“Karelin-Process” – New Method of Low-Cost Highly Pure Titanium Powders and Chemical Compounds Production

It has been proved, that processing titaniferous concentrates under the chloride technology with reduction of titanium tetrachloride purified from admixtures by metal magnesium or sodium, results in production of expensive metal titanium and high contamination of the environment by chemically harmful substances. There has been offered principally new non-polluting technology of production of low-cost highly pure titanium metal powders and submicronic ceramic constructional powders of titanium carbide, nitride, oxide, boride and silicide.

In a number of chemical elements prevalence, titanium takes the ninth place. Its weight content in the earth crust makes 0,61 % of masses. It belongs to the most widespread metals conceding in this respect only to aluminium, iron and magnesium. There are known about 70 titanium minerals. Among them, rutile, ilmenite, perovskite and sphenic concentrates, being naturally titanium minerals, are of the greatest industrial value.

Rutile and ilmenite concentrates are widely used for pigmentary titanium dioxide production about 4 million tons of it is produced annually in the world. The existing vitriolic and chloride methods of titaniferous concentrates processing do not provide complex extraction of all raw ingredients, therefore result in their dumping as sulfates and chlorides of elements to the environment. When producing pigmentary titanium dioxide, millions tons of chemically harmful substances are dumped annually to the oceans, seas, rivers, lakes and air atmosphere. The same situation is observed when producing metal titanium. In the world, all metal titanium is obtained on a commercial scale under the Kroll’s method, by metallothermal reduction of high-purified titanium tetrachloride by metal magnesium or sodium. Titanium obtained under the Kroll’s method is very expensive, approximately in 6 times more expensive the ordinary stainless steel X18H10T. When producing it, the environment is highly contaminated also by chlorine, hydrogen chloride and chlorides of other chemically harmful substances.

For these reasons, high-tech metal – titanium, having the unique physical, chemical and mechanical properties in comparison with other metals, has not found till now its wide industrial application, especially in life. In the world, needs for metal titanium and, correspondingly, its production do not exceed today only 60-70 thousand tons a year. Therefore, titanium is often refered to the rare metals group and called as rare metal. All numerous attempts to obtain metal titanium by electrolysis out of high-purified titanium tetrachloride had not a success for two reasons: low titanium tetrachloride solubility in melt of chloride salts eutectic and its high steam pressure under electrolyte melting point. One has not managed to realize the industrial production of electrolytically pure titanium also out of oxygen-containing compounds in chloride-fluoride eutectic. The same has happened with electrolytical method of titanium excretion from complex salts (K_2TiF_6 and others) in melt of chloride-fluoride salts eutectic under 750-850 ^{0}C . It seemed the problem of electrolytically pure titanium production has reached the deadlock, though Kroll himself, offering in the 40th years of the last century the metallothermal method, believed it to be replaced, say, in 15 years by more progressive and low-cost electrolytical method. However, the situation is the same.

And now – a new splash of the research works on electrolytical production of low-cost titanium out of natural oxygen-containing titanium concentrates. As a result – patenting of new FFC-process, creation of the special British Titanium Company for introduction of new technology of low-cost titanium production. The idea of FFC-process consists in electrolytical excretion on the cathode of metal titanium in melt of calcium chloride ($CaCl_2$ melting point is 772 ^{0}C) directly from solid titanium dioxide, without dissolving it in electrolyte. British Titanium Company, after pilot plant testing, schedules the construction in the nearest future of the larger experimental production plant. The authors of FFC-process consider that mastering of new technology will result in revolution in titanium production and consumption. The price for metal titanium should fall significantly, at least, in 75 % in comparison with the same under the Kroll’s method.

In this connection, the market of metal titanium should increase in the future 10 years not less than up to 1 million tons a year. Such are the FFC-process authors' forecasts.

We completely agree with the authors of FFC-process, that it is possible to obtain low-cost metal titanium out of natural concentrates on a commercial scale only by electrolytical method. Moreover, we consider that the cost price of production of electrolytically pure titanium obtained out of natural concentrates basically should not exceed the cost price of electrolytical aluminium production out of bauxites. Aluminium contents in bauxites (33-51 % of Al_2O_3 mass) are less than those of titanium in ilmenite and rutile concentrates (58-95 % of TiO_2 mass), and electric power consumption under electrolysis of aluminium (proceeding from electrochemical equivalents) is higher than of titanium.

