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RESEARCH ARTICLE

Fluorination of titanomagnetite concentrate with ammonium bifluoride

Alexander N. D'yachenko

MIREA – Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia

✉ *Corresponding author, e-mail: dyachenko@mirea.ru*

Abstract

Objectives. *To study the technological features of a new fluoride technology for the production of titanium dioxide by the decomposition of titanomagnetite concentrate with ammonium fluorides.*

Methods. *The chemical species of the titanium and iron components in the fluorination of titanomagnetite concentrate and sublimation separation of components were determined by means of X-ray powder diffraction analysis and inductively coupled plasma mass spectrometry. The kinetics of sublimation of the titanium component by the thermal decomposition of ammonium hexafluorotitanate was experimentally studied.*

Results. *The products of the fluorination of titanomagnetite concentrate with ammonium bifluoride are compounds $(NH_4)_2TiF_6$ and $(NH_4)_3FeF_6$, as proven by chemical analysis and X-ray powder diffraction analysis. The subsequent sublimation separation of the titanium component produced the target product: a mixture of ammonium fluorotitanates. The desublimation of the titanium-containing fraction gave an NH_4TiF_5–$(NH_4)_2TiF_6$–$(NH_4)_3TiF_7$ mixture, the titanium content of which is 30.6% and the content of impurities (Fe, V, Si) is a minimum (0.45%). The activation energy of the heterogeneous reaction and the rate-limiting step of the process were also determined.*

Conclusions. *A high-purity titanium product (a mixture of ammonium fluorotitanates) is obtained. This is a valuable commercial product for the industrial production of titanium dioxide pigment from titanomagnetite concentrate and ilmenite.*

Keywords: *ammonium fluorides, ammonium hexafluorotitanate, titanomagnetite concentrate, titanium dioxide*

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НАУЧНАЯ СТАТЬЯ

Исследование процесса фторирования титаномагнетитового концентрата дифторидом аммония

А.Н. Дьяченко

МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия
✉*Corresponding author, e-mail: dyachenko@mirea.ru*

Аннотация

Цели. *Исследование технологических особенностей новой фторидной технологии производства диоксида титана методом разложения титаномагнетитового концентрата с помощью фторидов аммония.*

Методы. *Формы нахождения титановых и железистых составляющих в процессе фторирования титаномагнетитового концентрата и сублимационного разделения компонентов определялись рентгенофазовым анализом и масс-спектрометрией с индуктивно-связанной плазмой. Кинетика сублимации титановой составляющей экспериментально изучена термическим разложением гексафторотитаната аммония.*

Результаты. *В результате фторирования титаномагнетитового концентрата дифторидом аммония образуются продукты реакции в виде соединений $(NH_4)_2TiF_6$ и $(NH_4)_3FeF_6$, что доказано химическим и рентгенофазовым анализом. С помощью последующего сублимационного отделения титановой составляющей получен целевой продукт, представленный смесью фторотитанатов аммония. Методом десублимации титансодержащей фракции выделена смесь NH_4TiF_5–$(NH_4)_2TiF_6$–$(NH_4)_3TiF_7$, содержание титана в которой находится на уровне 30.6%, а содержание примесей (Fe, V, Si) минимально (0.45%). Определена энергия активации гетерогенной реакции и лимитирующая стадия процесса.*

Выводы. *Получен высокочистый титановый продукт (смесь фторотитанатов аммония), который является ценным коммерческим продуктом для промышленного производства пигментного диоксида титана из титаномагнетитового концентрата и ильменита.*

Ключевые слова: *фториды аммония, гексафторотитанат аммония, титаномагнетитовый концентрат, диоксид титана*

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INTRODUCTION

Titanium dioxide is one of the main inorganic products of the chemical industry. It is used as a white pigment in paints and varnishes. Titanium dioxide is produced by two classical processes: the sulfate process and the chloride process whose optimization resource is currently exhausted. In order to reduce production costs, new approaches to processing titanium mineral raw materials are required [1]. Titanomagnetite concentrates (TMC) are refractory minerals, which cannot be processed by the classical sulfuric-acid and chlorine methods for titanium extraction. Our studies investigated the separation of a titanium-containing fraction from TMC fluorinated with ammonium bifluoride. In our previous works, an ammonium fluoride technology for the production of titanium dioxide was patented [2, 3]. However, it can be optimized, in order to reduce the cost of titanium dioxide pigment.

