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Production and Treatment of Zirconium Tetrafluoride from Zirconium-Containing Raw Materials Using Anhydrous (Dry) Technology

I. Yu. RUSAKOV[1], V. L. SOFRONOV[1], L. M. LEVCHENKO[2]

[1]*Seversk Technological Institute, Seversk, Russia*

E-mail: IYRusakov@mephi.ru

[2]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*

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Abstract

The paper describes testing of dry fluoride technology for processing of zirconium-containing raw materials and treatment of the resulting fluorides from impurities under semi-industrial conditions. Research results of the process of fluorination of zircon and baddeleyite with elemental fluorine in apparatuses of periodic and continuous action were given. The feasibility of efficient treatment of zirconium tetrafluoride from impurities via vacuum sublimation resulting in the production of high purity zirconium tetrafluoride was demonstrated. The design of the sublimation apparatus that had been manufactured and tested under operating production conditions was proposed.

Keywords: zirconium-containing raw materials, zircon, baddeleyite, zirconium dioxide, fluoride method, fluorine, sublimation, treatment from impurities

INTRODUCTION

To process zircon concentrates on an industrial scale three technologies, such as alkaline, chloride, and fluorosilicate are used; they are different by disclosure method [1–3]. However, all of them are low-productive and characterised by the multistage character of the process, insufficient product yields, the use of large volumes of aqueous salt solutions, *etc.*

In this regard, the All-Russian Research Institute of Chemical Technology (VNIIHT, Moscow) jointly with the Tomsk Polytechnical University (Tomsk) and Seversk State Technological Institute (Seversk) proposed dry fluoride technology of complex processing of zirconium-containing raw materials [1–3] that provides for fluorination of raw materials with gaseous fluorine, treatment of the resulting zirconium tetrafluoride (ZTF) from impurities by sublimation from the solid product of fluorination and the production of certified metalzirconium or its alloys by calciothermic reduction. This method allows additionally obtaining aerosil and silica white resulting from exhaust gas fluorination.

The proposed technology has a number of advantages:

i) The high reactivity of fluorine allows for full fluorination of almost any compounds including ore concentrates;

ii) The resulting fluorides are drastically different in their physicochemical properties, that allows purifying ZTF from impurities *via* the sublimation method ensuring high purity of the resulting fluoride;

iii) A small number of technological operations and, consequently, high productivity of the process;

iv)A minor amount of wastes including radioactive;

v) The opportunity of processing of solid fluoride wastes *via* the sulphuric acid method with the extraction of fluoride therefrom as hydrogen fluoride;

vi) The possibility of using technological techniques and equipment for their implementation used in large-tonnage uranium production.

A process flow diagram in view of the recommended technologies, including the production of anhydrous zirconium tetrafluoride is demonstrated in Fig. 1.

All stages of the fluoride technology were experimentally tested by us, mainly under experimental-industrial conditions. Zircon from Tugansk deposit (Tomsk region) and zirconium dioxide (baddeleyite) were used as raw materials. Chemical and phase compositions of the used materials are given in [5, 6].

ZIRCONIUM CONCENTRATE FLUORINATION

To assess the likelihood of fluorination process experiments of fluorination of zirconium concentrate with a mass of 0.08 and 10 kg were carried out.

Sample weights of zircon concentrate (0.08 kg) in the first series of experiments were loaded into nickel boats that were sequentially set in a horizontal tubular reactor. The fluorine produced in a laboratory medium-temperature electrolyser, heated to 300 °C and passed over portions of zircon heated to the same temperature in the amount of 10 and 20 % above the stoichiometrically required [1]. Consequently, ZTF in the main fluoride content of 95 and 99 % was obtained.

Fluorination process was accompanied by an increase in temperatures and the reaction rate due to high thermicity. In that way, the resulting ZTF was sublimated in the reacting front and became desublimated on the surface of the unreacted zircon in colder parts of the boat and the reactor as large needle-like crystals up to 10 mm length and 3 mm thickness.

