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Application of the electrolysis for the purposes of receiving titanium-based powders from fluoride fusions

V.A. Karelin[a],*, A.N. Strashko[a], A.V. Dubrovin[b], A.V. Sazonov[a]

[a]National Research Tomsk Polytechnic University, 30 Lenina St., Tomsk 634050, Russia
[b]New Technologies NTC, 34 Elizarovyx St., Tomsk 634012, Russia

Abstract

A short review of industrial technologies used for receiving titanic powders is provided. Shortcomings of existing industrial chloride production technologies of titanium are shown. The need to develop, the essentially new fluoride technology for the purposes of receiving titanic powders from low-temperature fluoride fusions is shown. The preparation technique for fluoride fusions uses the process of hydrofluoration of fluorides from lithium and sodium non-aqueous HF with the allocated decomposition of potassium hydrofluoride is given. The processes occurring during the electrolysis of titanic powders from fluoride fusions with the use of tetrafluoride as a reagent for the titanium are described.

Keywords: fluoride fusion ; electrolysis ; fluorine ; titanium ; impurities ; electrolyser ; cathode and anode processes

1. Introduction

Titanium possesses a number of valuable properties: high durability (carried to metal density), excellent chemical firmness in relation to many hostile environments and increased thermal stability. Now use this metal has a leading position in various areas of modern science and equipment. Over the last 60 years, new technologies focused on the reduction of titanium cost which led to the fact that Kroll-process[1] was offered. Nevertheless, the offered technologies didn't crown success, and researches were stopped in a period of economic crisis. Now, there is an

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* Corresponding author. Tel.: +7-382-2701-777 add. 2269.
  E-mail address: v.a.karelin@mail.ru

increase in demand for titanium and the fact that its production cost is high has resulted in the need to replace the outdated Kroll-process by more effective technologies.

Over the last 10 years, a number of technologies for obtaining titanic powders have been offered: PRP process (Great Britain)[2]; MER-process (Materials Electrochemical Research Corporation)[3] supported by the Agency of Defensive Research Projects (DARPA, Great Britain)[4]; OS-process[5,6] developed at Kyoto University (Japan)[7].

These processes are based only on using TiO_2 as the raw material. In the described ways, no data on the purity of dioxide in the composite and methods of receiving are found.

All described ways possess shortcomings: necessity of the excretion of a powder of the titanium from an initial briquette; difficulties in transfer of calcium to redox couples and control of the vapour content in calcium; sharp reduction of an exit current at the end of the process; electrolyte pollution by carbon at the expense of dissolution of the binding cathode at decomposition; need for the replacement of anodes due to their decomposition at the electrolysis with the allocation of a CO/CO_2 gas mixture.

2. Experimental results

We have conducted research on a high-purity metal powder of titanium by the electrolytic decomposition of titanium tetrafluoride or potassium hexafluorotitanate (K_2TiF_6) in the fusion of a low-melting eutectic fluoride salt of alkaline metal[8]. For these purposes, three-fold eutectic mixes of fluoride LiF/KF/NaF salts are investigated and the eutectic of structure of 0.5 M LiF/0.39 M KF/1 M NaF has a melting temperature of 472°C, and the greatest conductivity in comparison with eutectics on the basis of chloride salts[9] is recommended for practical use[8].

At absorption of the titanium tetrafluoride by fusion of fluoride, the electrolyte reaction proceeds:

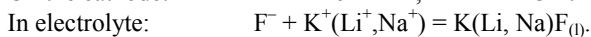$$TiF_{4(g)} + (LiF/KF/NaF)_{(l)} \rightarrow Li_2(K_2,Na_2)TiF_6(l) \tag{1}$$

The extent of saturation of fluoride fusion by titanium tetrafluoride totals 3-3.5%.

