

Preparation of cobalt titanates via co-precipitation while using industrial intermediates as titanium precursors

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This paper reports on the results of cobalt titanates preparation by calcination of green bodies obtained by a co-precipitation method. For the investigations were used: as titanium sources, acidic solutions of titanyl sulfate and hydrous titanium dioxide, originating from the production process of titanium dioxide by sulfate method. The composition of the obtained materials was determined using titration methods. The calcined powders were characterized by X-ray diffraction method. It has been found that the obtained products are composed of cobalt methatitanate CoTiO_3 or cobalt orthotitanate Co_2TiO_4 occurring as single phases, and also as cobalt titanates and titanium dioxide phase mixtures. The proposed method of proceeding can be used for the preparation of series of transition metals titanates, such as nickel, iron, zinc, copper and also aluminium titanates.

Keywords: titanium compounds, cobalt titanates preparation, titanyl sulfate, hydrous titanium dioxide.

INTRODUCTION

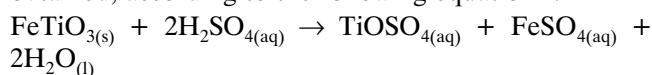
Cobalt titanates are known as useful materials because of the possibility of their technical application as green pigments, catalysts or in electric devices. Three cobalt titanates are known. They are the following: cobalt methatitanate, CoTiO_3 , having the ilmenite structure, cobalt orthotitanate, Co_2TiO_4 , with inverse spinel structure, and pseudobrookite-type cobalt dititanate, CoTi_2O_5 ¹. Among them CoTiO_3 is considered as the most important cobalt titanate due to its high thermal stability, even at temperatures above 1000°C, weak magnetism, semiconductivity, acousto-optic and electro-optic properties and high dielectric constant value of approximately $40^2 - 4$. Therefore, CoTiO_3 can be used, for example, as semiconducting device², hydrocarbonate catalyzer³, gas sensing material⁵⁻⁷ or pigment⁸.

There are known several methods for the preparation of cobalt titanates. The most popular is a solid-state reaction between titanium dioxide or hydrous titanium dioxide and cobalt oxide, hydroxide, or carbonate⁹. Although this method needs high temperature, about 1000°C, and long time, about 10 hours, small amounts of unreacted initial compounds can be expected¹⁰. Therefore, the methods based on the synthesis in the solution phase, like precipitation¹¹, sol-gel², or Pechini process¹², providing suitable mixing of the reagents, have recently been studied intensively.

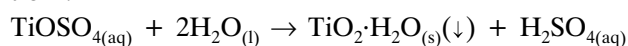
This work reports on the preparation of cobalt titanates by the co-precipitation method, using solutions of TiOSO_4 or $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ as titanium sources, CoSO_4 as cobalt source, H_2O_2 as a complexing agent, and NaOH as a precipitating agent. This approach is based on adding H_2O_2 to the acidic solution containing titanyl ion TiO^{2+} , in order to obtain titanium complex ion, $[\text{TiO}(\text{H}_2\text{O}_2)]^{2+}$. Complex ion of cobalt $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ can be easily prepared by dissolving of cobalt sulfate in water. The proceeding of the reaction between these two ions possessing the same charge requires the presence of OH^- ions, which were introduced with NaOH aqueous solution. With the gradual increasing of pH, as a result of NaOH dropping to the

starting solution, the formation of green precipitate took place. The principal advantage of this method is the short time of the co-precipitation process, (0.5 – 1 h), and the possibility of carrying out the process at room temperature. However, higher temperature is preferred to achieve quick sedimentation of the product.

The used titanyl sulfate solution and hydrous titanium dioxide paste were the intermediate products from the sulfate process of titanium dioxide production, as shown on the scheme in Figure 1^{9,13}. The raw material in this process is ilmenite, FeTiO_3 . As a result of decomposition of ilmenite by sulfuric acid the titanyl sulfate solution is obtained, according to the following equation¹⁴:



The prepared solution of a brownish black color is cooled in order to remove iron sulfate by crystallization. Then the purified and concentrated titanium sulfate solution is subjected to hydrolysis and the precipitation of colloidal titanium dioxide occurs by the following equation⁹:



