Ecologically clean fluoride conversion – New technology of tungsten production instead powder metallurgy

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Abstract

The fluoride conversion in the tungsten technology is based on three stages:

- electrochemical decomposition of HF with separate evolution of gaseous fluorine and hydrogen;
- fluorination of tungsten by evolved fluorine with further condensation of newly formed WF_6;
- reduction of gaseous WF_6 by evolved hydrogen followed by condensation of newly formed HF and its supply to electrochemical decomposition, thus providing the circulation of fluorine and hydrogen.

The processes optimization allowed finding equipment and technological solutions, which ensure industrial production of pore-free large-size workpieces and items of tungsten on technological line having productivity 6.6 kg/h (52 tons/year) at satisfying the environmental requirements. To improve the production efficiency, continuous operation of several lines in automatic mode is recommended.

Under equivalent productivity, specific energy consumption decreases 2-2.5 times comparatively with powder metallurgy.

The recommendations for production of tubes and crucibles in diameter up to 300 mm, plates from 22*60*500 to 47*305*1000 mm in size and bars ∅ 14-63 mm and 1000 mm long and examples of their deformation are discussed.

Keywords

Tungsten, fluorine, tungsten hexafluoride, hydrogen, fluoride cycle, productivity, ecology

Introduction

The tungsten metal production by power metallurgy involves tungsten powder pressing in molds, preliminary sintering of produced compacts in hydrogen at the temperature of 1200–1300 °C in indirect heating furnaces and final sintering in hydrogen at heating up to 2900–3000 °C by passing of the electric current through the compact. The above process requires great expenditures of electric power and does not allow producing pore-free semi-products [1]. The hydrostatic compaction of large-sized workpieces and their sintering in induction furnaces does not eliminate the cited problems.

Fluoride cycle with turnover of fluorine and hydrogen

The above cited problems are solved during the industrial production using the workpiece formation by gas-phase deposition of tungsten from the mixture of its hexafluoride with hydrogen. The expediency of using the technique is shown in [2–8] where the opportunity is substantiated to create an ecologically clean process cycle with circulation of fluorine-containing products and hydrogen based on three chemical processes, which are realized at the atmospheric pressure:

- Electrolytic decomposition of HF in KHF_2 + HF melt at the temperature of 80–100 °C with the separate evolution of fluorine and hydrogen:
  $$2HF_{(liquid)} = H_{2\ (gas)} + F_{2\ (gas)}\ ;$$
- Fluorination of tungsten powder (waste) by evolved fluorine at the temperature of 300–350 °C with condensation of the formed WF_6 at temperature 2.5–3.0 °C:
  $$W\ (solid) + 3F_{2\ (gas)} = WF_{6\ (liquid)};$$
- Reduction of WF_6 by evolved hydrogen at the temperature of 580–600 °C:
  $$WF_{6\ (gas)} + 3H_{2\ (gas)} = W_{(solid)} + 6HF_{(gas)}\ .$$

Intercoupling among these processes is shown in Fig. 1. Fluorine evolved in the course of electro-chemical decomposition of HF is supplied for tungsten metal fluorination where resultant WF_6 is gathered in the condensed form and transferred to its reduction by hydrogen. Produced after reduction HF is collected by condensation and supplied to electrolytic decomposition for fluorine and hydrogen production. As a result, the circulation of fluorine-containing products and hydrogen takes place.

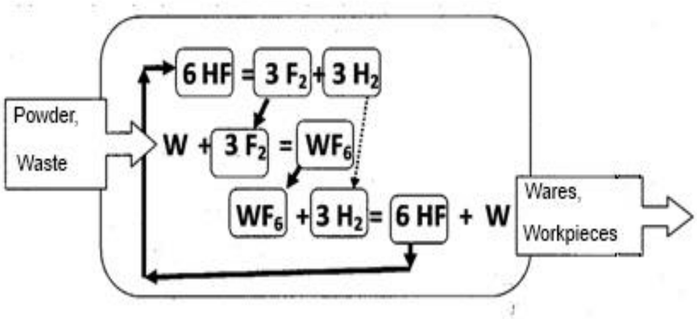

Figure 1: Ecologically clean fluoride scheme of production dence tungsten wares from powder and waste

Hydrogen being evolved during the electrochemical decomposition of HF is enabled to completely reduce newly formed WF_6.