The authors of this article are also engaged in a problem of low-cost highly pure titanium production out of natural titaniferous concentrates.

Having familiarized attentively with the patent and FFC-process studies, we would like to state some remarks and proposals on solution of the problem of low-cost highly pure titanium production.

In our opinion, it is possible to obtain metal titanium sponge or powder by electrolysis directly out of titanium dioxide without dissolving it in electrolyte melt. However, for these purposes, it is necessary to use pigmentary titanium dioxide as raw material, but it is very expensive. Under its electrolysis, in melt of calcium chloride only one raw component in cost price calculation reaches not less than:

$$A = \frac{M_{TiO2}}{M_{Ti}} \times C_{TiO2} / g = \frac{79,9}{47,9} \times 2,0 / 0,95 = 3,51 \text{ \$/kg.}$$

- A – cost of raw component in cost price of 1 kg titanium;
- M_{TiO2} – titanium dioxide molecular weight;
- M_{Ti} – titanium molecular weight;
- C_{TiO2} – cost of 1 kg titanium dioxide in $;
- g – titanium true output in % mass.

The consumption of auxiliary reagents (calcium chloride), electric power, labour expenditures, depreciation, overhead and other necessary charges for output will result in considerable increase of the commercial products cost price. With allowance for the firm-producer's profit, the price of metal titanium obtained under FFC-process will not differ considerably (in several times) from the price of titanium obtained under the Kroll's method. When using cheaper natural titaniferous concentrates as feed stock, without their pre-refining from admixtures, it is impossible to obtain electrolytically pure titanium or its alloys. To obtain alloys, input of components in strictly fixed proportion is necessary instead of a set of elements available in natural concentrates. If to take into account that pigmentary titanium dioxide is obtained under the contaminating technologies (vitriolic and chloride methods) with dump to the atmosphere of the great number of chemically harmful substances in kind of sulfates, chlorine, hydrogen chloride and chlorides of different elements, it becomes clear, that using pigmentary titanium dioxide as feed stock in the process of electrolytical metal titanium production under FFC-process, as a whole, will not exclude dumping the great number of chemically harmful substances to the environment. Processing or regeneration of the specified methods will cause the further increase of metal titanium price, and no revolution in its use will happen.

The authors of the article have elaborated another more perfect electrolytical method of low-cost metal titanium production out of natural titaniferous concentrates called by us as Karelin-process. The idea of it is demonstrated on the diagram (figure 1).

The advantages of the declared method of natural titaniferous concentrates processing are as follows:

- complete exclusion of chemically harmful substances dumping to the industrial premises and atmosphere;
- technological processes closure and practical exception of use of the reagents entered from outside (reagentless technology);
- complex extraction of all components from source natural concentrates;
- absence of explosive processes;
- simplicity of non-standard equipment manufacturing;
- high equipment productivity;
- high corrosion resistance of equipment, operation cycle without overhauling not less than 10-15 years;
- fluoride processes are easy for automation and computerization;
- flexible technology, easy and prompt equipment recustomizing from one kind of raw material to another;
- low commercial products cost price;
- low capital specific costs for creation of the production.

For today, the studies of Karelin-process in laboratory scale have been carried out; the design of pilot plant on working off the device of continuous output of metal titanium powders in intermixture with electrolyte from the trial electrolytic cell has been elaborated.

All technology of oxidic titaniferous concentrates processing offered is based on analogues and long-term industrial experience of oxidic concentrates of uranium, iron and rare-earth elements (Nd_2O_3) fluorination, the world's industrial experience of aluminium electrolytical production out of alum earth dissolved in melt of fluoride (cryolite) electrolyte, industrial experience of zirconium and tantalum electrolytical production out of complex salts K_2ZrF_6 and K_2TaF_7 in melts of fluoride-chloride salts.

