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PROCESSING OF RUTILE CONCENTRATES BY FLUORINATION

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ABSTRACT

The present paper substantiates the necessity of developing a new technology for processing titanium-containing concentrates. It describes a thermodynamic study of the process of rutile concentrate fluorination by elemental fluorine using "ASTRA" software. The study has shown that from a thermodynamic point of view, the process has no limitations. The article contains the description of the kinetic features of the process and their mathematical processing. It has been established that the process is limited by diffusion factors supply of a fluorinating reagent to the surface of a solid material. The article contains a brief overview of industrial technologies for producing titanium powders. The study substantiates the necessity of developing a fundamentally new fluoride technology for producing titanium powders from low-temperature fluoride melts. The authors describe a method for the preparation of fluoride melts using the process of hydro fluorination of lithium and sodium fluorides with anhydrous hydrogen fluoride obtained during the decomposition of potassium hydrogen fluoride. The article describes the processes occurring during the electrolytic production of titanium powders from fluoride melts using titanium tetra fluoride as a reagent. Since the potential of titanium extraction is much less than similar values of fluoride eutectic potential of fluoride salts, the process of titanium extraction proceeds with high efficiency. The paper describes the design of a laboratory unit for carrying out the electrolysis process and the sequence of operations for obtaining cathode deposit. The dependence of the effect of the cathode conductance on the titanium yield is investigated and the optimal conditions for electrolysis are selected. The paper presents the experimental results of electrolytic production of titanium and it shows that the cathode efficiency is not less than 93%. Two technologies are proposed for washing off the impurities from a titanium-containing cathode deposit washing off in a mixture of inorganic acids and anhydrous HF; the advantages of HF washing are shown; the content of impurities in the titanium powder obtained by washing in anhydrous HF is slightly lower than in the case of the "acidic" washing. This is due to the dissolution of these impurities in anhydrous HF during washing. In the industrial implementation of the washing of the cathode deposit in anhydrous HF, this reagent is recycled in the scheme, which ensures the environmental safety of production and low cost of the obtained titanium powder.

KEYWORDS: *Rutile Concentrate, Fluorination, Titanium Dioxide, Titanium Tetra fluoride, Electrolysis*

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INTRODUCTION

Titanium, which has a number of valuable properties such as high durability (due to the density of the metal), excellent chemical resistance to many corrosive environments and high heat resistance, has currently occupied the leading positions in application in various fields of modern science and technology. For the industrial production of titanium, sulfuric acid and chloride Kroll processes are used [1]. The sulfuric acid process pollutes the environment, and the produced titanium dioxide is expensive. Every year, hundreds of thousands of tons of toxic calcium sulphate are discharged into the environment. The chloride process is more environmentally friendly. However, during its application, great amounts of gaseous, liquid and solid toxic chloride wastes are formed, and the total extraction of titanium into purified titanium chloride does not exceed 89% by weight. With the world production of titanium dioxide pigment of 2,750 thousand tons/year, 1,467 thousand tons/year or 4,890 tons/day of harmful chloride solid wastes are formed [2–4]. At present, the growing demand for titanium and the high cost of its production have led to the need to replace the outdated Kroll process with more efficient technologies.

Over the past 10 years, a number of technologies have been proposed for the production of titanium powders:

- Preform Reduction process (PRP) process (UK), based on Cathermal reduction of preformedTiO_2[5];
- Fray-Farthing-Chen (FFC) process (Cambridge process), developed in 2000, in which electrolysis is carried out in molten calcium chloride using a preformed TiO2 cathode and a graphite anode [6]. It is expected that the industrial production of titanium using this method will be three times cheaper than the Kroll process;
- MER-process (Materials Electrochemical Research Corporation, DARPA, UK) [7]. To carry it out, the starting TiO_2-containing raw material is mixed with graphite-containing material and a binder or carbon, which is also used as a binder for sintering powders. By controlling the carbothermic reduction process, the following substances are obtained: Andersson-Magnelli compounds (Ti_nO_{2n-1}), anosovit (Ti_3O_5), titanium sesquioxide (Ti_2O_3), monoxide (TiO) and titanium carbide (TiC), as well as mixtures containing a small amount of free carbon. In addition, it is possible to synthesize pure titanium oxycarbide (Ti_2OC). The process is carried out in an inert gas environment or in vacuum at 1200-2100 °C [8]. The obtained semi-finished product is used for the manufacture of a composite anode in the process of metal titanium synthesis. Several methods have been developed for the synthesis of titanium from carbothermally reduced raw materials. If the oxide being reduced does not contain residual carbon as an impurity, it can be used as a cathode material. The cathode efficiency, determined according to Faraday's law, is rather low if the reducible oxide is used as a cathode. In the process, oxygen is released at the cathode. If alkali or alkaline earth metals are deposited on the cathode, which also contains a reducible oxide, cathode efficiency remains low. The diffusion of the metal-reducing agent used as the cathode of titanium oxide in the process of reduction also occurs at a limited rate. When using a composite anode, it is possible to conduct electrolysis of titanium from melts containing titanium ions (Ti^{2+}) or electrolysis of titanium cations (Ti^{4+}), which are released when the composite anode is dissolved.
- Ono & Suzuki(OS)-process [9, 10], developed at the University of Kyoto (Japan), is the result of combining electrolysis and calcium-thermal reduction of a mixture of oxides consisting of TiO_2, Nb_2O_5, Ta_2O_5, and $ZrO_2$to produce Ti-29Nb-23Ta-4,6Zr alloy ("TNTZ"alloy). CaO by-product is dissolved in the $CaCl_2$ melt near the cathode. It decomposes to metallic calcium and O^{2-}. This anion is removed from the melt in the form of CO and CO_2 gases formed at the anode. Ca released at the cathode also dissolves in the $CaCl_2$ melt and reduces the oxides in the melt [11].
- These processes are based solely on the use of TiO_2 as a feedstock. They do not provide information on the purity of titanium dioxide and methods of its obtaining.

All the described methods have a number of disadvantages, the main of which are:

- The need for leaching of titanium powder from the original perform,

- Difficulties in converting calcium into vapors and controlling the content of calcium vapor,
- A sharp decrease in cathode efficiency at the end of the process,
- Contamination of the electrolyte with carbon due to the dissolution of the binder during the decomposition of the cathode,
- The need to replace anodes due to their decomposition during electrolysis with the release of CO/CO_2 gas mixture.
- The development and creation of a more advanced and promising fluoride technology for processing titanium concentrates can reduce the harmful effects on the environment. One of the most common titanium concentrates, rutile, has the following composition (% wt.) [12]:TiO_2 – 93.2; SiO_2 – 1.8; FeO – 1.5; Fe_2O_3 – 1.2; Al_2O_3 – 1.0; MnO – 0.6; CaO – 0.4; MgO – 0.2; V_2O_5 – 0.1.

