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## **Deposition of Tungsten by Reduction of Its Hexafluoride with Hydrogen under the Stoichiometric Component Ratio: An Environmentally Pure Production Process**

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**Abstract**—The reduction of  $WF_6$  with hydrogen on a heated surface under atmospheric pressure, temperatures of 500–600°C, and a stoichiometric ratio of components with the subsequent additional reduction of tungsten hexafluoride at  $t = 800^\circ C$  and condensation of formed HF is described. The method of calculation of the completeness ( $\alpha$ ) of reduction of  $WF_6$  and productivity ( $M$ ) of deposition of tungsten depending on the temperature, gas flow rate, and sizes of the reaction surface is developed based on the physicochemical mechanism of the process. The possibility of attaining  $M = 5.1$  kg/h and  $\alpha = 80\%$  when fabricating crucibles 300 mm in diameter and 500 mm in height is shown. The additional reduction of  $WF_6$  provides the summary magnitude  $\alpha > 99.9\%$ . The almost complete condensation of HF initially at  $t = +1^\circ C$  and then at  $t = -78^\circ C$  makes it possible to decrease its concentration in exhaust gases below the maximum permissible concentration (MPC).

**Keywords:** tungsten, hexafluoride, hydrogen, hydrogen fluoride, deposition, additional reduction, condensation, productivity, maximum permissible concentration

**DOI:** 10.3103/S106782121502011X

The deposition of tungsten from the gaseous mixture of tungsten hexafluoride and hydrogen is a relatively new production process which enables the resolution of a wide circle of problems emerging when developing modern technology, including the deposition of coatings of various indentations and the fabrication of various tungsten wares, which are difficult or impossible to be fabricated by conventional methods [1–3].

The process is based on the chemical reaction



and possesses a series of advantages compared with other methods:

- (i) a low process temperature;
- (ii) high deposition rates of tungsten;
- (iii) the possibility of using metal equipment;
- (iv) the simplicity and reliability of dosing and transporting  $WF_6$  with a boiling point of  $17.3^\circ C$  [4];
- (v) a simple resolution of environmental problems because the gaseous hydrogen fluoride forming according to reaction (1) is lighter than air and moves up when entering the atmosphere.

The process is usually performed applying gas mixtures containing hydrogen excess over the stoichiometric component ratio [5]. This fact leads to the necessity of burning excess hydrogen at the output

from the production apparatus, which in turn complicates the hydrogen fluoride that is formed and unused tungsten hexafluoride to be caught. Due to this, HF and  $WF_6$  containing in exhaust gases are lost, while their catching and neutralization systems are transformed into cumbersome buildings not always guaranteeing the fulfillment of environmental requirements. In connection with this fact, it becomes necessary to develop an efficient production process ensuring emissions into the atmosphere in the limits of established sanitary norms.

If the ratio between  $H_2$  and  $WF_6$  is stoichiometric, it becomes possible to prepare a gas mixture containing mainly HF, which can be condensed almost completely because of the smallness of the amount of incondensable hydrogen in the mixture after their effective interaction. The use of the stoichiometric gas mixture under atmospheric pressure enables one to increase the process temperature to  $600^\circ C$  without worsening the precipitate quality [1, Fig. 17], which promotes an increase in process productivity. However, in order to attain the effective interaction between the starting components, the gas mixture should be directed to the additional reduction of  $WF_6$  at  $\sim 800^\circ C$  (post reduction) after the target fabrication process of a concrete ware.

To analyze the described processes quantitatively, a physicochemical model of deposition of tungsten from

the mixture of its hexafluoride with hydrogen with the stoichiometric component ratio is necessary. Based on this model, it would be possible to calculate the main process characteristics at specified parameters without performing numerous experiments. When developing the process model with the hydrogen excess [1, 6], assumptions were made which cannot be accepted in the case of the stoichiometric component ratio.

