The investigation of the chemical and phase composition as well as the size distribution of the powder produced allowed to consider the product obtained as a potassium polytitanate. The mechanism of the potassium polytitanate synthesis is analyzed. It is shown that the synthesized powder is a promising precursor to produce ceramics based on $K_2Ti_6O_{13}$ and characterized with high mechanical properties.

Keywords: $K_2Ti_6O_{13}$; Sintering; Mechanical properties; TiO_2

1. Introduction

Potassium titanates with high mechanical properties and thermal resistance are interesting for industrial applications as new and promising fillers for polymer and Al-based alloy composites. This type of materials is an alternative to silicon carbide, taking into account its lower price.[1–6] On the other hand, potassium titanate powders could be used to produce ceramics characterized with high mechanical properties and thermal resistance. However, the production of such powders (for example, $K_3Ti_9O_{13}$, $K_2Ti_6O_{13}$) is based on multistage methods that involve sintering at high temperatures (1000 °C).[7]

Molten salt synthesis allows low temperature preparation of nano-sized powders with properties that are interesting for different applications.[8] Some titanates have been reported as produced with this method;[9–11] nonetheless, the processes described were based on the use raw materials of $TiOCl_2$ as one of. The use of an alternative material to the toxic and expensive titanium oxochloride is desirable; in this regards the production of potassium titanates by means of the treatment of TiO_2 powders in molten nitrates seems quite promising in favoring cost reductions and avoiding the use of toxic substances. However, such synthesis is limited by the relatively low solubility of TiO_2 in the molten nitrates;[8] nonetheless, the introduction of alkali hydroxides in such salts mixture permits the regulation of the process of synthesis, since the TiO_2 dissolution is thus increased. Such modified molten salt synthesis has been previously reported,[12–15] where solid substrates (oxides or silicates) were treated in molten mixtures of KOH (or KOH–NaOH eutectic) and some salts (KNO_3, $NaNO_3$, $LiClO_4$, etc.) used as oxidizer. An initial induction period was recognized in these investigations and indicated as a stage of dissolution and transformation of solid raw materials.[15]

On this basis, it was attractive to investigate the possibility to produce potassium titanates by treatment of TiO_2 powder in molten salt mixtures of different basicity, regulated with the admixtures of alkali hydroxide. Moreover, to characterize the structure and properties of ceramic materials thus obtained with potassium titanate precursors.

2. Experimental procedures

The following substances of chemical grade (Aldrich, 99+%) were used for the experiments: TiO_2 (anatase),

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Table 1
Composition of mixtures used to produce potassium titanate precursors

No.	Concentration of components in wt.% (mol.%)			
	TiO_2	KNO_3	KOH	K_2CO_3
1.1	10.0 (12.3)	90.0 (87.7)		
1.2	10.0 (11.9)	85.0 (84.7)		5.0 (3.4)
2.1	10.0 (12.1)	88.0 (84.4)	2.0 (3.5)	
2.2	10.0 (11.8)	85.0 (79.7)	5.0 (8.5)	
2.3	10.0 (11.6)	82.0 (75.2)	8.0 (13.2)	
3.1	10.0 (12.0)	80.0 (76.0)	5.0 (8.6)	5.0 (3.5)

KNO_3, K_2CO_3, KOH. The mixtures investigated are those presented in Table 1. The mixtures of substances selected for the experiments, contained only one type of cations (K^+), which was considered convenient for the analysis of the experimental results taking into account the relatively simple compositions of the initial salt mixtures. A mixtures of K_2CO_3 were used as an additional regulation of molten salt mixture basicity.[8]

TiO_2 powder (average size of particles 0.4 μm) was introduced into alumina crucibles with the molten salt mixture, heated up to 450, 500, and 550 °C, and treated during 0.25, 0.50, 1.00, or 1.25 h. The synthesized powders were carefully washed with distilled water and separated with a paper filter (No. 42 Wathman). After that the powder was once more introduced in distilled water, washed, and filtrated. The powder was finally dried at 90 °C during 2 h and characterized as follows.

Particle size distribution analysis was carried out by laser diffraction (Coulter, model LS100, USA). Ten grams of the powders obtained was mixed with 100 g distilled water; the suspension was ultrasonically treated (Fisher Scientific, Model 550, USA) during 10 min (power of 80.75 kW at 20 kHz) before its particle size analysis.