EXPERIMENTAL RESULTS

One of the main processes of the proposed technology is the fluorination of rutile concentrate. The features of fluorination of titanium dioxide and compounds, included in the composition of rutile concentrate, by elemental fluorine (F_2) are described below [13]:

$$TiO_2 + 2F_2 \rightarrow TiF_4\uparrow + O_2; \tag{1}$$

$$SiO_2 + 2F_2 \rightarrow SiF_4\uparrow + O_2; \tag{2}$$

$$MgO + F_2 \rightarrow MgF_2 + 0.5O_2; \tag{3}$$

$$MnO + F_2 \rightarrow MnF_2 + 0.5O_2; \tag{4}$$

$$Al_2O_3 + 3F_2 \rightarrow 2AlF_3\downarrow + 1.5O_2; \tag{5}$$

$$FeO + 1{,}5F_2 \rightarrow FeF_3\downarrow + 0.5O_2; \tag{6}$$

$$Fe_2O_3 + 3F_2 \rightarrow 2FeF_3 + 1.5O_2; \tag{7}$$

$$CaO + F_2 \rightarrow CaF_2\downarrow + 0.5O_2; \tag{8}$$

$$V_2O_5 + 5F_2 = 2VF_5\uparrow + 2.5O_2. \tag{9}$$

As a result of fluorination, a gas phase containing TiF_4, SiF_4, VF_5, a solid product — FeF_3, AlF_3, MnF_2, CaF_2, MgF_2, and unreacted oxides are formed.

The equilibrium composition of the isolated thermodynamic system was studied using the ASTRA thermodynamic calculation software package [14]. These studies were carried out for a rutile concentrate having the following composition,% wt.: 48.43 TiO_2; 0.92 FeO; 1.03 SiO_2; 0.56 Al_2O_3; 0.15 Cr_2O_3; 0.12 CaO; 0.06 V_2O_5, which is 51.27% of the initial mixture. The rest is the amount which is stoichiometrically necessary for fluorination of fluorine and the excess of this amount.

Research at the said temperature range may result in the emergence of the following reaction products: O_2, CaF_{2s}, TiF_{4s}, TiO_{2s}, SiF_4, CrF_6, TiF_4, SiO_2F_2, AlF_{3s}, V_2O_{5s}, FeF_{3s}, FeF_3, AlF_3, V_4O_{10}, F_2, F, F_2O, FO, Fe_2F_6, Al_2F_6, TiF_3, FeF_2, Fe_2O_3. Due to the large number of components formed in this system, the analysis did not take into account the substances whose concentration in the temperature range under study was less than 0.0001 mol/kg, which does not exceed 0.01% of the concentration of the main products –TiF_4 and O_2.

Figure 1 shows the dependence of the change in the mass concentration of TiF_4 (*C,% wt.*) in the reaction products on the temperature (*T, K*) of the fluorination process.

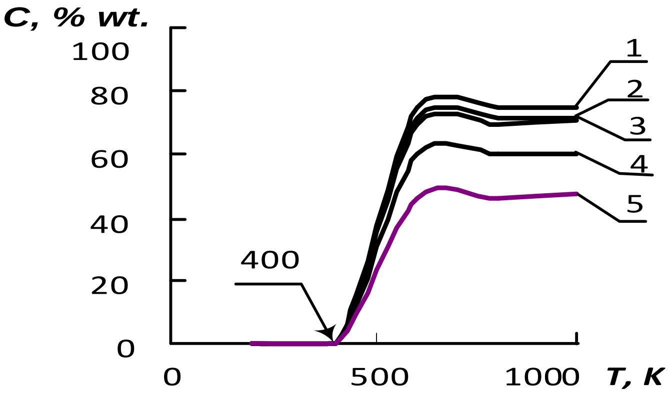

Figure 1: Dependence of TiF_4 Content on Temperature for Various Ratios of Reagents.

1) F_2 stoichiometry; 2) a 10% excess of F_2; 3) a 50% excess of F_2; 4) a 10% deficit of F_2; 5) a 50% deficit of F_2

Table 1 shows the equilibrium composition of the products of the fluorination process of rutile concentrate with a 10% excess of fluorine.

Table 1 The content of the products of the fluorination,% wt. (in the casewhen the content of the initial materials is 48.43% by weight of TiO_2, 53.63% F_2, the rest being impurities) P = 0.1 MPa. 10% excess of fluorine of stoichiometry*

Table 1

T, K	$TiF_{4\,(s)}$	$TiF_{4\,(g)}$	$V_2O_{5\,(s)}$	$F_{2\,(g)}$
200	72	0	$5.34 \cdot 10^{-2}$	4.4
400	72	$4.59 \cdot 10^{-2}$	$5.34 \cdot 10^{-2}$	4.4
600	0	71,6	$5.34 \cdot 10^{-2}$	4.4
800	0	71,6	$5.32 \cdot 10^{-2}$	4.3
1000	0	71,6	$5.29 \cdot 10^{-2}$	3.7

*The content of $O_{2(g)}$, $CaF_{2(s)}$, $SiF_{4(g)}$, $AlF_{3(s)}$and $FeF_{3(s)}$ in the reaction products practically does not change in the considered temperature range and is 20, $1.3\ 10^{-1}$, 1.7, $8.8 \cdot 10^{-1}$ and 1.38% wt. respectively.

To study the characteristics of the fluorination of TiO_2 (the main component of the rutile concentrate), kinetic studies were performed on an experimental laboratory unit, which is schematically shown in Figure 2.

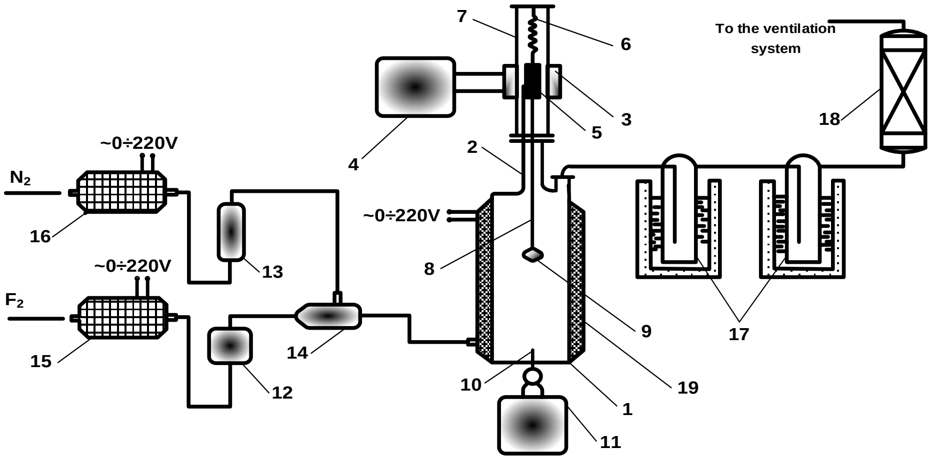

Figure 2: Scheme of the Experimental Unit for Fluorination of TiO_2, the Main Component of Rutile Concentrate.

1 - fluorination reactor; 2 - brass tube; 3 - induction coil; 4 - recording device; 5 - electromagnetic coil; 6 - Mo or W spring; 7 - measuring device; 8 - molybdenum thread; 9 - a cup of nickel foil; 10, 11 - temperature regulation and recording system; 12, 13 - gas flow control system; 14 - fluorine and argon supply unit; 15,16 - fluorine and argon electric heaters; 17 - volatile fluorides condensation unit; 18 - gas treatment line; 19 - reactor electric heater 1.

The main element of this unit is a vertical fluorination reactor 1. To start the process of fluorination, reactor 1 is heated by electric heater19. Brass tube 2 is soldered to reactor lid1, inside of which there is measuring element— annealed molybdenum or tungsten spring 6, one end of which is fixed to the plug, the other is connected to the steel plunger of induction coil 3 of recording device 4. A nickel foil cup 9 is attached to the lower end of the plunger of coil 3 with the help of molybdenum thread. In front of reactor 1, there is fluorine and argon supplying unit 14. Sensor 10 and system 11 are used to control and record the temperature. Fluorine and nitrogen gas flow rates are measured by systems 12 and 13. Heaters 15 and 16 are used for heating the initial gaseous reagents. Condensation unit 17 is located at the outlet of the reactor. The gases produced in the process are purified from fluoride-containing impurities on line 18.