Ammonium fluorides (a commercial technical mixture of ammonium fluoride NH_4F and ammonium bifluoride $NH_4F{\cdot}HF$ in known ratios) are solid fluorinating agents produced by the chemical industry. They allow the decomposition of ilmenite and TMC by solid-phase sintering followed by thermal distillation of the titanium phase. TMC is a mixture of ilmenite and excess oxidized iron (III) oxide [4]. Ilmenite ($FeTiO_3$) can be represented as an empirical mixture of titanium dioxide and iron oxide ($FeO{\cdot}TiO_2$). The titanium component of TMC and ilmenite reacts with ammonium fluorides to form ammonium fluorotitanates. Unlike iron fluorides, they are sublimated and separated from the fluorinated mixture [5–8].

$$TiO_2 + 3NH_4F{\cdot}HF \rightarrow (NH_4)_2TiF_6 + 2H_2O\uparrow + NH_3\uparrow \quad (1)$$

$$FeO + 2NH_4F{\cdot}HF \rightarrow (NH_4)_2FeF_4 + H_2O\uparrow \quad (2)$$

$$FeTiO_3 + 5NH_4{\cdot}HF = \\ = (NH_4)_2TiF_6 + (NH_4)_2FeF_4 + 3H_2O\uparrow + NH_3\uparrow \quad (3)$$

Other impurity compounds present in TMC also react with ammonium bifluoride to form ammonium fluoride complexes.

$$SiO_2 + 3NH_4F{\cdot}HF = (NH_4)_2SiF_6\uparrow + NH_3\uparrow + 2H_2O\uparrow \quad (4)$$

$$Al_2O_3 + 6NH_4F{\cdot}HF = 2(NH_4)_3AlF_6 + 3H_2O\uparrow \quad (5)$$

$$Cr_2O_3 + 3NH_4F{\cdot}HF = 2CrF_3 + 3NH_3\uparrow + 3H_2O\uparrow \quad (6)$$

When heated, fluorometalates decompose into metal fluorides, and excess ammonium fluoride enters the gas phase.

$$(NH_4)_2FeF_4 = FeF_2 + 2NH_3\uparrow + 2HF\uparrow \quad (7)$$

$$(NH_4)_2FeF_5 = FeF_3 + 2NH_3\uparrow + 2HF\uparrow \quad (8)$$

$$(NH_4)_3AlF_6 = AlF_3 + 2NH_3\uparrow + 2HF\uparrow \quad (9)$$

Excess ammonium bifluoride undergoes thermal decomposition.

$$NH_4F{\cdot}HF \rightarrow NH_4F + HF\uparrow \quad (10)$$

$$NH_4F \rightarrow NH_3\uparrow + HF\uparrow \quad (11)$$

The iron component of the fluorinated mixture upon heating with access to atmospheric moisture or water vapor formed by reaction (3) undergoes oxidative pyrohydrolysis to form iron(III) oxide.

$$2(NH_4)_2FeF_4 + 2H_2O + \tfrac{1}{2}O_2 = Fe_2O_3 + 4NH_3\uparrow + 8HF\uparrow \quad (12)$$

Upon further heating, ammonium hexafluorotitanate (AHFT) $(NH_4)_2TiF_6$ sublimates and is distilled off in the form of a gas phase from the fluorinated mass of ilmenite. The iron component in the form of ammonium tetrafluoroferrate $(NH_4)_2FeF_4$ decomposes to form solid iron difluoride with the release of gaseous hydrogen fluoride and water.

$$(NH_4)_2FeF_4 \rightarrow FeF_2 + 2NH_3\uparrow + 2HF\uparrow \quad (13)$$

The general principles of the fluorination of TMC with ammonium bifluoride are similar in process parameters to the fluorination of ilmenite.

An important economic aspect of this technology is the possibility of the complete regeneration of ammonium fluoride bifluoride, which shows the competitive advantages of the presented technology. Ammonium fluoride is regenerated by the subsequent treatment of the titanium fluoride desublimate with aqueous ammonia. Adding it to an AHFT solution leads to precipitation of hydrated oxy- and oxy-hydroxy compounds with the empirical formulas $TiOF_2{\cdot}nH_2O$ and $TiO(OH)F{\cdot}nH_2O$. Oxyfluoride monohydrate $TiOF_2{\cdot}H_2O$ is known to be released from aqueous solutions. The complex ions existing in aqueous solutions are assigned the formulas $TiOF^+$, $[Ti(OH)_2F]^+$, $TiOF_2$, $TiOF^{3-}$, $TiOF^{4-}$, and TiF^{2+} [9–12]. Next, by increasing pH,

these precipitates are converted into titanium hydroxide oxide; then, they are filtered off and, after calcination, transform into titanium dioxide.

