The mechanism for production of beryllium fluoride from the product of ammonium fluoride processing of beryllium-containing raw material

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Abstract. The technique of fluorite-phenacite-bertrandite ores from Russian Ermakovskoe deposit processing by ammonium bifluoride is described. To determine the temperature mode and the thermal dissociation mechanism of ammonium tetrafluoroberyllate (the product of ammonium-fluoride leaching of the ore) the TG/DTA have been carried out. By IR spectroscopy and XRD the semi-products of ammonium tetrafluoroberyllate thermal dissociation have been identified. The hygroscopic low-temperature beryllium fluoride forms higher than 380 °C. The less hydroscopic form of BeF_2 have been produced at 600 °C.

1. Introduction

In nature beryllium is mainly represented by nearly 30 minerals, the most important of them are: beryl, chrysoberyl, behoite, bertrandite, and phenacite [1-3]. In production of metallic beryllium and its compounds on industrial scale only beryl, bertrandite, and phenacite concentrates are used. The largest beryllium deposits with easy-to-break down ores (carbonate-containing bertrandite) are located in the United States: Spor Mountain, Sierra Blanca [4]. Today, beryllium is leached from ores of these deposits only by using an industrial method of hydrometallurgical processing of beryllium raw materials – the sulfuric acid method, without a preliminary preparation of raw materials [5]. There are only three states in the world that carry out hydrometallurgical processing of beryllium-containing raw materials: the United States, Kazakhstan, and China. At the same time, in the territory of the Russian Federation there are unique Orotskoe bertrandite and Ermakovskoe deposits, with the content 0.5-1.0 % of BeO in the ore. The capacity of the Ermakovskoe deposit in terms of commercial beryllium ore amounts to nearly 1400 thousand tons [6]. The Ermakovskoe deposit is represented by fluorite-phenacite-bertrandite ores; a concentrate with the content 24.44 % expressed in terms of Be_2SiO_4 is produced from the ore by flotation concentration (Table 1).

Table 1. Phase composition of the fluorite-phenacite-bertrandite concentrate

Be_2SiO_4	SiO_2	CaF_2	CaO	Fe_2O_3	MgO	Al_2O_3
24.44	13.01	23.65	27.27	1.07	2.51	8.04

Processing of the given raw material using the existing sulfuric-acid scheme is complicated by a number of problems: 1) in order to leach beryllium from the fluorite-phenacite-bertrandite concentrate (FPBC), the concentrate must be subjected to a dual thermal activation (1700 and 950 °C) and fusion with alkali fluxes ($CaCO_3$, Na_2CO_3); 2) a large amount of fluorine, which transitions into a soluble

form from fluorite (CaF_2), with further processing of the activated concentrate binds beryllium, which leads to losses of the target component [5]. The described phenomena adversely affect the cost of sulfuric-acid leaching of beryllium.

For efficient and cost-effective processing of FPBC for the purpose of production of metallic beryllium and its compounds the ammonium-fluoride technology has been developed.

2. Technology description

The ammonium-fluoride technology for processing of beryllium-containing raw materials (in this case FPBC) consists in fusion of the concentrate with ammonium bifluoride (NH_4HF_2) at 180-220 °C without a preliminary thermal and chemical treatment of the raw material. Interaction of the concentrate components NH_4NF_2 (except fluorite) proceeds according to chemical equations (1-6) [7,8]:

$$Be_2SiO_4 + 7NH_4HF_2 \rightarrow 2(NH_4)_2BeF_4 + (NH_4)_2SiF_6 + 4H_2O\uparrow + NH_3\uparrow, \quad (1)$$

$$Al_2O_3 + 6NH_4HF_2 \rightarrow 2(NH_4)_3AlF_6 + 3H_2O\uparrow, \quad (2)$$

$$Fe_2O_3 + 5NH_4HF_2 \rightarrow 2(NH_4)_2FeF_5 + 3H_2O\uparrow + NH_3\uparrow, \quad (3)$$

$$CaO + NH_4HF_2 \rightarrow CaF_2 + H_2O\uparrow + NH_3\uparrow, \quad (4)$$

$$MgO + NH_4HF_2 \rightarrow MgF_2 + H_2O\uparrow + NH_3\uparrow, \quad (5)$$

$$SiO_2 + 3NH_4HF_2 \rightarrow (NH_4)_2SiF_6 + 2H_2O\uparrow + NH_3\uparrow. \quad (6)$$