To reduce the effect of heat, released during the reaction, on the isothermal conditions of the process in the unit scheme provides for the dilution of fluorine with nitrogen. The resulting gas mixture is preheated in a coil located on the outer surface of the reactor. The use of a massive metal reactor and the above-described method for supplying the reaction gas mixture has made it possible to ensure a minimum temperature gradient between the sample contained in nickel foil 9 and the reaction gas mixture.

To study the kinetics of TiO2 fluorination with elemental fluorine, powders with a particle size distribution from $2\cdot10^{-6}$to $2\cdot10^{-5}$ m and a specific surface area of 3.5 m^2/g were used.

Studies were performed using TiO_2 samples weighing 280 mg and a sample layer thickness of up to 4 mm in the temperature range of 300–550 °C. During the fluorination process at controlled temperature and partial pressure of fluorine, the sample mass was continuously recorded. Fluorination was carried out with fluorine of commercial purity, which had been previously purified from HF by sorption on pelletized NaF at 370-380 K.

Studies of the process of obtaining high-purity titanium powder by electrolytic decomposition of titanium tetrafluoride or potassium hexafluorotitanate (K_2TiF_6) were carried out in a melt of a low-melting eutectic of fluoride salts of alkali metals [15]. For this, triple eutectics of a mixture of fluoride salts LiF-KF-NaF (FLiNaK) were studied and, for use in practice, it is recommended to use the eutectic of 0.5 M LiF - 0.39 M KF - 0.11 M NaF having a melting point of 472 °C and higher conductivity compared to eutectics of chloride salts [16]. To obtain FLiNaK, initial reagents of chemical degree of purity were used.

When TiF_4 is absorbed by the fluoride electrolyte melt, the following reaction proceeds:

$TiF_{4g} + (LiF\text{-}KF\text{-}NaF)_L \rightarrow Li_2(K_2,Na_2)TiF_{6L}$. (10)

The degree of saturation of fluoride melt with titanium tetrafluoride is 3-3.5%.

After saturation of the melt, dissociation processes occur in the fluoride electrolyte:

$Li_2(K_2,Na_2)TiF_{6L} \rightarrow 2K^+(Li^+, Na^+) + TiF_6^{2-}$, (11)

$TiF_6^{2-} = Ti^{4+} + 6F^-$.(12)

During electrolysis, titanium powder is formed at the cathode, and elemental fluorine is released at the anode:

at the cathode $Ti^{4+} + 4e \rightarrow Ti\downarrow$, (13)

at the anode $4F^- - 4e \rightarrow 2F_2\uparrow$, (14)

in the electrolyte: $F^- + K^+(Li^+,Na^+)_L = K(Li, Na)F_L$.(15)

Studies were performed on an experimental electrolytic unit, the scheme of which is shown in Figure 3.

The titanium tetrafluoride is heated with heater 8 to 300 °C in the tank 5. In this case, TiF_4 transforms from a solid to a gaseous state, i.e. it is sublimated. The mass of tank 5 is measured with the help of weighter 7, having a weighing error of ± 5 g. The flow rate of titanium tetrafluoride fed to the melt is changed by fine adjustment valve 5.

The initial fluoride salts have very high melting points: Tm FLiF = 870 °C, Tm KF = 857 °C, Tm NaF = 992 °C, therefore potassium hydrofluorides ($KF\cdot 2HF$, $KF\cdot HF$, Tm $KF\cdot 2HF$ = 80 °C Tm $KF\cdot HF$=239 °C) mixed with lithium and sodium fluorides are used to obtain fluoride eutectic. When such a mixture of $KF\cdot 2HF$ ($KF\cdot HF$) is heated, HF is released from it, which reacts with NaF to form $NaF\cdot 3HF$ (Tm = 70 °C) [17, 18]. LiF is highly soluble in HF, its solubility in the range of t = –23.0 ÷ 12.2 °C is 9.5 g/l [19, 20]. This mixture first transforms into the molten state, and then, as the temperature rises to 472 °C, sodium and potassium hydrofluorides decompose, and HF is released from the LiF-HF melt, and LiF-KF-NaF fluoride eutectics is formed. The released anhydrous HF is absorbed in absorber 3.

Eutectic of fluoride salts are prepared based on the following ratio:

0.5 M LiF – 0.39 M $KF_{anhydrous}$ – 0.11 M NaF

12.97 g 22.659 gKF 4.62 g

30.459 gKF· HF $\sum$= 48.05 g

$\left(\frac{12.97}{48.05}\right)\cdot 100 = 26.99$ % wt. –$\left(\frac{30.459}{48.05}\right)\cdot 100 = 63.39$ % wt. –$\left(\frac{4.62}{48.05}\right)\cdot 100 = 9.62$ % wt.

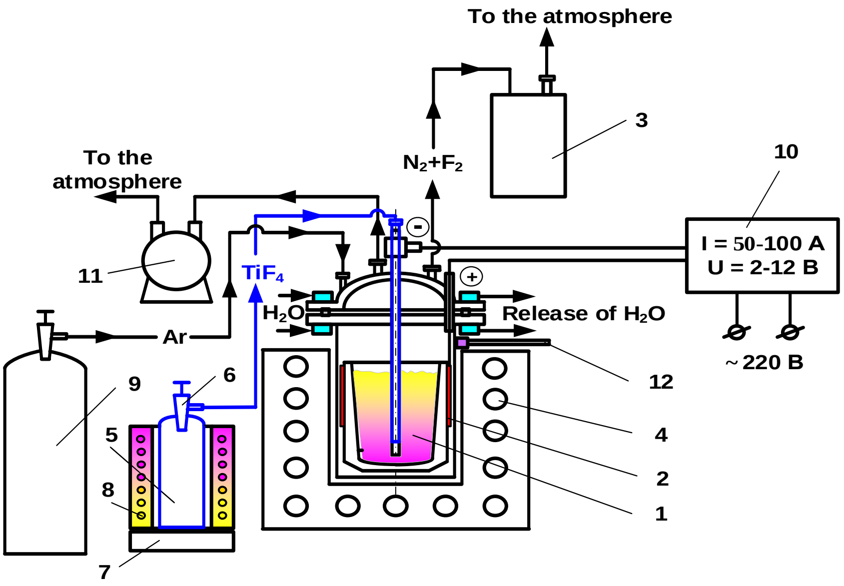

Figure 3: Scheme of Unit for Electrolytic Production of Titanium Powder.

1 - electrolyzer; 2 - muffle; 3 - chemical absorber (96% $Ca(OH)_2$ and 4% NaOH) for the absorption the released F_2; 4 - electric furnace; 5 - tank with TiF_4; 6 - fine adjustment valve; 7 - weighter; 8 - heater of tank with TiF_4; 9 - cylinder with inert gas (Ar); 10 - direct current source (rectifier); 11 - vacuum pump; 12 - thermocouple

The obtained fluoride eutectic is saturated with titanium tetrafluoride to a concentration of 7.75% or 3% in terms of the equivalent amount of Ti. In the process of saturation of fluoride melt at 500 °C complex salts are formed:

$$KF_L + TiF_{4g} \xrightarrow{500^0C} K_2TiF_{6L}, \qquad (16)$$

$$NaF_L + SiF_{4g} \xrightarrow{500^0C} Na_2SiF_{6L}. \qquad (17)$$

Fluorotitanate lithium is not formed, because at 500 °C on it decomposes.

