# APPLICATION OF FLUORIDE SALT SYSTEMS FOR OBTAINING TITANIUM
# BY THE METHOD OF ELECTROLYSIS
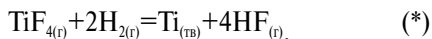
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*Fundamentally new fluoride method of synthesis of high-clean metal titanium powder from natural oxide concentrates has been proposed. In a closing stage of processing the electrolytic method of titanium tetrafluoride decomposition in soft eutectic of alkalis fluoride salts was used for the first time. Using this method in industrial practice allows excluding environment contamination with hazardous chemical substances and obtaining cheap high-clean metal titanium powder.*

Information about hydrogen reduction of gaseous fluorides of refractory metals is contained in numerous scientific publications [1–4].

Interaction of gaseous titanium tetrafluoride with hydrogen is described by summary reaction equation:

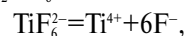$$TiF_{4(г)}+2H_{2(г)}=Ti_{(тв)}+4HF_{(г)}. \qquad (*)$$

Progressiveness of the given process becomes obvious in connection with the development of closed process flowsheet in which metal titanium wastes are fluoridated with elemental fluorine. The generated fluoride is reduced with hydrogen at obtaining semi-finished product and extracting hydrofluoric undergoes electrolysis in $KH_2F_3$ melt obtaining fluorine and hydrogen. Besides, blanks or products of various shape may be formed from gas phase $TiF_4$ with hydrogen. It is difficult and sometimes impossible to produce them by other known methods. The process of $TiF_4$ hydrogen reduction may be used for deposition from gas phase of titanium coating and its alloys of different purpose.

Significant and obvious disadvantages are inherent to hydrogen technique of titanium obtaining from its tetrofluoride. The main one consists in the fact that homogeneous reaction (*) is not observed at precipitation on the inner surface of heated tube up to 900 °C [5] and up to 1200 °C – at precipitation on substrate outer surface in reactor volume [6]. Homogeneous behavior of the given reaction in reactor volume occurs only at temperature higher than 1400 °C. The process of $TiF_4$ reduction with hydrogen at such high temperatures is stipulated by intensive corrosion of reactor material in hydrofluoric medium. Besides, carrying out the process, low straight titanium output from gas flow of titanium tetrafluoride strongly diluted with hydrogen and low reactor capacity is observed on the substrate.

We carried out investigations on obtaining high-clean titanium powders by electrolytic dissolution of titanium tetrafluoride or potassium hexafluorotitanate ($K_2TiF_6$) in the melt of soft eutectic of alkaline metal fluoride salts [7]. For these purposes triple eutectic mixtures of fluoride salts LiF-KF-NaF were studied and eutectic of the composition 0,5M LiF – 0,39M KF – 0,11M NaF, having $t_{пл}$=472 °C and the highest electrical conductivity in comparison with eutectics on the basis of chloride salts was recommended for practical use [8].

## Experimantal part and discussion of the results

To carry out experimental investigations on realization of the process of electrolytic dissolution of $TiF_4$ or potassium hexafluorotitanate ($K_2TiF_6$) in fluoride salt eutectic obtaining high-clean titanium powder at a cathode and elemental fluorine at anode by the reactions:

$$TiF_4 = Ti^{4+} +4F^-,$$
$$K_2TiF_6 = 2K^+ + TiF_6^{2-},$$
$$TiF_6^{2-}=Ti^{4+}+6F^-,$$
$$\text{at a cathode } Ti^{4+}+4e\rightarrow Ti^0,$$
$$\text{at anode } 4F^--4e\rightarrow 2F_2$$

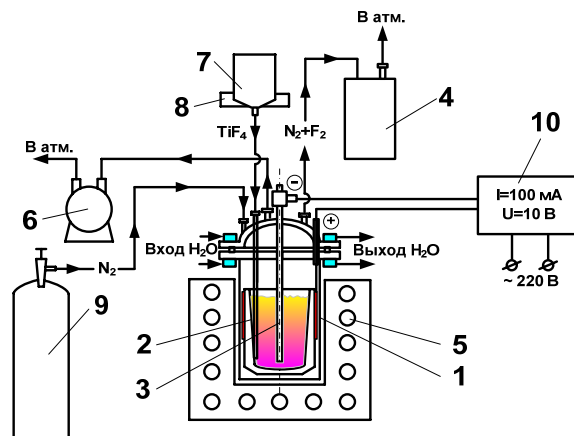a pilot electrolytic device was developed (Fig. 1).