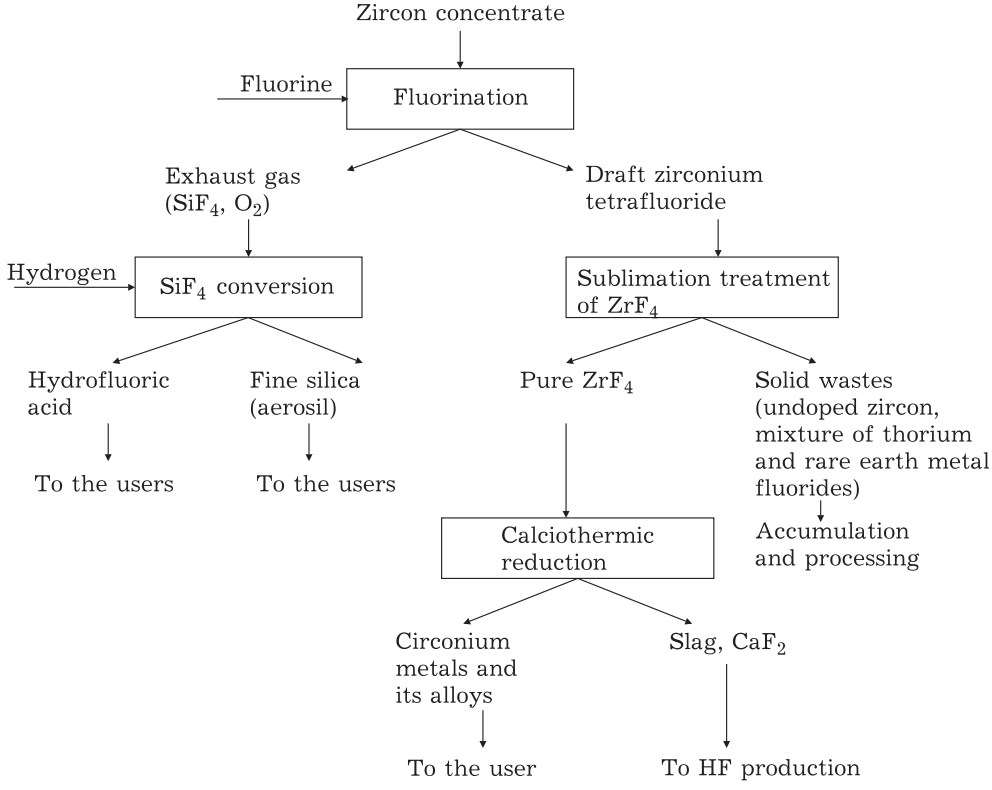

Fig. 1. Flow diagram of dry fluoride technology for processing of zircon concentrates.

In other experiment series, sample weights of zircon concentrate or baddeleyite (to 10 kg) were fluorinated with F_2 in a fixed bed. Fluorine was produced in an industrial medium-temperature electrolyser and fed in 20 % excess. The reactor is made of nickel tube with a length of 2 m and a diameter of 160 mm. The Initial concentrate was loaded in a nickel boat in 1.5 m length that was set into the reactor. Prior to experiments, the reactor was passivated with fluorine. The interaction of zircon concentrate with fluorine began at a temperature of 300 °C. The beginning of the reaction was judged by the intense temperature rise in the layer of zircon.

Zirconium tetrafluoride in the amount of 8.6–9.2 kg with the content of the main fluoride of no less than 99 % was obtained resulting from each experiment. By 50 % more of stoichiometrically required amount of fluorine was passed through the reactor during the experiment. Thus, fluorine specific consumption was 1.36 kg per 1 kg of ZTF. This indicator should substantially decrease when carrying out the fluorination process in apparatuses with the stirring of the solid product.

The results obtained during fluorination in reactors with a fixed bed of zircon were used when selecting technological parameters for fluorination of zirconium raw materials in an experimental-industrial apparatus used in uranium production. Plant scheme is presented in Fig. 2.

Fluorination was carried out in steel auger reactor *4* with rake stirrer *5* located in tube *2* with molten nitrate. To maintain a constant temperature of the tub electric heating elements *3* that are installed directly therein were used. The reactor is equipped with bunkers *7* and augers *13* and *6* for loading of raw material and unloading of the product, respectively. Exhaust gases were passed through electrostatic precipitator *9* with vibrator *18* and discharge device *8*. Fluorine was fed into the reactor at a temperature of 40–50 °C. Monitoring and regulating of fluorine flow rate was carried using dimensional diaphragm *16*, device *15* and valve *17*.

The reactor wall temperature was maintained constant during fluorination, namely 350 °C. Zircon concentrate in the amount of 360 kg was loaded into the reactor and 330 kg of fluorine was passed, which is by 30 % greater than the stoichiometrically required amount.