The electrolyte melt consists of:

$LiF_L + KF_L + NaF_L + (K_2TiF_{6\,L} + Na_2TiF_{6\,L})_L$

7,75 % wt. in terms of TiF_4

In this melt, dissociation processes occur:

$$LiF_L \leftrightarrow Li^+ + F^-, \qquad (18)$$

$$KF_L \leftrightarrow K^+ + F^-, \qquad (19)$$

$$NaF_L \leftrightarrow Na^+ + F^-, \qquad (20)$$

$$K_2TiF_{6L} \leftrightarrow 2K^+ + TiF_6^{2-}, \qquad (21)$$

$$Na_2TiF_{6L} \leftrightarrow 2Na^+ + TiF_6^{2-}, \qquad (22)$$

$$TiF_6^{2-} \leftrightarrow Ti^{4+} + 6F^-. \qquad (23)$$

To saturate the obtained fluoride eutectic by titanium tetrafluoride, a metal fitting is inserted through the central nozzle of muffle cap 2 (Fig. 3) down to the bottom of a graphite crucible, to supply TiF_4 gas. Then this pipe is raised upwards by 3 cm and a mark is made on it relative to the flange of the lid. The glands of the fitting and lid are then sealed. The supply pipe of TiF_4 is tightly connected by a metal tube with absorber 3 and tank 5. The absorber is filled with granules of 96% Ca $(OH)_2$ and 4% NaOH mixture. The lid of muffle 2 is cooled with water, then the furnace 3 heater is turned on. The temperature of muffle 2 is monitored using thermocouple 12, gradually increasing it to 500 °C. At muffle temperature of 2,500–550 °C, the eutectic melt is saturated with titanium tetra fluoride. To do this, in the tank 5 preheated to 300 °C, the fine adjustment valve 6 is opened and the flow of TiF_4 into the melt is adjusted by the weight loss of tank 5.

After the melt is saturated with titanium tetra fluoride, the fine adjustment valve 5 is closed. After loosening the gland seal, the metal pipe is replaced by a rod-cathode.

The electrolyser has the following technical characteristics: capacity up to 50 g/h for titanium tetra fluoride; muffle volume of 1.35 dm^3; electrolyte temperature of 450-500 °C; surface area of the anode 0.05872 m^2, cathode 0.0118 m^2; current density: anode 0.085-0.13 A/cm^2, cathode 0.42-0.63 A/cm^2.

For electrolysis, a graphite cathode (rod) and anode (crucible) are supplied with direct current, the value of which varies between 50-100 A, and the voltage between 2-12 V. During the electrolysis process, a precipitate forms at the graphite cathode (titanium powder in the melt of fluoride salts), and elemental fluorine at the anode, which is removed from the electrolyser and absorbed in absorber 2.

After electrolysis, the cathode with precipitated deposit consisting of titanium powder and fluoride salt melt is lifted above the electrolyte melt the furnace heater 4 is turned off. Electrolyser muffle 2 is cooled and in order to remove fluorine-containing gases, it is blown down with an inert gas (argon) from the cylinder 9. Then the muffle lid is taken off and the cathode with the *cathode deposit* obtained during the TiF_4 electrolysis in the melt of the alkali metal fluoride salt LiF-KF-NaF (FLiNaK) is removed. The cathode deposit has the following composition, % wt.: Ti - 42.5; LiF - 28.75; KF - 27.03; NaF - 1.72.

It should be noted that other elements, such as Si, B, P, the residual amounts of Na_2TiF_6, K_2TiF_6, etc., are also present in the cathode sediment. However, their content is incomparably small compared to the content of the main components; therefore, they cannot have a significant effect on the purity of the resulting titanium powder. Also, in the cathode deposit, there are complex titanium salts of the Me_2TiO_3type, where Me = Na, K, Li, which are absorbed on the resulting product during the course of the electrolysis process.

To obtain a pure titanium powder, it must be purified from electrolyte impurities of fluoride salts (FLiNaK) - LiF, KF, NaF; complex titanium-containing salts (formed by the absorption of TiF_4); micro impurities introduced by the original titanium-containing raw materials and fluoride electrolyte salts, as well as by corrosion of the equipment material. To carry out the washing-off, *a fundamentally new method* is needed allowing to regenerate the reagent used for washing-off and minimize the amount of waste, as well as to reduce the cost of titanium powder. Since the cathode deposit after the electrolysis process consists of fluoride electrolyte salts (FLiNaK) mixed with titanium powder, it should be expected that the best solvent of these salts is anhydrous HF.

In order to choose the washing-off temperature, let’s consider its effect on the equilibrium concentration of HF [21]. In order for the HF vapor pressure to be insignificant, the temperature should be (–40 ° C) at which the HF vapor pressure (p_{HF}) does not exceed 50 mm of mercury.

Let's study the effect of the temperature of washing-off by anhydrous HF in the range of (–50 ÷ –30 °C) on the quality (impurity content) of the resulting titanium powders. In this temperature range, p_{HF} does not exceed 75 mm of mercury. Such conditions are fairly easy to ensure using sealed equipment and a refrigeration unit.

In the process of washing-off by an hydrous HF, high purity reagents were used; therefore, contamination with impurities present in the reagents was insignificant (less than 10 ppm). Washing-off the cathode deposit with high-purity HF was carried out in an inert gas (argon) atmosphere. This is necessary in order to ensure that anhydrous HF does not react with moisture in the air. The washing-off process was carried out at –20 °C for 120 minutes. LiF, KF, NaF were dissolved in liquid HF and then the titanium powder was separated from the liquid phase. To remove insignificant amounts of HF, the titanium powder was purged with an inert gas (argon).

RESULTS AND DISCUSSIONS

The results presented in Figure 1 make it possible to conclude that all the fluorination processes have no limitations from the thermodynamic point of view, are irreversible and proceed with the formation of fluorides of the elements of rutile concentrate.

In Figure 1 it shows that a higher content of TiF_4 is provided at a stoichiometric ratio of phases, however, unreacted TiO_2 will be present in the system. Therefore, a 10% excess of F_2makes the optimal conditions for fluoridation. Table 1 shows that at temperatures above 400 K, the formation of gaseous TiF_4 begins and its amount dominates with increasing temperature.

The process of fluorination, which takes place on the contact surface of the solid and gaseous phases, consists of the following main stages: 1) transporting the reacting gas to the surface of the solid material; 2) gas chemisorption on the surface of the solid material; 3) chemical reaction of the sorbed gas with the solid; 4) desorption of gaseous TiF_4 from the surface of a solid product; 5) transporting of desorbed TiF_4.

The rate of interaction of TiO_2 with fluorine is determined by the slowest of these processes. Processes 1 and 5 are determined by diffusion factors; for a very thin layer of material, their role is relatively small, so the rate of fluorination is determined by processes 2, 3 and 4. The speed of these processes is determined by temperature; the speed of process 2 depends both on the size of the surface of the solid and on the partial pressure of fluorine p_{F_2} in the system. Thus, the rate of interaction of TiO_2 with fluorine is determined by the temperature, p_{F_2} and the physicochemical characteristics of the initial product.

It has been established that at 580 K and below, the fluorination proceeds slowly, probably with the formation of solid oxyfluoride or gaseous TiF_4. The first compound forms a film on the surface of titanium dioxide particles, which practically stops the process. At a rather high rate, the reaction proceeds only at 630 K, while at 830 K, the reaction rate gradually increases, and the volatilization of titanium in the form of TiF_4 ends within 12-14 minutes.