The iron component after fluorination of ilmenite with ammonium fluorides is iron tetrafluoroferrate. Upon heating, it transforms into iron difluoride and then undergoes pyrohydrolysis to produce iron(III) oxide, also a commercial product. The closed-loop material flow diagram (Fig. 1) of ammonium fluoride processing of ilmenite into titanium dioxide and iron(III) oxide with the return of all auxiliary reagents enables the so-called ammonium fluoride cycle of ilmenite processing.

This work studied the process parameters of the presented empirical diagram based on the example of the interaction of ammonium bifluoride with titanomagnetite concentrate.

The objects of research were TMC fluorinated with ammonium bifluoride (which was a mixture of AHFT and ammonium tetrafluoroferrate), titanium-containing sublimation products, and a nonsublimating iron-containing residue.

The purpose of the study was to confirm experimentally the above-mentioned chemical sequences of interaction of TMC with ammonium bifluoride, as well as the sublimation separation of the titanium component from the fluorinated mixture. A further aim was to determine the sublimation conditions, and the chemical species of the iron ferrous and titanium components in the products of the process under study.

EXPERIMENTAL

Table 1. Chemical composition of titanomagnetite concentrate (*Baikal-Amur Mining Corporation*, Russia)

Substance	TiO_2	Fe_2O_3	Al_2O_3	SiO_2	Cr_2O_3	V_2O_5
Content, %	15.2	68.3	5.2	7.0	0.34	0.69

Ammonium bifluoride (*Galogen*, Russia) used in the experiments complied with GOST 9546-75[1].

Chemical analysis was carried out over a wide concentration range by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7500cx mass spectrometer (*Agilent Technologies*, USA; low resolution, generator output power 1500 W, MicroMist nebulizer).

The fluoridation of TMC with ammonium bifluoride was studied using an SDT Q600 simultaneous TGA/DSC/DTA[2] analyzer (*NF Instruments*, USA) with software data processing using the Universal Analysis software (version V4.2E, *TA Instruments*, USA) according to standard ASTM methods[3].

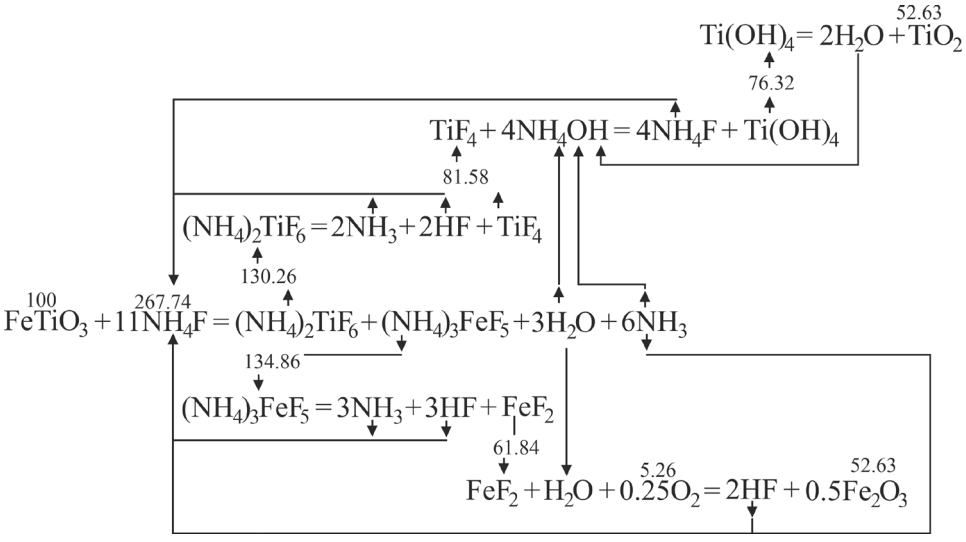

Fig. 1. Material flow diagram of the ammonium fluoride process.

[1] GOST 9546-75. State Standard of the USSR. Reagents. Ammonium fluoride (acid). Specifications. Moscow: Izdatelstvo standartov; 1981.

[2] TGA/DSC/DTA is the thermogravimetric analysis/differential scanning calorimetry/differential thermal analysis.

[3] American Society for Testing and Materials. ASTM E 473-00 (2000). Standard definition of terms relating to thermal analysis. https://cdn.standards.iteh.ai/samples/7305/ea45d8e86eff4027b88383a80db3c3a8/ASTM-E473-00.pdf. Accessed October 10, 2023.