The produced fluorinated sinter is then dissolved in water. Only beryllium and silicon completely go into solution (the degree of leaching is 97 %), iron (~ 55 %) and aluminum (~ 20 %) partially go into solution, calcium and magnesium form insoluble fluorides (the degree of leaching is ~ 0.2 %). The beryllium-containing solution is then purified from impurities using 25 % of ammonia solution. Ammonia hydrolysis of impurities proceeds according to chemical equations (7-9):

$$(NH_4)_2FeF_5 + 3NH_4OH = Fe(OH)_3\downarrow + 5NH_4F, \quad (7)$$

$$(NH_4)_3AlF_6 + 3NH_4OH = Al(OH)_3\downarrow + 6NH_4F, \quad (8)$$

$$(NH_4)_2SiF_6 + 4NH_4OH = Si(OH)_4\downarrow + 6NH_4F. \quad (9)$$

The pH level of precipitation of impurity hydroxides in this case is equal to 8. Such high pH of hydrolysis is related to the presence of an excessive amount of ammonium fluoride (NH_4F) in the production solution. Also, due to the presence of an excess of ammonium fluoride the destruction of the complex ion BeF_4^{2-} practically does not occur, even if raising the pH level to 10. The degree of beryllium hydrolysis at pH 10 does not exceed 5.2 %.

The purified beryllium solution is then evaporated to produce a crystalline ammonium tetrafluoroberyllate ($(NH_4)_2BeF_4$) which is then calcined to produce beryllium fluoride (BeF_2) – the initial compound for magnesiothermal reduction of beryllium [7, 9-11].

3. Experimental part

The aim of this study was to determine the temperature mode and the thermal dissociation mechanism of ammonium tetrafluoroberyllate.

Based on the information from literature sources, the decomposition of $(NH_4)_2BeF_4$ begins at 125 °C, at 230-260 °C ammonium trifluoroberillate (NH_4BeF_3) is formed, at temperatures higher than 270 °C beryllium fluoride is formed [1, 7, 9, 10]. A complete decomposition of ammonium tetrafluoroberyllate at an acceptable rate occurs at 400 °C, but the produced BeF_2 is hygroscopic and is not suitable for production of metallic beryllium, therefore the decomposition is carried out at 900 °C [9, 10]. For accurate identification of the decomposition mechanism of ammonium tetrafluoroberyllate a thermogravimetric and differential-thermal analyses of the mixture BeO-NH_4HF_2 have been carried out (Fig. 1). To carry out the analysis, ammonium bifluoride was taken with a 10 % excess relative to the stoichiometrically required quantity under the reaction (10):

$$BeO + 2NH_4HF_2 = (NH_4)_2BeF_4 + H_2O \quad (10)$$

Experiments were carried out using a combined TGA/DSC/DTA analyzer – derivatograph of the brand SDT Q600 with a software data processing TA Instruments Universal V4.2E. Crucibles: platinum: 40 mcl. Control of the sample atmosphere – argon. The heating rate was 5 °/min.