After carrying out the process of saturation in a fluoride electrolyte, the dissociation processes can be described by the following reactions:

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

$$TiF_6^{2-} = Ti^{4+} + 6F^-. \tag{3}$$

When carrying out pilot studies on the implementation of the electrolytic process on the cathode, there is a formation of a metal titanium powder. On the anode, however, elemental fluorine follows the reactions:

On the cathode: $Ti^{4+} + 4e \rightarrow Ti^0$,   On the anode: $4F^- - 4e \rightarrow 2F_2^0$,

In electrolyte: $F^- + K^+(Li^+,Na^+) = K(Li, Na)F_{(l)}$.

Investigations conducted on the skilled electrolytic installation scheme are given in Fig. 1.

TiF_4 is sublimated from the solid to the gaseous state (sublimation process). It occurs before carrying out the electrolysis process. Sublimation is performed at 300 °C in the reactor (position 4) which is located in the electric furnace (position 6). Under these conditions, TiF_4 passes from a solid state into a gaseous state, that is, it undergoes the sublimation. TiF_4, at the saturation of a eutectic fluoride salt, regulates by means of the gate of the thin adjustment installed on the case of a cylinder. The mass of a cylinder is measured by means of PV-10 scales with a margin error of ± 5 g which regulates the amount of TiF_4 in the composite. The general view of the installation of the electrolysis and separate knots are presented in Fig. 2.

Initial fluoride salts have very high melting temperatures: LiF=870 °C, KF=857 °C, NaF=992 °C. Therefore, potassium hydrofluoride (KF·HF, melting point of KF·HF = 239 °C) has been mixed with lithium and sodium fluorides to obtain the fluoride eutectic. When heating such a mixture, KF·HF decomposes and LiF·HF and NaF·HF are formed which have melting points that do not exceed 300 °C. Such mixtures first melt, and then, after increasing the temperature to 472 °C, the hydrofluorides of all alkaline metals decompose to the form a fluoride eutectic structure of LiF/KF/NaF. Anhydrous HF is assigned to the CA-L absorber.
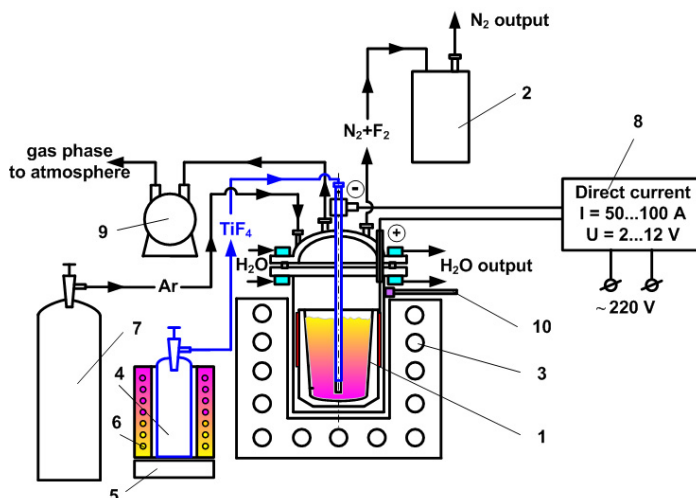
Fig. 1. Scheme of the installation for the electrolysis of a metal powder of titanium: 1 – electrolyser; 2 – absorber with mixture $(Ca(OH)_2$-NaOH) for absorption of allocated F_2; 3 – electric furnace; 4 – TiF_4 capacity; 5 – scales (PV-10); 6 – capacity electric furnace with TiF_4; 7 – cylinder with inert gas (Ar); 8 – rectifier; 9 – vacuum pump; 10 – thermocouple

Eutectic fluoride salts are prepared from their proceeding ratio:

0.5 M LiF – 0.39 M KF$_{non\ aqueous}$ – 0.11 M NaF

12.97 g   22.659 g KF   4.62 g

30.459 g KF· HF $\sum$ = 48.05 g
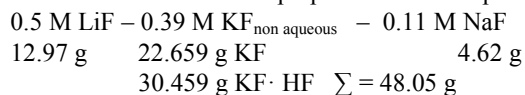
$(12.97/48.05) \cdot 100 = 26.99\%$ mass. – $(30.459/48.05) \cdot 100 = 63.39\%$ mass. – $(4.62/48.05) \cdot 100 = 9.62\%$ mass.
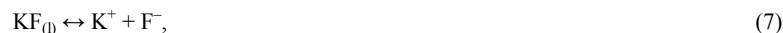
The received fluoride eutectic states with TiF_4 at concentrations of 7.75 or 3% in terms of Ti. At saturation of fluoride fusion at 500°C, complex salts are formed:

$$2KF_{(l)} + TiF_{4(g)} \rightarrow K_2TiF_{6(l)}, \tag{4}$$

$$2NaF_{(l)} + SiF_{4(g)} \rightarrow Na_2SiF_{6(l)}. \tag{5}$$

Complex compounds of lithium with the titanium, having the same structure, are not formed due to their low firmness at 500°C. Fusion of electrolyte consists of:

$LiF_{(l)} + KF_{(l)} + NaF_{(l)} + (K_2TiF_{6(l)} + Na_2TiF_{6(l)})_{(l)}$

7.75% mass of TiF_4
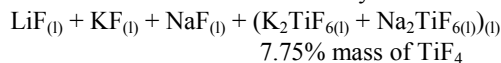
Fusion of electrolyte dissociation processes proceeds according to the following equations:

$$LiF_{(l)} \leftrightarrow Li^+ + F^-, \tag{6}$$

$$KF_{(l)} \leftrightarrow K^+ + F^-, \tag{7}$$

$$NaF_{(l)} \leftrightarrow Na^+ + F^-, \tag{8}$$

$$K_2TiF_{6(l)} \leftrightarrow 2K^+ + TiF_6^{2-}, \tag{9}$$

$$Na_2TiF_{6(l)} \leftrightarrow 2Na^+ + TiF_6^{2-}, \tag{10}$$

$$TiF_6^{2-} \leftrightarrow Ti^{4+} + 6F^-. \tag{11}$$

For the saturation of the received fluoride eutectic using TiF_4 through the central ion (Fig. 1), a metal branch pipe of working gas (TiF_4) has been used in the bottom of a graphite crucible. Then a metal branch pipe of working gas has been increased to 3 cm and in this situation a tag concerning a cover flange has been added. Junction of a cap of the reactor with the pipe duct pressurizes the polytetrafluoroethylene. The branch pipe of the working gas hermetically connects a metal tube to an absorber (2) with a capacity (4). The absorber was filled with a marble crumb or chemical absorber limy. After cooling down the cover of the muffle with water, a furnace (3) has been

used for electrical heating, increasing the temperature in the metal muffle, according to a thermocouple. The temperature has been gradually increased to 500°C. At a temperature of 450-500°C, eutectic fusion was achieved by TiF_4. For this purpose, the gate of the thin adjustment has been opened and TiF_4 has been regulated in capacities previously heated to 300 °C, providing the fusion with a decreased weight of capacity 4. After saturation of the fusion by TiF_4, the gate of thin adjustment is closed. Replacing a metal branch pipe with a core cathode has previously having weakened the consolidation. The electrolyser has the following technical characteristics: productivity is up to 50 g/h on TiF_4; the volume of the muffle is 1.35 dm^3; force of a direct current is up to 100 A; supply voltage of working electrodes 2-12 V; electrolyte temperature 500-550°C; working surface of the anode 0.0587 m^2; working surface of the cathode 0118 m^2; current density: anodic 0.85-0.13 A/cm^2, cathodic 0.42-0.63 A/cm^2.

Fig. 2. Electrolytic installation for the electrolytic decomposition of titanium tetrafluoride: a) General view of the installation; b) tight electrolyser; c) the nickel-plated cover of the electrolyser; d) graphite crucible: the anode with current conductor (below), the metal cathode (above) and an electrolyser retort (at the left)

Direct current varied within the range of 50-100A and the voltage within the range of 2-12V has been applied to carry out the process of the electrolysis on the graphite cathode (core) and the anode (crucible). During the electrolysis, a deposit (Ti powder in fusion of fluoride salts) is formed on the graphite cathode, and elemental fluorine is formed on the anode which comes from the electrolyser and absorbs into a chemical absorber, limy CA-L [a mix of 96% of $Ca(OH)_2$ and 4% of NaOH].

