Production and investigation into properties of high-pure rhenium fluorides

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Abstract. Two products of synthesis were obtained: synthesis product at a fluorination temperature of 300ºC, synthesis product at a fluorination temperature of 600ºC. Two source products were separated and rectified during this work. Monofraction of rhenium hexafluorides and heptafluorides were obtained. The temperatures of liquids in the system ReF_6 - ReF_7 were determined. Liquid-vapor equilibrium in the system was investigated. Viscosity and surface-tension at the liquid-to-vapor boundary are measured for liquid ReF_6 and ReF_7.A promising method of tungsten-rhenium alloys making is a gas-phase precipitation, namely joint hydrogen reduction of these metals fluorides.

1. Introduction

Higher volatile rhenium fluorides are of great interest for the production of high- purity precipitates of metallic rhenium and its alloys with tungsten by hydrogen reduction of their fluorides [1]. However, in the technical literature data on the synthesis and physico-chemical properties of rhenium hexa - and heptafluorides practically are not available or are contradictory.

The main technological production method is a direct interaction of elemental fluorine with rhenium powder [2,3]. Studies on the effect of fluorination temperature on the composition of the formed fluorides showed that at low temperatures the mixture enriched with rhenium hexafluoride and at high temperatures vice versa. The attempt to separate a mixture of fluorides by fractional distillation ended unsuccessfully. The studies on the chemical separation of fluorides mixture showed that at the interaction of mixture with fluorine at temperature of 400 ºC rhenium heptafluoride is formed, and rhenium hexafluoride is formed at interaction with metallic rhenium.

Quantitative determination of rhenium hexa- and heptafluorides in their mixture was unsuccessful. Chemical analysis method is not allowed to solve this problem due to the insufficient accuracy of concentration measurement of fluorine and rhenium. The study of the spectrum of infrared radiation of fluorides was inconclusive due to the proximity of their energy levels.

The purpose of this work is obtaining and investigation of the properties of higher rhenium fluorides.

2. Phase equilibrium in ReF6-ReF7 system

Liquidus temperatures in the system were measured by a visually- polythermal method [4]. The obtained data are given graphically in figure 1. Rhenium hexafluoride and heptafluoride formed a

diagram of a eutectic type with a degenerated eutectic from ReF6 side. Polymorphic transformation of ReF7 was revealed in the system at a temperature of ~ 24.5ºC.

Solution heat ofReF7 in ReF6 calculated from a tangent of a liquidus line slope in coordinates of lgN - 1/T (where N – a mole fraction of ReF7) is 13.2 kcal/mole. Melting temperature of pure ReF6 and ReF7 is respectively 18.5ºC for ReF6 and 48.3ºC for ReF7.

Liquid-vapor equilibrium in the system was investigated by an ebulliometric method by boiling points within a range of the pressures exceeding normal (from 760 to 1.085 mm Hg). The temperature was measured by thermometers with a division value of 0.1ºC. The measurements data are given in figures 1 and 2. It follows from the experiment data that ReF6-ReF7 system is practically ideal.

In the assumption that the system is ideal the components relative volatility is 3.5 at a normal pressure from the side of pure ReF6, and 4.2 from the side of pure ReF7. It specifies that separation ReF6 and ReF7 by a rectification method does not cause difficulties. The obtained data on boiling temperatures of pure fluorides were 33.4ºC for ReF6, and 72.2ºC for ReF7.

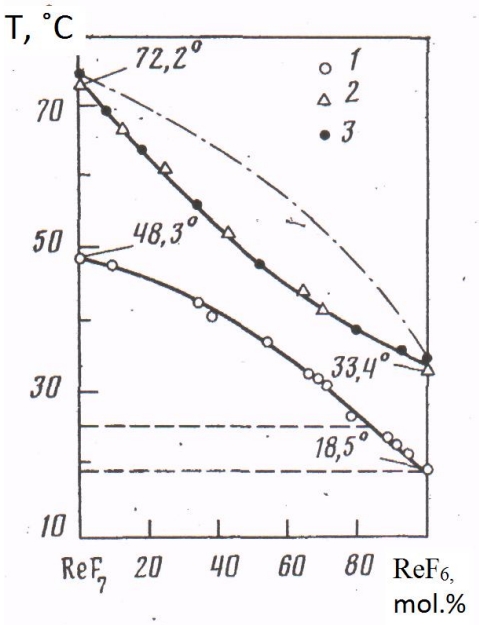

Figure 1. Crystal -liquid and liquid-vapor equilibria (at 760mmHg) in ReF_6-ReF_7 system: 1 - Liquidus temperatures under experimental data; 2 – Boiling temperatures of pure ReF_6 and ReF_7 and their mixture under experimental data; 3 – Data on the liquid line calculation in the assumption that the system is ideal; a dash-dotted line is a result of the vapor line calculation in the assumption that the system is ideal.