The sample weight was up to 25 mg; the sensitivity of the balance, 0.1 μg; the calorimetric accuracy/reproducibility, ±2% (metal standards); DTA sensitivity, 0.001°C; the thermocouples, Pt/Pt–Rh (type R); the crucibles, platinum (40 μL) and ceramic (Al_2O_3, 40 μL). The controlled atmosphere over the sample (argon, atmospheric air).

X-ray powder diffraction analysis (XRD) was performed using an XRD 7000S powder diffractometer (*Shimadzu*, Japan; sample weight, from 10 mg; sensitivity for phase composition, 3–5%).

The sublimation–desublimation process was modeled in a setup specially designed and constructed for these studies (*RTU MIREA*, Russia) (Fig. 2).

The mixture of the fluorinated TMC was transferred to a corundum boat, placed in a tubular furnace heated to 600°C and was kept for 5 h. To the outlet of the furnace, a desublimator was hermetically attached. This was a cooled fluoroplastic cup (100 mm in diameter and 300 mm in length) with an internal cooled coil made of a fluoroplastic tube (7 mm in diameter). Upon cooling, the mixture of sublimated titanium ammonium fluoride compounds desublimated again to form AHFT. As a result, the titanium component of TMC was separated from the ferrous component and distilled into the desublimator.

The kinetics of sublimation of the titanium product (containing mainly $(NH_4)_2TiF_6$) was studied in a setup (*RTU MIREA*, Russia) with continuous recording of changes in the weight of the sample. A 3-g AHFT sample in a platinum crucible was placed in a reactor preheated to a given temperature. The crucible diameter was 25 mm; the sublimation surface, 4.9 cm^2; the initial thickness of the bulk layer, 0.7 cm. After the completion of the experiment, the residue in the crucible was weighed and the degree of sublimation was calculated. The average deviation in a series of four experiments was within 3%. The activation energy of the process was calculated according to the published procedure [13].

RESULTS AND DISCUSSION

Study of the fluorination of TMC with ammonium bifluoride

The interaction of ammonium bifluoride with TMC and chemical reactions (1–10) were studied by means of differential thermal analysis (DTA) in a derivatograph with a load of 8 mg of TMC and 24 mg of ammonium bifluoride (Fig. 3).

At temperatures of 103–109°C, the water of crystallization is evaporated from ammonium bifluoride. At 123°C, ammonium bifluoride melts; at 242°C, excess ammonium bifluoride disproportionates to ammonia and hydrogen fluoride. The further changes in the weight of the reacting mixture are characteristic of the sequential formation and destruction of ammonium fluoride complexes of titanium and iron. The latest changes in the TGA and DTA curves in the range 400–450°C are due to the sublimation of the titanium component. The heat capacity of the system is most significantly affected by the melting and decomposition of ammonium bifluoride in the range 120–200°C, which occur with a total heat absorption of about 1 W/g of charge (300 kW/t of concentrate).

Ammonium bifluoride melts early in the process. This is accompanied by a decrease in the volume of the sample. However, at the same time, solid ammonium fluorometalates and gaseous reaction products begin to form, causing the

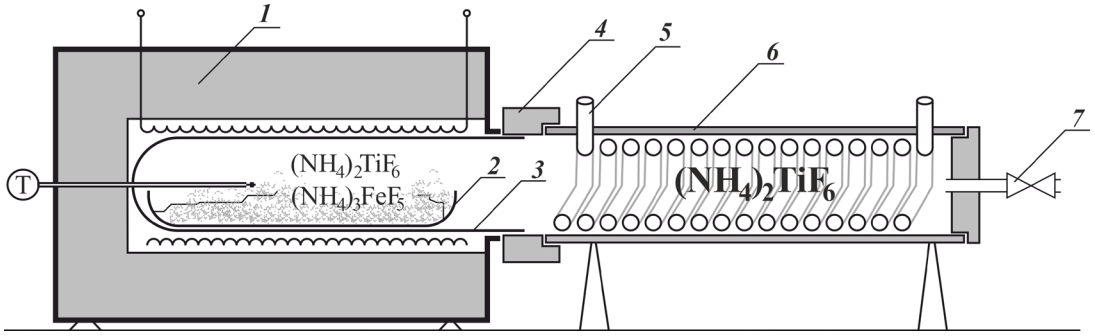

Fig. 2. Setup for separation of the titanium fraction from the ferrous fraction:
(*1*) furnace, (*2*) boat with a mixture of fluorometallates (corundum or stainless steel), (*3*) corundum cup, (*4*) gypsum coupling, (*5*) water cooling jacket (fluoroplastic), (*6*) desublimator housing (fluoroplastic), and (*7*) outlet.

