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Study of rhenium production process by hydrogen reduction of rhenium hexafluoride

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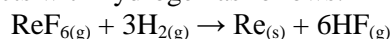
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Abstract. Study of heterogeneous reduction of rhenium hexafluoride with hydrogen was carried out. The dependence between the rate of rhenium deposition from mixture of rhenium hexafluoride and hydrogen and temperature and rhenium hexafluoride concentration has been studied. A study of structure of various rhenium precipitates was carried out. Microhardness of rhenium after deposition, and after one hour annealing at temperatures 1200 and 1800 °C was carried out.

1. Introduction

Gaseous rhenium hexafluoride reacts with hydrogen as follows:



Thermodynamic analysis shows that the process proceeds with heat liberation (~ 288 kJ / mol), and it becomes possible even at room temperature.

The minimum temperature at which the rhenium metal is obtained inside the copper tube (hot-well reactor) is 200 °C under atmospheric pressure [1,2,3]. The bulk of the metal was in powder form. With increasing temperature, the reaction has homogeneous-heterogeneous nature, a compact layer of rhenium forms together with the powder on the surface of the substrate.

Minimum powder formation is observed at 250 °C and ratio of H₂: ReF₆ = 25. These conditions provide a 95-100% conversion of ReF₆ to metal, including 70-75% - to compact. The density of the latter with thickness of 0.25-0.5 mm is 87-89% of the theoretical and the average microhardness (under a load of 1 ~ N) is 9100 MPa. The decrease of the system pressure to 267 Pa and the increase of ratio H₂: ReF₆ to 50-400 [4,5] do not result in formation of rhenium precipitates with density close to the theoretical value.

Plastic coatings with thickness 0.025-0.050 mm inside tube with diameter 19 mm and length 250 mm were obtained at a temperature of 600 °C, ratio of H₂: ReF₆ = 12.5, pressure of 1.3 kPa and flow rate of the gas mixture of 270 cm³ / min. Rhenium deposition rate under these conditions is 0.013 mm / h and completeness of ReF₆ recovery is 25%.

The coating has a columnar structure. X-ray studies showed that absence in it of any structure.

In [6,7] the dependence of rhenium deposition rate on the content of rhenium hexafluoride in gas mixture and deposition temperature was studied. Deposition of rhenium was carried out in the temperature range of the substrate (400-1500 °C) at a total pressure of 133 Pa, hydrogen flow rate of 5*10⁻⁷ m³ / s and rhenium hexafluoride flow rate (0.3-1.1)*10⁻⁷ m³ / s. Kinetic data at different temperatures are placed on one straight line that indicates on diffusive character of the reaction. Investigation of the effect of the substrate temperature on the deposition rate shows that there is a



weak dependence of the rhenium deposition rate on the temperature. At high temperatures, a large role is played by homogeneous nucleation.

Kinetic regularities of heterogeneous recovery of rhenium hexafluoride by hydrogen have not been investigated in these studies.

The purpose of this work is the study of heterogeneous recovery of rhenium hexafluoride by hydrogen.

2. Experimental part

Study of heterogeneous reduction of rhenium hexafluoride with hydrogen was carried out using the apparatus (figure 1) consisting of a reaction chamber (1), rhenium hexafluoride feeder (5), bottle gas purifier (8), gaseous components dosing units (3, 4), condensers (6). In cases when the experiments are carried out at lowered pressure, a forepump (9) and optical manometer (10) for pressure measurement inside the chamber.

The reaction chamber (figure 2) is a vertically arranged cylinder with water cooled jacket (1) and two removable flanges (4) which also function as mixers. Copper current leads were electrically insulated from the reaction chamber with fluoroplastic and rubber seals. To counterbalance substrate temperature elongation, one of the current lead was fitted with a movable electric contact. Hydrogen was purified from oxygen, moisture and dust particle impurities using a bottle gas purifier (dew point 70 °C).

Deep purification of rhenium hexafluoride was done using highly efficient rectifying columns [8].

Rhenium hexafluoride and hydrogen were dosed using a flow meter including a divided capillary and a differential manometer. The gas mixture consisting of rhenium hexafluoride and hydrogen were fed through the top of the reaction chamber. Unreacted rhenium hexafluoride and hydrogen fluoride produced by the reaction were collected in two tandem condensers cooled by liquid nitrogen.