Both the intermediate products originating from titanium dioxide manufacture are unstable regarding the time. In the titanyl sulfate solution the precipitation of hydrous titanium dioxide occurs, which results in decreasing of titanium content. The concentration of iron, whose small amounts remain after iron sulfate crystallization, also varies with time because it can be adsorbed on active surface of hydrous titanium dioxide precipitate. In addition, as the titanyl sulfate solution is stored, the oxidation state of iron is partially changing from Fe^{2+} to Fe^{3+} . During the storage of the hydrous titanium dioxide, decreasing of its hydration degree and increasing of titanium content takes place. Therefore, using TiOSO_4 and $\text{TiO}_2 \cdot n\text{H}_2\text{O}$, as the starting materials to prepare other titanium compounds, needs control of titanium and iron concentration.

The aim of our investigations was the elaboration of cobalt titanates preparation method by co-precipitation from solution using, as raw materials, titanyl sulfate solu-

tion TiOSO_4 , and hydrous titanium dioxide $\text{TiO}_2 \cdot n\text{H}_2\text{O}$, obtained under industrial conditions.

EXPERIMENTAL

Reagents

A composition of titanyl sulfate solution obtained from Chemical Works „Police”, Poland, [wt%]: TiO_2 -10.79, Fe^{2+} -2.68, Fe^{3+} -0.15, H_2SO_4 -20.

A composition of hydrous titanium dioxide paste obtained from Chemical Works „Police”, Poland, [wt%]: TiO_2 -89.12, SO_3 -5.85, moisture content-51.39 (determined in sample dried at 105°C).

Hydrogen peroxide p.a., 30%, POCH, Poland.

Cobalt(II) sulfate hexahydrate p.a., POCH, Poland.

Sodium hydroxide p.a., POCH, Poland.

Sulfuric acid p.a., 96%, POCH, Poland.

Experimental procedure

A volume of titanyl sulfate solution in the range of from about 2 to 17 ml was diluted with 100 ml of 20wt% H_2SO_4 . When hydrous titanium dioxide paste was used as titanium source then a sample of about 2 to 6 g was dissolved in 50 ml of boiling, concentrated sulfuric acid and diluted to 100 ml with water. Next, 2 ml of 30 wt% H_2O_2 was added to the prepared solution. Due to peroxide complex formation the color of the solution changed to dark red. Then a 50 ml volume of 5wt% CoSO_4 solution was added and the mixture was diluted to 400 ml of water.

The proper amounts of titanium sources, corresponding to the required weight ratio of Ti:Co in starting solution, were given in Table 1. The weight ratios of Ti:Co equal to 0.41, 0.81 and 1.62 were controlled according to a stoichiometric composition of Co_2TiO_4 , CoTiO_3 , and CoTi_2O_5 , respectively. Some of the experiments were carried out also at non-stoichiometric weight ratios of Ti:Co equal to 0.18, 0.2 and 0.98.

The starting mixture was placed in a three-necked flask provided with a stirrer, a reflux condenser, a dropping funnel and a pH measuring electrode. The precipitation was carried out with dropwise addition of 5n or 15n NaOH solution. The more concentrated NaOH was used when hydrous titanium dioxide was the starting material. All experiments were carried out at continuous stirring over the period of 1h at the temperature of 85°C . The green suspension was formed at pH about 5. The precipitating

agent was added until the pH of 7 – 8 was reached. It was necessary to achieve a high degree of conversion of the reactants. The precipitated solid substance was separated from the mother liquor and washed by decantation with hot distilled water. Next it was filtered out and dried in the oven to constant mass at 105°C . After grinding in the ball mill the obtained powder was calcined at 900°C for 1h.

Titration and instrumental methods

The composition of the obtained powders was determined by titration methods. The solid samples were dissolved in boiling, concentrated hydrochloric acid, then the content of titanium, cobalt, and total iron was determined.

Determination of Ti(IV) was carried out by the volumetric method based on the reduction of Ti(IV) ions to Ti(III) with aluminium metal powder in an acidic solution. The next stage was the titration of this solution with ferric ammonium sulfate to the sharp color change from violet to red. As the indicator of the end-point the ammonium thiocyanate solution was used.

Determination of Co(II) was carried out with the complexometric method based on titration with ethylenediaminetetraacetic acid disodium salt in alkali solution. The used end-point indicator was murexide, changing color from orange to violet.

