

Study on the process of Fe (III) oxide fluorination

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Abstract. The article deals with a fundamentally new fluoride technology for obtaining fluoride materials, provides data on the kinetics of the process of fluorination of Fe oxide with fluorine, fluoride and ammonium bifluoride. The physical and chemical properties of obtained fluorides are shown: a study of the elemental composition, grain-size composition using the method of scanning electron microscopy and laser diffraction.

1. Introduction

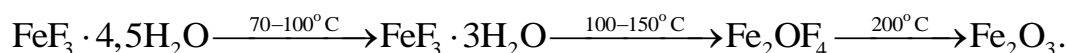
The fluoride technology of obtaining alloys for permanent NdFeB magnets is based on the process of ladle calciothermal reduction of the mixtures of non-aqueous REM fluorides and Fe. The description of fluoride technology and its advantages are given in papers [1-3].

The methods of obtaining inorganic fluorides, including Fe (FeF₂ и FeF₃), could be divided into two fundamentally different groups - hydrometallurgical and thermal.

Hydrometallurgical methods are based on deposition of metal fluorides from saline solutions or hydroxide sludges using a fluorinating agent, with their subsequent drying and calcination.

Unfortunately, Fe fluorides are unstable in water vapor atmosphere. So, FeF₂ and FeF₃, in the presence of water vapor, at 520 K, go into Fe₃O₄ and Fe₂O₃, respectively. Thus, the formation of Fe fluoride crystallohydrates with the number of water molecules from 1 to 6 is possible, and, at deposition of metal fluorides from saline solutions with fluorhydric acid, the formation of Fe fluoride crystallohydrates with a number of hydrogen fluoride molecules, e.g. FeF₃·3HF·3H₂O is possible. It is impossible to obtain non-aqueous fluorides from crystallohydrates by thermal treatment.

During heating of Fe (III) fluoride crystallohydrate the following processes could be observed:



Therefore, non-aqueous fluorides, which are suitable for metallothermic reduction, could not be obtained by aqueous methods.

Thermal methods. For obtaining non-aqueous trifluorides the methods of Fe oxides fluorination are preferable. As fluorinating agents gaseous F₂ and HF or NH₄F and NH₄HF₂ melts could be used.

The results of the studies of the process of Fe oxides fluorination with gaseous elemental fluorine and in the melt of ammonium fluoride are shown in the paper.