Pressure in the system was maintained within (1±1.5) kPa and measured with an optical manometer.

The average composition of the gas mixture fed into the reaction chamber was calculated according to known hydrogen consumption and loss of weight of the rhenium hexafluoride containing vessel. Temperature was measured with chromel-alumel thermocouple. Copper pipes with diameter 3 mm were used as substrates.

Rate of rhenium deposition was determined by change of precipitate diameter before and after the process.

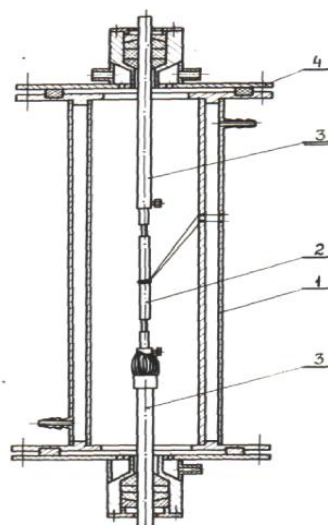
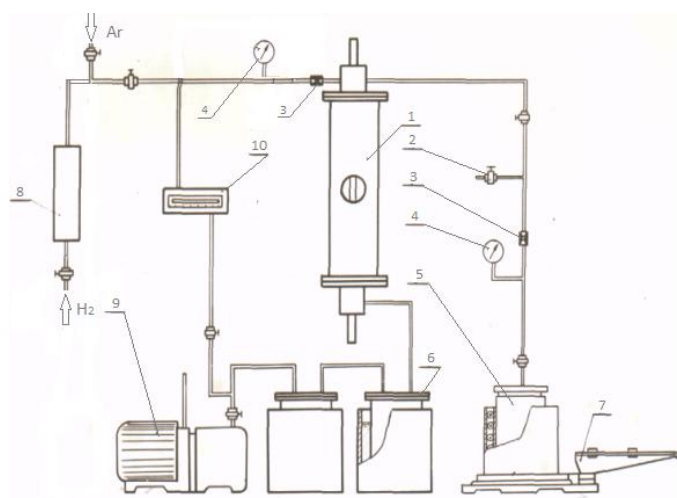


Figure 1. Diagram of the apparatus for rhenium precipitates production: 1 – reaction chamber; 2 – valve; **Figure 2.** Diagram of the reaction chamber for rhenium precipitates

3 – capillary; 4 – differential manometer; 5 – vessel with ReF_6 ; 6 – condenser; 7 – scales; 8 – bottle gas purifier; 9 – forepump; 10 – optical manometer. production: 1 – body; 2 – substrate; 3 – current lead; 4 – flange.

3. Results and discussion

Experimental results of study of temperature dependence of rhenium deposition obtained in this work are presented in figure 3.

As it can be seen from the data presented, the initial temperature of rhenium deposition is 350 °C, which is higher, than the temperature obtained in another work [1]. This result is probably related to the fact that the authors of the aforementioned work activated the gas mixture by heating it (rhenium deposited inside a tubular substrate). As the temperature rises above 350 °C, rhenium deposition rate increases exponentially, however at temperature over 450 °C reaction between rhenium hexafluoride and hydrogen proceeds throughout the whole volume with formation of fine-dispersed powder.

The results presented in figure 3 were obtained for rhenium hexafluoride concentration in gas phase equal to 0.015 molar fraction. Increase of rhenium hexafluoride content in gas phase results in rhenium deposition rate growth without changing its functional dependence; however that leads to decrease of volume reaction initiation temperature.