Four hundred kg of ZFT was obtained from the reactor and 65 kg of therefrom was uploaded from the electrostatic precipitator

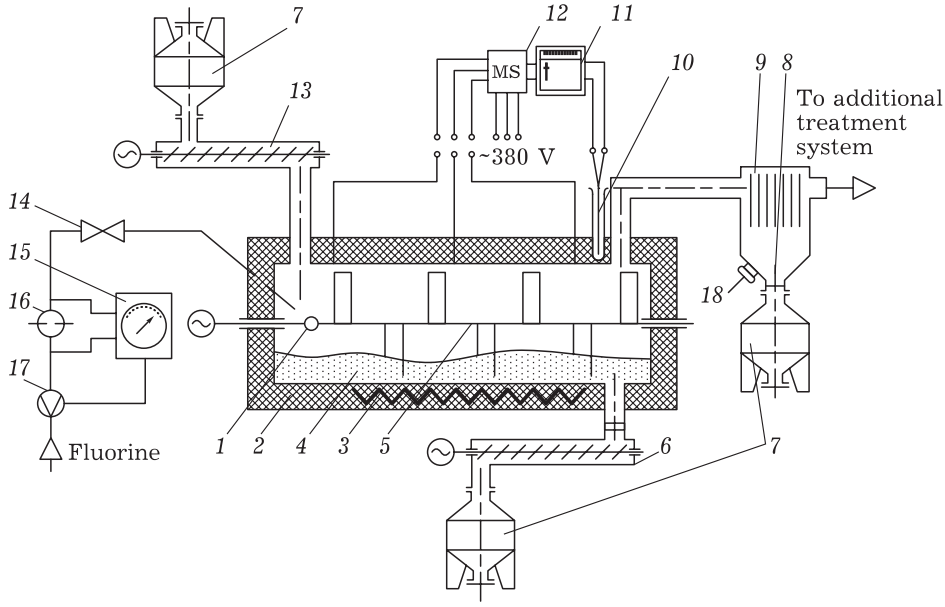

Fig. 2. Scheme of a pilot plant for fluorination: *1* – fluorine supply to the reactor; *2* – molten nitrate bath; *3* – electric heater; *4* – reactor; *5* – scraper stirrer; *6* – discharge auger; *7* – container; *8* – discharge device from the electrostatic precipitator; *9* – electrostatic precipitator; *10* – thermocouple; *11* – potentiometer; *12* – magnetic starter; *13* – screw download; *14* – valve; *15* – flow meter; *16* – dimensional diaphragm; *17* – valve; *18* – vibrator.

resulting from the 110 h experiment. Herewith, the fluorine specific consumption was 0.92 kg per 1 kg of concentrate, which was by 67 % lower than that under stationary conditions. Fluorine excess can be decreased in case of carrying out continuous fluorination process as in uranium production, up to 5–10 %, which may additionally enhance the process efficiency [8].

The resulting ZFT is a white crystalline powder with the yellowish tint and a granulometric composition from 0.05 to 1 mm. The colour is driven by minor amounts of nickel (less than 0.02 %) and other products of corrosion of the apparatus and stirrer in its composition. For this reason, and also due to high oxygen contents, this tetrafluoride is unsuitable for direct calciothermic reduction and the production of metal zirconium [1, 7]. To use this ZFT as a metallurgical semi-product it should be treated from oxygen and other corrosion products of the reactor material. Sublimation and desublimation processes are recommended to be used for this purpose.

SUBLIMATION TREATMENT OF ZIRCONIUM TETRAFLUORIDE

To carry out sublimation treatment of ZFT a laboratory setup was developed, the scheme of which is presented in Fig. 3.

Zirconium tetrafluoride obtained after zircon fluorination was loaded into corundum glass *7* that was set in sublimator *5*. The sublimator was placed into shaft furnace *10* and sealed. The setup includes vacuum pump *3*, absorption column *2*, traps *8* and *9* for gaseous and solid reaction products from the sublimator, valve *14* and cylinder *4* to flow argon to the sublimator, means of temperature control *12* and vacuum control *1*.

At a temperature of 700–850 °C, ZFT was sublimated from the glass and was desublimated from the precipitated surface of desublimator *6* as a dense spherical druse of crystals (Fig. 4).

