OBTAINING NIOBIUM CONCENTRATE FROM NIOBIUM-CONTAINING FLUORIDE CINDERS

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ABSTRACT

The paper presents the results of processing niobium-containing fluoride cinders to obtain niobium concentrate from them. The material composition of the cinder was studied by chemical and X-ray methods. X-ray phase analysis showed the presence of ammonium aluminium fluoride, ammonium iron fluoride, ammonium titanium fluoride, as well as niobium-containing sodium niobium fluoride. Leaching of the fluoride cinder was carried out with ammonia water at temperatures of 60 - 80°C until a precipitate was formed at pH = 9 with vigorous stirring at 300 rpm, for 90 min. Nitric acid purification of the sludge was performed with a nitric acid solution within 4 - 10 %, at 60°C, with a S:L ratio of 1:5 and an agitation time of 120 min. 8 % HNO_3 was chosen as the optimum concentration of nitric acid. After washing the obtained cake was calcined at 500°C for 120 min. The niobium concentrate containing 57.5 % Nb_2O_5 was obtained according to the study results.

Keywords: fluoride cinders, niobium, ammonia water, nitric acid, leaching.

INTRODUCTION

Niobium is a bright silvery grey metal that belongs to the class of refractory rare metals. The terrestrial crust contains 0.002 % (wt.) of niobium. High strength and good corrosion resistance, even at high temperatures, allow niobium to be used as a construction material. Such use is typical for the manufacture of aircraft parts, pipes and containers for the transfer and storage of liquid metals, and casings for radioactive heat-producing elements [1].

Niobium ores, natural mineral formations containing Nb in quantities at which it is economically feasible to extract Nb and its compounds. The minimum grades at which it is profitable to develop primary niobium ores are about 0.15 - 0.2 % Nb_2O_5; the average content of Nb_2O_5 in most deposits of niobium ores of the world is 0.2 - 0.6 %; rich deposits contain 1 % or more Nb_2O_5 [2]. One of the important features of niobium is its high affinity for titanium. Numerous minerals of niobium with titanium are found in nature. In this regard, titanium raw material is one of the main sources of niobium production [3]. In the process of obtaining sponge titanium at "Ust-Kamenogorsk titanium-magnesium plant" JSC a large number of rare metals is lost annually with production waste. In these wastes, the content of niobium is comparable to the content of niobium in industrial ores. At the same time, these wastes are not processed and all the valuable components in them are accumulated in sludge reservoirs [4, 5].

Scientific team of the laboratory of titanium and rare refractory metals from the Institute of Metallurgy and Ore Beneficiation JSC conducted studies devoted to the recycling problem of Ust-Kamenogorsk Titanium Magnesium Plant JSC waste for many years. The method for extracting niobium from titanium production waste, including melting, chlorination, distillation and

condensation of niobium chlorides, in which the process is carried out in vacuum at a rarefaction of 133.3 - 1333 Pa and the condensation of niobium chlorides is carried out at a temperature of 150 - 200°C, was proposed in [6]. The technical result of the invention was to increase the extraction degree of niobium with obtaining a more concentrated product.

Besides, the authors proposed the method of titanium chloride sludge processing that included leaching, filtration to get titanium-niobium sludge and solution, whereby the leaching solution was sent for Fe^{3+} reduction to Fe^{2+}, neutralized up to pH 2.0 - 3.0 with magnesium production sludge, filtered with separation of the sediment containing recovered titanium and niobium, and the obtained titanium-niobium sludge was combined [7]. The result of the proposed invention was an increase in the extraction degree of niobium and titanium into the titanium-niobium sludge.

Fluorammonium processing has recently become one of the promising methods of rare metal extraction. There are enough studies in the literature devoted to the processing of titanium-containing raw materials with the use of fluorammonium compounds [8, 9]. Fluorammonium treatment of cakes after nitric acid leaching of titanium sludge with ammonium bifluoride was used and showed the possibility of selective sublimation of silicon and titanium and possibility to produce niobium-enriched cinder [10]. The present work is devoted to the study of this niobium-containing cinder with the purpose to obtain niobium concentrate in oxide form from it.

EXPERIMENTAL

Materials and apparatus: Ammonia solution 25 % pure (NH_4OH), nitric acid 65 % ultrapure (HNO_3). Cinder composition, wt. %: 9.7 Al, 8.2 Fe, 6.5 Nb, 2.1 Ti, 0.7 Ca, 0.2 Si, 65.5 F, 3.0 O etc. Heating plate, SNOL 58/350 drying oven and SNOL 7.2/1300 muffle furnace (Lithuania) were used in the experiments.

