

**SYNTHESIS OF HIGH-PURE TITANIUM CONCENTRATES
BY THE ELECTROLYTIC METHOD FROM FLUORIDE MELTS**

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Annotation

The short review of industrial technologies of processing titanium concentrates is spent. Lacks of existing industrial production technologies of the titan are shown. Necessity of working out essentially new fluoride technologies of processing titanium concentrates is proved. The reactions proceeding at fluorination of a rutile concentrate by element fluorine are described, and thermodynamic research of fluorination process with use of *the computer program "ASTRA" is executed. It is shown that from the thermodynamic point of view fluorination process has no restrictions. Dependence of change of mass concentration titanium fluoride in products of reaction from process temperature fluorination is investigated and the choice of optimum surplus of element fluorine is proved. The equilibrium structure of products of fluorination process a rutile concentrate is defined at the chosen surplus of fluorine. The basic stages of fluorination process are described and its kinetic features are studied. Factors influencing speed of fluorination process are defined. Temperature influence at kinetics fluorination process is investigated and optimum conditions are chosen. Mathematical processing of results of the executed kinetic researches on the equations is spent: Gistling, "reduced" sphere and Jander. It is shown that for the description fluorination kinetics it is necessary to use the Jander equation. It is established that process is limited by diffusive factors – a supply of a fluorinating reagent to a surface of a firm material. The size of energy of activation of fluorination process is defined. Conditions of carrying out of process in the industrial equipment are discussed.*

Key words: fluoride melt, electrolysing process, the fluorine, dioxide and tetrafluoride of titanium, fluorides of impurity, the electrolyzer, processes on the cathode and the anode.

Titan possessing the row of valuable properties: high durability (attributed to the density of metal), excellent chemical firmness in relation to many aggressive environments and inhanceable hot – resistance, presently occupied leading positions on the use in different areas of modern science and technique.

For the last 60 years the great number of the new technologies directed to reduction of cost of titan produced Kroll – by a process is offered [1]. Nevertheless, offered technologies were not crowned by success, and researches on them were stopped in the period of economic crisis. Presently, the height of demand on titanium and high cost of his receipt resulted in a necessity to replace out – of – date Kroll – process with more effective technologies.

For the last 10 years for receipt of titanium concentrates a number of technologies is offered:

- PRP process (Great Britain) [2],
- FFC process (Cambrigian process) [3],
- MER process (Materials Electrochemical Research Corporation) [4].

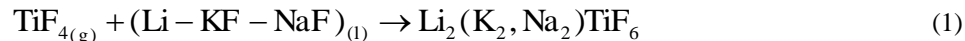
These processes are based exceptionally on using TiO_2 as a feedstock. In the described methods there is no information about the cleanness of titanium and methods of its receipt.

All described methods possess the row of main defects of which are:

- A necessity of lixiviating of titanium concentrates from the initial cake,
- difficulties of transfer of calcium in to vapors and monitoring of the content of vapors of calcium,
- sharp reduction of output on current at the end of a process,
- electrolyte pollution by carbon due to dilution of the binding cathode in case of decay,
- a necessity of changeover of anodes because of their decay when electrolysing with separation of a gas compound of CO/CO_2 .

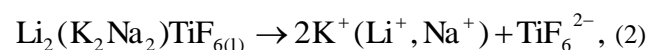
We conducted researches on receiving high – pure metal concentrates of titanium by electrolytic edecay of tetrafluoride of titanium or hexafluorotitanate potassium (K_2TiF_6) in a eutectic compounds of fluoride salts of alkali metals [5]. For these purposes triple eutectic compounds of fluoride $\text{LiF} - \text{KF} - \text{NaF}$ salts are probed and the composition 0,5M LiF eutectic – 0,39M KF – 0,11M NaF having a melting temperature of 472 °C and the greatest conductance in comparison with eutectics on the basis of chloride salts is recommended for practical use [6].

In case of absorption of tetrafluoride of titanium by a melt of a fluoride electrolyte response proceeds:

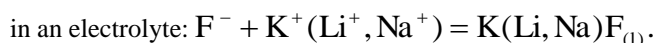
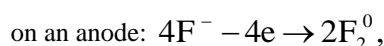
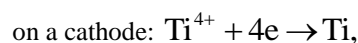


The level of saturation of a fluoride melt tetrafluoride of titanium makes up 3–3,5%.