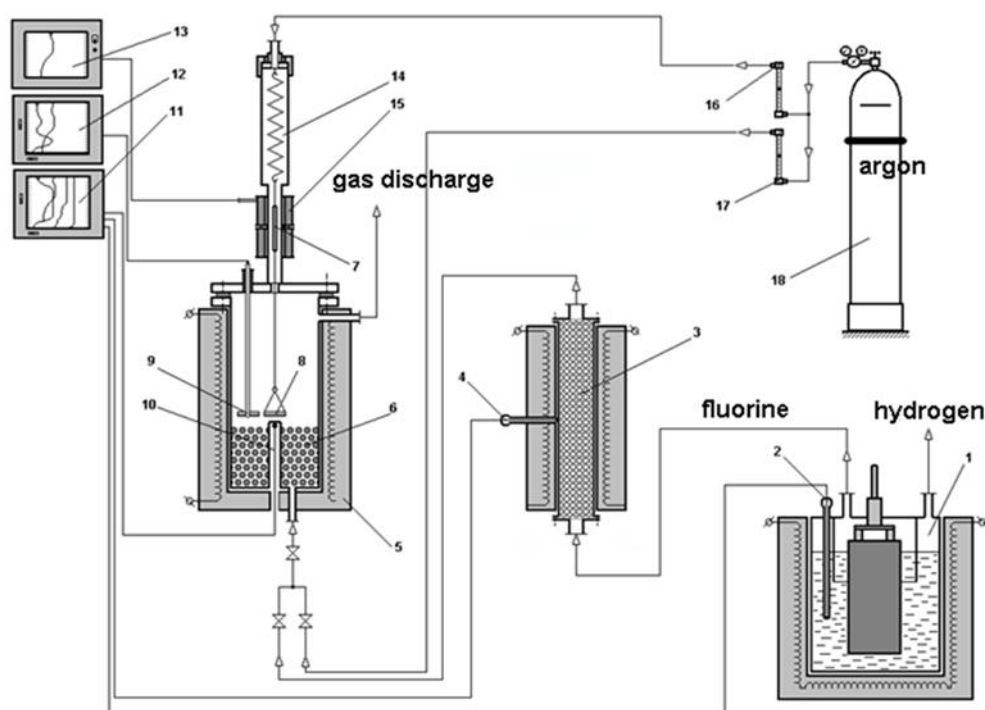
2. Kinetics of fluorination process

2.1 The fluorination with elemental fluorine

Study of the kinetics of the process of Fe oxide fluorination was conducted using thermogravimetric installation with nickel retort, shown in Figure 1. The installation can operate in isothermal conditions, both in pure fluorine atmosphere and in the atmosphere of a gas mixture of fluorine-argon or nitrogen at the temperatures up to 600 ° C and permanent recording of the sample mass and temperature.

Fe (III) oxides of Ch.p brand (Ch.p. – chemical purity) were chosen as the objects of the studies. The research was carried out at the temperatures from 420 ° C to 550 ° C and in the following constant conditions: initial sample weight is 150 mg; gas flow (composition: F₂- 96-97%, HF – in res.) is 2 l / h; argon flow is 4 l/h; particles size is less than 100 microns.

The results of kinetic studies and experimental data processing for the Fe oxide fluorination process are shown in Figures 2 and 3.



1 - electrolyser; 2, 4, 10 - thermocouples for recording the temperature of the electrolyte in electrolyser, the sorbent agent in a column and the gas in the reactor, respectively; 3 – the column with the sorbent agent (NaF); 5 - fluorination reactor; 6 - nickel filler; 7 - nickel core; 8 - a cup with the product; 9 - thermocouple with a cup; 11 - multi-channel recording device of temperature mode of adsorption column and electrolyser; 12 - recording device of the product temperature; 13 - recording device of the product mass changing; 14 - weighing spring; 15 - measuring inductors; 16, 17 - flow rotameters; 18 – a tank with an inert gas

Figure 1. Experimental installation for thermogravimetric studies of fluorination processes

In Fe₂O₃ fluorination degree dependence on the process duration at various temperatures, shown in Figure 1, we could see that the degree of fluorination increases with increasing the temperature.

Thus, if the temperature increases from 420 ° C to 550 ° C, the degree of fluorination at the time of fluorination of 2400 sec. increases from 14% to 93%.

When the results of kinetic studies of Fe₂O₃ fluorination were processed, several mathematical models were used to describe the chemical: for the kinetic region the equation of districting sphere and

surface was used, for diffusion region Todes and Yander equations were used, for description of the processes in the initial period of the reaction Kazeev-Erofeev-Kolmogorov equation was used [4].

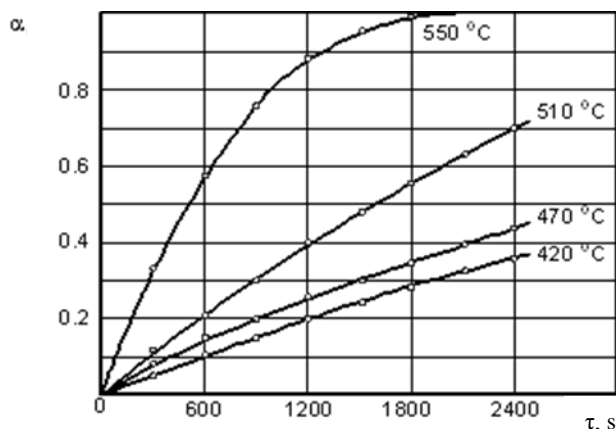


Figure 2. Fe₂O₃ fluorination degree dependence on the duration of the process at different temperatures

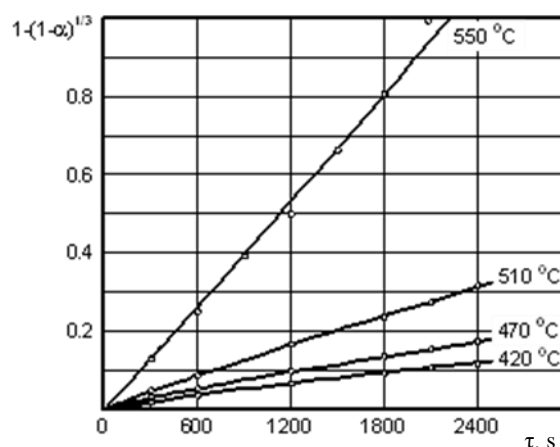


Figure 3. The results of experimental data processing using the districting surface equation

It should be noted that, at high temperatures (over 500 ° C), there is some melting and sintering of solid fluoride films based on the Fe₂O₃ powder particles, which decreases the fluorine access to the surface and reduces the degree of resulting product fluorination.