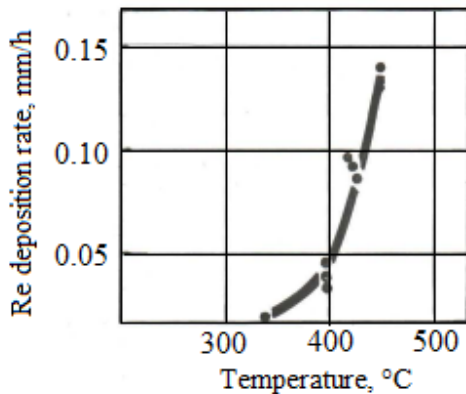


Figure 3. Dependence of rhenium deposition rate from substrate temperature

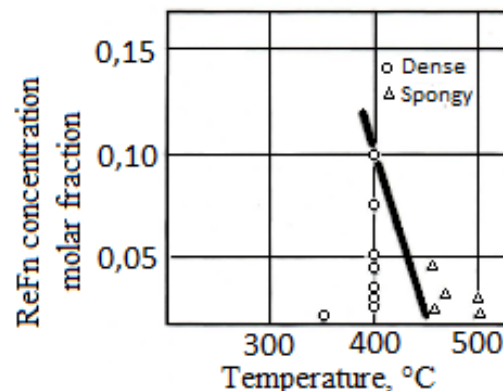


Figure 4. Conditions of formation of various rhenium precipitates depending on the parameters of the process

To obtain high-quality rhenium precipitates on large diameter substrates it is necessary to increase the gas flow velocity, and at higher temperatures the gas mixture should be fed in such way, that it would get simultaneously to entire reactive surface of the substrate (e.g. gas mixture feeding through a muzzle towards the whole generatrix of the rotating product).

The structure of rhenium precipitates was studied using metallographic slices with 10÷500-fold magnification, and the microhardness was measured using PMT-3 device with 100 g load.

The analysis of precipitates structure has shown that three types of precipitates form within the studied intervals of temperature and rhenium hexafluoride concentration in gas phase. These precipitates types are columnar, laminated and loose spongy. The conditions of these precipitates formation are presented in the figure 4.

In the area of relatively low temperatures and rhenium hexafluoride concentrations dense columnar precipitates form (figure 5a). Increase of the temperature results in formation of laminated precipitates (figure 5b). Further increase of the aforementioned parameters is attended by the reaction proceeding throughout volume and at the near-surface layer of the substrate with simultaneous heterogeneous reaction running on the substrate as well. These conditions result in formation of loose spongy precipitates which are a mixture of powder and solid rhenium. (figure 5c).