The powder products obtained from the treatment of the mixture 2.2 during 1 h at 500 and 550 °C were used to produce potassium titanate ceramics. Tablets of 3.2 ± 0.3 mm in thickness and 9.7 ± 0.5 mm in diameter were prepared in green state with a static pressure (750 N). The tablets were dried at 100 °C during 1 h in an oven and then heated up 1100 °C at 3 °C/min and soaked for 2 h in an electrical muffle (Thermolyne). After this, the tablets were cooled down to room temperature at 5 °C/min. The sintering temperature was selected considering the temperature resistance of potassium titanates (1100–1200 °C)[5] and the temperature of solidus (1114 °C) in the K_2O–TiO_2 phase diagram related to the TiO_2/K_2O mole ratio obtained in the product.[7]

The mechanical strength of ceramic discs (dimensions) was measured by the splitting (Brazilian) tensile strength test method (ASTM D 3967-95a).

The chemical and phase compositions of obtained powders and synthesized ceramics were determined by Scanning Electron Microscopy (SEM, Jeol, Model Jeol-6300, Japan) equipped with an X-ray microanalysis (EDS-S60 DX90) and also by X-ray diffractometry (Philips, Model X'Pert-MPD, The Netherlands).

3. Results

The treatment of TiO_2 by molten KNO_3 from the series 1.1 and 1.2 did not result in the formation of the desired products for the selected conditions of treatment.

For the series 2.2, the X-ray diffractograms (Fig. 1) indicated that the use of KOH admixtures to KNO_3 melts promoted structural decomposition of titanium oxide and the formation of new products at all temperatures used.

The synthesized product was characterized with the following changes of its size fractions. Short treatments (15 min) resulted in the formation of different particles with sizes from 0.4 to 200 μm (local maxima at 1, 4, and 32 μm). Increased treatment times to 1 h promoted disappearance of particles larger than 100 μm as well as formation of three local maxima at 0.9, 25, and 50 μm (Fig. 2); SEM micrographs (Fig. 3) present the powders obtained after treatment at 500 °C for 1 h, showing particles of 0.5–4 μm and agglomerates of 10–50 μm.

The kinetics of TiO_2 transformation into products was determined as the time dependence of the ratio between the intensities of the main reflections of the product (I_P, 29.1°) and anatase (I_T, 25.4°). The data obtained in the experiments with different admixtures of KOH is presented in Fig. 4.

Generally, increased KOH contents promoted a faster formation of the product; however, the ratio of I_P/I_T strongly depended on the temperature of treatment. The maximal contents of the product was obtained at 550 °C after 30 min but decreased with further treatment times.

The influence of K_2CO_3 admixture (3.5 mol.%), introduced into the molten system of KNO_3 and KOH (series

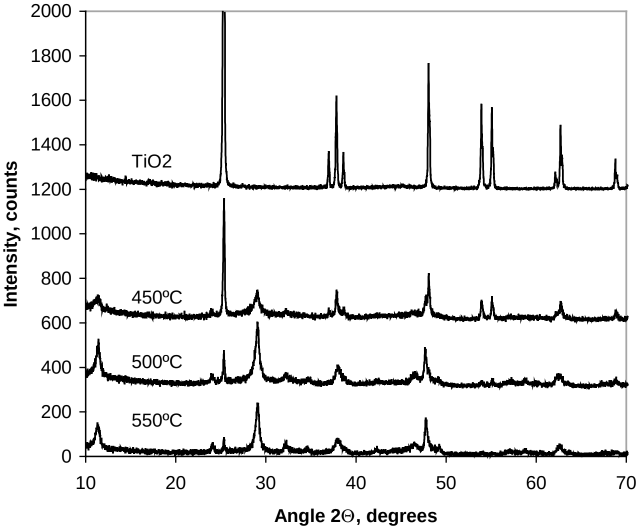

Fig. 1. X-ray diffractograms of the product obtained by treatment of TiO_2 in the molten mixture of KNO_3 and KOH (series 2.2) at different temperatures for 1 h.