The results of experimental data mathematical processing concerning Fe oxide fluoridation using the different models have shown that the districting surface equation gives the smallest error in the linear approximation. The reaction order, determined using this model, is close to 1, and the apparent activation energy is $E_a = (43,0 \pm 3,0)$ kJ/mol.

To describe the kinetics of Fe oxide fluorination in the range of 420-550 ° C the following equation could be used:

$$1 - (1 - \alpha)^{\frac{1}{3}} = (0,087 \pm 0,007) \cdot \tau^{\frac{(43000 \pm 3000)}{R \cdot T}}$$

2.2 Fluorination with ammonium fluoride

Fe fluoride was obtained using the reaction of Fe oxide and ammonium fluoride interaction according to the scheme:



For this purpose, Fe oxide sample was mixed with NH₄F in a molar ratio of 1: (8-9) and placed into the reactor preheated to 300 ° C. The sample was being kept there for 1.5 hours, then the system was vacuum-processed to a residual pressure of $1 \cdot 10^{-3}$ mm. of mercury and accommodated.

The products research was carried out using the installation of combined heat and differential calorimetric analysis SDT Q-600, produced by Intertech instruments company (hereinafter, thermal analyzer). Derivatographic analysis allowed us to determine the areas of chemical and phase transformations, while diffraction method (XRD) analysis - structural constitution.

Results of the study of the process of Fe oxide fluorination are shown in Figure 4.

X-ray diffraction analysis shows the absence of the fluorination reaction at the temperature of up to 120 ° C, but at the temperature of 175 ° C ammonium complex composition NH₄FeF₄ appears.

Heating the mixture of reactants up to 206 ° C leads to the formation of the complex with (NH₄)₃FeF₆ composition. This complex is thermally unstable and with further temperature increase decomposes into two compounds: NH₄FeF₄ and FeF₃. At the temperature of 365 ° C, the product of fluorination in 99% consists of NH₄FeF₄ complex. With further temperature increase up to 450-600 ° C tetra-ammonium fluoride complex is destroyed in the air with forming Fe oxide.

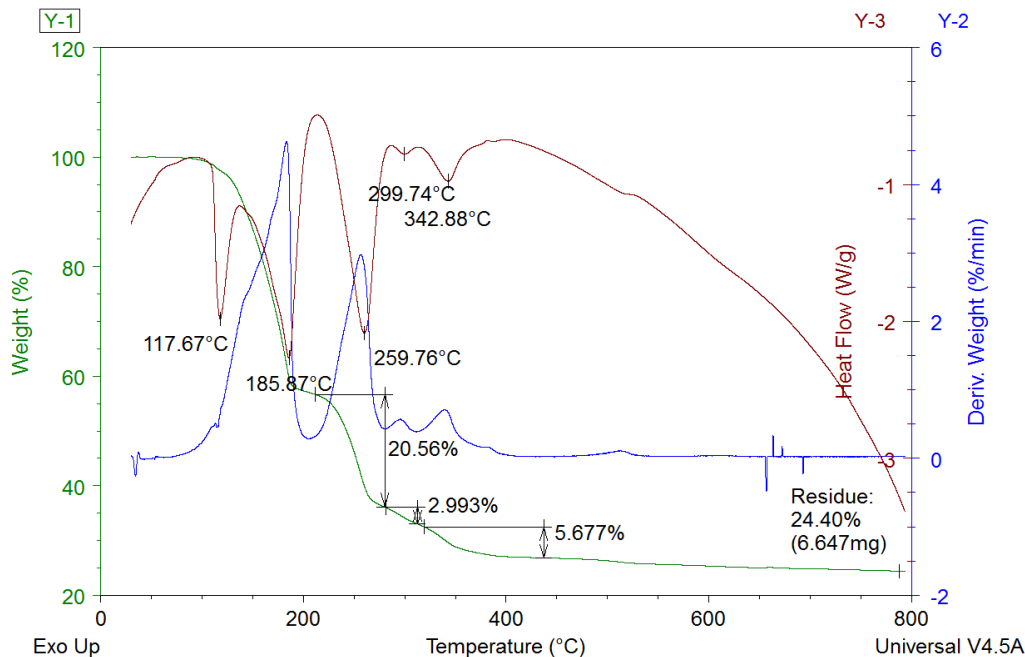
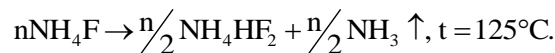