The process cycle described above consumes powder metal and/or waste and produces tungsten wares and/or semi-products. For realization of the cycle, two process lines are necessary:

- Fluorination line, including an electrolizer for producing fluorine (and hydrogen), sorption columns with NaF for cleaning of fluorine from HF and a below described chain of fluorators and condensers (Fig. 2);
- Line of reduction WF_6 by hydrogen, which consists of reaction chambers for tungsten deposition on a substrate of prescribed shape for the purpose of production of wares, an apparatus for final reduction of unreacted WF_6 , and condensers for collection of newly formed HF (Fig. 3).

Using of harmful compounds and difficulties for make them safe after dilution by ventilated gases require capturing maximum quantity of deleterious products in every line.

Fluorine and hydrogen production

In the industry, the fluorine production is carried out by KHF_2 – HF melt electrolysis [9,10]. Under the effect of electric current at the temperature of 80–100 °C and voltage of 10–12 V, hydrogen fluoride decomposes into hydrogen evolved on the steel cathode and fluorine evolved on the carbon anode. The electric current intensity varies from 4 to 20 kA . The current output is 90–93 %. Fluorine is cleaned from HF by sorption over granulated (porous) NaF at the temperature of 100 120 °C [9-10].

Hydrogen is also cleaned from HF by sorption over NaF. After the subsequent desorption at the temperature of 300–350 °C, HF is supplied to electrolysis.

Fluorination of tungsten

After cleaning from HF, fluorine is supplied into the tungsten fluorination reactor. Such a scheme does not allow significant volumes of gaseous fluorine to give off into the atmosphere in case of an emergency, since its evolution ends up after power-off.

Fluorine flow rate is regulated by current consumed by the electrolytic cell. As shown in Fig. 2 [6, 7], gaseous fluorine is passed over tungsten-containing nickel boats located inside the nickel reactor where it interacts with tungsten producing WF_6 with liberation of 9.3 kJ per 1 g of reacted tungsten [11], allowing maintaining the required temperature (~300 °C) in the first reactor using reaction heat. In moving the gas, the fluorine content in it decreases and that of WF_6 increases. As a result, the fluorination rate decreases. The fluorine use completeness calculation ($\propto_{\mathrm{F}_2}$, fractions) can be performed with equation [6, 7]:

$$\propto_{\mathrm{F}_2} = 1 - \mathrm{e}^{-0{,}000939\ \mathrm{K}_{\mathrm{F}_2}\ \frac{S\ \ell}{\mathrm{q}^0_{\mathrm{F}_2}}} \qquad (1)$$

where $\mathrm{K}_{\mathrm{F}_2}$ is the process rate constant; S and ℓ are the width and length of tungsten layer (mm); $\mathrm{q}^0_{\mathrm{F}_2}$ is the initial fluorine flow rate (mole/h).

The values of ($\mathrm{K}_{\mathrm{F}_2}$) for different temperatures and kinds of fluorinated tungsten are given below [6,7] in Table 1.

The parameters and the results of fluorination of tungsten powder with particle size < 5 µm are given in Table 2 [6,7]. Row 1 shows the rated values, which have been confirmed experimentally in producing WF_6.

Table 1: Value of (K_{F_2}) for different temperatures and kinds of fluorinated tungsten. The parantheses contain the values deduced by extrapolation.

Temperature, °C	W-powder, < 5 µm	W-powder, < 80 µm	W-waste, ~2 mm
300	(0.155)	(0.134)	(0.103)
380	(0.30)	0.277	0.213

Gas mixture of unreacted fluorine and newly formed WF_6 after the first fluorination stage is supplied into the condenser (K1, Fig. 2) made of stainless steel as a heat exchanger with 7 tubes of Ø 80 mm and 800 mm long. In passing the mixture unside the tubes cooled down to the temperature of 2.5–3 °C, the partial condensation of liquid WF_6 takes place, which flows down into a accumulator leaving the condensation surface clean (without skull). The fluorine content in the gas increases and that of WF_6 decreases to equilibrium pressure of WF_6 equal to 57 kPa [12], i.e. to WF_6 content of 57 % mole.

