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STUDY OF FLUOROAMMONIUM PROCESSING OF REDUCTION SMELTING DUSTS FROM ILMENITE CONCENTRATE

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The article presents the results of studies on the processing of fine waste dusts of electric smelting of ilmenite concentrates. The main silicon impurity was preliminarily removed from the dusts. The process of dust fluorination with titanium fluorides extraction is studied. The influence of temperature and time on sublimation degree of titanium fluorides was studied. The optimum conditions for sublimation of titanium fluorides were determined: T = 600 ± 10 °C, time - 2 hours. The extraction of titanium in sublimations was up to 99 %. The XRD method showed that phases of heptofluorotitanate, hexafluorosilicate and ammonium hexofluoroferrate are present in the sublimations. The impurity components of iron, manganese, chromium are sublimated at a sufficiently low degree during titanium fluorination.

Keywords: ilmenite concentrate, waste, dust, sublimation, titanium fluoride

INTRODUCTION

Existing industrial technologies for the stripping of titanium raw materials are the sulphuric acid and chlorine methods. In the sulphuric acid process, low-grade titanium-containing raw materials are acceptable, but large quantities of hydrolysis acid and contaminated wastewater are generated. In chlorine technology synthetic rutile and titanium slag, previously prepared from ilmenite raw material, are used as initial raw materials. At Ust-Kamenogorsk Titanium-Magnesium Plant JSC (UKTMK JSC) electric melting of ilmenite concentrates to produce titanium slag and cast iron is applied, the process is accompanied by high dust emissions. Due to the high silica content, the dust cannot be returned to the technological process, so it is stored in landfills. It is relevant to find ways to process electric smelting dust of ilmenite concentrates with the extraction of valuable components from them.

Recently, fluoroammonium processing has become one of the most promising methods of rare metal extraction.

There are studies on the processing of titanium-containing raw materials with the use of fluoroammonium compounds. Processing method 1 for ilmenite concentrate, includes fluorination of raw materials by sintering with fluoride reagent, heat treatment of profluorinated mass for separation of fluorination products through sublimation, pyrohydrolysis of residue after sublimation to produce iron oxide. In the process of fluorination ammonium fluoride, ammonium bifluoride or a mixture of them are used as a fluoride reagent in a stream of inert gas. Substance is collected with water to produce solution of ammonium fluorotitanate and titanium dioxide hydrate is precipitated with water ammonia solution, followed by heat treatment of precipitation to produce anhydrous titanium dioxide.

In work [2], at fluorination of titanium slag with ammonium bifluoride after hexafluoride sublimation there remained titanium dioxide with admixtures of other oxides which were separated from them using ammonium bifluoride solution of different concentrations.

In study [3] the method of fluoroammonium-fluoride treatment of cakes after leaching of titanium sludge with nitric acid [4] with ammonium bifluoride was used and it showed the possibility of separation of silicon from titanium.

The use of fluoroammonium bifluoride method for treatment of fine dusts of reduction electrical smelting of ilmenite concentrates is of interest.

MATERIALS AND METHODS

Materials and equipment: pure ammonium fluoride GOST 9546-72, 10 and 25 % ammonia, sleyeve filter dust of electrical melting of ilmenite concentrates provided by UK TMK JSC (Republic of Kazakhstan). Content of the main components of electric smelting dust of ilmenite concentrate (converted to oxides) / wt. % : 27,53 SiO_2, 34,29 TiO_2, 18,19 FeO, 4,17 MnO, 0,79 Cr_2O_3.

A sample of thoroughly mixed ammonium bifluoride and dust or cinder in a certain ratio was placed

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in an alundumina boat, which was placed in a steel tube placed in a horizontal LOIP LF-50/500-1200 tube furnace. Argon was fed through the steel tube and the furnace was heated to a predetermined temperature within a certain time interval. At the end of the experiment the fumes of ammonium hexafluorosilicate or titanium fluorides were collected at the end of the steel tube and the gas-air mixture was collected in a flask with ammonia water. The degree of fluorination was estimated by the change of content of controlled components in the solid residue. The rate of argon feed was 1,0 – 1,5 dm^3/h.