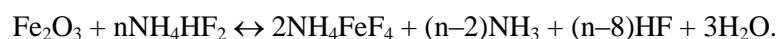
Figure 4. Thermogram of Fe oxide fluorination with 100% of ammonium fluoride excess (heat flux)

Fe oxide fluorination with ammonium difluoride is similar to the reaction with ammonium fluoride, as fluoride decomposes at the temperature over 120 °C, becoming a bifluoride. The study finds out that the reactions of non-aqueous Fe fluoride formation is a complex mechanism with forming intermediates.

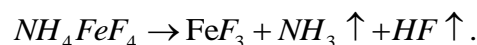
At the first stage, the formation of ammonium bifluoride occurs:



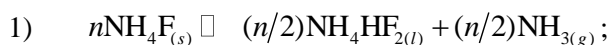
At a subsequent stage, interaction of formed molten NH_4HF_2 with Fe oxide occurs according to the scheme:



At further heating, the formed compounds complex decomposes with forming non-aqueous Fe fluoride according to the scheme:



Identification of endothermic processes, recorded according to DSC data, is confirmed with the results of differential scanning calorimetry simultaneous analysis - mass spectrometry - x-ray diffraction analysis (DSC - MS - XRD). The interconnection of the temperature and the activation energy of the process of Fe oxide fluorination is determined by the process of ammonium fluoride melting and the formation of a heterophase liquid - solid system, that provides a significant change in the diffusion coefficients and, thus, - reaction acceleration, which correlates properly with the mechanism of ammonium fluoride interaction, proposed in K. Rajeshwar work [5]:



and decomposition of obtained complexes according to the scheme:

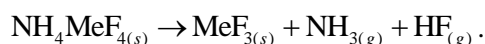


Table 1. The results of differential scanning calorimetry of $\text{NH}_4\text{F}-\text{Fe}_2\text{O}_3$ system

Stage №	Temperatures region, °C	E_a , $\frac{\text{kJ}}{\text{mol}}$	T_{max} , °C	Process characteristics
I	30–75	38.5	44.8	HF desorbtion
II	30–140	163.2	81.7	H_2O desorbtion
III	115–145	510.0	135.0	NH_4F melting
IV	150–210	150.7	183.0	Complex formation
V	205–230	269.0	214.2	Complex decomposition
VII	305–338	273.0	338.8	Removal of the evolved NH_4F

XRD pattern of NH_4FeF_4 complex is shown in Figure 5 (a), where I is relative intensity, and 2θ is determined in angular degree. Subsequent thermal decomposition of this product leads to the formation of non-aqueous Fe fluoride. XRD pattern of obtained non-aqueous Fe fluoride is shown in Figure 5 (b).

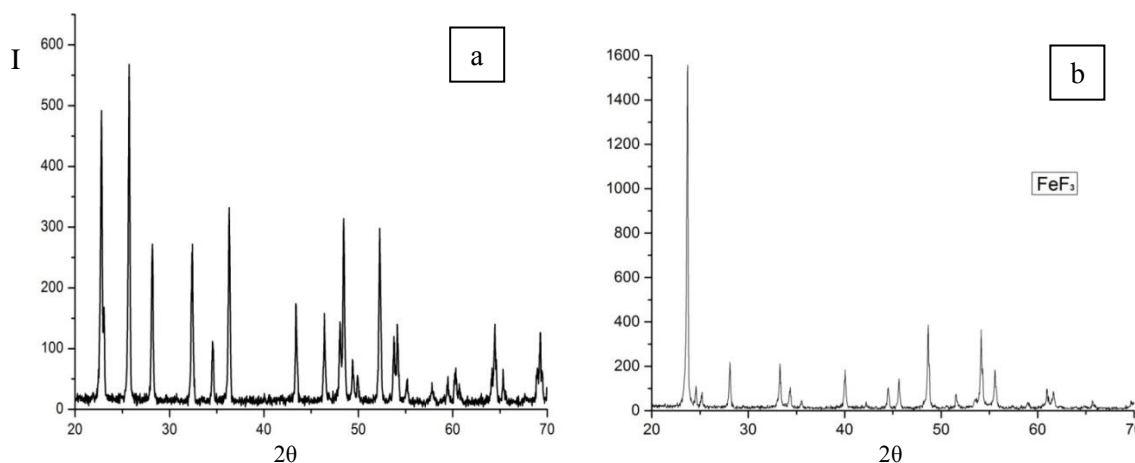


Figure 5. NH_4FeF_4 XRD pattern (a) and FeF_3 XRD pattern (b)