The kinetic curves of fluorination of titanium dioxide with fluorine have an S-shaped form, characteristic of heterogeneous "gas-solid" processes [22]. Three areas are visible on the kinetic curves: 1 — an induction period characterized by low speed and associated with the transformation of the initial TiO_2 into intermediate oxyfluorides. During this period, the interface is formed, consisting of an intermediate compound (titanium oxyfluoride). Fluorine atoms diffuse inside the initial solid reagent, forming nuclei of intermediate compounds. At stage 2, as new nuclei appear, the velocity increases, reaching a maximum value, and the further course of the kinetic curves is determined by the advancement of the interface. At stage 3, the reduction of the surface area occurs due to the consumption of solid reagent, the rate of transformation decreases [23].

The kinetic curve of fluorination at 580 K is characterized by a large induction period. The rate of fluorination in the range of 780-830 K increases dramatically due to the fact that the reaction goes into combustion mode. It should be noted that fluoridation proceeds with a significant release of heat, so it is quite difficult to ensure isothermal conditions of the process.

Mathematical processing of the obtained values of the interaction of titanium dioxide with fluorine was carried out in three equations: the Gistling equation, the "shrinking" sphere and the Jander equation.

The Gistling equation is used to describe the kinetics of the process in the external diffusion area:

$$1-(1-\alpha)^{2/3}=k\tau,$$

where α is the degree of substance transformation, k is the rate constant, $\tau$is time.

The equation of the "shrinking" sphere is applied to the kinetic field:

$$1-(1-\alpha)^{1/3}=k\tau,$$

and to describe the kinetics of reactions, during which sufficiently dense films are formed, slowing down the flow of fluorine to the reaction surface (diffusion area), the Janderequation is used:

$$(1-(1-\alpha)^{1/3})^2=k\tau.$$

The possibility of using these equations to describe the fluorination mechanism was determined by calculating the maximum correlation coefficient of the $k=f(\alpha,t)$ dependences for each kinetic equation. Figures 4-6 show the corresponding dependences (the temperatures of the fluorination process are shown in parentheses).

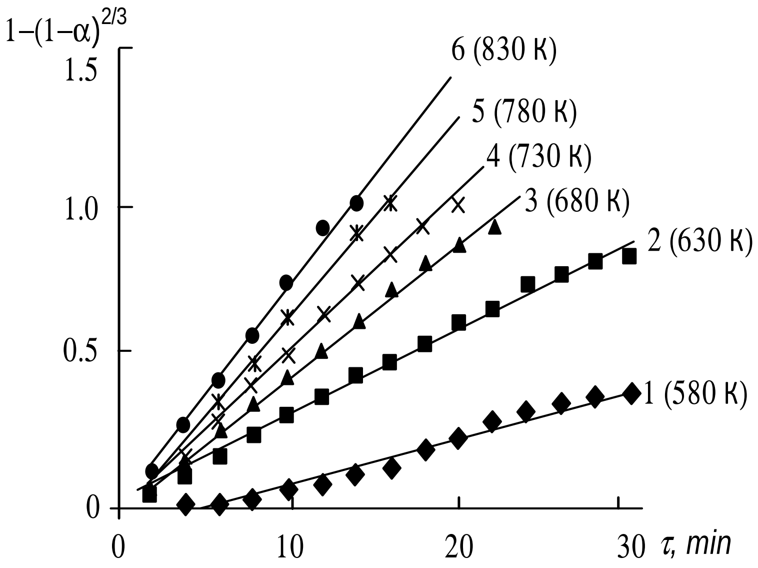

Figure 4: $1-(1-\alpha)^{2/3}=f(\ln\tau)$ Dependence for the Gistling Equation.

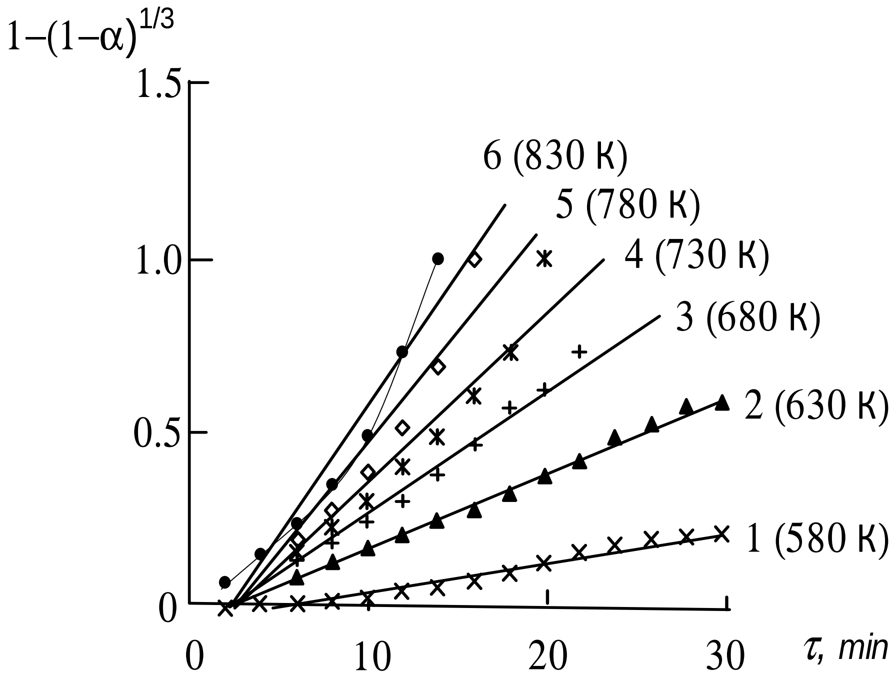

Figure 5: 1–(1–α)$^{1/3}$=f(lnτ) Dependence for the "Shrinking" Sphere Equation.

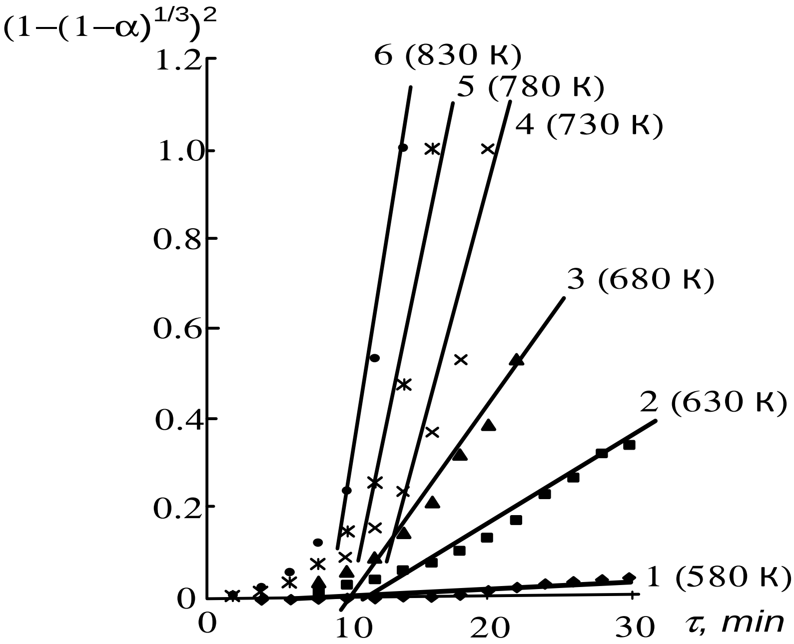

Figure 6: (1–(1–α)$^{1/3}$)^2=f(lnτ) Dependence for the Jander Equation.