Today, the group of specialists has designed the constructions practically of all non-standard equipment working not in cyclic, but in continuous mode. All this allows us stating that the first plant on production of electrolytically pure titanium powders ($\geq$ 99,99 % mass) and highly pure constructional ceramic submicronic powders of titanium carbides, nitrides, pigmentary titanium dioxide with the use of Karelin-process, by productivity up to 1000 tons a year (by titanium) could be created within not more than two years at capital investments reaching 30 million US$.

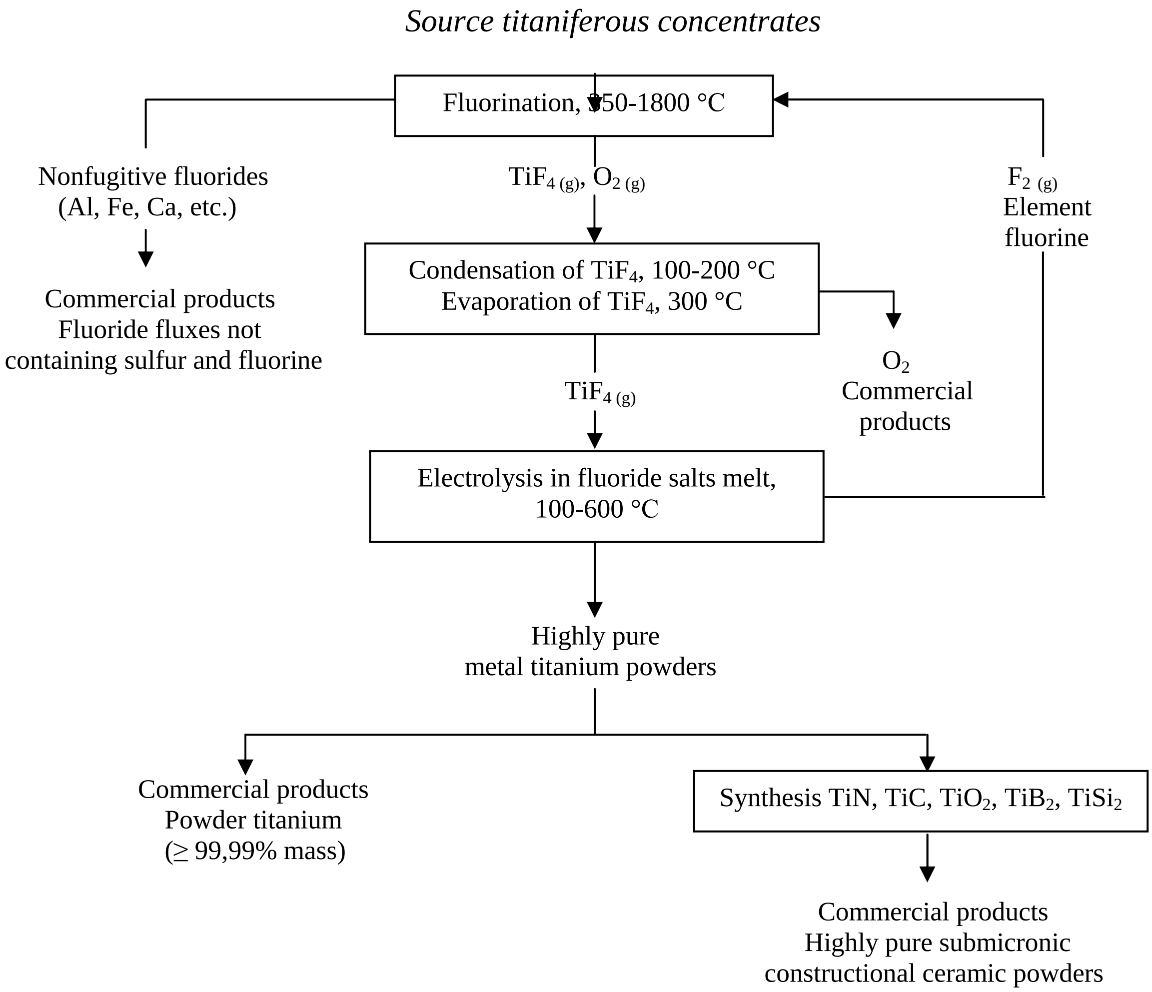

Figure1. Key diagram of Karelin-process

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