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Research of fluorination process of rutile concentrate

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Abstract

The brief review of industrial technologies of titanium-containing concentrates processing has been carried out. Drawbacks of the existing titanium manufacture schemes are shown and the necessity of the essentially new fluoride technologies development has been proved. The reactions proceeding during the fluorination of rutile concentrate with element fluoride are described in the given work. The thermodynamic research of the process has been carried using ASTRA software. Dependence of mass concentration change of titanium tetrafluoride has been investigated in products of reaction on the temperature of the process, and the choice of optimum excess of fluoride has been proved.

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1. Introduction

Now there are two schemes of recycling the titanium containing concentrates: sulfuric-acid and chloride. The sulfuric-acid technology leads to environmental pollution due the fact that annually thousands of tons of sulfur containing wastes in the form of CaSO_4 are dumped. The received titanium dioxide has a high cost. The chloride way is considered to be more favorable in the ecological aspect. However, here a big deal of gas, liquid and solid industrial chloride wastes are dumped again and total extraction of titanium into the purified chloride does not exceed 89% (by mass)¹. At multiphase recycling of titanium raw material in the final production (products), the

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content makes up only 10% to 50% of metal, entering at the initial phase of processing which essentially increases its cost².

Given the current world's pigmentary TiO₂ production rate of 2750 thousand ton/year, there are 1467 thousand t/year or 4890 t/day of harmful chloride industrial solid wastes formed (under condition of transition of all factories to the chloride technology)^{3,4}. In the nearest future we can expect the breakthrough of industrial technology in the "know-how" of titanium that will allow essentially lowering its cost, so that it can become commensurable to the cost of stainless steel. It will lead to the fact that high corrosion stability of titanium along with its low density will allow covering ~10% of the corrosion-proof steel market.

The demand will increase prospectively upon decrease in titanium prices.

2. Experimental results

All of this is the precondition for the development and creation of more advanced and perspective technologies of processing the titanium containing concentrates, in particular the rutile concentrate, the most widespread one of them. In the given work the rutile concentrate of Tarsky deposit (Omsk Region)⁵ was used. It has the following composition, % (mass): 93,2 TiO₂; 1,8 SiO₂; 1,5 FeO; 1,2 Fe₂O₃; 1,0 Al₂O₃; 0,6 MnO; 0,4 CaO; 0,2 MgO; 0,1 V₂O₅.

The developed fluoride technology of producing titanium in the form of highly purified metal powder includes processes of rutile concentrates fluorination, extraction of the formed TiF₄ from a gas stream and electrolytic reduction of the titanium in fluoride melt⁶. One of the basic processes of the given technology is rutile concentrate fluorination. For the purposes of its industrial application, the fluorination features of the titan dioxide and the compounds that are a part of rutile concentrate, by means of element fluorine (F₂)⁵ have been studied:



As a result of fluorination, there is a gas phase which contains TiF₄, SiF₄, VF₅, the solid residuum – FeF₃, AlF₃, MnF₂, CaF₂, MgF₂, and non-reacted oxide formed. Dependence of the change on the equilibrium constant logarithm of these reactions on temperature $\lg Kp = f(T)$ is presented in Fig. 1. All fluorination processes from the thermodynamic point of view have no limits, are irreversible, and proceed with the formation of target products in the form of fluorides. Researches of the equilibrium structure of the isolated thermodynamic system have been conducted with the use of the ASTRA software package⁷. These researches have been conducted for the rutile concentrate of the following structure, % (mass): 48.43 TiO₂; 0.92 FeO; 1.03 SiO₂; 0.56 Al₂O₃; 0.15 Cr₂O₃; 0.12 CaO; 0.06 V₂O₅, that makes 51.27 % of initial mixtures, and the rest is stoichiometrically necessary for fluorination of the fluoride quantity and its excess.

When carrying out tests within the specified temperature range, it is most likely that the following products of reactions exist: O₂, CaF_{2(TB)}, TiF_{4(TB)}, TiO_{2(TB)}, SiF₄, CrF₆, TiF₄, SiO₂F₂, AlF_{3(TB)}, V₂O_{5(TB)}, FeF_{3(TB)}, FeF₃, AlF₃, V₄O₁₀, F₂, F, F₂O, FO, Fe₂F₆, Al₂F₆, TiF₃, FeF₂, Fe₂O₃.