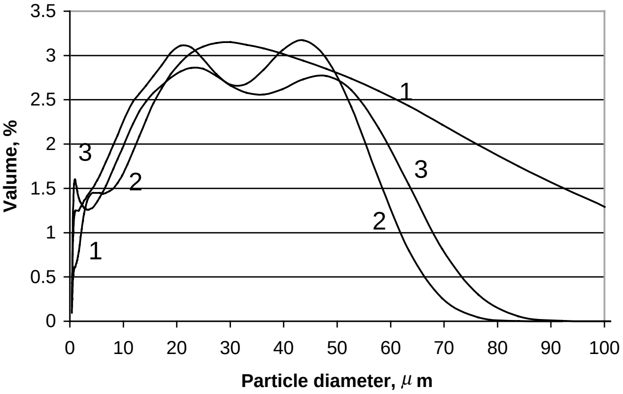

Fig. 2. Size distribution of particles after the treatment of TiO_2 by molten mixture of KNO_3 and KOH (series 2.2) at 500 °C during 0.25 h (1), 0.5 h (2), and 1.5 h (3).

3.1), on the kinetics of the potassium titanates formation in comparison with the data for the series 2.2, is presented in Fig. 5. These curves show an induction period, which length depends on the temperature. This induction period is characterized by a relatively low rate of product formation and is followed by a fast increase of the rate of transformation. However, increasing the time of treatment for more than 1 h resulted in the formation of less product, as compared to the treatment with the basic mixture of KNO_3–KOH (series 2.2).

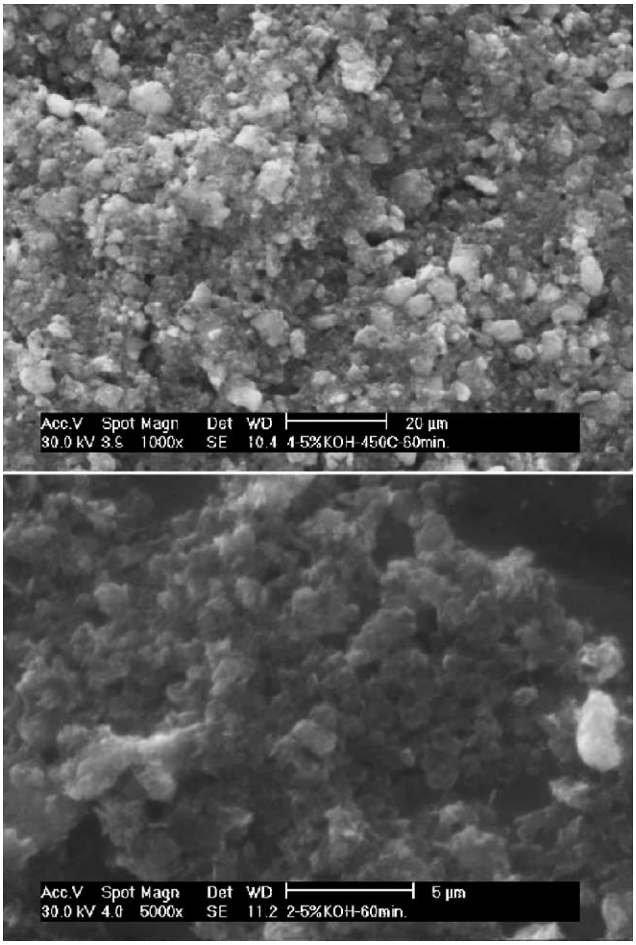

Fig. 3. Electron microphotographs of precursor material synthesized at 500 °C (1 h, mixture 2.2).