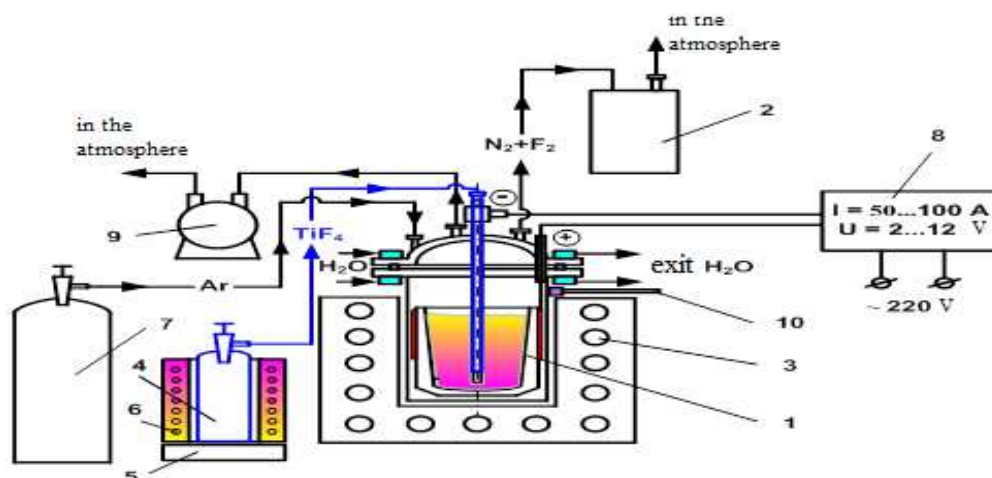
After carrying out the process of saturation in a fluoride electrolyte the dissociation processes, being described responses proceed:



During carrying out of experimental researches on realization of process electrolytic there is formation of metallic titanium concentrates on cathode, and on an anode – element fluorine on reactions:



Researches conducted on the experimental electrolytic installation which diagram is given in figure 1.



1 – electrolytic cell; 2 – absorber with an absorber (HP-I) for absorption of distinguished F_2 ; 3 – electrical furnace; 4 – capacity with TiF_4 ; 5 – PV-10 scales; 6 – the capacity electric furnace with TiF_4 ; 7 – bulb with inert gas (Ar); 8 – rectifier; 9 – vacuum pump; 10 – thermocouple.

Figure 1 – Installation diagram of electrolytic receiving metal concentrates of titanium.

The tetrafluoride of titanium which is in the capacity 4, heat in the electric furnace 6 to 300 °C. In case of this TiF_4 transfers from a solid status in gaseous, that is there is its sublimation. The expenditure TiF_4 in case of saturation of eutectic of fluoride salts is regulated by means of the valve of thin regulation set on the casing of a bulb. Measuring bulb mass by means of PV–10 scales with a margin error weighings ± 5 g the amount of tetrafluoride of titanium given to a melt is regulated.

The general view of installation of electrolysing and separate nodes are provided in figure 2.

The initial fluoride salts have very high temperatures of melt: $T_{melting} LiF = 870$ °C, $T_{melting} KF = 857$ °C, $T_{melting} NaF = 992$ °C therefore for receiving fluoride eutectic potassium hydrofluoride ($KF \cdot HF$, $T_{melting} KF \cdot HF$ of = 239 °C) in a compound with lithium and sodium fluorides is used. In case of heating up of such compound there is $KF \cdot HF$ decay with formation of $LiF \cdot HF$ and $NaF \cdot HF$ having melting temperature, not exceeding 300°C. Such compound at first passes into the melted status, and then, in case of increase in temperature to 472 °C, there is an decay of hydrofluorides of all alkali metals with formation of fluoride eutectic of $LiF-KF-NaF$ composition. Being selected waterless HF is caught by on HP–I absorber.

Eutectic of fluoride salts are prepared proceeding from their ratio:



$$12,97g \quad 22,659gKF \quad 4,62g$$

$$30,459gKF \cdot HF \quad \sum = 48,05g$$

$$\left(\frac{12,97}{48,05}\right) \cdot 100 = 26,99\% \text{ mas.} - \left(\frac{30,459}{48,05}\right) \cdot 100 = 63,39\% \text{ mas.} - \left(\frac{4,62}{48,08}\right) \cdot 100 = 9,62\% \text{ mas.}$$



a) b)



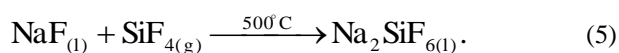
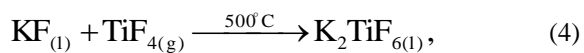
c)

d)

a) general view of installation; b) hermetic electrolytic cell; c) the nickelized cover of the electrolytic cell; d) the graphite crucible – anode current conductors to the anode (below), The metallic cathode (above) and an electrolytic cell retort (at the left).

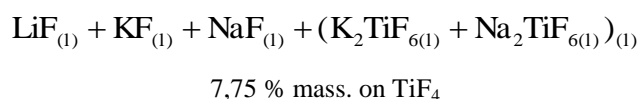
Figure 2- Experimental electrolytic installation of electrolytic expansion of tetrafluoride of titanium.