After the process of the electrolysis, the cathode with the allocated deposit consisting of powdered titanium in a fusion of fluoride salts is lifted over the electrolyte fusion and the electrolyser cools down before its depressurisation blows inert gas (argon) from a cylinder (7).

Appearance of the cathode with the formed deposit is shown in Fig. 3. The formed deposit is crushed mechanically and washed away from fluoride salts with anhydrous HF solution at 20°C. Thus, Li, K, and Na fluorides are well dissolved in HF. Their solubility yields 9.3%, 9.1%, and 19.2% at –20°C, respectively. Titanic powders in these conditions remain in a solid state. Final washing is carried out in acetone and ethyl alcohol.

3. Results and discussion

In Fig. 4, the influence of the cathodic current density (I_k) on an exit of the titanium current (η_τ, %) is shown in the cathodic product. It can be seen that, at a current density over 0.4 A/cm^2, the exit current of titanium exceeds 90% and it remains almost unchanged with the increasing current density.

The concentration of titanium in the cathodic product during the TiF$_4$ electrolysis in a fluoride salt fusion was 35-40% by mass. The optimum exits of Ti as the current made η_τ~90-95%. Experimental electrolysis results for the titanium are presented in Table 1 in fluoride LiF/KF/NaF/TiF$_4$ electrolyte.
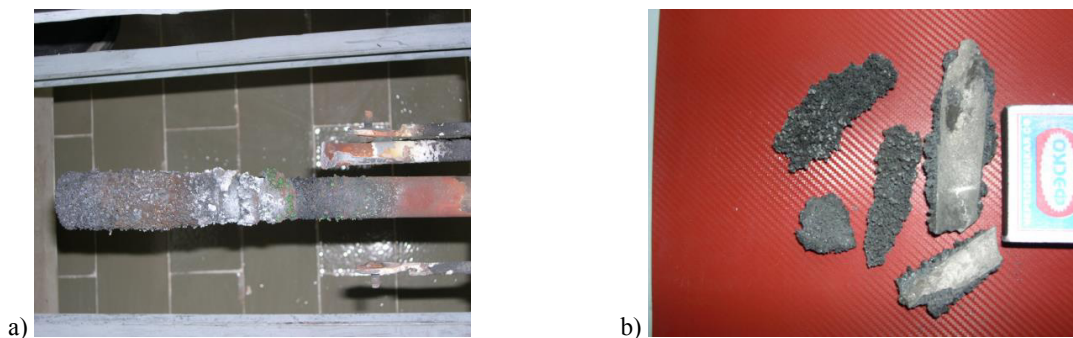

Fig. 3. Appearance of the cathode after the electrolysis and the cathodic deposit removed from the cathode: a) The metal cathode with the silicon powder on it in a mixture with the electrolyte; b) the powdery silicon removed from the cathode in a mixture with the electrolyte.
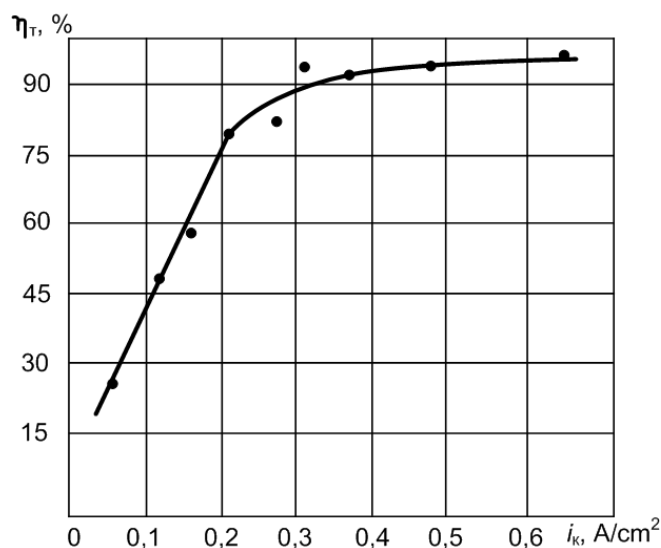

Fig. 4. Influence of the cathodic current density (I_k) on an exit current of titanium (η_τ, %)

Electrolysis conditions: composition of electrolyte, % mass: KF (29.98)/LiF (52.17) LiF/NaF (10.66)/TiF$_4$ (7.19); parameters: I_a = 0.09-0.13 A/cm^2, t = 500-550 °C, τ = 6 h.