In the actual process, a gaseous mixture of  $WF_6$  and  $H_2$  is passed along the heated surface on which tungsten is deposited. The content of initial components in the gas mixture decreases upon its motion, while the content of the reaction product (HF) increases. Due to this, a decrease in the process rate along the length of the reaction surface is observed. This decrease depends on the surface sizes, deposition temperature, and composition and consumption of the gas mixture. The quantitative interrelation between the listed parameters and main process characteristics—the completeness ( $\alpha$ ) of reduction of  $WF_6$  and productivity ( $M$ )—can be established by a mathematical analysis of the apparatus operation.

If we isolate an infinitely small zone over the length of the reaction surface ( $d\ell$ , mm), in the limits of which the process parameters and deposition rate can be considered constant, then a decrease in the molar fraction of  $WF_6$  in the gas mixture ( $\partial N_{WF_6}$ ) for this segment is directly proportional to the amount of tungsten deposited for time unit ( $\partial m$ , g/h) and inversely proportional to the consumption of the gas mixture ( $q$ , mol/h), which passes through the cross-section of the reactor:

$$-\partial N_{WF_6} = \partial m / (184q), \quad (2)$$

where 184 is a g-atom of tungsten.

During the deposition of tungsten on the surface,

$$\partial m = 0.0192 \Pi V \partial \ell, \quad (3)$$

where  $V$  is the deposition rate of tungsten, mm/h; 0.0192 is the tungsten density, g/mm<sup>3</sup>; and  $\Pi$  is the perimeter of the surface, mm.

The deposition rate of tungsten is described by the following equation [1, p. 23]:

$$V = \frac{3.6 \times 10^{19} N_{H_2} N_{WF_6} T^{-3} e^{\frac{58500}{RT}}}{\left( \frac{1}{P} + \frac{21500}{\sqrt{T}} N_{H_2} e^{\frac{840}{RT}} + \frac{25600}{\sqrt{T}} N_{WF_6} e^{\frac{6700}{RT}} + \frac{20000}{\sqrt{T}} N_{HF} e^{\frac{3860}{RT}} \right)^2}, \quad (4)$$

where  $R = 8.3$  J/(mol K) is the universal gas constant;  $P$  is the pressure, MPa (usually  $P = 0.1$  MPa); and  $T$  is the temperature, K.

For the atmospheric pressure ( $P = 0.1$  MPa), we can write (4) in a form convenient for further integration:

$$V = K_t N_{H_2} N_{WF_6}, \quad (5)$$

where

$$K_t = \frac{3.6 \times 10^{17} T^{-3} e^{\frac{58500}{RT}}}{\left( 1 + \frac{2150}{\sqrt{T}} N_{H_2} e^{\frac{840}{RT}} + \frac{2560}{\sqrt{T}} N_{WF_6} e^{\frac{6700}{RT}} + \frac{2000}{\sqrt{T}} N_{HF} e^{\frac{3860}{RT}} \right)^2}. \quad (5a)$$

In the case under consideration,  $N_{H_2}/N_{WF_6} = 3$ . Therefore, Eq. (5) is transformed to the form

$$V = 3K_t N_{WF_6}^2. \quad (6)$$

In the beginning of the reaction zone,  $q = q^0$ . Upon reaching the reduction completeness of  $WF_6$ ,  $\alpha \sim 80\%$  and, according to Eq. (1),  $q = 1.4q^0$ .

The average consumption of the gas mixture is

$$q_{av} = 1/2(q^0 + 1.4q^0) = 1.2q^0. \quad (7)$$

Substituting Eqs. (3), (6), and (7) into Eq. (2), we derive

$$\begin{aligned} -\partial N_{WF_6} &= \frac{0.0192 \times 3K_t N_{WF_6}^2 \Pi \partial \ell}{184 \times 1.2q^0} \\ &= 2.6 \times 10^{-4} K_t N_{WF_6}^2 \frac{\Pi}{q^0} \partial \ell. \end{aligned} \quad (8)$$

