

APPLICATION OF FLUORIDE SALT SYSTEMS FOR OBTAINING TITANIUM BY THE METHOD OF ELECTROLYSIS

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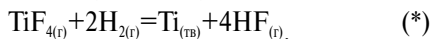
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Fundamentally new fluoride method of synthesis of high-clean metal titanium powder from natural oxide concentrates has been proposed. In a closing stage of processing the electrolytic method of titanium tetrafluoride decomposition in soft eutectic 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:



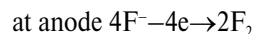
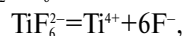
Progressiveness of the given process becomes obvious in connection with the development of closed process flowsheet in which metal titanium wastes are fluoridated with elemental fluorine. The generated fluoride is reduced with hydrogen at obtaining semi-finished product and extracting hydrofluoric undergoes 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 tetrafluoride. 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 $t_{\text{m}} = 472$ °C and the highest electrical conductivity in comparison with eutectics on the basis of chloride salts was recommended for practical use [8].

Experimental 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:



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

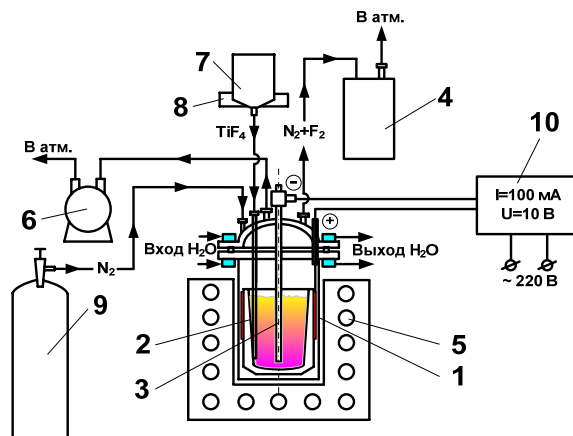


Fig. 1. Diagram of the device for obtaining titanium electrolytic powder: 1) electrolytic cell, 2) anode, 3) cathode, 4) absorber with calcium oxide and sodium dioxide for absorption F_2 , 5) electric stove, 6) vacuum pump, 7) capacity with TiF_4 , 8) electron scales, 9) bottle with inert gas N_2 , 10) 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 sodium 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/cm²; cathode current density is 0,42...0,63 A/cm².

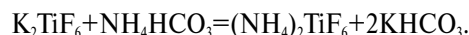
Electrolytic cell assembled and filled with eutectic mixture fluoride salt was filled up with nitrogen after preliminary sealing and heated up to the salt melting temperature (472 °C). TiF_4 was supplied from the capacity – 7 into salt melt to the concentration of ~8 %. Original TiF_4 was supplied in 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 sodium dioxide (mixture of 96 % $\text{Ca}(\text{OH})_2$ 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:



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_k) on current titanium output (η_t , %) into cathode product is shown in Fig. 2.

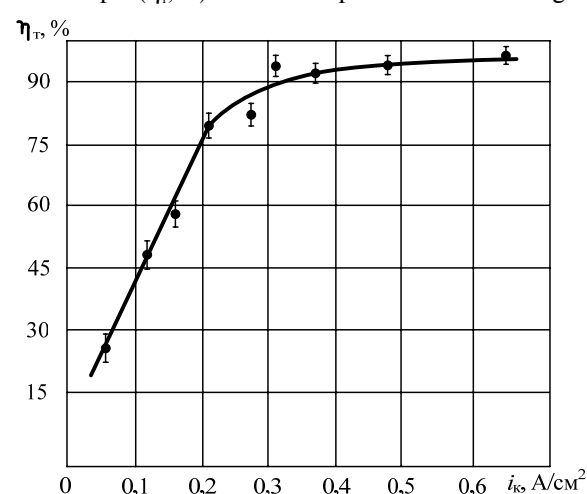


Fig. 2. Influence of cathode current density (i_k) on current titanium output (η_t , %)

At current density up to 0,2 A/cm² titanium current output increases linearly. In the range η_t electrolytic cell operates in transient condition. At current density higher than 0,4 A/cm² 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 $\eta_t \sim 90...95$ %.

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

The conditions of electrolysis: electrolyte composition, %: $\text{LiF}(43,5)\text{-KF}(47,1)\text{-NaF}(1,4)\text{-TiF}_4(8,0)$; parameters: $i_a = 0,09...0,13$ A/cm², $t = 500...550$ °C, $\tau = 6$ h.

Table 1. Experimental results of titanium electrolysis in fluoride electrolyte

Mass of original electrolyte, g	Treated, g		Obtained Ti, g	η_t , %
	TiF_4	Ti c 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 Loebel 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	$3 \cdot 10^{-3}$		

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Conclusions

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

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_2TiF_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/cm² 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.

Received on 07.12.2006