Methods of analysis: X-ray phase analysis was performed with the help of BRUKER D8 ADVANCE device (Germany), X-ray fluorescent analysis was performed with Venus 200 PANalyical B.V. spectrometer (Holland), chemical analysis of samples was performed on optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA).

RESULTS AND DISCUSSION

X-ray phase analysis was performed to study the composition of the main phases of the cinder and associated formations. The X-ray phase analysis result of is shown in Fig. 1.

X-ray phase analysis showed the presence of ammonium aluminium fluoride, ammonium iron fluoride, ammonium titanium fluoride, as well as niobium containing sodium niobium fluoride in the studied samples.

Then, alkaline hydrolysis was carried out to convert

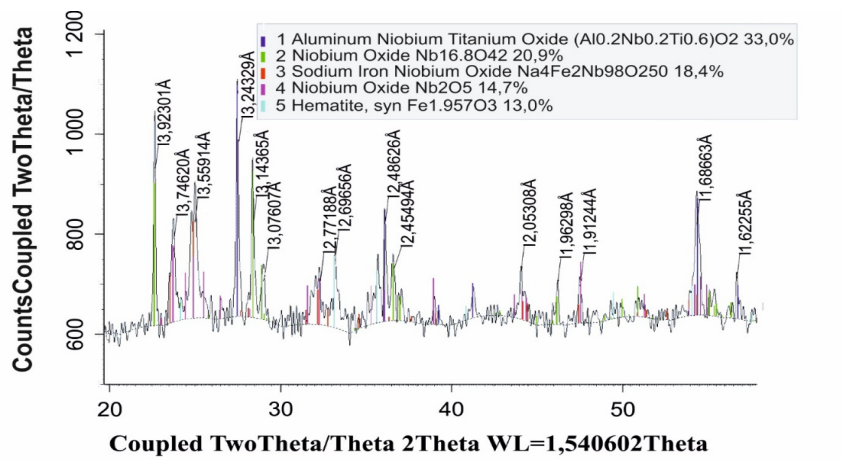

Fig. 1. X-ray phase analysis of the cinder.

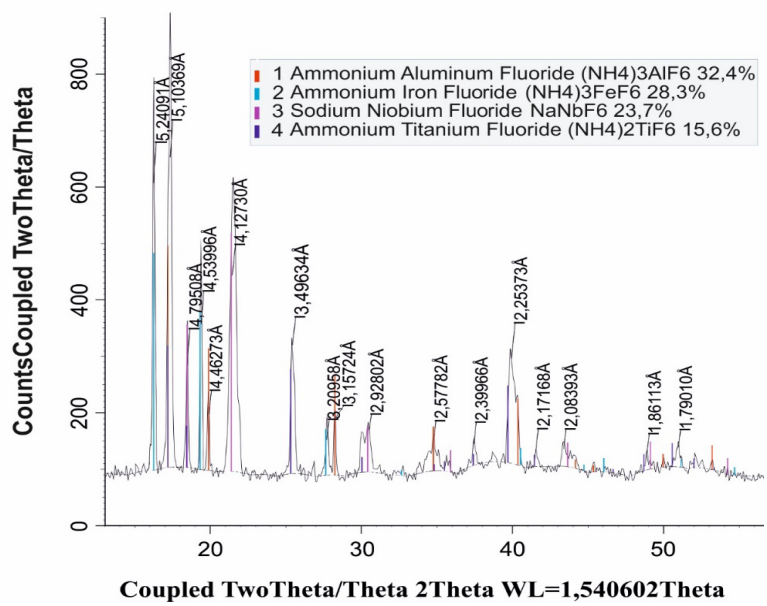

Fig. 1. X-ray phase analysis of the cinder. - *continued*

Table. 1. Thermodynamic parameters of alkaline hydrolysis of main fluoride compounds present in carbon black.

No.	T, K	293	313	333	353	373
1	$(NH_4)_3AlF_6 + 3NH_3 + 3H_2O = Al(OH)_3\downarrow + 6NH_4F$					
	ΔG, kJ	-41.11	-48.65	-56.05	-63.54	-71.1
2	$(NH_4)_3FeF_6 + 3NH_3 + 3H_2O = Fe(OH)_3\downarrow + 6NH_4F$					
	ΔG, kJ	-54.88	-48.317	-41.443	-34.268	-26.804
3	$(NH_4)_2TiF_6 = TiF_4 + 2NH_4F$					
	$TiF_4 + 2NH_4F + 4NH_4OH = TiO_2\downarrow + 6NH_4F + 2H_2O$					
	ΔG, kJ	-338.71	-332.262	-325.485	-318.414	-311.081
4	$NaNbF_6 = NbF_5 + NaF$					
	$2NbF_5+10NH_4OH = Nb_2O_5\downarrow +10NH_4F+5H_2O$					
	ΔG, kJ	-888.563	-873.024	-856.66	-839.541	-820.378
	$NaF + NH_4OH = NaOH + NH_4F$					
	ΔG, kJ	31.927	33.558	35.283	37.091	38.974