The received fluoride eutectic sated with tetrafluoride of titanium to concentration of 7,75% or 3% in terms of Ti. In case of saturation of a fluoride melt complex salts will be formed in case of 500 °C.

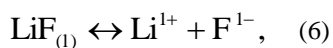


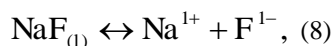
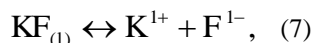
Fluorotitanat of lithium will not be formed since they are unstable in case of 500 °C.

The melt of an electrolyte consists from:



In fusion of electrolyte the processes of dissociation flow:





For the saturation of the fluoride eutecticum of tetrafluoride titan got through the central carbine of lid of muffle (figure 1) insert the metallic union coupling of working gas (TiF_4) to support in the bottom of graphite crucible. Then the metallic union coupling of working gas is lifted upwards on 3 cm and in this position nick in relation to flange of lid is made on it. The stuffing-boxes of the union are made more coupling and lid. The union coupling of working gas is hermetically connected by a metallic tube with an absorber 2 and by a capacity 4. an Absorber-absorber is filled with a marble crumb or chem. HPI absorber.

Cooling of a cover of a muffle with water is included, then a furnace 3 electrical heating is included, temperature in a metal muffle is increased, controlling temperature according to thermocouple 10 indications and gradually increasing it to 500 °C. At a temperature of muffle of 450–500 °C an eutectic melt is sated with tetrafluoride of titanium. For this purpose in beforehand heated to 300 °C capacities 4 a valve of thin regulation is opened and TiF_4 submission in a melt is regulated on a decrease of mass of capacity 4.

After saturation of melt by tetrafluoride of titanium a valve of thin regulation is closed. A metal branch pipe with the rod cathode is replaced, having weakened a glandsealing beforehand.

The electrolyzer has the following technical characteristics:

- productivity is up to 50 g/hour on tetrafluoride of titanium;
- the volume of a muffle is 1,35 dm³;
- force of a direct current is up to 100 A;
- supply voltage of working electrodes 2...12 V;
- temperature of an electrolyte 50...550 °C;
- working surface of the anode 0,0587 of m²;
- working surface of the cathode 0,0118 of m²;
- current density: anode 0,085...0,13 A/cm²;
- the cathode 0,42...0,63 A/cm².

For carrying out the process of electrolysing on the graphite cathode (rod) and the anode (crucible) give the direct current which value varies within 50...100 A, and tension – within 2...12 Century. During electrolysing process on the graphite cathode there is a formation of a precipitate (powder of titanium in a melt of fluoride salts), and on the anode – the element fluorine which brings out the electrolyzer and is absorbed in an absorber – 2 on a chemical absorber lime HP-I (a compound of 96% of $\text{Ca}(\text{OH})_2$ and 4 of % of NaOH).

After the end of process of electrolysing the cathode with the selected precipitate consisting of powder of titanium in a melt of fluoride salts, is lifted over an electrolyte melt, the electrolyzer is cooled and before its depressurization is blown with inert gas (argon) from a bulb – 7.

Appearance of the cathode with the formed precipitate is shown in figure 3.



a)

b)

a) the metallic cathode with the powder of titanium received on it in a compound with an electrolyte; b) the powdery titanium removed from the cathode in a compound with an electrolyte

Figure 3 – Appearance of the cathode after electrolysis and the cathode precipitate removed from it

The formed precipitate is ground mechanically and washed from fluoride salts waterless HF solution – 20 °C. Thus Li, K and Na fluorides are well dissolved in HF. Their solubility in case of – 20 °C makes respectively 9,3; 9,1 and 19,2% Mas. Titanic powder in these conditions remains in a solid status.

Final scrub is carried out in acetone and ethyl alcohol.

In figure 4 influence of the cathode current density (I_k) on an output of titanium on current (η_T , %) in the cathode product is shown. It is visible that in case of current density higher than 0,4 A/cm² the output of titanium on current intensity exceeds 90% and in case of increase in current density practically doesn't change.

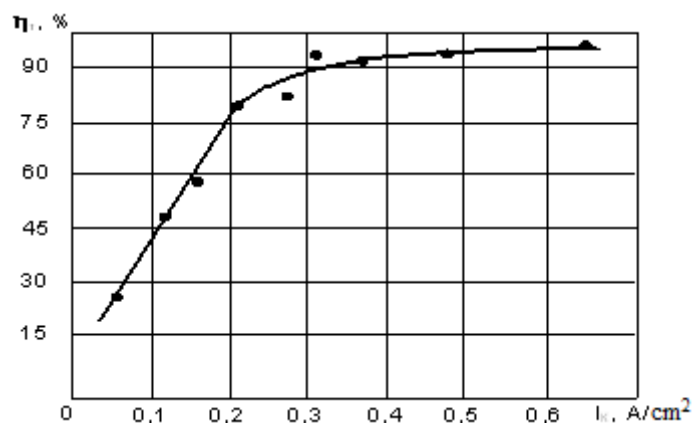


Figure 4 – Influence of the cathode current density (I_k) on an output of titanium on current (η_T , %)

The content of titanium in the cathode product when electrolysis TiF_4 in a fluoride salt melt makes 35–40% Mass output Ti of on current made $\eta_c \sim 90$ –95%.