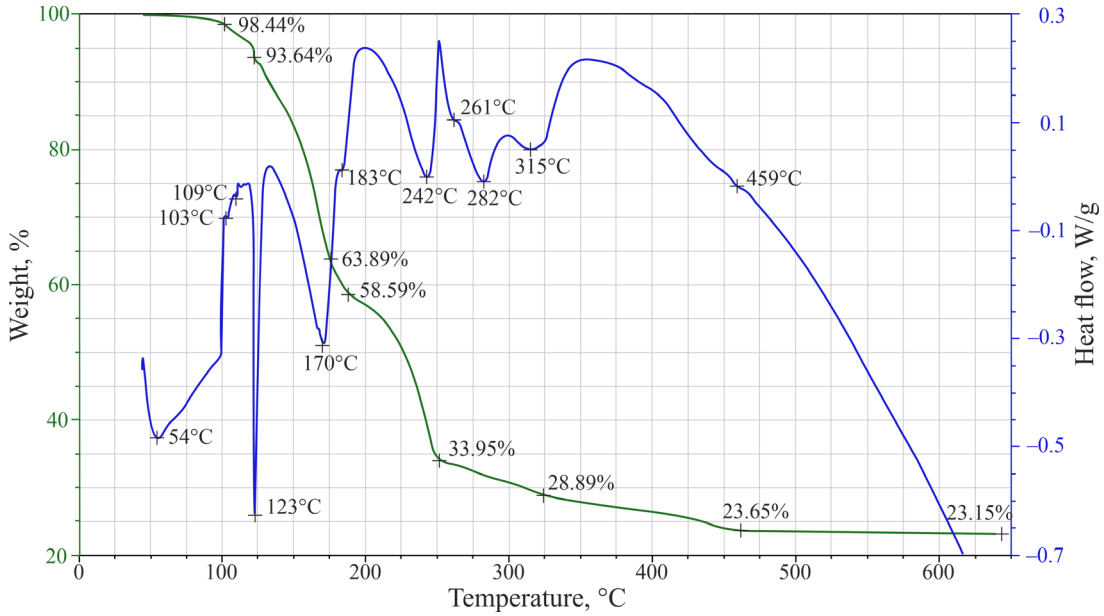

Fig. 3. DTA of the reacting mixture of TMC and ammonium bifluoride.

mixture to foam and leading to an increase in the volume of the sample. Filling the crucible to 80% ensures acceptable accuracy of weight measurements and calculation of observed thermal events, as well as the absence of errors due to sticking to the crucible lid or leakage of part of the reaction mixture.

The chemical composition of the reaction products $(NH_4)_2TiF_6$ and $(NH_4)_3FeF_6$ was confirmed by XRD (Fig. 4), showing complete agreement between the products and the reference samples. XRD did not detect an unreacted residue, indicating that the reaction had almost completed and the concentration of the original ilmenite was below the level of determination by XRD, i.e., less than 2%.

The fluorinated mixture was calcined in an atmosphere of natural (undried) air. As expected, ammonium tetrafluoroferrate underwent pyrohydrolysis and was converted into iron(III) oxide which upon calcination transforms into magnetite. XRD (Fig. 5) confirmed the predominance of Fe_3O_4 in the calcined residue, and also detected an admixture of unreacted ilmenite, which fully confirms the occurrence of chemical reaction (4).