The obtained results are most correctly processed by the Gistling equation (the correlation coefficient being 0.96-0.99). This equation is derived from the assumption that the process rate is determined by the diffusion of the fluorinating reagent molecules and sublimated fluorination products (TiF_4, SiF_4, O_2, etc.) into the space between the grains. This space is supposed to be infinite [24].

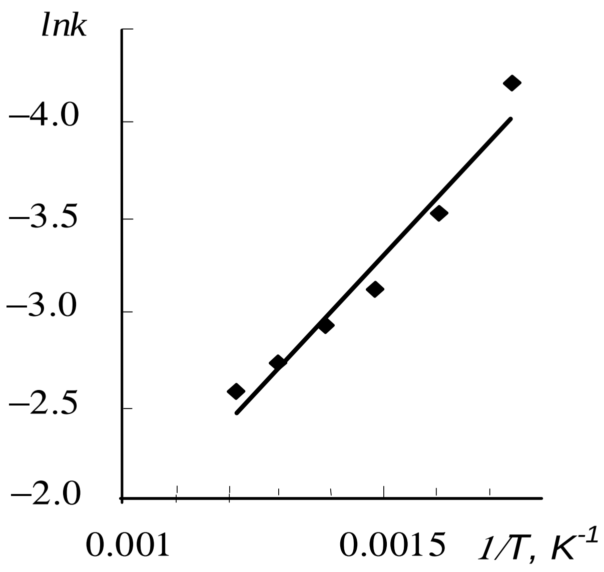

Figure 7: lnk Dependence on Absolute Temperature.

The effect of temperature on the fluorination rate of TiO_2, calculated by the Gistling equation, is shown in Figure 7. To determine the activation energy of the process (Ea), this dependence was linearized. A direct proportional dependence is observed throughout the whole fluorination process, except for the initial and final stages. The deviation from the linear dependence at the beginning of the process can be explained by filling the system with inert gas (nitrogen), which is necessary to remove air from the system. During the last stage of the process, it is not TiO_2that is fluorinated, but the resulting intermediate titanium oxyfluoride.

The slope of the straight line in the Arrhenius coordinates is used to determine the value of apparent *Ea* (24,600 J/mol) and the multiplier by the pre-exponent (k_0 = 3.063 min^{-1}). The kinetic equation for the fluorination of TiO_2 is:

$$\left(1-(1-\alpha)^{1/3}\right)^2 = 3.063 \cdot e^{\frac{24600\pm100}{RT}} \cdot \tau.$$

It should be noted that all the patterns described above are valid when using a large excess of fluoride. In practice, its minimum excess is usually used. During the formation of intermediate fluorides from TiO_2, the process rate is quite high, and fluorine can be used almost completely. When obtaining TiF_4 from its intermediate fluorides, fluorine is used almost completely (quantitatively) only when the solid and gas phases are in contact. This process is carried out in countercurrent reagents when fresh fluorine is supplied to the interaction with a partially fluorinated product, and the fresh TiO_2 is fluorinated by the released gases.

Under static conditions (or with insufficient mixing intensity) and at high concentrations of fluorine, considerable overheating of the solid material can occur. Since the intermediate titanium oxyfluoride and impurities present in the rutile concentrate can be sintered, poor mixing of the solid and gas phases leads to the melting of the material and further deterioration of the contact conditions of the phases. Therefore, it is more reasonable to carry out the process of TiF_4 formation in gas mist. Under these conditions, the heating of the particle can be neglected, since its temperature is almost equal to the gas temperature [25, 26].

When conducting TiF_4 electrolysis, the effect of cathode current density (I_c) on the current output of titanium (ηt,%) in the cathode product is shown (see Fig. 8). When the current density is higher than 0.4 A/cm^2, the titanium yield in current strength exceeds 90% and practically does not change with an increase in I_c. The optimal values of Ti current output are$\eta_{\text{т}}$~90-95 %. Table 2 shows the experimental results for Ti electrolysis in the fluoride electrolyte LiF-KF-NaF-TiF_4.

During the research, it was established that the processes of surfacing of fluoride eutectic, its saturation with titanium tetra fluoride, and the electrolytic recovery occur stably in accordance with the regulatory (pre-determined) standards. Due to the ingress of moisture from the air through the gland seals of the electrodes, as well as overheating of the walls and the retort lid of the electrolyser due to the need to ensure the temperature mode of the electrolyte melt, the formation and penetration of corrosion products into the electrolyte and the pollution of the obtained titanium powder were observed. To eliminate corrosion, the lid and all parts of the electrolyser made of stainless steel and located above the electrolyte melt, had previously been covered with a layer of electrolytic nickel.

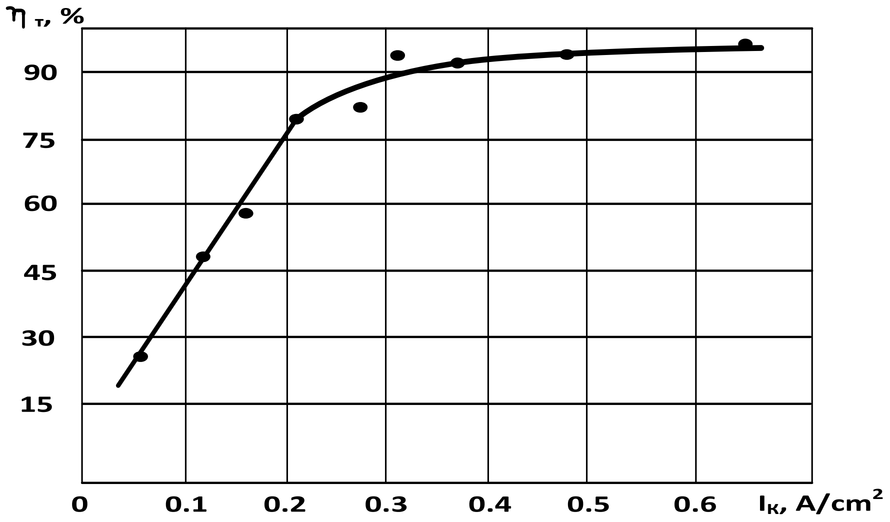

Figure 8: Effect of Cathode Current Density (Ic) on Titanium Current Output (ηt,%).

Table 2: Experimental Results for the Electrolysis of Titanium in Fluoride Electrolyte

No	Mass of the Initial Electrolyte, g	Processed, g		ObtainedTi, g	$\eta_{\text{т}}$, %
		TiF_4	Ti c TiF_4		
1	1250	100	38.7	38.1	98.5
2	1875	150	58.1	56.2	96.7
3	1250	100	38.7	38.1	98.5
4	1875	150	58.1	66.2	96.7
5	1625	130	50.3	47.0	93.4
6	1250	100	38.7	38.1	98.5

Electrolysis conditions: electrolyte composition,% wt.: LiF(29.98)-KF(52.17)-NaF(10.66)-TiF_4 (7.19); parameters: $I_a = 0.09\text{-}0.13$ A/cm^2, t = 500-550 °C, $\tau = 6$ h.

Titanium powder with electrolyte (cathode deposit) is very firmly attached to the base of the cathode when the cathode is cooled to room temperature. Thus, when using a graphite cathode, it is almost impossible to remove the deposit from its surface. The deposit was removed from other tested cathode materials only when the cathode was cooled in liquid nitrogen. At the same time, together with the cathode deposit, a 1-2 mm thick visible film consisting of the cathode material was removed from the cathode. When grinding the deposit and washing it off, the titanium powder was contaminated with impurities of the cathode material. This contamination of titanium powder with metal impurities was eliminated when using a titanium cathode.