The dependence of sublimation degree and impurity amount content in a desublimate on a number of factors, such as the granulometric composition of the initial ZFT, sublimation

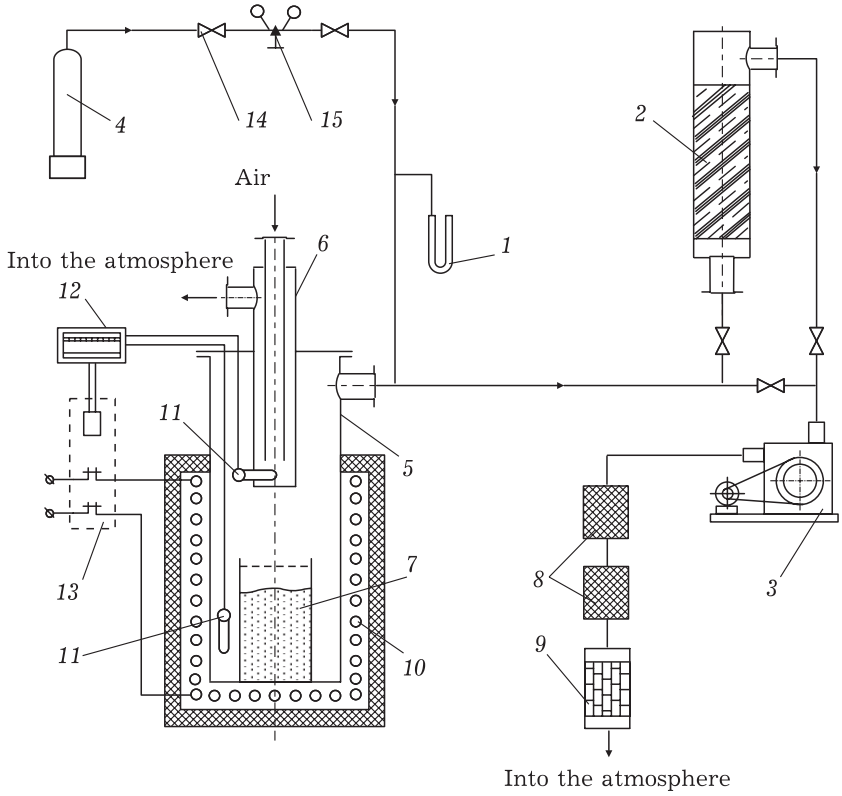

Fig. 3. Scheme of a laboratory setup for sublimation treatment of zirconium tetrafluoride (ZTF): *1* – U-shaped vacuum gauge, *2* – absorption column, *3* – vacuum pump, *4* – cylinder with an inert gas, *5* – sublimator, *6* – desublimator, *7* – corundum glass, *8* – oil filter, *9* – filter, *10* – electric shaft furnace, *11* – thermocouple, *12* – potentiometer KSP-4, *13* – electromagnetic relay, *14* – valve, *15* – gas reducer.

TABLE 1

Content of impurities in zirconium tetrafluoride (ZTF) desublimate, depending on number of treatment cycles, mass %

Number of treatment cycles	Fe	N	O	Ti	C	Al	Ni	Hf
One-time	0.04	0.006	0.01	<0.003	0.003	0.005	0.02	1.18
Two-time	0.01	0.004	<0.01	<0.003	0.002	ND	<0.02	0.81
Three-time	0.001	ND	<0.01	ND	ND	ND	0.001	0.49

Note. ND – not determined.

temperature, and process time, and also number of sublimation cycles was studied.

A number of recommendations to carry out experiments on sublimation treatment of ZFT under experimental-industrial conditions was developed:

i) To reach the sublimation degree of no less than 95% particle size of the initial powdery ZFT should not exceed 0.2 mm;

ii) Vacuum sublimation of ZFT should be carried out in the temperature range of 750–800 °C;

iii) The number of cycles of re-sublimation of ZFT depends on the purpose of the final product (Table 1).

As it follows from the data of Table 1, ZFT sublimated once contains totally 0.087 % of impurities including 0.009 % of nitrogen and carbon alongside with hafnium tetrafluoride. This product is applicable to obtain zirconium metal powders and alloys on its basis that are used in the manufacture of alloy steels [8].

Two-time sublimation may reduce the total content of impurities in ZFT to 0.049 %, and with the three-time sublimation of ZFT sublimated in each subsequent cycle for no less than 95 %, the total content of impurities is reduced to 0.012 %. It can be seen that hafnium content in ZFT after three-time sublimation decreased from 2.0 to 0.49 %. Thus, nuclear quality ZFT according to hafnium content too can be obtained via repeated sublimation.

To produce treated ZFT on a semi-industrial scale a vacuum sublimation apparatus "Ts" of periodic action with single charging of the initial ZFT to 20 kg was manufactured and launched into action.