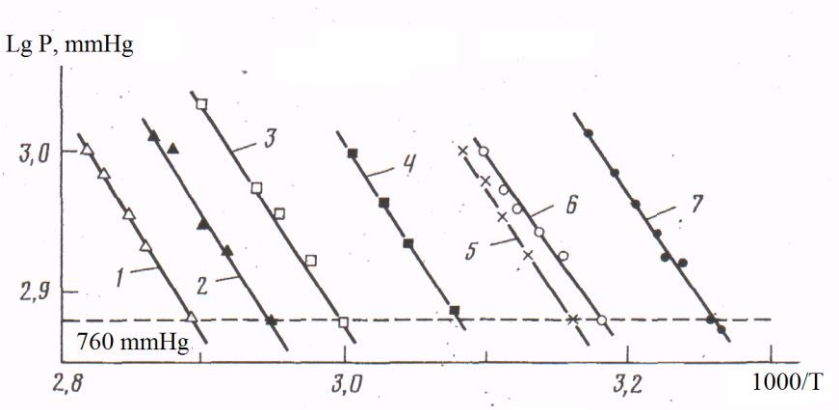

Figure 2. Dependence of ReF_6 and ReF_7 and their mixes saturated vapors pressure on temperature: 1 – pure ReF_7; 2 – 11.9 mol.% ReF_6; 3 – 24.5 mol.% ReF_6; 4 -43.0 mol.% ReF_6; 5- 64.3 mol.% ReF_6; 6 -69.2 mol.% ReF_6; 7 – pure ReF_6.

3. Synthesis of rhenium fluorides

Rhenium hexafluoride (ReF6) and rhenium heptafluoride (ReF7) used for researches were synthesized by fluorination of a rhenium powder of brand Re-0. The impurity composition of a source powder is given in Table 1.

For removing oxides and moisture, a rhenium powder was subjected to thermal treatment in a hydrogen flux at a temperature of 900-1000ºC for two hours. Rhenium fluorination was performed in a horizontal cylindrical reactor made of nickel with a diameter of 100 mm and length of 1m. Two products of synthesis were obtained: synthesis product at a fluorination temperature of 300ºC, synthesis product at a fluorination temperature of 600ºC.

When the end product should be ReF6 and fluorination were too deeply with formation of significant amounts of ReF7 in the mixture, the situation can be corrected by adding metal rhenium to the mixture with conversion of superfluous ReF7 into ReF6. In paper [4] it was pointed to ease of ReF7 interaction with metal rhenium already at the temperatures close to its melting temperature (~50ºC). We have specified a kinetic characteristic of the process.

4. Separation and purification of rhenium hexa - and heptafluorides by rectification

Investigation into liquid-vapor equilibrium in the ReF6-ReF7 system shows that their mutual separation and purification by a rectification method can be performed very effectively.

Two source products were rectified during this work. The rectification was carried out at atmospheric pressure with the use of a plate- and- sieve columns made of quartz glass with a diameter of 30 mm.

During the first experiment a synthesis product at a fluorination temperature of 300ºC was rectified with the use of a column with 15 real plates. Selection of fractions lasted for 8.5 hours. The product mainly consisted of ReF6. Five fractions of purified ReF6 (1-5 fractions) were obtained. The fractions were selected with reflux ratios (R): fractions 1-5 at R from 70 to 60; fractions 6-8 at R from 150 to 200; fraction 9 at R = ~ 20; and fraction 10 at R close to 1.

During the second experiment a synthesis product at a fluorination temperature of 600ºC was rectified with the use of a column with 25 real plates. Selection of fractions lasted for 7 hours. The product mainly consisted of ReF7. Four fractions of purified ReF7 (4-7 fractions) were obtained. The fractions were selected with reflux ratios (R): fraction 1 at R =200; fractions 2-3 at R from 90 to 70; the other fractions at R from 15 to 10.

The temperature of distillation curves are graphically shown in figure 3.

The results of analysis on the impurities content in the source sample and purified fraction are given in Table 1.The analysis was made by chemical- spectral method after the samples dissolution in the deionized water.

Gas chromatography analysis of rhenium fluorides purified by rectification showed that they did not contain any volatile impurities at a sensitivity of 10^{-3} volume percents.