Methods of analysis: The X-ray experimental data were obtained on BRUKER D8 ADVANCE device with copper radiation at an accelerating voltage of 36 kV, current 25 mA. X-ray fluorescence analysis was performed on a Venus 200 PANalytical B.V. wave dispersion spectrometer. (PANalytycal B.V., Holland). Chemical analysis of samples was performed on optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA, Perkin Elmer).

RESULTS AND DISCUSSION

Distillation of silicon from dusts

With the purpose of complete removal of silicon-containing phases and separation of silicon impurity from titanium, the high-temperature ammonium-fluoride pre-treatment of electrofusion dust of ilmenite concentrate at the following fluorination conditions was carried out: temperature 260 °C, duration 6 h, mass ratio dust : ammonium bifluoride = 1 : 1 [5]. At the same time silicon was almost completely extracted in substrates (Table 1).

Table 1 **Results of X-ray phase analysis of the residue from the fluorination of the electrowinning dust of the ilmenite concentrate**

Component	Formula	Phase content / %
Ammonium Titanium Oxide Fluoride	$(NH_4)_{0.8}TiOF_{2.8}$	9,4
Iron Fluoride	FeF_3	16,7
Ammonium Titanium Fluoride	$(NH_4)_2TiF_6$	28,3
Zinc Titanium Fluoride Hydrate	$ZnTiF_6(H_2O)_6$	5,7
Titanium Oxide	$TiO_{0.428}$	9,3
Ammonium Iron Fluoride	$NH_4(FeF_4)$	5,2
Titanium Oxide	Ti_6O_{11}	25,5

Determination of optimum conditions for the sublimation of titanium fluoride compounds

The interaction of ammonium fluoride with ilmenite is accompanied by formation of non-stoichiometric compounds ammonium fluorotitanate, ammonium fluoroferrate [6,7].

In [6] the dependence of ilmenite transformation upon fluorination with ammonium fluoride is given. It was proved, that at 225 – 250 °C the degree of transformation is 90 %.

Titanium sublimation depends on the conversion degree of titanium compounds in the raw material during sublimation of silicon fluorides. In this connection the evaluation of titanium transformation degree into fluorides was carried out by the method [8]. The results are shown in Figure 1.

The diagram shows that the maximum degree of conversion is 45,6 %. The low degree of transformation is connected with the large amount of silicon compounds in the initial dust. So, in ilmenite concentrates the ratio of silicon to titanium is 1:3÷4, in the investigated object it is 1:1.3.

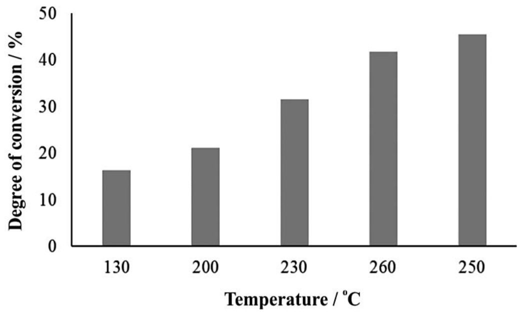

Figure 1 Dependence of the degree of conversion of titanium compounds contained in smelting dust of ilmenite concentrate on the fluorination temperature

Studies on determining the optimum conditions for sublimation of titanium fluorides were carried out from fluorinated dust after removal of the main part of silicon.

The influence of temperature on sublimation degree of titanium fluorides was investigated in the temperature range 450 – 650 °C. Experimental results are shown in Figure 2. When temperature increases from 450 to 600 °C the sublimation degree increases up to 99 %. 600 ± 10°C should be considered as an optimal temperature of titanium sublimation.

Study of the decomposition of fluorinated ilmenite concentrate showed [9], that at 350 °C the decomposition of heptafluorotitanate ammonium to hexafluorotitanate $(NH_4)_3TiF_7 \rightarrow (NH_4)_2TiF_6$ occurs. Sublimation of the ammonium hexafluorotitanate takes place from 371 °C up to 683 °C.