After the separation of variables and integration, we have

$$\frac{1}{N_{WF_6}} = 2.6 \times 10^{-4} K_t \frac{\Pi \ell}{q^0} + \text{const}, \quad (9)$$

where const is the integration constant. It is determined from the condition at  $\ell = 0$ ,  $N_{\text{WF}_6} = N_{\text{WF}_6}^0 = 0.25$ , where  $N_{\text{WF}_6}^0$  is the molar fraction of  $\text{WF}_6$  in the initial gas mixture. Then  $\text{const} = 4$ , while Eq. (9) takes the form

$$N_{\text{WF}_6} = (4 + 2.6 \times 10^{-4} K_t \Pi \ell / q^0)^{-1}. \quad (10)$$

The reduction completeness of  $\text{WF}_6$  ( $\alpha$ , in fractions) can be expressed as the ratio of the amount of reacted  $\text{WF}_6$  to its amount entered the reactor:

$$\alpha = \frac{q^0 N_{\text{WF}_6}^0 - q N_{\text{WF}_6}}{q^0 N_{\text{WF}_6}^0}. \quad (11)$$

The relation between  $q$  and  $N_{\text{WF}_6}$  can be established as follows. For the instant when the  $\text{WF}_6$  content in the gas mixture became equal to  $N_{\text{WF}_6}$ ,  $(q^0 N_{\text{WF}_6}^0 - q N_{\text{WF}_6})\text{WF}_6$  and  $3(q^0 N_{\text{WF}_6}^0 - q N_{\text{WF}_6})\text{H}_2$  reacted. Simultaneously,  $6(q^0 N_{\text{WF}_6}^0 - q N_{\text{WF}_6})\text{HF}$  formed and  $(q N_{\text{WF}_6})\text{WF}_6$  and  $3(q N_{\text{WF}_6})\text{H}_2$  remained in the gas mixture. Correspondingly,

$$\begin{aligned} N_{\text{WF}_6} &= \frac{q N_{\text{WF}_6}}{q N_{\text{WF}_6} + 3q N_{\text{WF}_6} + 6(q^0 N_{\text{WF}_6}^0 - q N_{\text{WF}_6})} \\ &= \frac{q N_{\text{WF}_6}}{6q^0 N_{\text{WF}_6}^0 - 2q N_{\text{WF}_6}}, \end{aligned} \quad (12)$$

from where

$$q = \frac{6q^0 N_{\text{WF}_6}^0}{1 + 2N_{\text{WF}_6}}. \quad (12a)$$

Substituting (12a) into (11), we derive

$$\alpha = 1 - \frac{6N_{\text{WF}_6}}{1 + 2N_{\text{WF}_6}}. \quad (13)$$

Substituting (10) into (13), we have

$$\alpha = \frac{4.33 \times 10^{-5} K_t \Pi \ell / q^0}{1 + 4.33 \times 10^{-5} K_t \Pi \ell / q^0}. \quad (14)$$

Remark: A more rigorous mathematical solution can be found if we substitute Eq. (12a) into formula (2) instead of expression (7). The separation of variables, integration, and calculation of the integration constant lead to the equation

$$\frac{1}{N_{\text{WF}_6}} - 2 \ln \frac{1 + 2N_{\text{WF}_6}}{N_{\text{WF}_6}} = 0.416 + 2.09 \times 10^{-4} K_t \frac{\Pi \ell}{q^0}. \quad (14a)$$

We can determine  $N_{\text{WF}_6}$  from (14a) by the trial-and-error method or graphically. Quantity  $q$  can be found from Eq. (12a), after which the reduction completeness of  $\text{WF}_6$  ( $\alpha$ ) can be found from (11). Values of  $\alpha$  found using Eqs. (14) and (14a) for the range of varying  $\alpha$  from 0 to 0.8 differ no more than by 1%.