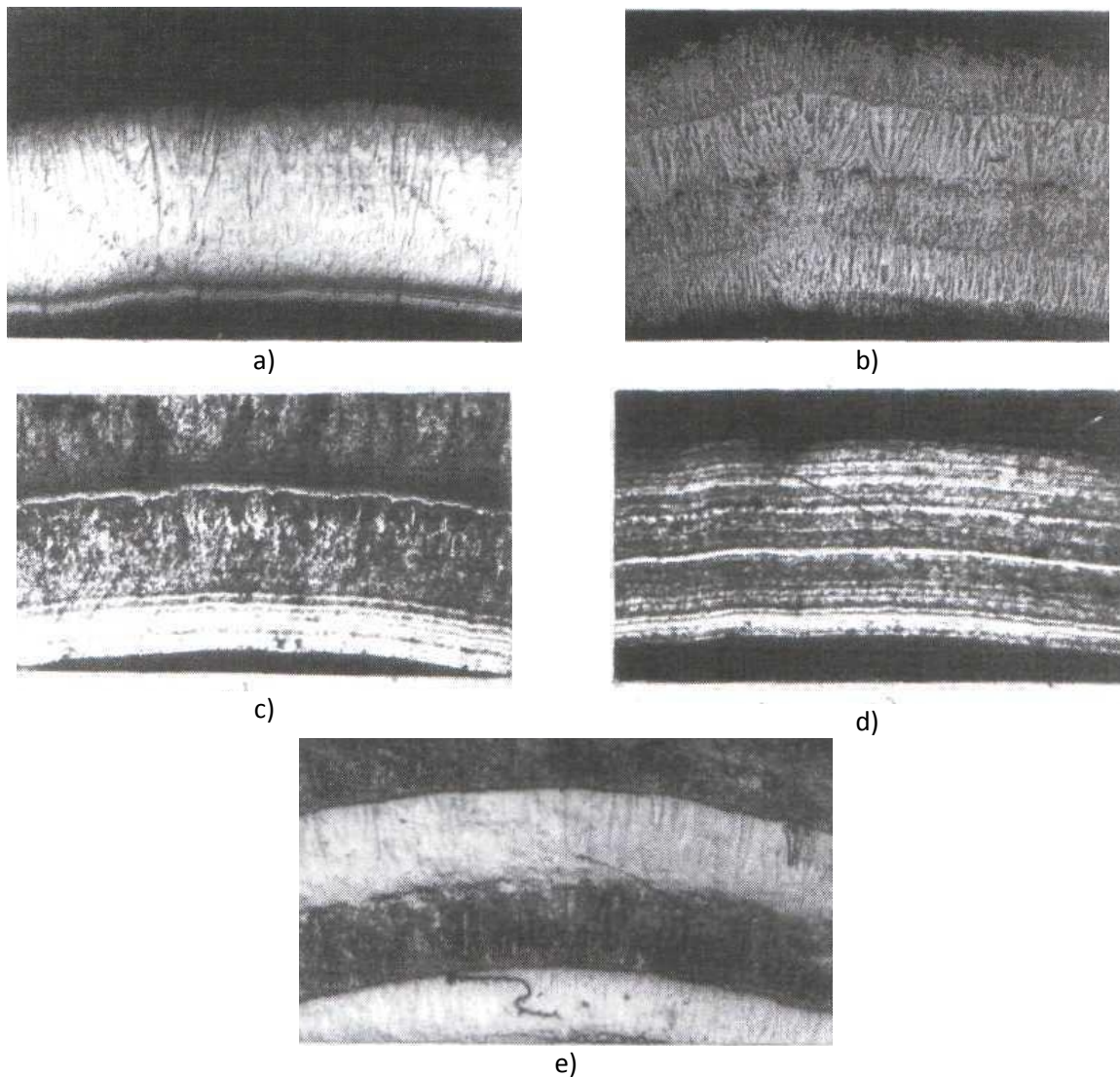


Figure 5. Structure of rhenium precipitates ($T = 400\text{ }^{\circ}\text{C}$, $C_{\text{ReF6}} = 0.02$ molar fraction): b) $T = 420\text{ }^{\circ}\text{C}$, $C_{\text{ReF6}} = 0.015$ molar fraction; c) $T = 450\text{ }^{\circ}\text{C}$, $C_{\text{ReF6}} = 0.05$ molar fraction; d) $T = 450\text{ }^{\circ}\text{C}$, $C_{\text{ReF6}} = 0.02$ molar fraction; e) $T = 400\text{ }^{\circ}\text{C}$, $C_{\text{ReF6}} = 0.05$ molar fraction

Laminated precipitates form within the dense-to-spongy structure transition area. On the one hand, in this area homogeneous reaction starts to run, while a slight change of the process parameters results in prevalence of heterogeneous or homogeneous reaction. Apparently, that circumstance may explain varying thickness of layers of the laminated precipitates (figure 5d). At the same time, laminated precipitates with greater thickness of layers form inside the area where dense precipitates crystallize (Fig. 5e). Such lamination is related to instability of the process parameters. Therefore, production of dense precipitates with homogeneous structure requires automatic maintenance of the parameters at a preset level.

Initially, microhardness of obtained rhenium precipitates was $(600\text{-}650)\text{ kg/mm}^2$. After one hour annealing at 1200 and $1800\text{ }^{\circ}\text{C}$, obtained levels of microhardness were $(400\text{-}450)\text{ kg/mm}^2$ and $(300\text{-}350)\text{ kg/mm}^2$ respectively.

4. Conclusion

The dependence between the rate of rhenium deposition from mixture of rhenium hexafluoride and hydrogen and temperature and rhenium hexafluoride concentration has been studied. It has been demonstrated, that at rhenium hexafluoride concentration 0.015 molar fraction within temperature range (350 – 400) °C the reaction proceeds at the surface of the substrate, while at 400 °C it runs both at the surface and throughout the whole volume. Increase of rhenium hexafluoride concentration in the gas mixture lowers the region where heterogeneous reaction runs.

Conditions of formation of different types of rhenium precipitates were defined. Microhardness of rhenium after deposition – (600 – 615) kg/mm², while after one hour annealing at temperatures 1200 and 1800 °C – (400 – 450) kg/mm² and (300 – 350) kg/mm² respectively.

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