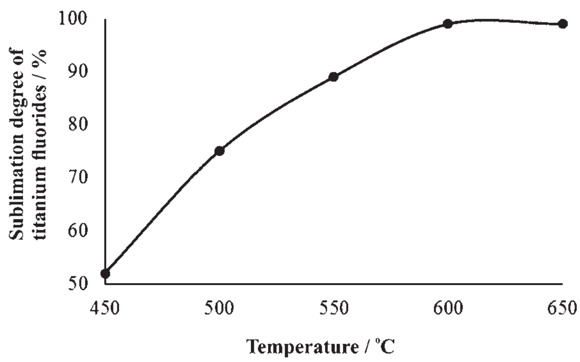

Figure 2 Dependence of titanium fluoride sublimation degree on process temperature

Table 2 **Dependence of titanium sublimation degree and phase composition of the slag composition on process time**

Duration duration / min.	Cake output / %	TiO_2 content in the slag, wt. / %	Titanium extraction into the distillation / %	Phase composition of the slag	
				Component	Component fraction in the slag / %
30	20,4	12,18	85,4	$(NH_4)_2SiF_6$•NH_4F $(NH_4)_3TiF_7$ $(NH_4)_3FeF_6$ NH_4HF_2 NH_4F	28,3 18,0 16,4 37,3
60	19,8	5,00	94,2	-	-
90	19,2	1,99	97,8	$(NH_4)_3FeF_6$ $(NH_4)_2TiF_6$ $(NH_4)_3TiF_7$ NH_4HF_2	28,7 27,1 23,6 21,2
120	19,1	0,84	99,0	-	-
180	19,2	0,69	99,2	$(NH_4)_3FeF_6$ $(NH_4)_2TiF_6$ $(NH_4)_3TiF_7$ NH_4HF_2	28,7 17,1 33,0 21,2
240	19,0	0,64	99,3	$(NH_4)_3TiF_7$ $(NH_4)_3FeF_6$ NH_4HF_2 $(NH_4)_2TiF_6$	50,3 28,4 13,3 8,0

Influence of duration of sublimation process. Results of studies of dependence of sublimation degree of titanium and phase composition of the slag on process time are resulted in Table 2. From Table 2 it is visible that sublimation of titanium is almost completely passed in 2 hours of the process at 610 °C. The study of sublimations by X-ray phase analysis showed that during the first 30 minutes of the process the main phase in sublimations is ammonium hexafluorosilicate. Ammonium heptofluorotitanate and ammonium hexofluoroferrate are present.

When the process time increases, a hexafluorotitanate of ammonium appears in the distillates, the fraction of which is approximately the same as the fraction of $(NH_4)_3TiF_7$. Further prolongation of the process up to 3 – 4 h resulted in a significant increase of the fraction of ammonium heptafluorotitanate. The process conditions have an influence on the phase composition of the substrates. Thus the optimum conditions for sublimation of titanium are: temperature 600 ± 10 °C, duration 2 h.

Due to the strict requirements for the content of chromophoric impurities which impart different colours to white pigment even at their very low concentrations the behaviour of iron, manganese, chromium and residual silicon impurities in the sublimation of titanium fluoride compounds was studied [10-11].

The study of sublimation of impurity components during the sublimation of titanium fluorides at 610 °C in the range of 30 – 240 min showed that the silicon in the form of ammonium fluorosilicate is almost completely removed into sublimations during the first 30 min of the process. Sublimation of iron over 2 h takes 15,1 %, of manganese 9,3 % and of chromium 13,6 %. At the same time, despite a certain sublimation of iron, manganese and chromium, their content in the residue increases. In 2 hours the iron content increased by 1,8, manganese by 1,9 and chromium by 2,0.

CONCLUSIONS

The influence of temperature and process duration on sublimation degree of titanium fluorides was studied. The optimum sublimation conditions of titanium fluorides are temperature 600 ± 10 °C, the duration 2 h. The extraction of titanium in sublimations can be up to 99 %. The X-ray phase method of analysis showed that the phases of heptofluorotitanate, hexafluorosilicate and ammonium hexofluoroferrate are present in the substrates. The predominance of this or that phase in sublimations strongly depends on the process conditions. The study of sublimation of impurity components during fluorination of titanium from sinter showed that iron, manganese and chromium sublimate together with titanium with a rather low degree.

Studies on fluoroammonium treatment of ilmenite concentrate electrofusion dusts have shown that it is possible to separate silicon from titanium during sublimation of their fluoride compounds which are suitable for their further processing and yield valuable products.

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