Due to a big amount of chemical compounds formed in the given system during the analysis, those substances have been rejected if their concentration at the investigated temperatures <0,0001 mole/kg that does not exceed 0,01% from the quantity of target products TiF₄ and O₂. In Fig. 2 the dependence of the TiF₄ mass concentration change [C, % (mass)] is presented in reaction products according to the temperature of fluorination process. The

higher content of TiF_4 is observed at stoichiometrical proportion of phases, however, in the system there is no reacted TiO_2 . Therefore, the optimum condition of carrying out the fluorination process is 10% excess of F_2 .

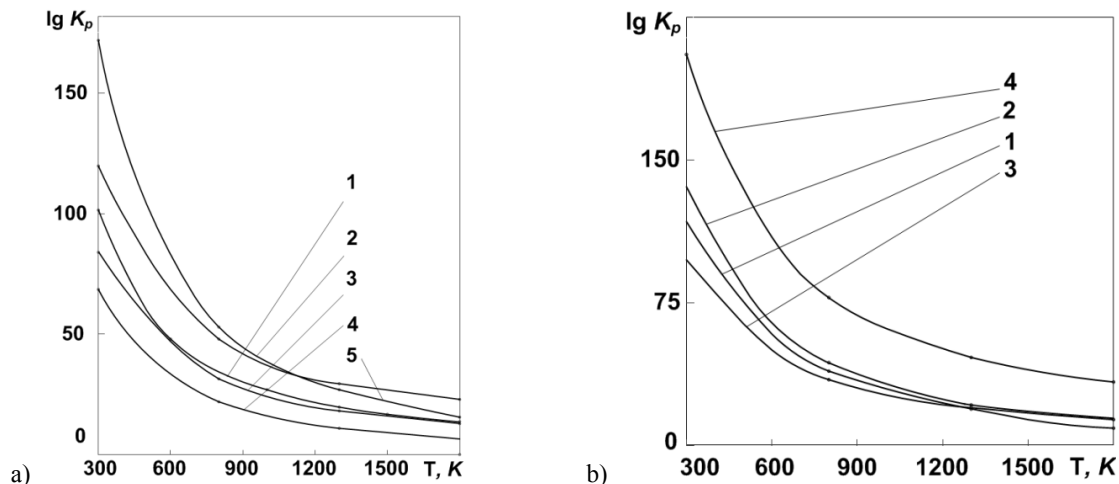


Fig. 1. Dependence of the $\lg K_p$ change on the temperature of fluorination reactions of rutile concentrate components: 1-9 – numbers of reactions (See in the text)

In the table the equilibrium composition of products of the rutile concentrate fluorination process is presented at the 10% excess of fluoride and with the content of initial substances, % (mass): 48,43 TiO_2 , 53,63 F_2 , the rest of them is admixtures.

The content of $\text{O}_{2(g)}$, $\text{CaF}_{2(s)}$, $\text{SiF}_{4(g)}$, $\text{AlF}_{3(s)}$ and $\text{FeF}_{3(s)}$ in products of the reaction generally does not change in a considered temperature range and it makes up 20, 0.13, 1.7, 0.88 and 1.38% (mass.) accordingly.

The noticeable occurrence of gaseous TiF_4 begins above 400 K and its quantity dominates over all the temperature range. At fluorination nonvolatile fluorides – CaF_2 , AlF_3 and FeF_3 are also formed.

The kinetic research on experimental installation (Fig. 3) has been carried out for the purposes of studying features of fluorination of the rutile concentrate basic component (TiO_2).