fluoride cinders into oxides. Fluoride cinder batches were preliminarily worked out to study the alkaline hydrolysis process. The conversion of fluoride cinders into oxides was performed with ammonia water (25 wt. % NH_3) at 60 - 80°C to form a precipitate at pH = 9, with vigorous stirring at 300 rpm, for 90 min. Then the precipitate was separated from ammonium fluoride solution by filtration. It can be reused for fluorination of feedstock.

The thermodynamic probability of ammonia hydrolysis of the main fluoride compounds which are present in the sludge is shown in Table. 1.

Temperature range 60 - 80°C was selected under the results of thermodynamic studies for the process of alkaline hydrolysis of cinder. Increase in the temperature above 80°C leads to intense evaporation of the solution, and less than 60°C, as studies have shown, we get a product of the worst quality. Keeping the suspension at this temperature interval for 90 min contributed to

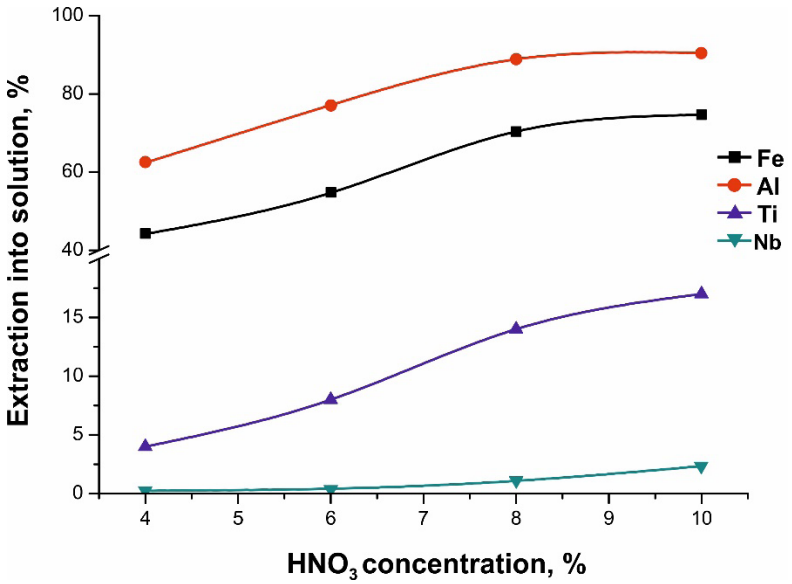

Fig. 2. Influence of HNO_3 concentration on extraction of cinder components into solution.

