Investigation into Rhenium Fluorination Process

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Abstract. The process of rhenium and fluorine interaction in the interval of temperatures from 200 ºC up to 600 ºC has been investigated. Influence of fluorine charge, fluorination square and temperatures on the process efficiency and fluorine use efficiency have been determined. Presence of two areas of process behavior, namely kinetic and diffusion has been demonstrated. It was shown that in the course of fluorination a mixture of hexafluorides and heptafluorides was formed. Dependence of rhenium fluorides composition on temperature has been determined

1. Introduction
A promising method of obtaining tungsten-rhenium alloys is vapor deposition, namely joint hydrogen reduction of metal hexafluorides [1,2].

Tungsten hexafluoride is currently produced on an industrial scale. The main technological production method is direct interaction of elemental fluorine with tungsten powder [3]. Information about the fluorination process of rhenium powder is contradictory. The first studies of the interaction of rhenium with elemental fluorine were published in [4]. The authors determined the initial reaction temperature (125 ºC) at which there was formation of a gaseous product and condensates of deep purple and green colors. They concluded that it was rhenium hexafluoride on the basis of chemical analysis of the obtained product. By optimizing the installation of fluorination, the authors of [5, 6] obtained a more pure rhenium hexafluoride due to pre-treatment of fluorine and improvement of technological methods. The obtained compound in the liquid and solid phases had pale yellow color. The melting temperature of ReF$_6$ (18.8 ºC) and dependence of its density on temperature were determined. The authors did not find rhenium heptafluoride in the obtained product.

The authors of [7], exploring the interaction process of rhenium with fluorine, determined that a mixture hexa- and heptafluorides were formed at temperature of 400 ºC. The studies on the effect of fluorination temperature of rhenium on the composition of formed fluorides are given in [8]. It was shown that with increasing temperature the mixture is enriched with rhenium heptafluoride. Attempt of quantitation of rhenium hexa- and heptafluorides and fractional separation of the mixture were unsuccessful.

This work was carried out to study the fluorination process of rhenium metal powder.

2. Plant, Source Materials and Experimental Technique
A technological process of rhenium fluorides synthesis includes: fluorine making, a rhenium powder fluorination, and condensation of the made fluorides (figure 1).
Fluorine was produced by electrolysis of potassium bifluoride melt. Fluorine was purified from fluoric hydrogen by its passing through the grained fluoric sodium heated up to 100 °C. Rhenium fluorination was performed in a horizontal cylindrical reactor made of nickel with 100 mm in diameter and 1,000 mm in length (figure 2).

Fluorine charge was specified by current loading on an electrolyzer and changed from 50 up to 200 g/hour (figure 3).
The process temperature was controlled by changing the power of the radiator placed outside the fluorination reactor and measured by a chromel-alumel thermocouple placed into a nickel cover. One to four boats having a reaction surface square of ~ 1 dm$^2$ each were loaded into the fluorination reactor. Formed reaction products were trapped in a tank made of stainless steel cooled by liquid nitrogen. Upon the process completion condensed fluorine was distilled out of the tank, and analysis sample was selected for determination rhenium and fluorine content in it. Powdery metallic rhenium of P-1 TU 48-4-195-87 brand was used as a feed stock. For purifying from oxides and moisture the rhenium powder was exposed to heat treatment in hydrogen at a temperature of 1000 °C for 2 hours.

3. Influence of fluorine charge on fluorination rate and its efficiency

Figure 4 shows dependence of fluorination rate and also output by fluorine on its charge at the process temperatures from 200 to 600 °C and fluorination square of 1 dm$^2$.

![Figure 3. Dependence of fluorine charge on current loading on electrolyzer](image)

![Figure 4. Dependence of fluorination rate output by fluorine on its charge](image)
In the field of low charges of fluorine a fluorination rate varies in proportion to the quantity of fluorine carried. In this case the output by fluorine is 50 % at 200 °C, and 90 % at 600 °C. At increase in the charge of fluorine (more than 75 g/hour) a fluorination rate is slowing down, and this effect occurs in a greater degree at a temperature of 200 °C. At large fluorine charges a fluorination rate is almost constant, and output by fluorine sharply decreases from 90 % to 40 % at 600 °C, and from 45 % to 18 % at 200 °C. The specified decrease in the output by fluorine is connected with a high linear speed and short time of its contact with a rhenium powder.

Analysis of the dependences given in figure 4 shows that at increasing in the fluorination process efficiency by 10 g/hour dm$^2$ the output by fluorine decreases by 10 % at the average for all range of temperatures investigated.