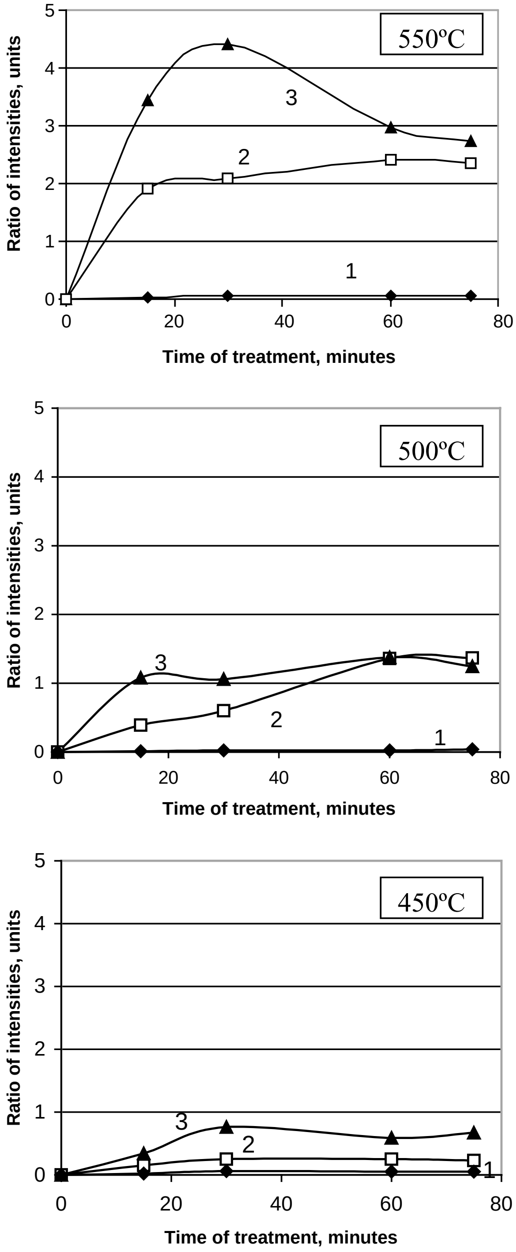

Fig. 4. Kinetics of TiO_2 transformation into the potassium polytitanate in the case of different admixtures of KOH: 3.5 mol.% (1; series 2.1), 8.5 mol.% (2; series 2.2), 13.2 mol.% (3; series 2.3).

The diffractograms of ceramics obtained with the powders synthesized during 1 h at 500 and 550 °C (Fig. 6) indicate $K_2Ti_6O_{13}$ as the main crystalline phase, along some rutile and unidentified phases. The content of the latter was proportional to that of anatase in the precursors. $K_2Ti_6O_{13}$ (fiber crystals identified by SEM in the pores) formed dense

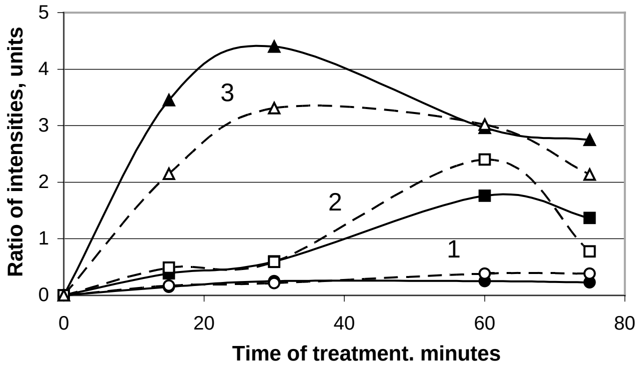

Fig. 5. Influence of K_2CO_3 admixture (dashed curves) on the kinetics of TiO_2 transformation into the potassium titanate at 500 °C in the case of different admixtures of KOH: 3.5 mol.% (1; series 2.1), 8.5 mol.% (2; series 2.2), 13.2 mol.% (3; series 2.3).

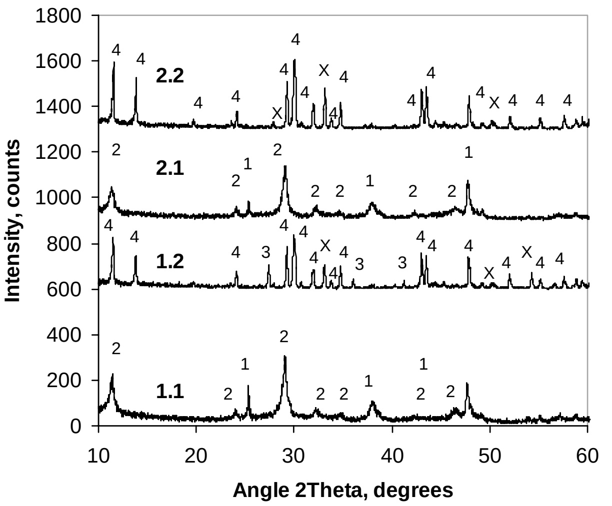

Fig. 6. X-ray diffractograms of precursors synthesized at 500 (1.1) and 550 °C (2.1) and ceramics sintered on the base of these precursors at 1100 °C (1.2 and 2.2 correspondingly). (1) TiO_2 (anatase), (2) potassium polytitanate, (3) TiO_2 (rutile), (4) $K_2Ti_6O_{13}$.

ceramic structure (Fig. 7). The ceramic articles obtained from the precursors synthesized at 500 and 550 °C, and after sintering both at 1100 °C, had average tensile strengths of 600 and 702 MPa, respectively.

4. Discussion

According to XRD and SEM-EDS results, the products obtained by treatment of TiO_2 with KNO_3–KOH molten mixtures included crystals of potassium titanate ($K_xTi_yO_z$) and some titanium dioxide (anatase).