**Fig. 1.** *Diagram of the device for obtaining titanium electrolytic powder: 1) electrolytic cell, 2) anode, 3) cathode, 4) absorber with calcium oxide and natrium dioxide for absorption $F_2$, 5) electric stove, 6) vacuum pump, 7) capacity with $TiF_4$, 8) electron scales, 9) bottle with inert gas $N_2$, 10) straighten device*

Pilot electrolytic device consists of:
— hermetic electrolytic cell – 1, body and cap of which are made of stainless steel 12X18H10T. Body and cap flanges are cooled with running water; sealing is realized by vacuum rubber. Crucible serves as anode – 2, and cathode is made in the form of bar – 3. Anode and cathode are made of high-clean graphite of ARVU type. Inert gas (nitrogen) is supplied from the bulb into electrolytic cell body for dilution of $F_2$ separated at anode up to concentration of

10...15 rev. % and cooling titanium sediment at the cathode after its rising over eutectic melt from fluoride electrolytic salts;

— absorber — 4, filled up with calcium oxide and natrium dioxide or another solid sorbent for absorption of elemental fluorine extracted at anode;

— electric stove — 5 for melting fluoride salt eutectic (of fluorides Li, K and Na) and keeping preset electrolyte temperature (500 °C) at electrolysis;

— vacuum pump — 6 for air and moisture removal after system sealing;

— capacitor (capacity) — 7 for supplying consumed substance — titanium tetrafluoride. To determine the quantity of supplied substance the capacity is placed on electron scales — 8;

— bottle with inert gas (nitrogen) — 9 for blowing the system at the beginning and at the end of the process;

— straighten device — 10.

To prevent emissions during the process the electrolytic cell, absorber and vacuum pump are set in the exhaust hood. Electrolytic cell has the characteristics: $TiO_2$ capacity is up to 80 g/h; electrolyte temperature is 500...550 °C; $TiF_4$ saturation of eutectic melt is 4...8 %; anode current density is 0,085...0,13 $A/cm^2$; cathode current density is 0,42...0,63 $A/cm^2$.
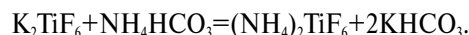
Electrolytic cell assembled and filled with eutectic mixture fluoride salt was filled up with nitrogen after preliminary sealing and heated up to the salt melting temperature (472 °C). $TiF_4$ was supplied from the capacity — 7 into salt melt to the concentration of ~8 %. Original $TiF_4$ was supplied in portions of 50...100 g for preventing blockage of tube output part with potassium hexafluorotitanate generated in the melt. Then the tube for supplying $TiF_4$ was raised over fluoride salt melt having weakened preliminary the sealing in electrolytic cell cover. Electrolytic cell was cooled and after then the tube for supplying titanium tetrafluoride was substituted for graphite cathode.

Electric stove — 5 was switched on for warming up electrolyte melt and graphite cathode was dropped into fluoride electrolyte. At electrolysis continuous current was supplied to the graphite cathode (bar) and anode (crucible). Its value varied in the range of 50...100 mA and voltage was in the range of 2...10 V. In the course of electrolysis sediment (titanium powder in fluoride salt melt) was formed at graphite cathode and at anode elemental fluorine which was removed from electrolytic cell and absorbed in the absorber — 4 at chemical absorber with calcium oxide and natrium dioxide (mixture of 96 % $Ca(OH)_2$ and 4 % NaOH) was formed. Elemental fluorine was diluted with nitrogen up to the concentration of 10...15 rev. % to prevent absorber sealing due to its warming up at fluorine absorption. The amount of supplied nitrogen was preliminary calculated based on fluorine quantity separating at electrolysis.

After electrolysis cathode with segregated sediment consisting of titanium powder in fluoride salt melt was raised over electrolyte melt; electrolytic cell was cooled

and blown with inert gas (nitrogen) from the bottle — 9 before its depressurization.

The generated sediment was ground mechanically and washed from fluoride salts with solution of ammonium hydrocarbonate $NH_4HCO_3$ at pH=8,0...9,0 units by the reaction:

$$K_2TiF_6 + NH_4HCO_3 = (NH_4)_2TiF_6 + 2KHCO_3.$$

To remove hydrogen particles being in electrolytic titanium powder the flotation washing was carried out in the mixture of emulsifier: diesel fuel in ratio 1:3. Final washing was carried out in acetone and ethyl alcohol.

Influence of cathode current density ($i_к$) on current titanium output ($\eta_т$, %) into cathode product is shown in Fig. 2.
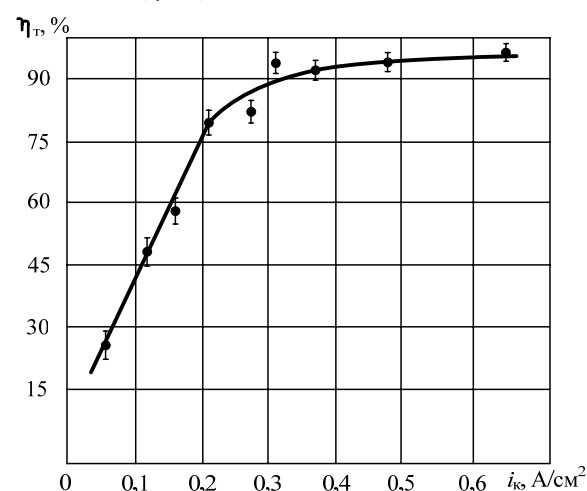