When carrying out research, it is known that the process of depositing a fluoride eutectic, its saturation by TiF$_4$, and electrolytic restoration proceed steadily in strict accordance with procedural (established in advance) norms. Owing to the moisture from the air, due to the consolidation of electrodes, and as a result of the overheating of walls and the cover of the electrolyser for providing a temperature mode of the fusion in the electrolyte, products of corrosion and pollution of the electrolytic titanium powder have been observed. With the exception of the formation

of such pollution, the cover and details of the electrolyser have been made of stainless steel which had to be covered with a thin film of electrolytic nickel.

Table 1. Experimental results for the electrolysis of titanium in the fluoride electrolyte

№	Mass of initial electrolyte, g	Amount processed, g		Ti received, g	η_τ, %
		TiF_4	Ti with 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

Results of the analysis of the titanium powder, received as a result of the TiF4 electrolysis in a eutectic mixture of fluoride salts (LiF/KF/NaF), are presented in Table 2.

Table 2. Chemical composition of the electrolytic titanic powder

Element	Content, % mass	Element	Content, % mass
Ti	Basis	Cr	$3 \cdot 10^{-3}$
Ni	0.17	Mo	$2 \cdot 10^{-3}$
Cu	$6 \cdot 10^{-2}$	Co	$1 \cdot 10^{-3}$
Mg	$3 \cdot 10^{-2}$	Sn	$1 \cdot 10^{-3}$
Fe	$2.4 \cdot 10^{-2}$	Mn	$< 1 \cdot 10^{-4}$
Nb	$1.2 \cdot 10^{-2}$	Ca, Si	$< 5 \cdot 10^{-3}$
W	$< 1 \cdot 10^{-2}$	Al, Mg, Pb, Zr	$1 \cdot 10^{-3}$
Zn	$9 \cdot 10^{-3}$		

When carrying out research, it has been established that the deposit of titanium powder in the electrolyte was very strongly fastened to the base upon cooling down of the cathode to room temperature.

So, when using a graphite cathode, it is almost impossible to remove a deposit from its surface. From other tested cathodic materials, the deposit has been only removed when the cathode has been cooled down in liquid nitrogen. Thus, the cathode material could be removed together with a cathodic deposit from the cathode film that was approximately 1-2 mm thick. There was a mechanical pollution of the electrolytic silicon powder by metal impurities when crushing a deposit and washing it has been observed. Such a pollution of the silicon powder by metal impurities has been avoided when using a cathode produced from titanium.

4. Conclusion

Thus, when carrying out the process of electrolytic obtaining of the titanic powder:
- It is established that when the TiF_4 dissolution occurs in a fluoride eutectic of salts of alkaline LiF/KF/NaF metal-complex salts – Li$_2$ (K$_2$, Na$_2$) TiF$_{6\,(l)}$, a well dissolved fluoride fusion is formed.
- It is established that at TiF_4 dissolution during the Li$_2$ (K$_2$, Na$_2$) TiF$_6$ electrolysis on the titanic cathode, the titanium powder is formed in a mixture with a fluoride eutectic.
- Under the optimum conditions for carrying out the electrolysis of titanium tetrafluoride in fluoride salt fusion, the exit of the titanium substance in a cathodic product reaches 93.4-98.5% by mass which is much higher than that observed in the Mg-thermal restoration of titanium tetrachloride in the Kroll-process.

- The impurity content in the titanium powder after washing it from a fluoride eutectic doesn't exceed 0.1% which is much less than in titanic powder received by means of the Kroll-process, etc.

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