Determination of Fe(II) and total iron (after reduction of Fe(III) ions with stannous chloride) was carried out by titration of the solution with potassium dichromate using, as the end-point indicator, the sodium salt of diphenylaminosulfonic acid. The color change at the end-point was from green to violet.

The phase composition of solid compounds was identified with the X-ray diffractometry on the Philips PW 1710 goniometer using $\text{Cu K}\alpha$ radiation at the voltage of 45 kV and the 40 mA current.

RESULTS AND DISCUSSION

It has been found that precipitation of green bodies takes place in the whole examined range of Ti:Co weight ratio from 0.18 to 1.62. The precipitation is not affected by the presence of iron ions when the titanyl sulfate solution is used as titanium source, however iron is coprecipitated. Therefore, to obtain the cobalt titanate single phase using both, the titanyl sulfate solution containing iron ions and also hydrous titanium dioxide, different weight ratio of Ti:Co must be used. As it is shown in Table 1, the lower Ti:Co weight ratio is needed when the

Table 1. The conditions of cobalt titanates preparation and their elemental and phase composition

Sample code	Titanium source	Amount of titanium source	Ti:Co weight ratio in starting solution	Elemental composition, wt%, 105°C			Δm , % 900°C	Phase composition 900°C
				Ti	Co	Fe		
Ti-Co1	Titanyl sulfate solution	1.87 ml	0.18	9.8	36.7	5.9	25.6	Co_2TiO_4
Ti-Co2		2.08 ml	0.20	12.5	28.8	7.7	25.5	$\text{CoTiO}_3 + \text{Co}_2\text{TiO}_4$
Ti-Co3		4.26 ml	0.41	18.3	25.0	8.2	21.6	$\text{CoTiO}_3 + \text{Co}_2\text{TiO}_4$
Ti-Co4		8.41 ml	0.81	21.8	21.2	9.4	19.8	CoTiO_3
Ti-Co5		16.82 ml	1.62	25.0	14.8	12.5	8.5	$\text{CoTiO}_3 + \text{CoTi}_2\text{O}_5$
Ti-Co6	Hydrous titanium dioxide	0.74 g	0.20	17.4	38.4	–	22.1	Co_2TiO_4
Ti-Co7		1.52 g	0.41	19.4	36.8	–	20.8	$\text{CoTiO}_3 + \text{Co}_2\text{TiO}_4$
Ti-Co8		3.00 g	0.81	26.0	30.3	–	16.5	$\text{CoTiO}_3 + \text{Co}_2\text{TiO}_4$
Ti-Co9		3.63 g	0.98	26.3	25.5	–	16.3	CoTiO_3
Ti-Co10		5.99 g	1.62	27.0	16.4	–	15.5	$\text{CoTiO}_3 + \text{TiO}_2$

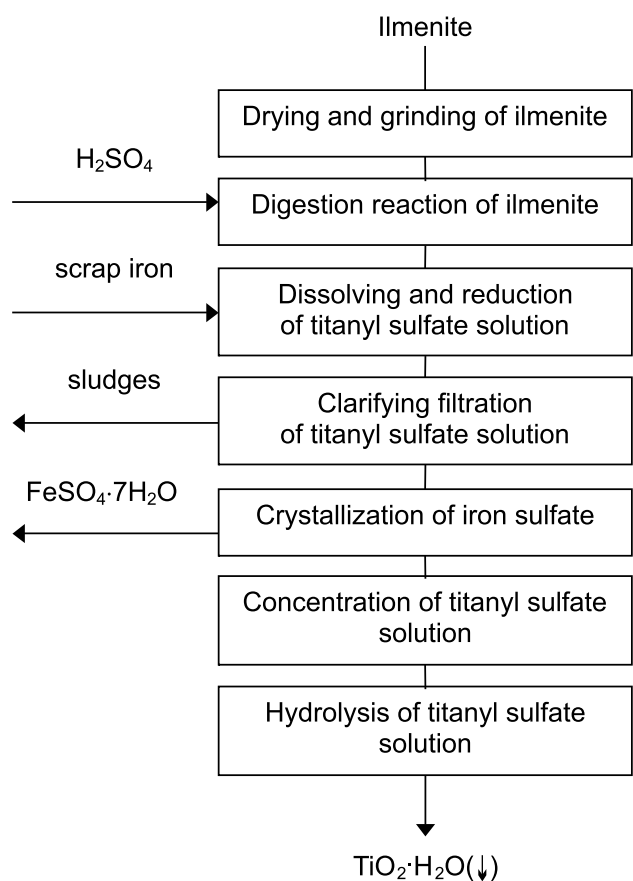


Figure 1. The block diagram of TiOSO_4 and $\text{TiO}_2 \cdot \text{H}_2\text{O}$ preparation in the titanium dioxide technology