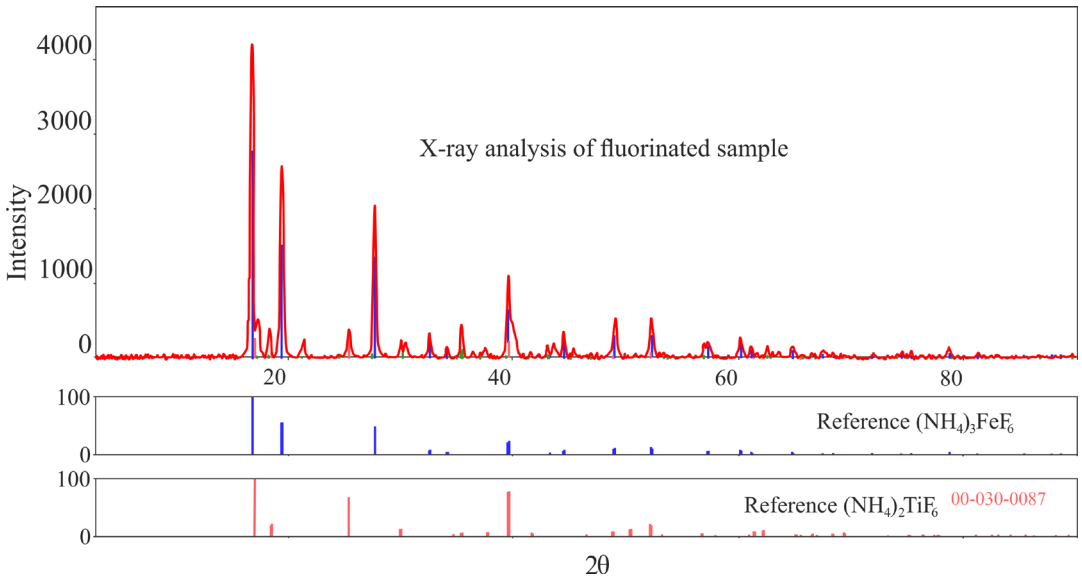

Fig. 4. XRD of the fluorinated sample.

Study of the separation of the titanium-containing fraction of AHFT

With regard to the technological development of the separation of the titanium component from the ilmenite fluorinated with ammonium fluorides, it was necessary to study the rate and completeness of AHFT sublimation. During the experiment, the weight of the residue was recorded and the degree of sublimation was calculated from it (Fig. 6).

The AHFT sublimation rate increases with increasing temperature. Above 650°C, the rate increases significantly, reaching 3.87 and 4.21 g/(h·cm^2) at 650 and 700°C, respectively (Table 2). At 700°C, the degree of sublimation of AHFT reaches 85% within 10 min.

The experimental data on the kinetics of AHFT sublimation was mathematically processed using the Crank–Gistling–Brownstein equation.

The calculated activation energy is E = 52336 J/mol.

$$1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}=0.183\cdot\tau\cdot\exp\left(-\frac{52336}{RT}\right).$$

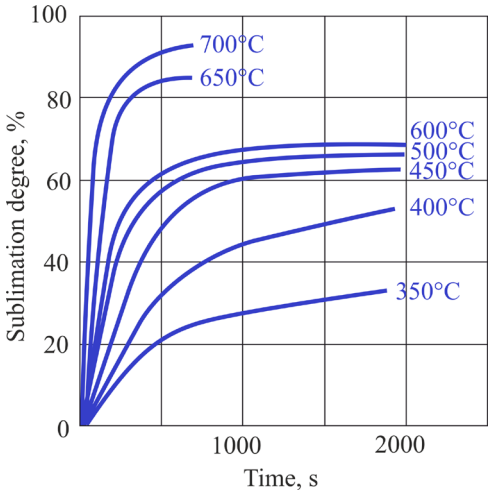

Fig. 6. Dependence of the sublimation degree on temperature and heating time.

The activation energy of the process is 52336 J/mol, indicating that the process is under kinetic (rather than diffusion) control. The process can be enhanced by increasing process temperature.

With a decrease in the AHFT sublimation temperature, the conversion in the pyrohydrolysis

Table 2. AHFT sublimation rate in the temperature range of 350–700°C

Temperature, °C	700	650	600	500	450	400	350
Sublimation rate, g/(h·cm^2)	4.21	3.87	1.55	1.27	0.50	0.31	0.12