When mixing pure beryllium oxide and ammonium bifluoride the reaction begins immediately with the release of heat. The moisture allocated prior to loading of the reaction mixture into the analyzer is removed at 53 °C. At 129 °C melting of ammonium bifluoride in the mixture takes place, and the flow of the fluorination process accelerates. The fluorination ends at 160 °C. In the temperature range of 185-255 °C the decomposition of $(NH_4)_2BeF_4$ up to NH_4BeF_3 takes place (Fig.1). The decomposition of NH_4BeF_3 up to beryllium fluoride proceeds in the range of 255-300 °C, while on the TGA curve an inflection at 275 °C is observed. At 549 °C a peak on the DTA curve is observed, which corresponds to melting of the quartz form of beryllium fluoride with subsequent recrystallization and solidification of a new crystalline structure (tridimitic, α-cristobalitic) [11]. Melting of a new form of BeF_2 begins at 811 °C. Since the sample is under argon and there is a constant removal of beryllium fluoride vapors from the surface of the melt, a complete evaporation of the sample takes place when reaching 926 °C.

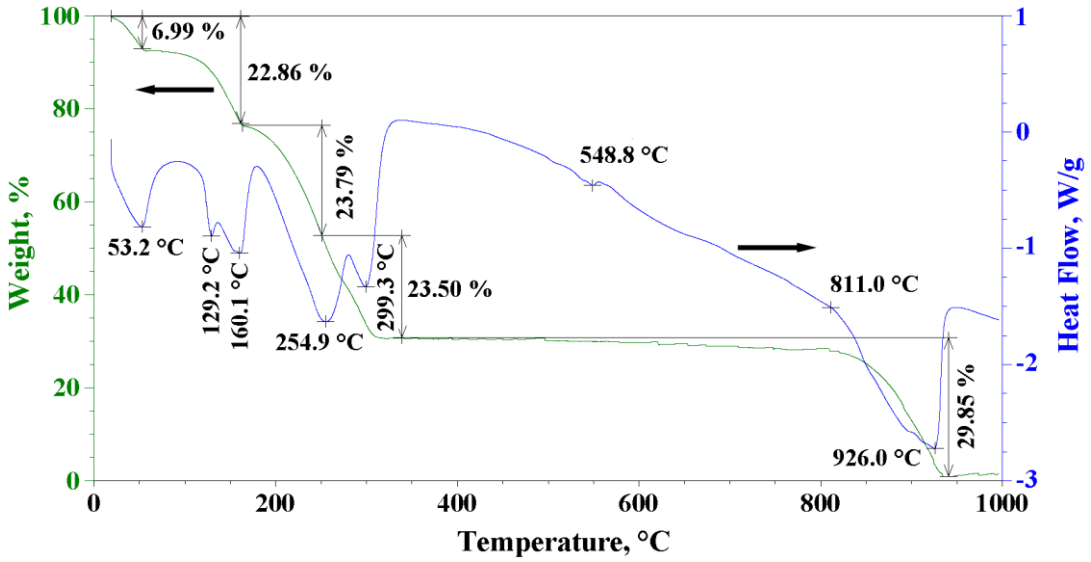

Figure 1. The derivatogram of the system BeO-NH_4HF_2

To determine the composition of produced substances during the decomposition, an analysis of products in critical points of the DTA curve has been carried out using methods of infrared (IR) and X-ray spectroscopy (X-ray diffraction analysis – XRD). To prepare the samples 5 g of beryllium oxide and 24 g of NH_4HF_2 were taken. The powders were mixed, abraded, and the mixture was filled into a graphite crucible. The reaction mixture was first heated at 150 °C, then at 250 °C, 280 °C, and 310 ° C, in each temperature mode the mixture was incubated for 1 hour. The reaction proceeded under argon.

Analysis of the sample maintained at 150 °C

IR-spectra were recorded on a Fourier spectrometer NICOLET 6700 Thermo Electron Corporation in the wavenumber range of 600 – 4000 cm^{-1}, the acceptable error threshold of the wavenumber scale ± 0.5 cm^{-1}, under nitrogen. For the given range of 4000–600 cm^{-1} the samples were prepared by compression of tablets, the ratio of the investigated material: KBr – 1:300.