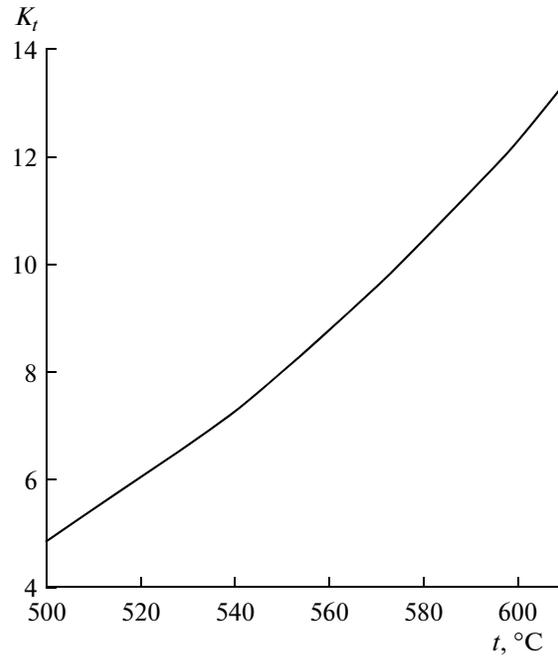


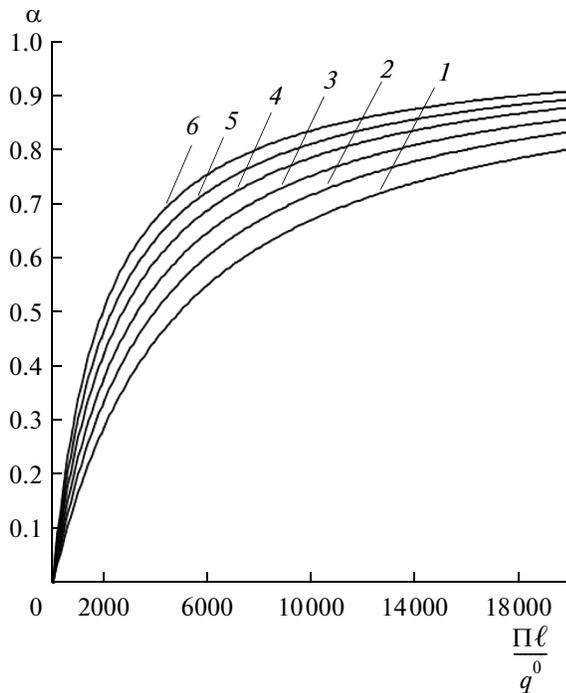
Fig. 1. Temperature dependence of  $K_t$  under the atmospheric pressure.

It follows from expression (14) that the reduction completeness of  $\text{WF}_6$  under the atmospheric pressure is determined by two factors. Quantity  $K_t$ , which is calculated according to Eq. (5a), reflects the rate of reaction (1) and depends mainly on the temperature of the reaction surface. As for quantity  $\Pi \ell / q^0$ , which can be considered the criterion of the process efficiency, it is proportional to the contact time of the gas mixture with the reaction surface.

Figure 1 shows the temperature dependence of  $K_t$ . Dendritic precipitates can form at  $t \geq 610^\circ\text{C}$  and the accepted component ratio in the gas mixture [1, Fig. 17]. It is difficult or unreasonable to provide the same temperature over the entire reaction surface in practice. Sometimes, in order to increase the deposition uniformity of tungsten, a positive temperature gradient is created in the motion direction of the gas mixture. Therefore, the magnitude of  $K_t$  should be determined for the average temperature on the reaction surface. Below we give the values of  $K_t$  for the most applicable temperatures:

t, °C	500	520	540	550	560	570	580	590	600
$K_t$	4.86	5.98	7.29	8.01	8.78	9.60	10.45	11.39	12.37

The variation in the reduction completeness of  $\text{WF}_6$  depending on the process efficiency criterion ( $\Pi \ell / q^0$ ) is presented in Fig. 2.



**Fig. 2.** Dependence of the reduction completeness of  $\text{WF}_6$  ( $\alpha$ ) on the "process efficiency criterion" ( $\Pi\ell/q^0$ ) at various temperatures under the atmospheric pressure.  $t$ : (1) 500, (2) 520, (3) 540, (4) 560, (5) 580, and (6) 600°C.