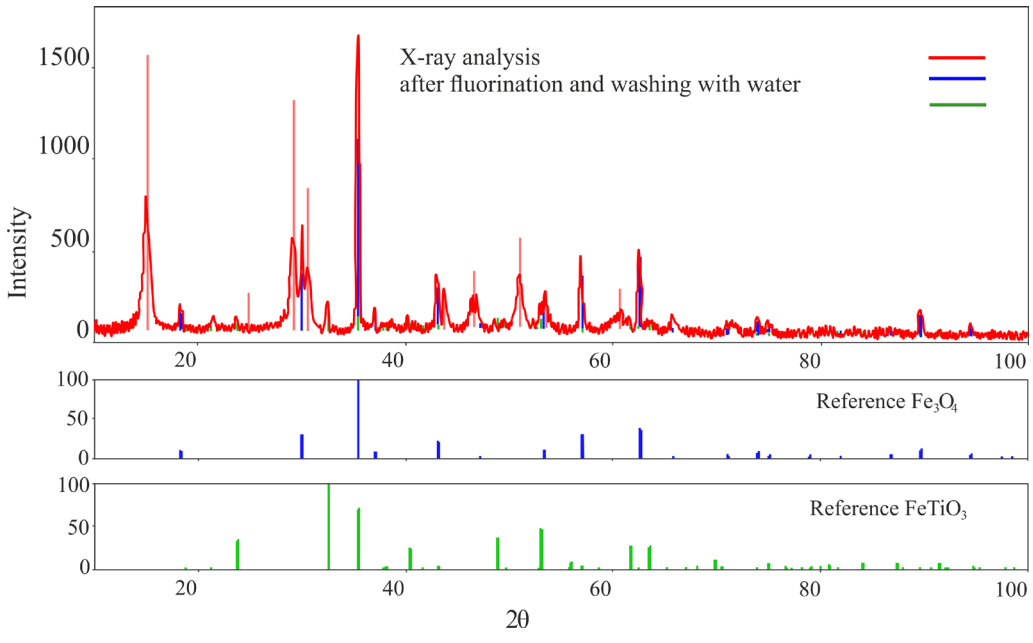

Fig. 5. XRD of the products after fluorination and calcination of the residue.

to form titanium oxide and gaseous products (NH_3, HF) increases. This increases the loss of titanium in the form of TiO_2 in the residue after sublimation.

$$(NH_4)_2TiF_6 + H_2O \rightarrow TiO_2 + NH_3 + HF \quad (14)$$

The degrees of pyrohydrolysis of AHFT at 650 and 700°C were 17 and 15%, respectively. The conversion and rate of sublimation of AHFT depend on non-linear time and behave differently in the three temperature ranges.

In the temperature range 350–450°C, the increase in the degree of pyrohydrolysis is at its maximum in the first five minutes after the start of the process. During this period of time, the weight loss is 20%. The further weight loss is described by a linear change in the weight of the sample, which characterizes the sublimation of AHFT.

In the temperature range 500–600°C, the sublimation is accompanied by the removal of the water of crystallization. Within 25 min, the weight loss is intense and a high degree of sublimation is achieved: 65 and 73% at 500 and 600°C, respectively.

In the temperature range 650–700°C, AHFT sublimates more intensely in comparison with the low-temperature ranges; the maximum degree of sublimation (83%) is achieved within the first 10 min.

According to previously proposed chemical reaction (1), the products should contain AHFT and ammonium tetrafluoroferrate. In order to confirm this assumption, experiments were conducted with fluorination of ilmenite under various conditions. Table 3 presents fluoridation conditions. These include: fluorination reagent (ammonium fluoride or bifluoride); fluorination temperature; number of fluorination operations (number of passes through the furnace); ratio of ilmenite and ammonium fluoride/bifluoride reagents; and reagent feed rate. Based on the results of ICP-MS chemical analysis of the unreacted ilmenite residue (from the contents of Ti, Fe, and silicon oxide impurity in the residue), the degrees of fluorination were determined (Table 3).

Study of the titanium-containing desublimate

The previously obtained sample of fluorinated TMC, a mixture of $(NH_4)_2TiF_6$ and $(NH_4)_3FeF_6$, was studied in a sublimation-desublimation apparatus (Fig. 2), in order to determine the quality of the desublimated titanium-containing product. ICP-MS chemical analysis of the desublimate showed minimum contents of impurity elements in the titanium-containing product isolated by sublimation-desublimation from the fluorinated ilmenite (Table 4).

XRD analysis of the desublimated titanium-containing product (Fig. 7) showed that it consists of a mixture of $(NH_4)_2TiF_6$, $(NH_4)_3TiF_7$, and NH_4TiF_5. Chemical analysis showed that the titanium content in the desublimate (after with a single sublimation–desublimation cycle) is about 30.6%. The total amount of impurities (Fe, V, Si) is 0.45%,

Table 3. Process parameters and degrees of fluorination of TMC components

No.	Fluorination temperature, °C	Reagent	Time of reaction per operation (total time), min	Number of operations (number of passes through furnace)	Reagent ratio	Feed flow rate of mixture of reagents, g/h	Degree of fluorination, %		
							Ti	Fe	Fe
1	210	NH_4F	60 (240)	4	1:3	900	81	73	95
2	210	$NH_4F·HF$	60 (120)	2	1:3	900	94	92	99
3	210	$NH_4F·HF$	60 (120)	2	1:2.43	900	92	91	99