From the above-stated follows that an optimal mode of the process for the fluorination square of 1 dm$^2$ is a temperature of 300 – 400 °C and fluorine charge is equal 100-120 g/hour, at which the efficiency of 95 g/hour is reached at the output by fluorine of 50-55 %. Increase in temperature up to 600 °C leads to insignificant increase in the process efficiency and output by fluorine, but in this case the fluorination reactor material stability decreases with respect to fluorine.

4. Influence of reaction surface square on process rate and its efficiency

One of the ways to raise the fluorination process efficiency is expansion in a reaction surface. Figure 5 shows dependences of fluorination rates and output by fluorine on the reaction surface at temperatures of 200, 300, 400, 500 and 600 °C and constant charge of fluorine equal to 200 g/hour.

It can be seen from the given data that expansion in the reaction surface from 1 to 4 dm$^2$ leads to decrease in a specific rate of fluorination; however the process efficiency rises from 60 to 130 g/hour for 200 °C and from 80 to 200 g/hour for 600 °C. And for a temperature of 200 °C the most appreciable raise in the process efficiency is observed at expansion of the square of fluorination from 1 to 3 dm$^2$. For temperatures of 300, 400, 500 and 600 °C expansion of the fluorination square leads to uniform raise of fluorination rate.

From the above-stated follows that different character of the process is observed at a fluorination temperature of 200 °C at changing the square of fluorination. At transition from one area of a reaction to another one a fluorination rate sharply changes. This conclusion is also confirmed by dependence of a fluorination rate on the temperature in Arrhenius coordinates.

![Figure 5. Dependence of fluorination rate and output by fluorine on reaction surface size](image-url)
Analysis of the dependences given in figure 4 shows that optimal conditions for the process are the following: a temperature of 350–400 °C, the square of fluorination of 4 dm2. At these parameters the fluorination rate of 160–170 g/hour is reached at the output by fluorine equal to 45–55 %. At a temperature of 600 °C and fluorination square of 4 dm2 the process efficiency and output by fluorine increase slightly in comparison with normal conditions, 200 g/hour and 62 % respectively.

Based on experimental dependences of fluorine charge and reaction surface square influence on a fluorination rate which are given in figures 4 and 5, a dependence of a fluorination rate and output by fluorine on the process temperature was made at constant fluorine charge of 200 g/hour (figure 6).

From the results given in figure 6 it can be seen that influence of process temperature on the fluorination rate at various reaction surfaces is not the same. So, at the rhenium powder square of 1 dm2 up to a temperature of 300–350 °C a proportional increase in the fluorination rate can be observed, and above 350 °C – insignificant increase. These dependences are less typical at a reaction surface of 2 and 3 dm2, and they are practically absent at a reaction surface of 4 dm2. Processing of the integrated data on a rhenium fluorination rate in Arrhenius coordinates given in figure 7 demonstrates a different character of the process.

Transition from one area of the process to another is observed at the temperature change, and at expansion of the reaction surface a transition point on the curves moves to the area of lower temperatures in which a dependence of the fluorination rate on temperature becomes more apparent, and a limiting factor of the process is chemical interaction of rhenium powder with fluorine. The activation energy in this area is $E = 25$ kcal/mole.

In the area of higher process temperatures (300 °C) the fluorination rate slowdown can be observed that is typical for transition from a kinetic to diffusion area. The temperatures of the process transition from a kinetic area to diffusion one at different fluorination squares and fluorine charge of 200 g/hour, which were determined in accordance with the data in figure 7, are given below.

![Figure 6. Dependence of fluorination rate and output by fluorine on process temperature](image-url)
5. Determination of rhenium fluorides chemical composition

Rhenium fluorides were analyzed for rhenium and fluorine content in them under a procedure of specifications TU 2134-035-076.22928-2003; according to them rhenium was determined by a gravimetric method, and fluorine – by an ionometry method.

The gained analysis results showed that rhenium fluoride in all samples consisted of a mixture of hexafluorides and heptafluorides (figure 9). Increase in the fluorination temperature leads to more rhenium content in the mixture of heptafluorides.
6. Conclusion

The process of rhenium and fluorine interaction in the interval of temperatures from 200 ºC up to 600 ºC has been investigated. Influence of fluorine charge, fluorination square and temperatures on the process efficiency and fluorine use efficiency have been determined. The maximal process efficiency was 210g/hour at a temperature of 600 ºC and fluorine charge of 200 g/hour; in this case the fluorine use efficiency was 60%. Apparent activation energy of the process was 25kcal/mole.

Presence of two areas of the process going and areas of their existence has been demonstrated. Dependence of rhenium fluorides composition on temperature has been determined. It was shown that in the course of fluorination a mixture of hexafluorides and heptafluorides was formed. Rise of the process temperature leads to increase in rhenium heptafluoride content in the mixture and on the contrary temperature decrease leads to increase in hexafluoride content.

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