2.3 The study of fluorides physical and chemical properties

To determine fluorides physical and chemical properties modern analytical equipment and instrumental methods of analysis: X-ray fluorescence method of scanning electron microscopy and laser diffraction method were used.

To measure the moisture content (mass fraction of moisture) of Fe trifluoride weight hydrometer MH-50 was used. The moisture of the sample was 0.76 % (wt).

A study of the elemental composition of Fe fluoride. To determine the elemental composition of the Fe fluoride X-ray fluorescence method was used. The study was conducted using X-ray spectrometer (XRF-1800 model), produced by SHIMADZU company. Averaged results of three simultaneous determinations of the elemental composition of Fe fluoride samples: the content of Fe – 50.56%; F - 46.91% wt.; degree of Fe oxide fluorination with fluorine content - 93%. The magnitude of the mass fraction error for determined elements is (± 5)%.

The studies of Fe fluoride grain-size composition. The research was carried out using a scanning electron microscope (Quanta 200 3D SEM, produced by FEI company) and laser diffraction method (analyzer SALD-7101 (Shimadzu, Japan)).

Micrograph of Fe fluoride samples are shown in Figure 6 (a), and a bar graph of particle size distribution - in Figure 6 (b).

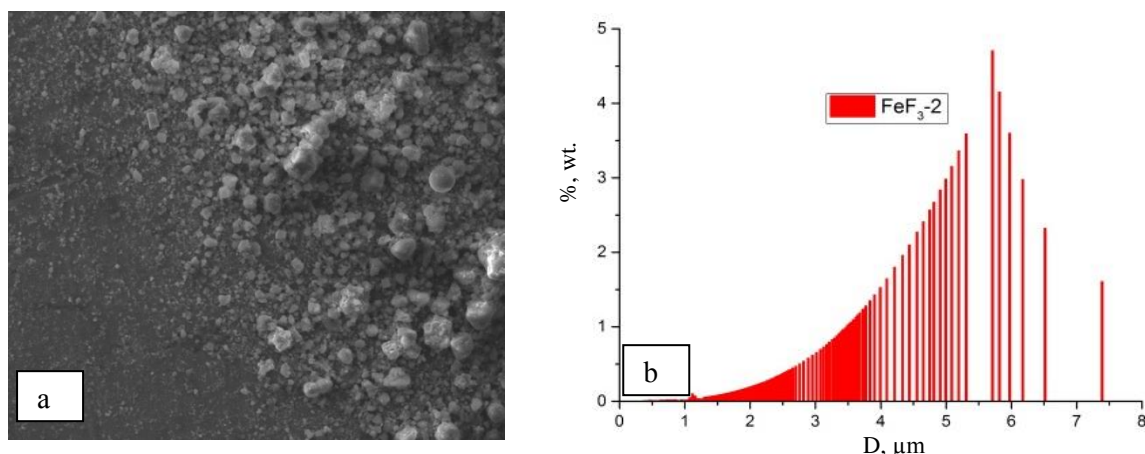


Figure 6. The micrograph (a) of Fe fluoride samples and the particles distribution based on Fe fluoride sample sizes (b)

Particles average diameter was 5.3 microns.

The XRD pattern of obtained non-aqueous Fe is identical to the XRD pattern presented in Figure 5b, which shows that the product is composed of FeF_3 in almost 100% .

Conclusion

1 The kinetics of Fe (III) oxide powder fluorination with elemental fluorine and ammonium fluoride is studied. The activation energies of the processes and reaction order of gaseous fluorine are determined.

2 The physical and chemical properties (moisture content, elemental composition, grain size and phase compositions) of Fe fluoride samples, that were obtained with the method of metal oxides interaction with fluoride and ammonium fluoride.

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