In the IR-spectrum of the investigated product in the wavenumber range of 600 – 4000 cm^{-1} there are bands characteristic of the bond N-H (NH_4^+) – 3266, 1427, for the bond of ammonium cation and fluoride-ion – 1101, bands for the bond Be-F are distinct – 793, 552 (Fig. 1). The fluorination product of the mixture BeO-NH_4HF_2 at 150 °C consists of a complex fluorine-containing compound of beryllium.

In order to establish a more specific structure of the fluorination product the sample was tested using the method of X-ray spectroscopy on X-ray diffractometer MiniFlex 600. The analysis

conditions: X-ray power – 40 kW, 15 mA; detector – SC-70; scanning rate – 2 deg./min; step width – 0.02 deg .; scanning range – from 15.0 to 80.0 degrees.

The fluorination product at 150 °C consists of ammonium tetrafluoroberyllate (Fig. 1).

Analysis of the sample maintained at 250 °C

In the IR-spectrum of the investigated product in the wavenumber range of 600 – 4000 cm^{-1} there are bands characteristic of the bond N-H (NH_4^+) – 3251, 1440, for the bond of ammonium cation and fluoride-ion – 1101, 478, bands for the bond Be-F are distinct – 792, 638, 552, 436 (Fig. 2). The product of thermal dissociation at 250 °C consists of a complex fluorine-containing compound of beryllium.

XRD data indicates that the product of thermal dissociation at 250 °C consists of NH_4BeF_3 and $(NH_4)_2BeF_4$ (Fig. 3). The intensity of trifluoroberyllate bands is much greater than of tetrafluoroberyllate, which indicates an incomplete decomposition of $(NH_4)_2BeF_4$.