The EDS analyses of powders with the highest yields of transformation of TiO_2 into $K_xTi_yO_z$ indicated that the ratio x/y in the product obtained was close to 0.33. Taking into account that the products obtained at all temperatures had similar features in the diffractograms, as related to the reflections not corresponding to the potassium titanates, as available in the XRD database ICDD-1999, it is possible that such products are some kind of polytitanate.

The probable mechanism of the processes taking place in the systems investigated, is presented in Fig. 8. Two routes could be considered for the formation of titanate ions in the investigated mixtures:

1. Dissolution of TiO_2 in the melt by OH^- ions, followed by the interaction of TiO_2 structural fragments with O^{2-} ions (Lux–Flood interaction, labeled processes 1 and 2).
2. Direct Lux–Flood acidic–basic interaction of O^{2-} ions with TiO_2 particles (process 3).

The processes 2 and 3 promote the formation of simple titanate ions, a possible product of their interaction with K^+ ions (K_2TiO_3) was not recognized, because of the high solubility of K_2TiO_3 in the melt used and the hydrolysis of this product in water during the washing of sediments.[16] The simple titanate anions, formed in the processes 2 and 3, could have also been polymerized into the polytitanate form (process 4). The subsequent interaction of such polytitanate anions with K^+ promoted the crystallization of potassium polytitanate (process 5).

Increased KOH contents in the melt promoted faster dissolution of TiO_2 (process 1), but in the case of long treatments at 500–550 °C, the solubility of the polytitanate product in the melt also increased. That is why the yield of potassium polytitanate obtained for a long treatment at high temperatures decreases as a result of the process 6 (see Fig. 4).

The introduction of K_2CO_3 increases the concentration of O^{2-} ions, as a result of ${CO_3}^{2-}$ ions decomposition,[8] and accelerates formation of ${TiO_3}^{2-}$ ions in the melt (processes 2 and 3). However, this favors the potassium polytitanate formation only after the induction period (curves 1 and 2 in Fig. 5), this shows the predominant role of the process 1 in the formation of simple titanate ions. On the other hand, high concentration of OH^- decreases the influence of K_2CO_3 (curve 3, Fig. 5).

Different contents of potassium polytitanate and anatase in the precursors formed at 500 and 550 °C influenced the phase composition and mechanical strength of ceramics obtained after sintering. Crystals of rutile, formed from anatase at 1100 °C, take place in the ceramic matrix produced from the precursor synthesized at 500 °C and are absent in the case of the precursor obtained at 550 °C. Thus, an increase of potassium polytitanate contents and decrease of anatase concentration in the precursor promotes better mechanical strength of ceramics produced. It seems that the regimes of $K_2Ti_6O_{13}$ ceramics production on the base of potassium polytitanate precursors can be improved, taking into account that the mechanical strength of some ceramic samples, obtained with the powders synthesized at 550 °C, was of 1100–1200 MPa.