The experimental results on electrolysis of titanium are provided to tabel 1 in a fluoride electrolyte of $LiF-KF-NaF-TiF_4$.

Table 1 – The experimental results on electrolysing of titanium in a fluoride electrolyte

n/n	Mass of the initial electrolyte,g	It is processed,g		Ti is received,g	η_r , %
		TiF ₄	Ti whith TiF ₄		
	1250	100	38,7	38,1	98,5
	1875	150	58,1	56,2	96,7
	1250	100	38,7	38,1	98,5
	1875	150	58,1	66,2	96,7
	1625	130	50,3	47,0	93,4
	1250	100	38,7	38,1	98,5

Electrolysing conditions:

- composition of an electrolyte, % Mas. : (29,98) – KF(52,17) LiF – NaF(10,66) – TiF₄ (7,19);
- parameters: $I_a = 0,09 \dots 0,13 \text{ And/cm}^2$, $t = 500 \dots 550 \text{ }^\circ\text{C}$, $\tau = 6 \text{ h}$.

Analysis results of powder of the titanium received as a result of electrolysing of TiF₄ in eutectic of fluoride salts (LiF–KF–NaF) are provided to tabale 2.

Table 2 – Chemical composition of electrolytic titanium concentrates.

Element	Contents, % Mas.
Ti	basis
Ni	0,17
Cu	$6 \cdot 10^{-2}$
Mg	$3 \cdot 10^{-2}$
Fe	$2,4 \cdot 10^{-2}$
Nb	$1,2 \cdot 10^{-2}$
W	$< 1 \cdot 10^{-2}$
Zn	$9 \cdot 10^{-3}$
Cr	$3 \cdot 10^{-3}$
Mo	$2 \cdot 10^{-3}$
Co	$1 \cdot 10^{-3}$
Sn	$1 \cdot 10^{-3}$
Mn	$< 1 \cdot 10^{-4}$
Ca, Si	$< 5 \cdot 10^{-3}$
Al, Mg, Pb, Zr	$1 \cdot 10^{-3}$

When carrying out researches it is set that processes of a hardfacing of fluoride eutectic, its saturation by tetrafluoride of titanium, electrolytic restoration proceed stably in strict accordance with the regulated (in advance set) norms. Due to the moisture hit from air because of its suction through glandsealings of electrodes, and also as a result of overheating of walls and a cover of a retort of the electrolyzer for support of a temperature mode of a melt of an electrolyte education and hit in an electrolyte of products of corrosion and pollution of electrolytic powder of titanium by them was watched. For an exception of formation of such pollution a cover

and all details of the electrolyzer from the stainless steel, being over an electrolyte melt, were stimulated to cover with a thin film of electrolytic nickel.

When carrying out researches it is set that the precipitate of powder of titanium with an electrolyte when cooling cathode to indoor temperature is very strongly fastened to its basis.

So, when using cathode from graphite, it is almost impossible to remove a precipitate from its surface. From other tested cathode materials of settlings cathode precipitate was he moved only when cooling cathode in liquid nitrogen. Thus together with the cathode precipitate from the cathode the film 1–2 mm thick seen approximately from a cathode material was deleted. When grinding a precipitate and its scrub there was a mechanical pollution of electrolytic powder of silicon by metal impurity. Such pollution of powder of silicon by metal impurity managed to be excluded when using cathode from titanium.

Thus, when carrying out process of electrolytic receiving titanic powder:

– it is set that in case of TiF_4 dilution in fluoride eutectic of salts of $LiF-KF-NaF$ alkali metals complex salt – $Li_2(K_2, Na_2)$ by TiF_6 is dissolved well in a fluoride and melt will be formed;

– when electrolysing $Li_2(K_2, Na_2) TiF_6$ the powder of titanium which is in a compound with fluoride eutectic will be formed on the titanic cathode;

– under optimum conditions of carrying out electrolysing of tetrafluoride of titanium in a fluoride salt melt the output of titanium on substance in the cathode product reaches 93,4 – 98,5% Mas. that is much higher, than in case of magniyetermichesky restoration of tetrachloride of titanium when carrying out Kroll-process;

– the content of impurity in powder of titanium after washing from fluoride eutectic does not exceed 0,1% that is much less, than in titanic powder of the TG–Tv brands, etc.

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