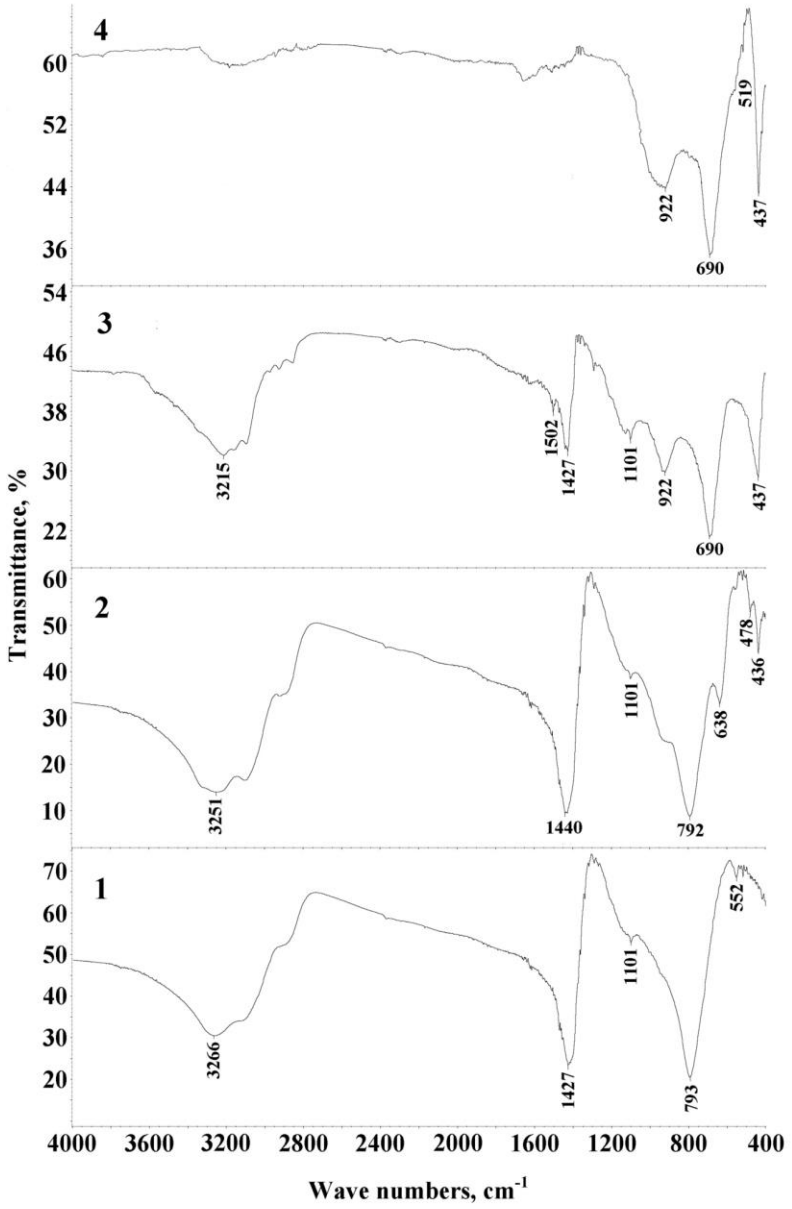

Figure 2. IR-spectra of samples: 1 – maintained at 150 °C; 2 – at 250 °C; 3 – at 280 °C; 4 – at 380 °C.

Analysis of the sample maintained at 280 °C

In the IR-spectrum of the investigated product in the wavenumber range of 600 – 4000 cm^{-1} there are bands characteristic of the bond N-H (NH_4^+) – 3215, 1427, for the bond of ammonium cation and fluoride-ion – 1502, 1101, 478, bands for the bond Be-F are distinct – 922, 690, 437 (Fig. 3). The product of thermal dissociation at 280 °C consists of a complex fluorine-containing compound of beryllium.

XRD data indicates that the product of thermal dissociation at 280 °C (in the region of the TGA curve, where the change in the inclination angle of the line takes place) consists of $NH_4Be_2F_5$ (Fig. 3). The reference on the formation of such a compound during the decomposition of $(NH_4)_2BeF_4$ is present in [11].

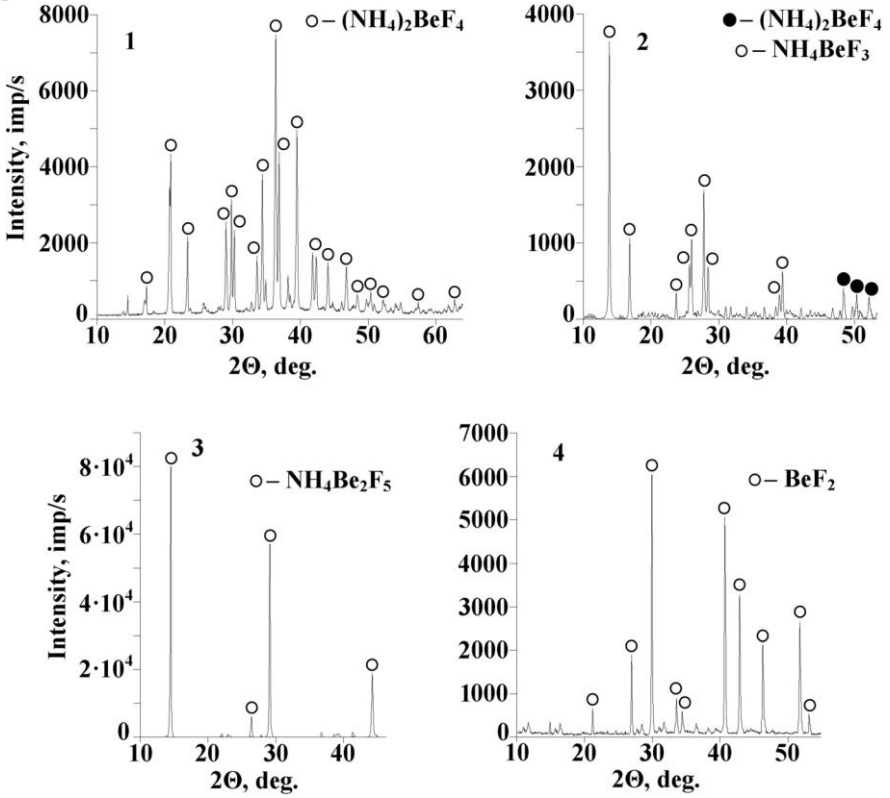

Figure 3. Diffraction patterns of samples: 1 – maintained at 150 °C; 2 – at 250 °C; 3 – at 280 °C; 4 – at 380 °C.