A steel cylindrical case of the apparatus made of 12 X18H10T ovenproof steel is provided on the outside by a water-cooled jacket. A desublimator in the form of a removable cup made of copper was installed into the case with minimum clearance with the wall of the apparatus. A sublimator in the form of a tube was mounted coaxially inside the case and secured to the lid of the apparatus. A few round plates were secured along its height, in which the initial TFTS was loaded. An electric heater was mounted in the inner cavity of the sublimator of heat-resistant ceramic core on

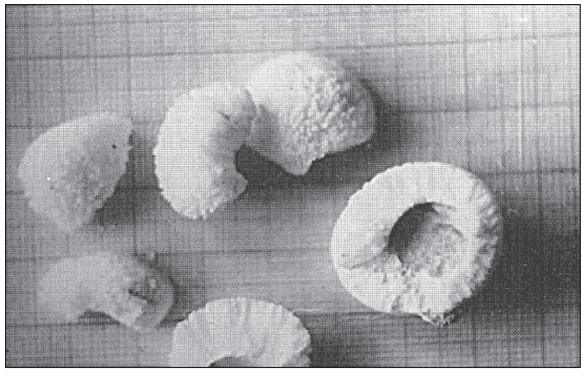

Fig. 4. Druses of zirconium tetrafluoride (ZTF) crystals after desublimation in the surface of a desublimator.

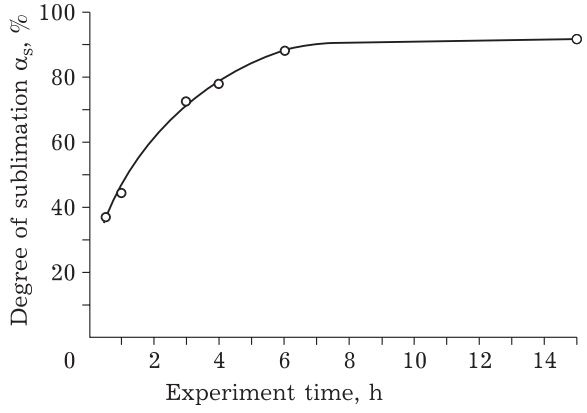

Fig. 5. Degree of sublimation of zirconium tetrafluoride (ZTF) versus experiment time

TABLE 2

Chemical composition of desublimate obtained in the apparatus "Ts"

Impurtity	Content, mass %	Impurtity	Содержание, мас. %
O	≤0.02	Be	10^{-3}
N	$<1\cdot10^{-4}$	Sn	ND
C	$1\cdot10^{-3}$	V	ND
Si	$<1\cdot10^{-3}$	Cr	$<10^{-3}$
Ti	$<1\cdot10^{-3}$	Pb	$<10^{-3}$
Ni	$<1\cdot10^{-3}$	Mn	$<10^{-4}$
Fe	$<3\cdot10^{-3}$	Ca	$3\cdot10^{-3}$
Al	10^{-2}	Hf	0.7–1.1
Cu	$2\cdot10^{-3}$	Mo	н/о

Note. ND – not determined

which the spiral of EI-935 alloy was wound.

The pressure and temperature of ZFT directly in the plate of the medium sublimator part were monitored during sublimation in the apparatus.

The sublimation process was carried out in the temperature range of 750–800 °C at a residual pressure of 10 Pa. Upon the completion of the experiment, the electric heater in the sublimator was turned off and the plant was filled with an inert gas up to atmospheric pressure. The effect of experiment time on the degree of sublimation of ZFT with apparatus load of 18 kg of ZFT was studied. Having determined the residual mass of ZFT, the degree of sublimation was calculated. Research and calculation results are given in Fig. 5.

It can be seen that the degree of sublimation of tetrafluoride increases, however, its full sublimation does not occur. About 45 % of the product is sublimated during the first hour, after 6 h – 90 %. The chemical composition of the residues after sublimation demonstrated that they consisted of non-volatile corrosion products of fluorination apparatus, sublimator, and also of not completely fluorinated zircon, ZFT residues, and a mixture of rare-earth element (REE) fluorides.

The resulting product corresponds to the composition given in Table 2, as demonstrated by multiple analyses of sublimated ZFT.

As if follows from the data of Table 2, the ZFT purified by vacuum sublimation in apparatus "Ts" is comparable with potassium hexafluorozirconate that corresponds to TU 6-09-3934–75 and is used as a metallurgical semi-product for the production of metal zirconium and its alloys.

CONCLUSION

The fluoride technology of processing of zircon concentrates has been proposed and experimentally proven using elemental fluorine and producing zirconium tetrafluoride under industrial conditions. The feasibility of treatment of zirconium tetrafluoride from impurities via vacuum sublimation has been demonstrated. The design of the sublimation apparatus manufactured and tested under current production conditions has been proposed.

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