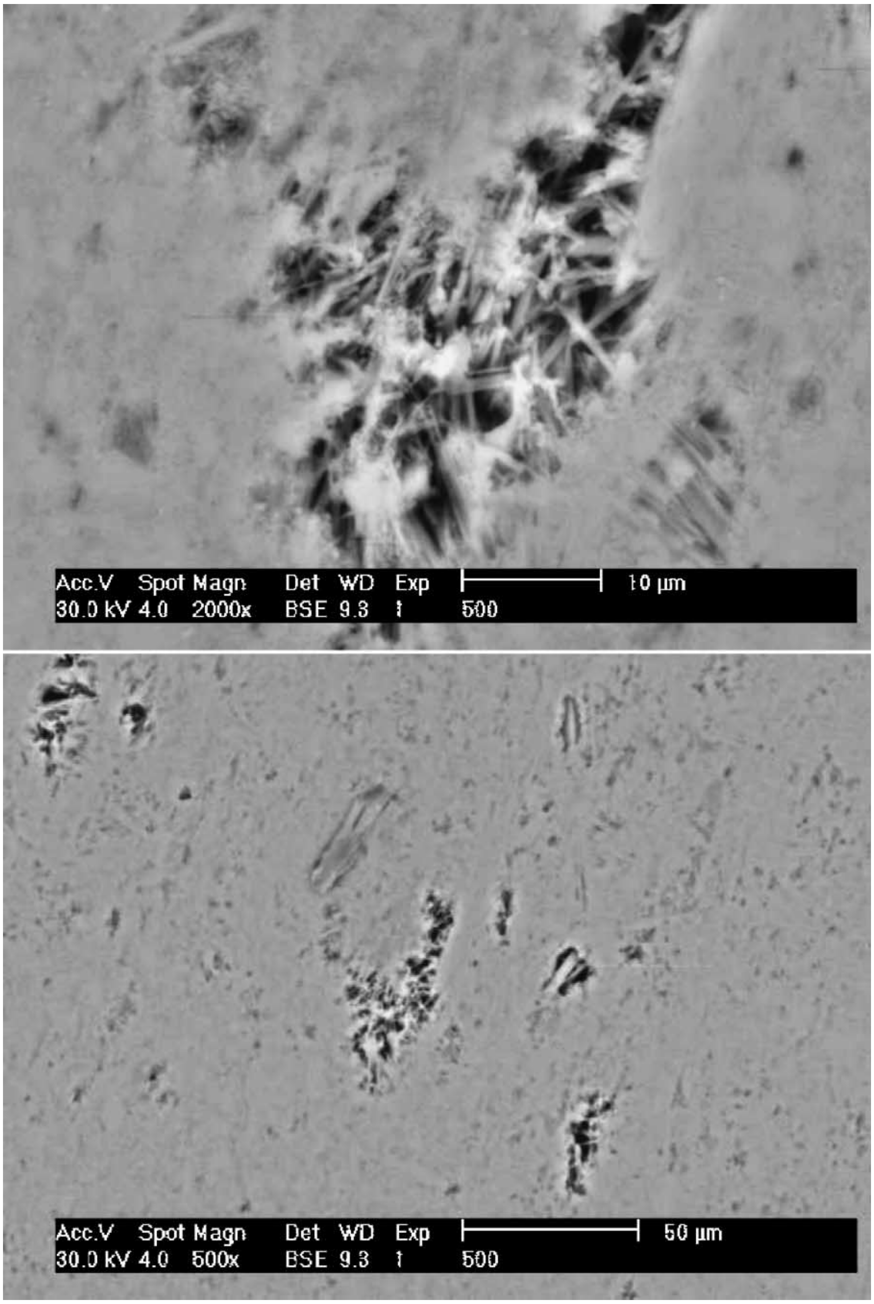

Fig. 7. Electron micrographs of ceramics obtained on the base of precursor synthesized at 550 °C (1 h, mixture 2.2).

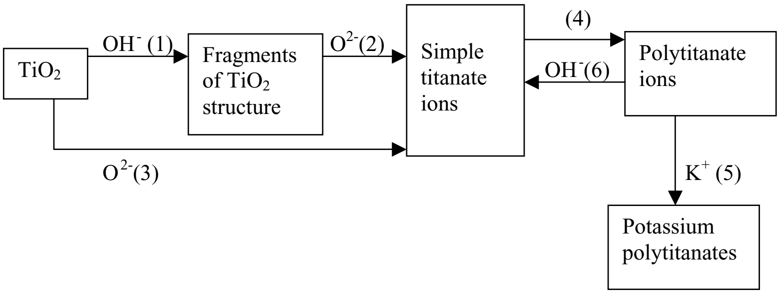

Fig. 8. Scheme of chemical processes in the system TiO_2–molten mixture of KNO_3–KOH–K_2CO_3.

5. Conclusions

The chemical interaction of TiO_2 with molten mixtures of KNO_3 and KOH allows to synthesize potassium polytitanate with [K]/[Ti] ratio about of 0.33. The mechanism of the process investigated included the stages of TiO_2 powder dissolution in the melt, Lux–Flood transformation of TiO_2 fragments into the simple titanate ions, polymerization of titanate ions and their interaction with K^+ cations to form crystalline potassium polytitanate. The product of TiO_2 treatment with molten mixture of KNO_3 and KOH can be considered as a promising precursor material to synthesize potassium titanate ceramics. A particle size distribution, from 0.4 to 80 μm, of the powder obtained is favorable to produce compact structures of green body articles and low porosity of the ceramics after sintering. The ceramic precursors formed at 500–550 °C during 1 h have minimal admixtures of TiO_2 and an optimal ratio of K/Ti, which allows crystallization of $K_2Ti_6O_{13}$; as the main phase, promoting high mechanical strength of ceramics obtained by sintering at 1100 °C.

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