titanyl sulfate solution is used. It is caused by the occurring in the solution Fe^{2+} ions which are oxidized to Fe^{3+} ions during the co-precipitation reaction and can substitute Ti^{4+} ions in the precipitate, due to similar ionic radii size. The determination of iron in dried samples confirmed that it occurs only in the +3 oxidation state. The presence of iron in the prepared materials have an influence on their color which changes from bluish green to brownish black in the case of CoTiO_3 and from emerald green to black in the case of Co_2TiO_4 .

The samples dried at 105°C are X-ray amorphous. After their thermal treatment at 900°C for 1h the crystalline phases of cobalt titanates are formed. It has been found that when the titanyl sulfate solution is used it is possible to obtain Co_2TiO_4 and CoTiO_3 single phases at Ti:Co weight ratio equals 0.18 and 0.81. When, the hydrous titanium dioxide is used as the reagent, the appropriate Ti:Co weight ratio is 0.2 and 0.98, respectively. The results of diffractometric investigations are shown in Figure 2. The standard patterns of cobalt titanates shown at the bottom of the figure are taken from the ICPDS X-ray diffraction database. As it is shown in this figure, the samples containing iron preserve the same crystallographic structure as cobalt titanates without forming the additional phases originating from iron oxides like hematite. However, peak shifts can be observed due to the lattice distortion affected by the iron ions substitution. Figure 3 shows the most intense peak of Ti-Co1 and Ti-Co4 samples referred to the corresponding standard pattern of Co_2TiO_4 and CoTiO_3 . It is seen that peaks are shifted