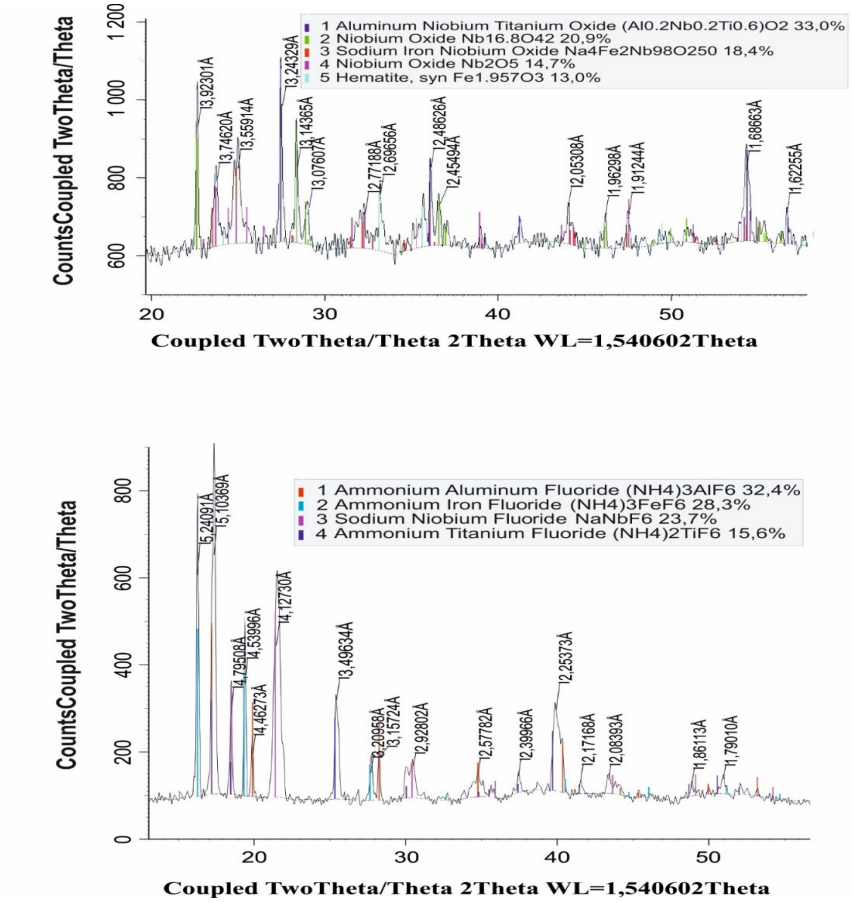

Fig. 3. A diffractogram of niobium concentrate.

stabilization of the system and significant improvement of its filterability. The resulting sludge was dried at 105 - 110°C to constant weight.

Then purification experiments for the obtained sediment from iron, aluminium and titanium impurities were performed with nitric acid. It is known that iron and aluminium dissolve well in non-concentrated nitric acid but remain resistant to concentrated acid. Besides, when nitric acid purification is performed for sludge from impurities, it is necessary to minimize dissolution of the main product and to transfer iron and aluminium into solution as much as possible. Therefore, nitric acid purification was carried out with a weakly concentrated nitric acid solution in the range of 4 - 10 % at 60°C with a ratio of S:L = 1:5 and an agitation time of 120 min. The pulp mixing speed was 300 rpm. Experiments to study the effect of HNO_3 concentration on the purification of the resulting sludge from impurities of iron, aluminum and titanium are shown in Fig. 2.

Fig. 2 shows that there is concentration of the niobium concentrates in the cake with the increase of HNO_3 and with a significant decrease in the extraction of aluminium, iron and titanium into the cake.

Consequently, the optimum concentration of nitric acid is 8 % to avoid significant losses of niobium, with sufficiently high extraction of aluminium, iron and titanium in the solution. After washing, the resulting cake was dried at 105 - 110°C to constant weight, then calcined in a chamber furnace at 500°C for 120 min.

The chemical analysis of the obtained product was carried out after calcination, mass %: 40.2 Nb, 10.55 Fe, 6.3 Ti, 5.5 Al, 0.37 Na, 0.28 Ca, 31.4 O etc. (57.5 Nb_2O_5, 15.1 Fe_2O_3, 10.5 TiO_2, 10.4 Al_2O_3 etc.). X-ray phase analysis of the obtained niobium concentrate is presented in Fig. 3.

It is clear according to the XRD results of the obtained niobium concentrate shown in Fig. 3 that the product consists mostly of niobium oxides Nb_2O_5, $Nb_{16.8}O_{42}$. Besides, niobium is found in the phases $(Al_{0.2}Nb_{0.2}Ti_{0.6})O_2$, formed most likely due to the high calcination temperature of the cake. And the phase analysis showed the presence of iron in the form of Fe_2O_3.

Thus, niobium concentrate containing 57.5 % Nb_2O_5 in terms of oxides was obtained according to the results of studies. It can be used as an intermediate product in the production of metallic niobium.

CONCLUSIONS

Chemical and X-ray fluorescence analyses determined the content of the main components of fluoride cinders, wt. %: 9.7 Al, 8.2 Fe, 6.5 Nb, 2.1 Ti, 0.7 Ca, 0.2 Si, 65.5 F, 3.0 O etc. X-ray phase analysis showed the presence of the following phases: $(NH_4)_3AlF_6$, $(NH_4)_3FeF_6$, $NaNbF_6$, $(NH_4)_2TiF_6$.

The fluoride cinder was converted into oxides by agitation leaching with ammonia water (25 wt. % NH_3) at 60 - 80°C to form a precipitate at pH = 9 which was kept at a given temperature for 90 min. Then the precipitate was separated from the ammonium fluoride solution by filtration. The resulting precipitate was dried to a constant weight.

Nitric acid purification was performed with a nitric acid solution in the range of 4 - 10 % at 60°C with a ratio of S:L = 1:5 and an agitation time of 120 min. 8 % HNO_3 was chosen as the optimum concentration of nitric acid. The pulp mixing speed was 300 rpm. After washing the obtained cake was calcined at 500°C for 120 min. Niobium concentrate containing 57.5 % Nb_2O_5 in terms of oxides was obtained according to the study results. X-ray phase analysis showed the presence of Nb_2O_5, $Nb_{16.8}O_{42}$, $(Al_{0.2}Nb_{0.2}Ti_{0.6})O_2$, $Na_4Fe_2Nb_{98}O_{250}$, Fe_2O_3.

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