To calculate the reduction completeness of  $\text{WF}_6$  when using two sequentially connected apparatuses, Eq. (14) should be varied:

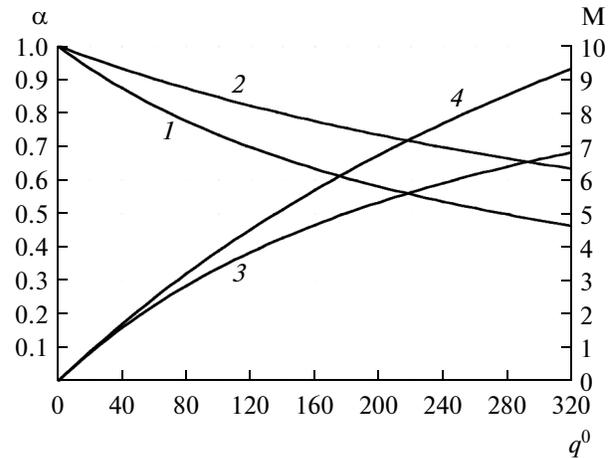
$$\alpha = \frac{4.33 \times 10^{-5} \left( K_t^1 \frac{\Pi^1 \ell^1}{q^0} + K_t^2 \frac{\Pi^2 \ell^2}{q^0} \right)}{1 + 4.33 \times 10^{-5} \left( K_t^1 \frac{\Pi^1 \ell^1}{q^0} + K_t^2 \frac{\Pi^2 \ell^2}{q^0} \right)}, \quad (15)$$

where  $K_t^1$ ,  $\Pi^1$ ,  $\ell^1$  and  $K_t^2$ ,  $\Pi^2$ ,  $\ell^2$  are the parameters for the first and second apparatuses, respectively. In this case, we initially calculate the reduction completeness of  $\text{WF}_6$  for the first apparatus and then for two apparatuses. The fraction of  $\text{WF}_6$  reduced in the second apparatus is determined from our data. Similarly, we can perform the calculation for three and more apparatuses in which the process is performed at various temperatures.

A comparison of the calculated and experimental reduction completeness of  $\text{WF}_6$ , which is shown in the table for typical implementation variants of the process, opens up the possibility to use the described computational procedure for a broad analysis of possibilities of the process.

The process productivity is described by the equation

$$M[\text{g/h}] = 184q^0 N_{\text{WF}_6}^0 \alpha. \quad (16)$$



**Fig. 3.** Dependence of (1, 2) the reduction completeness of  $\text{WF}_6$  ( $\alpha$ ) and (3, 4) productivity ( $M$ ) on the consumption of the gas mixture ( $q^0$ ) under the atmospheric pressure and  $t = 580^\circ\text{C}$ . (1, 3) For one apparatus and (2, 4) for two apparatuses.

In a practice activity, the sizes of the reaction surface ( $\Pi$  and  $\ell$ ) are specified by the configuration of the ware, which should be fabricated or covered with the coating. The aspiration to high process productivity dictates the selection of the maximal deposition temperature in the above-defined range. To optimize the process, the technologist can vary only the consumption of the gas mixture ( $q^0$ ). Dependences of the reduction completeness of  $\text{WF}_6$  ( $\alpha$ ) and productivity ( $M$ ) on the consumption of the gas mixture ( $q^0$ ) for the deposition of tungsten on a crucible-shaped substrate 300 mm in diameter and 550 mm in length at an average temperature of 580°C are presented in Fig. 3 as an example.

It is seen from Fig. 3 that  $\alpha = 0.8$  and  $M = 2.55$  kg/h are attained for one apparatus upon the consumption of a gas mixture of 69.3 mol/h, which corresponds to the deposition rate of tungsten  $V \approx 0.22$  mm/h. Higher process productivity  $M = 5$  kg/h ( $V \approx 0.43$  mm/h) is observed for the consumption of a gas mixture of 180 mol/h, but the reduction completeness of  $\text{WF}_6$  lowers to  $\alpha = 0.6$ .