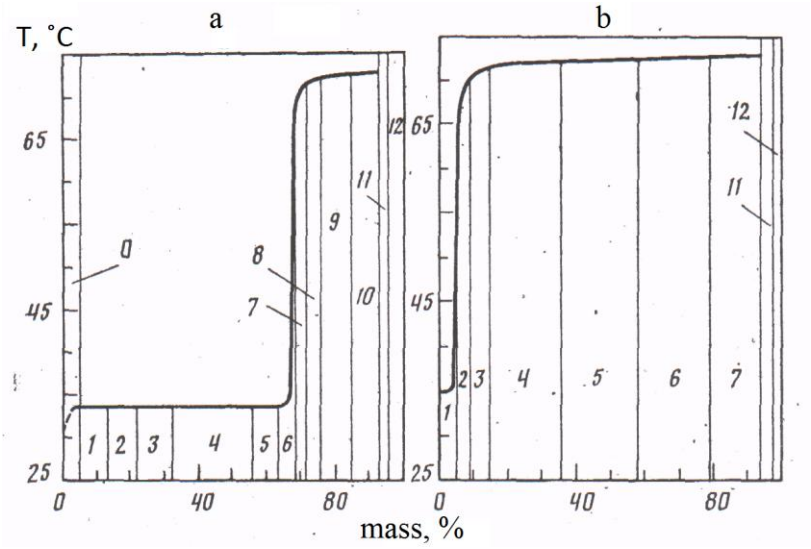

Figure 3. Temperature curve of rhenium hexa - and heptafluorides distillation: a mass percent of fractions from the initial loading is given on the X-axis, and fractions selection temperature is given on the Y-axis. The head fraction is presented by a zone zero; vat residue is presented by zone 11, and losses – by zone 12; *a*- Rectification of a synthesis product at a fluorination temperature of 300ºC; *b*- Rectification of a synthesis product at a fluorination temperature of 600ºC.

Table 1. Impurity composition of rhenium powder, source fluorides mixture and rhenium hexafluoride purified by rectification (10^{-4} mass %).

Impurity	Re powder of brand Re-O	Source fluorides mixture ReF_6+ReF_7	Purified fraction ReF_6
Al	5	0.6	0.05
Fe	7	0.1	0.05
K	10	<0.01	<0.01
Ca	10	2	0.2
Cu	3	2	0.1
Na	3	0.5	<0.05
Ni	2	<0.04	<0.01
Si	30	0.2	0.01
Mo	3	1	<0.2

5. Density, viscosity and surface tension of liquid rhenium hexafluoride and heptafluoride

In this work, density, viscosity and surface tension at the liquid-to-vapor boundary were measured in temperature range from fluorides melting point to the temperatures exceeding their normal boiling point for 20-40ºC.

All physical and chemical studies were carried out inside evacuated and sealed off devices made of quartz glass. Each property was measured with three different devices. Density was measured with pyknometers-dilatometers according to techniques described in papers [6-8]. Viscosity was measured with capillary efflux viscometer [6, 9]. Design of the viscometers used was presented in [10]. Surface tension was measured using liquid capillary ascension technique, similar to paper [11].

Table 2. The experimental data on density, viscosity and surface tension were processed using least square method and formulated using respective interpolation equations

Compound	Equation	Range of measurement, ºC	Standard deviation of measurement
ReF_6	ρ_l=3.717-0.00587*t, g/cm^3 Lgη_l=-0.945+261.4/t, cP Б=25.0-0.136*t, dyne/cm	18-76 20-76 20-76	$\Delta\rho_{st}$=0.0025 $\Delta\eta_{st}$=0.04 ΔБ$_{st}$=0.1
ReF_7	ρ_l=3,909-0,00488*t, g/cm^3 Lgη_l=-1.359+446.7/t, cP Б=28.8-0.086*t, dyne/cm	50-96 51-96 52-96	$\Delta\rho_{st}$=0.002 $\Delta\eta_{st}$=0.005 ΔБ$_{st}$=0.3

Regarding the density of liquid, our data correlate well with the data [12] presented for one temperature $\rho_l(ReF_6)$=3.58(22ºC) g/cm^3 and $\rho_l(ReF_7)$=3.65(52ºC) g/cm^3.

Processing of experimental data on liquid ReF_6 and ReF_7 viscosity in 1/ρ-1/η coordinates showed that liquid ReF_6 and ReF_7 are non-associated liquids.

6. Process operations in production of ReF_6 monofraction

The studies performed made it possible to develop the following sequence of process operations to produce ultra-pure rhenium hexafluoride monofraction:

1. Production of rhenium powder by hydrogen reduction of ammonium perrhenate at temperature (800÷850)°C:
$$2NH_4ReO_4 + 7H_2 \rightarrow 2Re + 2NH_3 + 8H_2O$$
2. Two-hour purification of rhenium powder from oxides and moisture in hydrogen flow at temperature (900÷1000) °C;
3. Fluoridation of rhenium powder:
$$2Re + 7F_2 \rightarrow 2ReF_7$$
$$Re + 3F_2 \rightarrow ReF_6$$
4. Transformation of ReF_7 into ReF_6:
$$6ReF_7 + Re \rightarrow 7ReF_6$$
5. Purification of ReF_6 from attending impurities by rectification

7. Conclusions

1. Higher rhenium fluorides were synthesized.
2. Separation and purification of rhenium hexafluoride and heptafluoride were performed
3. Phase equilibria in rhenium hexafluoride and heptafluoride system were studied
4. Density, viscosity and surface tension of liquid rhenium hexafluoride and heptafluoride were measured.
5. A process for ultra-pure rhenium hexafluoride monofraction production was developed.

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