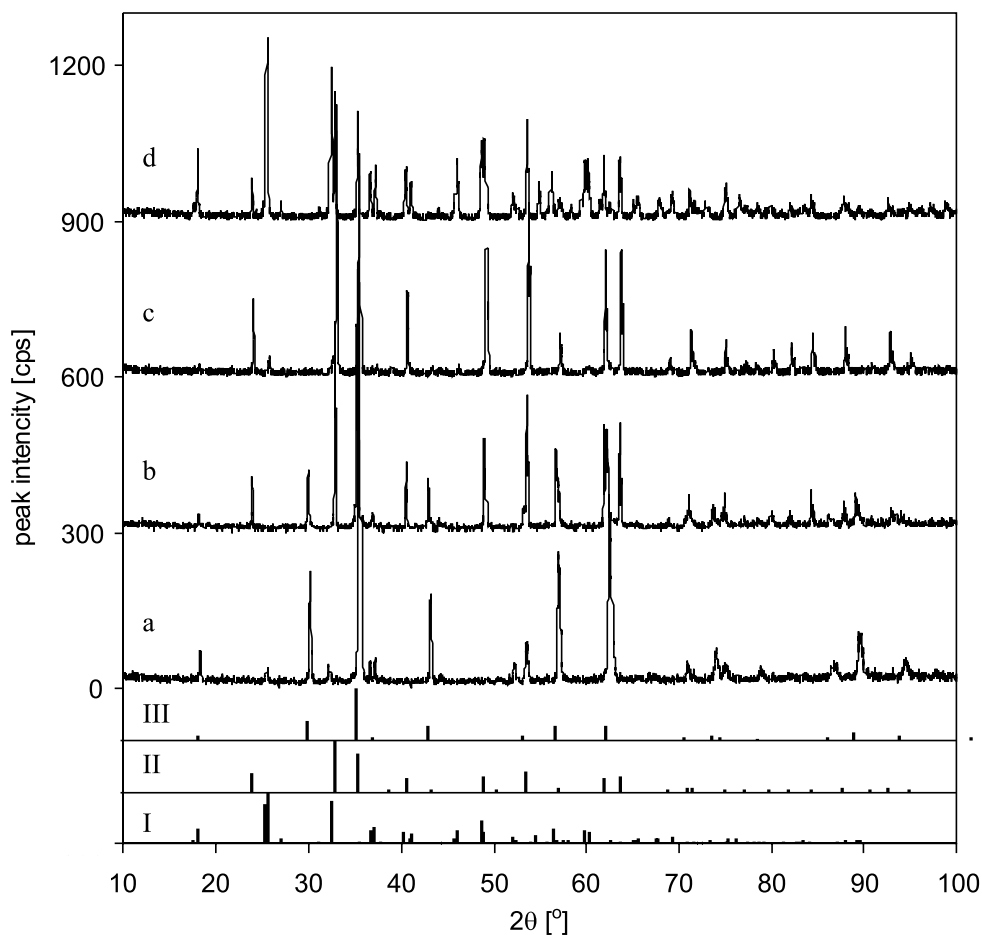


Figure 2. The diffraction patterns of the calcined samples and standard patterns of cobalt titanates: a-Ti-Co1, b-Ti-Co2, c-Ti-Co4, d-Ti-Co5, I- CoTi_2O_5 , II- CoTiO_3 , III- Co_2TiO_4

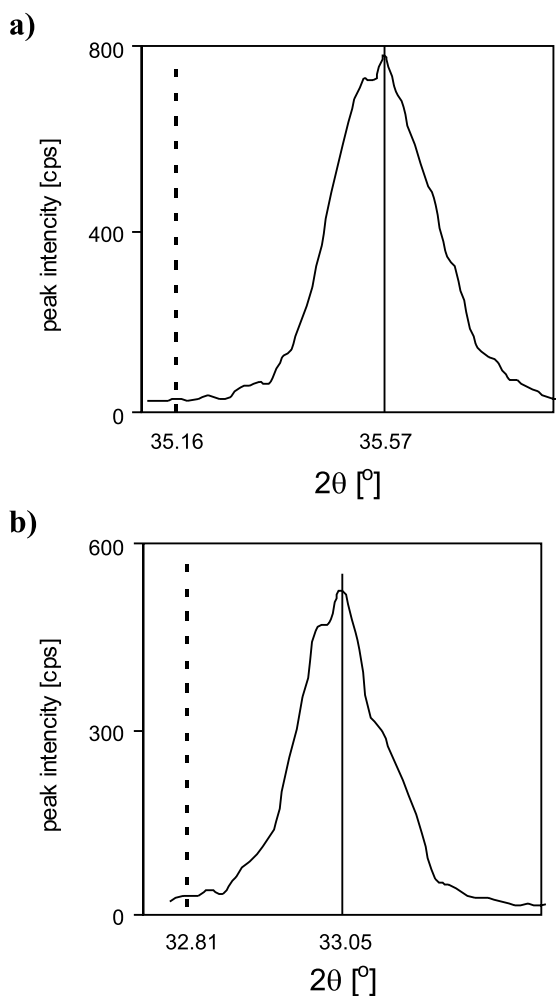


Figure 3. The most intense peak and corresponding standard pattern of: a) Ti-Co1 sample and Co₂TiO₄, b) Ti-Co4 sample and CoTiO₃

towards higher 2θ value. This indicates a decrease of the unit cell volume of iron-doped samples.

CONCLUSIONS

The method of co-precipitation has been successfully applied to obtain the green bodies. Their thermal treatment at 900°C allowed to distinguish the crystalline single phases of CoTiO₃ and Co₂TiO₄, in dependence on Ti:Co weight ratio in the starting solution.

We have found that the intermediate products of ilmenite decomposition, originating from industrial conditions, are suitable for the preparation of cobalt titanates. In the case of the titanyl sulfate solution, used as titanium source, the obtained cobalt titanates contain from 5.9 to 12.5 wt% of Fe³⁺, which results in the darkening of their color. The iron containing samples can be applied as electrical materials. On the contrary, the samples prepared from the hydrous titanium dioxide, not containing iron, can be applied as pigments due to their intensive colors varying from emerald green to bluish green, in dependence on phase composition.

A series of experiments with other transition metals salts has been performed, using industrial titanium intermediate products and adopting the described method. We have stated that when, instead of cobalt sulfate solution, the solutions of Ni, Fe, Zn, Cu and Al sulfates are used, then it is possible to obtain the corresponding metals titanates.

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