Analysis of the sample maintained at 310 °C

During the analysis of the sample maintained at 310 °C, using methods of IR-spectroscopy and XRD, strips of ammonium cation were found in the sample, indicating an incomplete decomposition of $NH_4Be_2F_5$. Experiments on decomposition of salt in the temperature range of 320-400 °C have been also carried out. Ammonium bands were detected up to 380 °C.

In the IR-spectrum of the given product in the wavenumber range of 600 – 4000 cm^{-1} there are peaks characteristic for the bond Be-F – 922, 690, 519, 437 (Fig. 4). The product of thermal dissociation at 375-380 °C consists of beryllium fluoride.

The produced beryllium fluoride at 380 °C, after exposure to atmospheric environment for 30 minutes, begins to cohere and becomes viscous. This fact indicates high hygroscopicity of the synthesized compound. When BeF_2 was dried in a muffle furnace at 110 °C for 3 hours, a grayish powder was obtained, the IR-spectrum of which does not match with the spectrum of the freshly produced compound. XRD indicated the presence of an oxide component in the dried powder. The

produced compound was beryllium oxyfluoride, whose properties are described in [6]. This structure of beryllium fluoride is not suitable for storage and transport, and, consequently, for production of metallic beryllium.

During thermal decomposition of $(NH_4)_2BeF_4$, beginning from 25 °C, a white mass of beryllium fluorocomplex melted at 220 °C and boiled at 310 °C, with allocation of gaseous products. Then the reaction mass solidified forming a transparent amorphous material at 350 °C. With further increase in the temperature up to 380 °C the amorphous mass melted again turning into a thick liquid grayish substance. Upon reaching 500 °C there was an intense boiling of the formed mass with its parallel recrystallization. This phenomenon was accompanied by an intense increase in the volume and splashing of the substance from the reaction zone. Above 560 °C recrystallization of the substance ended, a decrease in the volume of the reaction material took place. The formed mass acquired a crystalline shape and a grayish color at 600 °C.

XRD data indicates that the product of thermal dissociation at 600 °C consists of BeF_2 (Fig. 3). Beryllium fluoride produced at a temperature of ≥ 600 °C, after being exposed to atmospheric environment during one day, does not cohere and does not become viscous. The difference between diffraction patterns of the freshly produced beryllium fluoride and the sample maintained in atmospheric environment has not been revealed.

4 Conclusion

1. As a result of the study, the temperature mode and the thermal dissociation mechanism of ammonium tetrafluoroberyllate up to beryllium fluoride have been established (Table 2).

Table 2. Stages of thermal dissociation $(NH_4)_2BeF_4$

Temperature range, °C	Process
185-255 °C	$(NH_4)_2BeF_4 = NH_4BeF_3 + NH_4F$
255-280 °C	$2NH_4BeF_3 = NH_4Be_2F_5 + NH_4F$
280-380 °C	$NH_4Be_2F_5 = 2BeF_2 + NH_4F$
525-565 °C	Melting and recrystallization BeF_2

2. It is established that beryllium fluoride produced at 380 °C is a hygroscopic substance. Production of beryllium fluoride at a temperature over 600 °C allows forming a less hygroscopic type of substances suitable for storage.

3. The process of thermal dissociation of $(NH_4)_2BeF_4$ is accompanied by liberation of fluorinated gases (NH_4F) and splashing of beryllium-containing compounds. To reduce losses of the target component and toxic contamination of the laboratory it is recommended to use a stage mode of thermal dissociation of $(NH_4)_2BeF_4$.

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