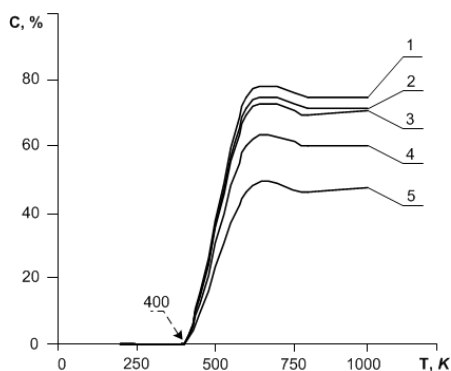


Fig. 2. Dependence of the TiF_4 content on temperature for different reagents relations: 1 – stoichiometry by F_2 ; 2 – excess of 10 % by F_2 ; 3 – excess of 50 % by F_2 ; 4 – lack of 10 % by F_2 ; 5 – lack of 50 % by F_2

The basic element of this installation is a vertical reactor 1. To start the process, an electrical heater 18 is used. In the lid of the reactor, which is a brass tube, is soldered in to the place with a measuring element, which is an annealed tungsten spring, one end is fixed on the plug, another is connected with the plunger of the induction coil 2

of the measuring and registering device 3. The cup made from the nickel foil 8 is attached to the bottom end of the plunger on the alumel wire bracket. In front of the reactor there is a unit of fluoride and argon submission 13. For regulation and registration of temperature, the measuring element 9 and system 10 are intended. Charges of gaseous fluoride and nitrogen are measured by systems 11 and 12. At the exit of the reactor, there is the unit of the volatile fluoride condensation 16. Sanitary purification of departing gases from fluoride containing admixtures is conducted on the line 17.

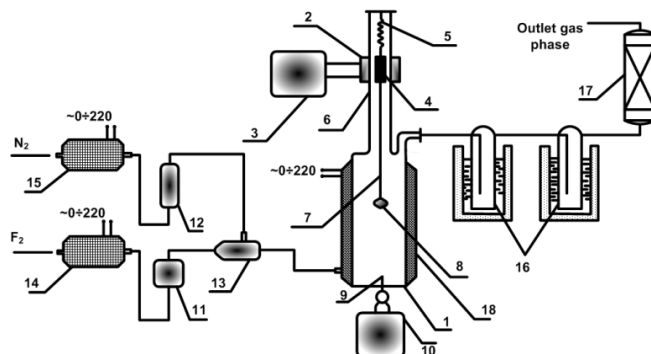


Fig. 3. The scheme of experimental installation for TiO_2 fluorination: 1 – reactor for fluorination; 2 – induction coil; 3 – registering device; 4 – electromagnetic coil; 5 – spring made of Mo; 6 – measuring device; 7 – molybdenum string; 8 – nickel foil cup; 9, 10 – system of temperature regulation and registration; 11, 12 – system of regulation of gas discharge; 13 – unit of fluorine and argon supply; 14, 15 – heaters of fluoride and argon; 16 – unit of flying fluorides condensation; 17 – line of purifying the departing gases; 18 – heater of the reactor 1

Fluoride dilution is provided by nitrogen to reduce the influence of reaction heat on isothermal conditions in the scheme of experimental installation. Preliminary heating of the reaction gas mixture is carried out in a coil located on an external surface of a reactor. Use of a massive metal reactor and the applied method of supply of the reactionary gas mixture have allowed reducing gradient of a bracket-reaction gas mixture system to a minimum temperature.

3. Results and discussion

Kinetics of the TiO_2 fluorination process by elemental fluoride has been studied on powders with granulometric content from $2 \cdot 10^{-6}$ to $2 \cdot 10^{-5}$ m with a specific area of $3.5 \text{ m}^2/\text{g}$. Researches have been carried out on samples of TiO_2 with a mass of 280 mg and with a thickness of a bracket layer up to 4 mm in the temperature range from 300 to 550°C . During the process the mass of the sample has been continuously fixed at the controllable temperature and partial pressure of fluoride. Fluorination has been carried out by technical fluoride which had been purified from HF by means of sorption on tableted NaF at 370-380 K.

The fluorination reaction, proceeding on a surface of the contact of solid and gaseous phases is developed with the following basic stages: 1) transportation of the reacting gas to the surface of a solid material; 2) chemisorption of gas on the surface of the solid substance; 3) chemical reaction of the adsorbed gas with a solid substance; 4) desorption of gaseous TiF_4 from the surface of a solid product; 5) transportation of desorpted TiF_4 .