**Fig. 2.** Influence of cathode current density ($i_к$) on current titanium output ($\eta_т$, %)

At current density up to 0,2 $A/cm^2$ titanium current output increases linearly. In the range $\eta_т$ electrolytic cell operates in transient condition. At current density higher than 0,4 $A/cm^2$ titanium output by current strength exceeds 90 % and when current density increasing it does not practically change.

Titanium content in cathode product at $TiF_4$ electrolysis in fluoride melt changed in the range of 4...8 wt. %. Optimal current outputs of Ti amounted to $\eta_т$~90...95 %.

The results of titanium electrolysis in fluoride electrolyte $LiF-KF-NaF-TiF_4$ are given in Table 1.

The conditions of electrolysis: electrolyte composition, %: $LiF(43,5)-KF(47,1)-NaF(1,4)-TiF_4(8,0)$; parameters: $i_a$=0,09...0,13 $A/cm^2$, $t$=500...550 °C, $\tau$=6 h.

**Table 1.** Experimental results of titanium electrolysis in fluoride electrolyte

| Mass of original electrolyte, g | Treated, g | | Obtained Ti, g | $\eta_т$, % |
|---|---|---|---|---|
| | $TiF_4$ | Ti с $TiF_4$ | | |
| 1250 | 100 | 45,7 | 45,0 | 98,5 |
| 1875 | 150 | 68,6 | 66,3 | 96,7 |
| 1250 | 100 | 45,7 | 45,0 | 98,5 |
| 1875 | 150 | 68,6 | 66,3 | 96,7 |
| 1625 | 130 | 59,4 | 55,5 | 93,4 |
| 1250 | 100 | 45,7 | 45,0 | 98,5 |

The results of analysis of titanium powder obtained as a result of titanium tetrafluoride electrolysis in eutectic of fluoride salts (LiF-KF-NaF) are given in Table 2.

Impurity composition of titanium powder was determined by the method of spark mass-spectrometry at mass-spectrometer with double focusing JMS-01-BM-2, of the company JEOL (Japan). For quantitative interpretation of mass-spectra microdensitometer MDM6 of Joyce Loebl company (Great Britain), matched with mini-computer NOVA 4 (USA) was applied.

Random error of the analysis results is characterized by the value of relative standard deviation 0,15...0,30. Inert gas contents are lower than their detection limit 0,01 ppm (1 ppm=$10^{-4}$ %).

***Table 2.*** *Chemical composition of electrolytic titanium powder*

| Element | Content, wt. % | Element | Content, wt. % |
|---------|----------------|---------|----------------|
| C | $<8 \cdot 10^{-3}$ | Nb | $1,2 \cdot 10^{-2}$ |
| Cu | $6 \cdot 10^{-2}$ | Ni | 0,17 |
| Fe | $2,4 \cdot 10^{-2}$ | Sn | $1 \cdot 10^{-3}$ |
| K | $1 \cdot 10^{-3}$ | Zn | $9 \cdot 10^{-3}$ |
| Li | $<1 \cdot 10^{-4}$ | W | $<1 \cdot 10^{-2}$ |
| Mg | $3 \cdot 10^{-2}$ | Ca, Si | $<5 \cdot 10^{-3}$ |
| Mo | $2 \cdot 10^{-3}$ | Al, Pb, Zr | $1 \cdot 10^{-3}$ |
| Na | $3 \cdot 10^{-3}$ | | |

Sum content of impurities in electrolytic titanium powder did not exceed 0,32 %. Titanium powder purity is not less than 99,7 %.

**Conclusions**

1. Electrolytic way of obtaining titanium powder from fluoride melts was studied. It was stated that at TiF$_4$ dissolution in fluoride eutectic of alkali salts LiF-KF-NaF complex salt K$_2$TiF$_6$ is formed.

2. At electrolysis of potassium hexafluorotitanate titanium powder being in the mixture with fluoride eutectic is formed on graphite cathode.

3. It was shown that at electrolysis of titanium tetrafluoride at 500...550 °C, TiF$_4$ content in fluoride eutectic ~8 %, time of electrolysis 6 h and anode current density 0,4...0,8 A/cm$^2$ titanium substance output into cathode product achieved 93,4...98,5 wt. %. It is 2,5...3 times higher than at hydrogen reduction of titanium tetrafluoride or titanium dioxide calciumthermie.

4. Impurity content in titanium powder after washing from fluoride eutectic does not exceed 0,32 % that indicates high quality of titanium powder.

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