The process productivity can be increased using two sequentially connected apparatuses; in this case, the gas mixture after the first apparatus is directed into a second similar apparatus. The motion direction of gas changes after passing through the system of  $\sim 50\%$   $\text{WF}_6$ ; i.e., it is initially supplied into the second apparatus and then into the first one. The process productivity at  $\alpha = 0.8$  can be increased to 5.1 kg/h in such a manner with a simultaneous increase in the consumption of the gas mixture to 138.6 mol/h. To fabricate crucibles with a 12-mm-thick wall,  $\sim 55$  h is necessary.

After the target deposition of tungsten to fabricate the concrete ware, gas is directed into a postreduction apparatus of  $\text{WF}_6$ , which is fulfilled in the form of a

Comparison of the calculated and experimental reduction completeness of  $WF_6$

No.	Ware type	Reaction surface		Average temperature, °C	Consumption of gas mixture, mol/h	Deposition time, h	Reduction completeness	
		length, mm	average diameter, mm				calculation	experiment
1	Crucible	300	112.0	500	23.2	29.0	0.510	0.500
2	Tube	1020	34.5	510	16.0	10.8	0.624	0.616
3	Tube	1020	44.0	560	25.8	7.8	0.670	0.665
4	Tube	1020	34.5	510	16.0	10.8	0.762*	0.777*
	+ tube	1020	13.0	610	16.0	10.8		
5	Tube	1020	44.0	560	25.8	10.8	0.953**	0.97**
	+ tube	1020	15.0	560	25.8	10.8		
	+ postreduction	800	120.0	750	25.8	10.8		

\* For two apparatuses.

\*\* For three apparatuses.

cylinder with an inner diameter of 200 mm and length of the heating zone of 1200 mm. The working part of the apparatus is heated to  $t = 800^\circ\text{C}$ . To increase the reduction completeness of  $WF_6$ , the internal volume

of the apparatus is filled with tungsten wire waste ("tangle wire").

The magnitude of  $\alpha$  for the system as a whole can be performed using the expression

$$\alpha = \frac{4.33 \times 10^{-5} \left( K_t \frac{\Pi^1 \ell^1}{q^0} + K_t \frac{\Pi^2 \ell^2}{q^0} + K_t \frac{\Pi^3 \ell^3}{q^0} \right)}{1 + 4.33 \times 10^{-5} \left( K_t \frac{\Pi^1 \ell^1}{q^0} + K_t \frac{\Pi^2 \ell^2}{q^0} + K_t \frac{\Pi^3 \ell^3}{q^0} \right)}, \quad (17)$$

where  $K_t^3 = 42$  is the average value of  $K_t$  calculated for  $t = 800^\circ\text{C}$  and range  $\alpha = 0.8-0.99$ ;  $\Pi^3 \ell^3$  is the area of the reaction surface in the postreduction apparatus, which is formed by the surface of inner apparatus walls and surface of tungsten wire placed into the apparatus. If 1.5 kg of tungsten wire with diameter 0.005 mm, which has a surface area of  $6.255 \times 10^6 \text{ mm}^2$ , is placed into the apparatus, then  $\Pi^3 \ell^3 = (0.754 + 6.255) \times 10^6 \text{ mm}^2$ .

The reduction completeness of  $WF_6$  calculated according to Eq. (17) is as follows:

$\alpha_1 = 0.995$  when using one target apparatus and  $q^0 = 69.3 \text{ mol/h}$ ;

$\alpha_2 = 0.990$  for two target apparatuses and  $q^0 = 138.6 \text{ mol/h}$ . Correspondingly, tungsten in an amount of 0.26 kg/h will be additionally deposited in the first case, and a gas mixture in an amount of  $\sim 2545 \text{ L/h}$  which contains (mol %) 99.64 HF, 0.09  $WF_6$ , and 0.27  $H_2$  will be formed at the output. Tungsten in an amount of 1.22 kg/h will be additionally formed in the second case, and gas in an amount of  $\sim 5100 \text{ L/h}$  which contains (mol %) 99.33 HF, 0.17  $WF_6$ , and 0.5  $H_2$  will be formed at the output.