Cathode deposits were washed-off in a mixture of inorganic acids (“acidic” washing) or anhydrous HF. For this, cathode deposits weighing 50 g were used. The Ti content in the deposits was 30-35% by weight (17.5 g), and the content of the fluoride electrolyte salts was LiF-KF-NaF - 70-65% wt. (32.5 g), respectively.

Samples of the washed-off electrolytic titanium powder after the "acidic" washing were analyzed for the content of impurities. The results of the analysis are shown in Table 5. The content of impurities in the titanium powder obtained using fluoride technology and the titanium powder washed-off with an acidic method is significantly lower than in the Kroll titanium sponge.

Despite the fact that during the “acidic” washing the quality of the obtained titanium powders is high, however, such washing requires significant quantities of chemical reagents that cannot be regenerated and returned to the washing process. Therefore, the "acidic" method of washing can be used only under laboratory conditions to obtain experimental batches of titanium powder.

The results of studies of the change in the mass of the cathode deposit depending on the temperature during washing with anhydrous HF are shown in Figure 9 [27]. The results obtained show that at –40 °C a decrease in the mass of the cathode deposit occurs in a minimum time of 20-22 minutes. As the washing temperature increases, the amount of HF in the gas phase increases dramatically, and the washing process becomes ineffective.

The effect of HF excess on the dissolution rate of fluoride salts contained in the cathode deposit at –40 ° C was studied. The research results are presented in Figure 10. It is shown that with an increase in the excess of HF from 5 to 20% by volume, the time of dissolution of fluoride salts in the cathode deposit is reduced. These salts are almost completely dissolved in 20% vol. HF excess in 10-12 minutes. The increase in HF excess to 30% vol. does not reduce the time of dissolution of the cathode deposit. Therefore, the process of dissolving the deposit should be carried out with a 20% excess of HF.

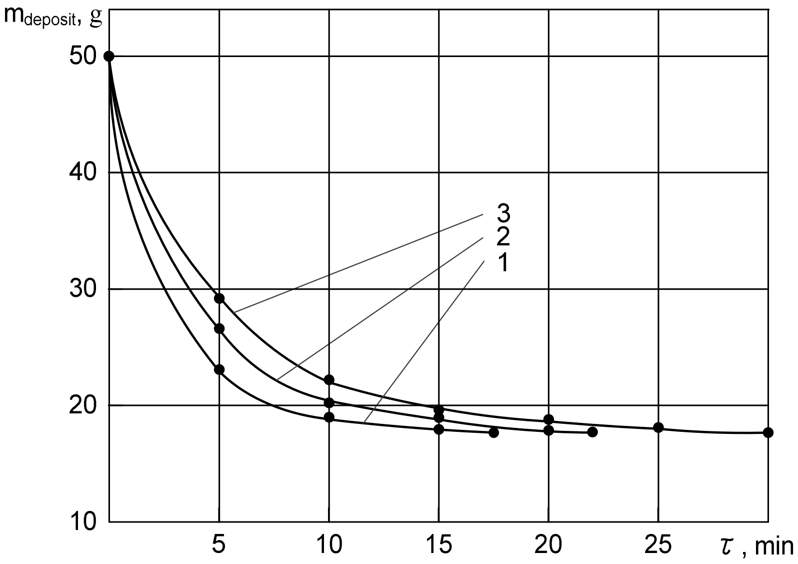

Figure 9: Effect of the Temperature of Washing with Anhydrous HF on the Change in Mass of the Cathode Deposit. The Temperature of the Washing-off Process: 1 – -50 °C; 2 – -40 °C; 3 – -30 °C.

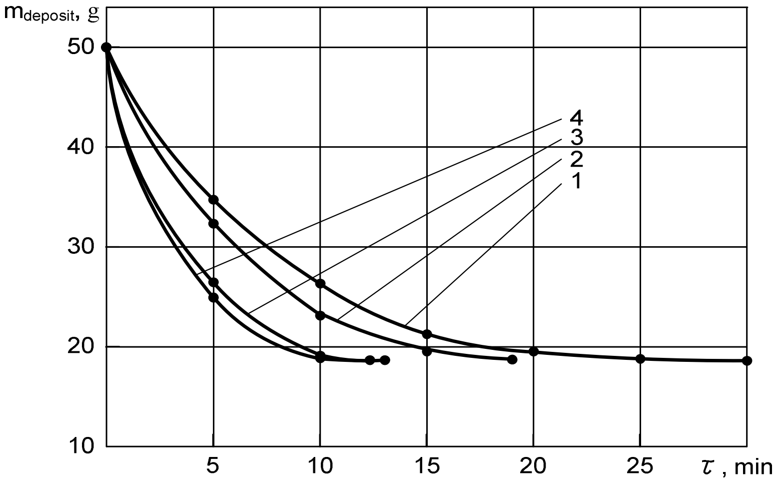

Figure 10: Effect of HF Excess on the Dissolution Rate of Fluoride Salts of the Cathode Deposit. Washing-off Temperature –40 °C; Excess HF:1 – 5 % Vol.; 2 – 10 % Vol.; 3 – 20 % Vol.; 4 – 30 % Vol.

The chemical composition of titanium powder, obtained by washing-off with anhydrous HF and dried in an inert medium, is presented in Table 5.

Table 5: Composition of Titanium Powder after Washing-Off with Anhydrous HF

Element	Content after Washing-Off with Anhydrous HF, % Wt.	Content of Titanium Synthesized in the Kroll Process
Ti	основа	99.74
Ni	$9 \cdot 10^{-4}$	0.04
Cu	$5 \cdot 10^{-4}$	Not pre-determined
K	$6 \cdot 10^{-4}$	
Li	$4.5 \cdot 10^{-4}$	
Na	$8 \cdot 10^{-5}$	
Mg	$8 \cdot 10^{-3}$	
Fe	$5.7 \cdot 10^{-3}$	
Nb	$2.9 \cdot 10^{-3}$	
W	$< 1 \cdot 10^{-2}$	
Zn	$7 \cdot 10^{-3}$	
Cr	$9 \cdot 10^{-4}$	
Mo	$6 \cdot 10^{-4}$	
Co	$8 \cdot 10^{-4}$	
Sn	$3 \cdot 10^{-4}$	
Mn	$< 1 \cdot 10^{-4}$	
Ca, Si	$< 5 \cdot 10^{-3}$	0.01
Al, Mg, Pb, Zr	$8 \cdot 10^{-4}$	Not pre-determined

CONCLUSIONS

To obtain titanium powder from rutile concentrates, a fluoride process has been proposed, in which the initial material is fluorinated with elemental fluorine, and the resulting TiF_4 is separated from the fluoride impurities. The purified TiF_4 is electrolyzed in the melt of fluoride salts of alkali metals, and the obtained cathode deposit is washed-off with anhydrous HF. In fluoride technology, two main reagents are recycled - elemental F_2 and anhydrous HF. Due to this, high economic performance is ensured, and the environment is not polluted by hazardous waste technology.