The speed of interaction between TiO_2 and fluoride is defined by the slowest of these processes. Stages 1 and 5 have diffusion character; their role is rather insignificant for a very thin layer of a material, so the fluorination speed caused by temperature is defined by processes 2-4. The speed of the process 2 depends on both surface area of solid substance and fluoride partial pressure in system. Thus, speed of TiO_2 and fluoride interaction is defined by temperature, partial pressure of fluoride, and physical and chemical characteristics of an initial product.

By means of a qualitative observation, it was determined that at the temperatures of 580 K and below fluorination proceeded slowly, possibly with the formation of solid oxyfluoride or gaseous titanium tetra fluoride. The first compound makes a film on a surface of the titanium dioxide particles which practically stops the process. With a noticeable speed the reaction proceeds only at 630 K; at 830 K, the speed of reaction gradually increases, and the escape of titanium in the form of TiF_4 comes to an end within 12-14 minutes.

The kinetic curves of the titanium dioxide fluorination by fluoride have the S-shaped form which is characteristic for heterogeneous processes of the gas-solid status system⁸. It is possible to allocate the following three sections on kinetic curves:

- The first induction period, described by the low speed and connected with the transformation of initial titanium dioxide into intermediate oxyfluorides. During the induction period there is a formation of the surface of phases' partition that consists of intermediate compound (titanium oxyfluoride). Fluoride atoms diffuse inwards the initial solid reagent, forming nucleus of intermediate connections.
- In the second phase, during the process of generating of new nucleus, the speed begins increasing, reaching maximum values, and the further course of kinetic curves is defined by the promotion to the surface of phases' partition.
- In the third phase, the reduction of the surface area can be explained due to the expense of a solid reagent leads to reduction of the transformation speed⁹.

The kinetic fluorination curve at 580 K is characterized by a longer induction period. Substantial growth of fluorination speed in the range of 780-830 K is explained by the fact that the reaction begins transforming into burning. It is necessary to note that fluorination runs with heat release, therefore it is difficult to endure the isothermal conditions of process.

Mathematical processing of quantitative data on interaction between titanium dioxide and fluoride has been conducted according to three equations: Gistling's equation, Yander's equation, and the "reduced" sphere equation⁹. Applicability of these equations for description of the fluorination mechanism has been defined by the maximal correlation factor of the dependences $k = f(\alpha, t)$ for each kinetic equation. In Fig. 4 and 5 corresponding dependences (in brackets temperatures of fluorination process are specified) are given.

Experimental results are processed most correctly (correlation factor 0.96-0.99) by Gistling's equation which is eliminated from the assumption that the speed of the process is defined by diffusion of molecules of a fluorination reagent and sublimated products of fluorination: TiF_4 , SiF_4 , O_2 , etc. into the space between grains which is assumed to be infinite⁸. Temperature influences on the speed of titanium dioxide fluorination, being calculated by the Gistling's equation, and that is shown in Fig. 6. The linearization of this dependence has been carried out for the purposes of definition of the energy activation process (E_a).

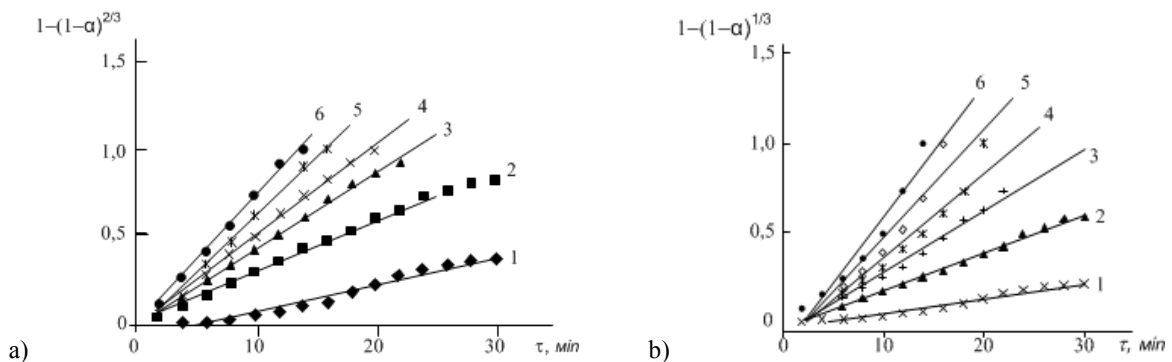


Fig. 4. Dependencies: a – for Gistling's equation; b – for the "reduced" sphere equation; at T, K: 1 – 580; 2 – 630; 3 – 680; 4 – 730; 5 – 780; 6 – 830

Linear dependence is observed during the entire process, except for initial and final phases. The deviation from rectilinear dependence in the beginning of process is caused by the fact that the system is filled with inert gas nitrogen which is necessary for air removal; during the last phase of the process it is not TiO_2 which is fluorinated, but the formed intermediate titanium oxyfluoride.