It is reasonable to condense HF ( $t_{\text{boil}} = 19.5^\circ\text{C}$  [4]) and  $WF_6$  at  $+1^\circ\text{C}$  using a vertically arranged tubular heat exchanger made of stainless steel. In order to condense HF and  $WF_6$  almost completely, the heat exchanger should have 19 or 37 tubes 18–20 mm in diameter with a cooling region of 1 m. Coolant passes through the tube space, while the gas mixture moves in tubes downwards. Effective condensation is provided due to two factors:

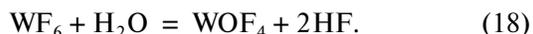
(i) liquid condensate drains into the collector tank conserving the condensation surface pure (without wall accretion) overall the process;

(ii) when gas moves in tubes, its volume decreases from 5100 to  $\sim 50 \text{ L/h}$  (by a factor of  $\sim 100$ ), which provides its effective cooling and attainment of equilibrium vapor pressures of HF and  $WF_6$ .

The equilibrium pressure of HF vapor at  $t = +1^\circ\text{C}$  is 49.3 kPa [7]; from here, it follows that HF is carried with incondensable hydrogen in amount of  $\sim 20 \text{ g/h}$ . Approximately the same ratio will be in the condensate and gas mixture after condensation, which allows us not to take into account  $WF_6$  in calculations.

To catch HF more completely, the gas mixture after the condensation at  $t = +1^{\circ}\text{C}$  should be passed through a small vessel (4–6 L) cooled with dry ice (solid  $\text{CO}_2$ ) to  $t = -78^{\circ}\text{C}$ , where HF will be additionally condensed, and its partial pressure will reduce to 0.67 kPa [7]. This operation will result in a decrease in the volume of uncondensed gas to  $\sim 26$  L/h, and it will carry out HF from the system in an amount of  $\sim 137$  mg/h. The HF concentration in air upon the emission of exhaust gases in amount of  $\sim 26$  L/h into the vent system with a productivity of  $3000$  m<sup>3</sup>/h will be  $0.046$  mg/m<sup>3</sup>, which is lower than the maximum permissible concentration (MPC) of  $0.05$  mg/m<sup>3</sup> [8]. Vent gases emitted into the atmosphere are diluted multiply, which excludes the appearance of environmental problems.

Such technology provides the almost complete condensation of gaseous hydrogen fluoride formed according to reaction (1). The fabricated product contains  $\text{WF}_6$  in an amount of  $\sim 0.17$  mol % (2.56 wt %). The removal of  $\text{WF}_6$  can be performed by the regulated hydrolysis method [9] according to the reaction



Water in an amount of 1.7–1.8 g should be added per 1 kg of the prepared product. Tungsten oxyfluoride forming during the hydrolysis ( $\sim 25$  g/kg) has a boiling point of  $186^{\circ}\text{C}$  [10], which makes it possible to separate HF by evaporation. Residual  $\text{WOF}_4$  is subjected to complete hydrolysis and is directed to the hydrometallurgical stage of manufacturing tungsten-containing production. Purified HF can be used in other technologies.

### CONCLUSIONS

The described production process of reducing  $\text{WF}_6$  with hydrogen under atmospheric pressure, temperature of  $580^{\circ}\text{C}$ , and stoichiometric component ratio makes it possible to fabricate wares (coatings) made of tungsten with sufficiently high productivity (5.1 kg/h)

with the usage completeness of  $\text{WF}_6$   $\alpha = 0.8$ . More than 99.99% of the HF that is formed is caught, and its content in exhaust gases does not exceed the MPC.

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Translated by N. Korovin