Table 4. Content of target components in the desublimate

Substance	Ti	Fe	V	Si	Al
Content, %	30.6	0.2	0.16	0.1	0.3

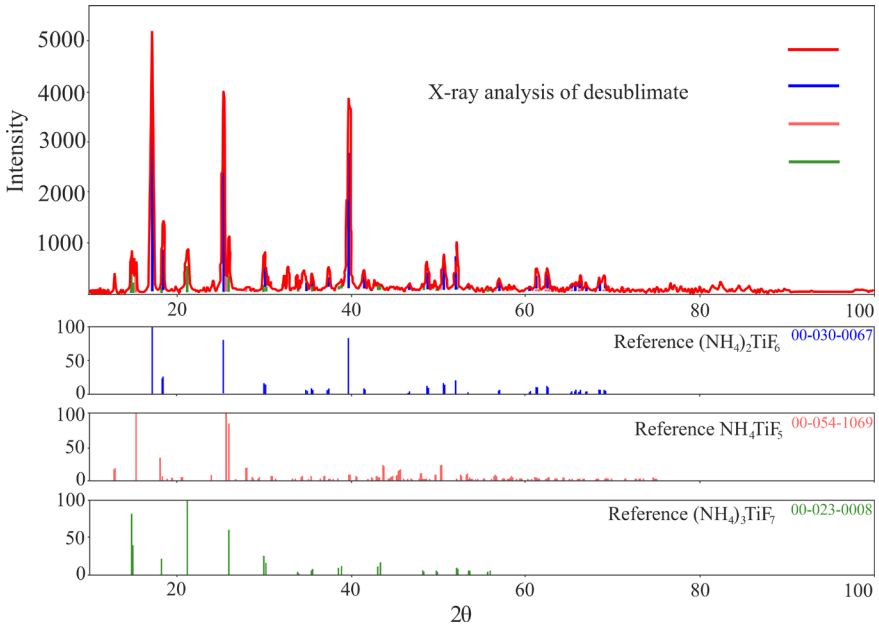

Fig. 7. XRD of the desublimated titanium-containing product.

including only 0.2% Fe. Redistillation of the product reduces the content of impurities in the ammonium fluorotitanate mixture to 0.1%.

Thus, XRF proved that the method of fluorination of TMC with ammonium bifluoride produced a high-purity titanium product: a mixture of ammonium fluorotitanates. The resulting intermediate product—a mixture of NH_4TiF_5, $(NH_4)_2TiF_6$, and $(NH_4)_3TiF_7$—is a valuable commercial product for the industrial production of titanium dioxide pigment from titanomagnetite concentrate and ilmenite.

CONCLUSIONS

The study of the fluorination of TMC by means of ammonium bifluoride followed by the separation of titanium and iron fractions allows us to draw the following conclusions:

(1) The general principles of fluorination of TMC by means of ammonium bifluoride are similar in process parameters to the fluorination of ilmenite.

(2) Chemical analysis and X-ray powder diffraction analysis have proven that the products of the fluorination of TMC with ammonium bifluoride are compounds $(NH_4)_2TiF_6$ and $(NH_4)_2FeF_4$.

(3) The residue after the fluorination of TMC mainly consists of Fe_2O_3 with an iron content of 40.2% and impurities of unreacted TMC and ilmenite, containing up to 1.1% titanium. This confirms the almost complete fluorination of TMC.

(4) The AHFT sublimation rate increases with increasing temperature, and above 650°C, the rate increases significantly, reaching 3.87 and 4.21 g/(h·cm^2) at 650 and 700°C, respectively. At 700°C, the degree of sublimation of AHFT reaches 85% within 10 min.

(5) The titanium-containing fraction separated by sublimation undergoes desublimation. XRD determined that the desublimate consists of a mixture of $(NH_4)_2TiF_6$, $(NH_4)_3TiF_7$, and NH_4TiF_5. Chemical analysis showed that the titanium content in the desublimate (after a single sublimation–desublimation cycle) is about 30.6%. The total amount of impurities (Fe, V, Si) is 0.45%, of which 0.2% Fe. Redistillation of the product reduces the amount of impurities in the ammonium fluorotitanate mixture to 0.1%.

(6) The resulting high-purity titanium product (a mixture of ammonium fluorotitanates) is a valuable commercial product for the industrial production of titanium dioxide pigment from titanomagnetite concentrate and ilmenite.

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The author declares no conflicts of interest.

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About the author:

Alexander N. Dyachenko, Dr. Sci. (Eng.), Professor, Head of the K.A. Bol'shakov Department of Chemistry and Technology Rare Elements, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: dyachenko@mirea.ru. Scopus Author ID 7006148917, RSCI SPIN-code 7929-7127, https://orcid.org/0000-0003-3490-4713

Об авторе:

Дьяченко Александр Николаевич, д.т.н., профессор, заведующий кафедрой химии и технологии редких элементов им. К.А. Большакова, Институт тонких химических технологий им. М.В. Ломоносова, ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: dyachenko@mirea.ru. Scopus Author ID 7006148917, SPIN-код РИНЦ 7929-7127, https://orcid.org/0000-0003-3490-4713

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