It is shown that fluorination proceeds at high speed in the temperature range of 300-550 ^{o}C. Diffusion factors limit this process, since the activation energy E_a is 24,600 J/mol. Studies of the electrolytic production of titanium powder have shown that when TiF_4 dissolves in the alkali metal salts fluoride eutectic FLiNaK, a complex salt is formed - $(K_2,Na_2)TiF_{6L}$which is well dissolved in the fluoride melt and during its electrolysis, titanium powder is formed on the titanium cathode, which is mixed with fluoride eutectic. The yield of Ti in the cathode product reaches 93.4-98.5 wt.%, which is much higher than with the magnesium-thermal reduction of $TiCl_4$ in the Kroll process. The proposed technology of washing Tipowder from cathode deposit using an hydrous HF almost completely eliminates the emissions of solid, liquid and gaseous chemically harmful substances into the environment. The content of impurities in the Tipowder after washing off the fluoride eutectic does not exceed 0.1%, which is much less than in the Tipowder obtained in the Kroll process.

ACKNOWLEDGMENTS

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REFERENCES

1. *Kroll W.J. Ductile titanium. // Trans. Electrochem.Soc. –1940. Vol. 112. – P. 35-47.*
2. *Lane D.A. Pollution caused by waste from the titaniumdioxide industry: Directive 89/428 // Boston College International and Comparative Law Review. – 1991. Vol. 14. Issue 2 Symposium on European Community. Article16. Environmental Law. URL:lawdigitalcommons.bc.edu/cgi/viewcontent.cgi?referer=https://www.google.com/&httpsredir=1&article=1500&context=iclr*
3. *Agreement reached with Belgium to end waste acid discharges into north sea by 1990,10 Int'l Env't Rep. (BNA) №. 4, at 174 (Apr. 8, 1987); Case 68/81, Commission of the European Communities v. Kingdom of Belgium, [1982] E.C.R. 153, 156 (1982).*
4. *Vondruska M., Bednarik V., Sild M.Stabilization/solidification of waste ferrous sulphate from titanium dioxide production by fluidizedbed combustion product. // Waste Management. – 2001 Vol. 21, № 1. – P.6-11.*
5. *Okabe T.H.,Oda T., Mitsuda Y.Titanium powder production by preform reduction process (PRP) // Journal of Alloys and Compounds. Vol. 364, Issues 1-2, 11 February 2004. – P. 156-163. URL:sciencedirect.com/science/article/pii/S0925838803006108*
6. *Fray D.J., Farthing, T., and Chen G.Z. Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. // Nature, 407 (2000) 361-364. URL:nature.com/articles/35030069*
7. *Withers J.C., Cardarelli F., Laughlin J., Loutfy R.O.Recent improvements for electrowinningitanium metal from composite anodes // Materials Electrochemical Research (MER) Corporation7960 S. Kolb Road, Tucson AZ 85706 United States. URL:francoiscardarelli.ca/PDF_Files/Article_Cardarelli_MER_Process.pdf*
8. *Loutfy R., Withers J.C. Thermal and Electrochemical Process for Metal Production. US Patent App. 2007/0029208*

9. *Ono K. and Suzuki R.O.: A new concept for producing Ti sponge: Calciothermic reduction. JOM Mem. J. Min. Met. Mater. Soc., 2002, Vol. 54 (2), p. 59-61.*

10. *Suzuki R.O., Teranuma K., Ono K. Calciothermic reduction of titanium oxide and in-situ electrolysis in molten* $CaCl_2$*. //Metall. Mater. Trans. B 34B (2003) 287-295.*

11. *Osaki S., Sakai H., Suzuki R.O.Direct Production of Ti–29Nb–13Ta–4.6 Zr Biomedical Alloy from Oxide Mixture in Molten* $CaCl_2$*. //J. Electrochem. Soc. 157 (2010) E117–E121.*

12. *Kanari N., Gaballah I. and Allain E. A study of chromite carbochlorination kinetics.// Metall.Mater. Trans. B, 30B, 1999, 577-587.*

13. *Karelin V.A., Karelin A.I. Fluoride technology of processing of concentrates of rare metals. – Tomsk: NTL publishing house, 2004. – 184 p.*

14. *Sinyarev G.B., Vatolin N.A., Trusov B.G., Moiseyev G.K. Use of the COMPUTER for thermodynamic calculations of metallurgical processes. – M.: Science, 1986. – 261 p.*

15. *Karelin V.A., Strashko A.N., Dubrovin A.V. Electrolytic production of titanium powders in fluoride fusions // News of the Tomsk Polytechnic University. – 2013. Vol. 323, № 3. – P. 82-87. URL:file:///C:/Users/vakarelin/Downloads/elektroliticheskoe-poluchenie-titanovyh-poroshkov-vo-ftoridnyh-rasplavah%20(1).pdf*

16. *KarelinV.A., StrashkoA.N., DubrovinA.V., SazonovA.V.Application of the electrolysis for the purposes of receivingtitanium-based powders from fluoride fusions // Procedia Chemistry.2014. Vol. 11. P. 49-55. URL:file:///C:/Users/vakarelin/Downloads/application-of-the-electrolysis-for-the-purposes-of-receiving-titanium-based-powders-from-fluoride-fusions.pdf*

17. *Adamszak R.L., Mattern J.A., Tiecelmann. A partical phase study of the system NaF–HF. // Journal of Physical Chemistry, 1959, V. 63, № 12, p. 2063-2065.*

18. *Fischer J. The dissociation pressure of sodium bifluoride – the free energy and enthalpy change for the reaction* $NaHF_2 \rightarrow NaF + HF$ *from 157 to 269. // Journal of American Chemical Society, 1957, V. 79, p 6363-6364.*

19. *Miller A.R. Sodium bifluoride decomposition preassure by the knudsen effision method // Journal of Physical Chemistry, 1967, V. 71, p 1144-1145.*

20. *Morrison J.S., Jache A.W. The system NaF–HF at 0 and -15°C. // Journal of American Chemical Society, 1959, V. 81, № 8, p. 1821-1823.*

21. *Hydrofluoric Acid properties / V. 1.1, January 2002. Honeywell 2002. URL:http://www3.imperial.ac.uk/pls/portallive/docs/1/7276108.PDF*

22. *KarelinV.A., Strashko A.N., Dubrovin A.V., Sazonov A.V. Research of fluorination process of rutile concentrate // Procedia Chemistry.– 2014, №11. P. 56-62.*

23. *Karelin V.A., StrashkoA.N., DubrovinA.V. Research of fluorination process of rutile concentrate // International Symposium on Inorganic Fluorides: Chemistry and Technology: book of abstracts, 2-6 June 2014, Tomsk / National Research Tomsk Polytechnic University (TPU); edit. V.N. Mitkin; R.V. Ostvald. – Tomsk: TPU*

Publishing House, 2014. – [P. 103]. URL: http://www.lib.tpu.ru/fulltext/c/2014/C75/057.pdf

24. *Levenspiel O.Chemical reaction engineering. John Wiley and Sons, Inc.– New York London. – 1965. – 624 p.*
25. *Kopyrin A.A., Karelin A.I., Karelin V.A.The nuclear fuel production technology and radiochemical processing. – M.:ZAO «Atomenergoizdat». – 2006. – 576 p.*
26. *Lawroski S. et al. Production of Refined Uranium Hexafluoride from OreConcentrates by Fluidization and Fractional Distillation Technique, p. 1552,USA; Geneva, 1958.*
27. *KarelinV.A., StrashkoA.N., SobolevV.I.,SazonovA.V., KarelinaN.V.Titanium powder segregation outof cathode deposit of titanium electrolyzers // Journal of Chemical Technology and Metallurgy, 53, 5, 2018, 856-863.*