By the inclination of a straight line in the Arrenius' coordinates the value of a seeming activation energy (24 600 Joules/mole) and a pre-exponential multiplier ($k_0 = 3,063 \text{ min}^{-1}$) of fluorination process of titanium dioxide by element fluoride have been determined. The kinetic equation of TiO_2 fluorination looks like this:

$$(1 - (1 - \alpha)^{\frac{1}{3}})^2 = 3.063 \cdot e^{\frac{24600 \pm 100}{RT}} \tau \quad (10)$$

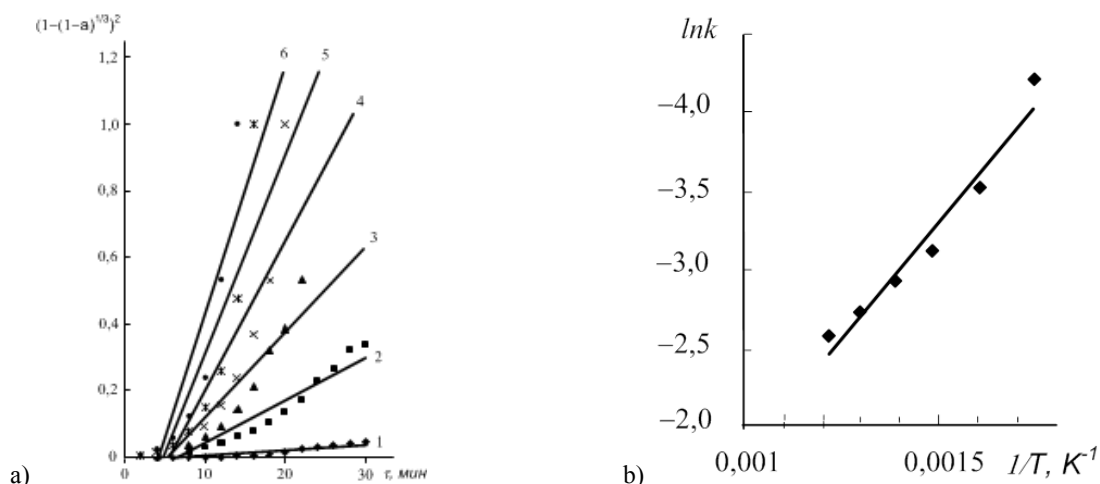


Fig. 5. Dependencies: a – for the Yander’s equation at T, K: 1 – 580; 2 – 630; 3 – 680; 4 – 730; 5 – 780; 6 – 830; b – ln k on absolute temperature;

4. Conclusion

It is necessary to note that all the mechanisms described above concern a case of use of the big excess of fluoride, whereas in practice the minimal excess is usually used. When generating intermediate fluorides from TiO_2 , the process speed is fast enough, and fluoride can be used almost totally. When producing titanium tetra fluoride from intermediate fluorides, one can achieve quantitative usage of fluoride only during a very long contact of solid and gaseous phases; it is possible under counterflow process when fresh fluoride is supplied for processing of a partially perfluorinated product and departing gases treat the fresh TiO_2 . In static conditions (or at insufficient intensity of stirring) and at high concentration of fluoride, we have observed significant overheating of a solid material. Since intermediate titanium oxyfluoride and admixtures, containing in the rutile concentrate, can sinter, the bad stirring of solid and gaseous phases leads to the fusion of material and to even greater deterioration of conditions of phases contact. Therefore, it is more favorable to carry out the process of titanium tetra fluoride formation in gaseous suspension. Under these conditions, the heating of a particle is insignificant, as its temperature is practically equal to the gas temperature^{10,11}.

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