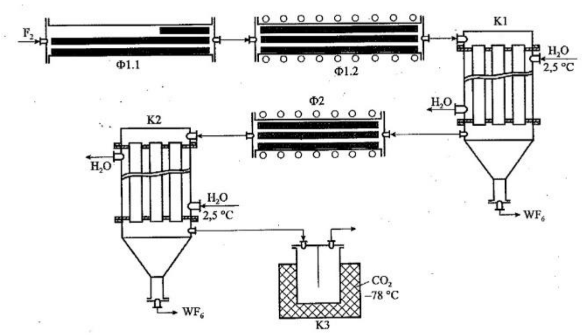

Figure 2: Fluorination unit scheme. Φ 1.1 and Φ 1.2 – First and second sections of first stage fluorator; Φ 2 – Reactor of second stage of fluorination; K1 and K2 – Condensers being cooled down to the temperature of 2.5–3 °C; K3 – condenser being cooled down to the temperature of -78 °C.

The expression for WF_6 concentration ($N^{k}_{WF_6}$, fractions) calculation along the length of the condenser depending on the process parameters is given below [7]:

$$\frac{\left(1-N^{k}_{WF_6}\right)\left(N^{0k}_{WF_6}-N^{p}_{WF_6}\right)}{\left(1-N^{0k}_{WF_6}\right)\left(N^{k}_{WF_6}-N^{p}_{WF_6}\right)} = e^{0,04\frac{\Pi_k \ell_k \left(1-N^{p}_{WF_6}\right)}{q^{0k}\left(1-N^{0k}_{WF_6}\right) d}} \qquad (2)$$

where $N^{p}_{WF_6}$= 0,57 is the equilibrium WF_6 vapor fraction at the condensation temperature; $N^{0k}_{WF_6}$ and q^{0k} are the mole fraction of WF_6 and the gas mixture rate (mole/h) in supplying into the condenser; Π_k and ℓ_k are the perimeter and the length of the condensing surface (mm); d is the inner diameter of the condenser tubes (mm).

With known value ($N^{k}_{WF_6}$), the gas flow rate in the given point (q^k ,mole/h) and the mass of condensed WF_6 (m_{WF_6}) is determined from the equations:

$$q^{k} = \frac{q^{0k}\left(1-N^{0k}_{WF_6}\right)}{1-N^{k}_{WF_6}} \qquad (3)$$

and

$$m_{WF_6} = (q^{0k}N^{0k}_{WF_6} - q^{k}N^{k}_{WF_6}) \qquad (4)$$

The gas mixture after condensation, which contains 43 mole % fluorine, is supplied into the fluorator (Φ2, Fig. 2), which is heated by an electric furnace. The expression for fluorine use completeness calculation ($\propto^{s}_{F_2}$) with such an incoming gas composition is transformed [6,7]:

$$\propto^{s}_{F_2} = 1 - e^{-0,0004388\ K_{F_2} \frac{S_s\, \ell_s}{q^{0s}}} \qquad (5)$$

where S_s and ℓ_s are the width and length of the reaction surface at this stage (mm); q^{0s} is the incoming gas flow rate (mole/h).

Fluorine use completeness at the second fluorination stage is > 99.9 %.

Summary fluorine use completeness at two stages ($\propto^{1+s}_{F_2}$) reaches > 99,99 %.

$$\propto^{1+s}_{F_2} = 1 - (1 - \propto_{F_2})(1 - \propto^{s}_{F_2}) \qquad (6)$$

The gas mixture containing > 99.9 % WF_6 from the second fluorator is supplied into the second condenser of the similar design (K2, Fig. 2) with the temperature of 2.5–3 °C, where practically complete condensation of WF_6 takes place. About 0.2 l/h of the mixture outflows from the second condenser carrying off 140 mg/h F_2 and 1460 mg/h WF_6. With the volume of ventilated gases of 5,000 m^3/h the concentration of F_2 and WF_6 in them amounts to <0.03 and <0.3 mg/m^3, being below the permissible concentrations 0.15 and 0.5 mg/m^3 [13] respectively.

The condensation at the temperature of 2.5–3 °C allows producing WF_6 with low concentration of SiF_4 and other low boiling fluorides, which result in uprising of inner stresses in the tungsten to be deposited.

The process optimization in locating the boats containing tungsten powder in three tiers in such a manner to avoid overheating of the first fluorator walls without forced cooling allowed reaching the same results in decreasing by half the total fluorator length (Table 2, row 2) [7].

Table 2: Parameters and results of the fluorination processes at various equipment and technological solutions

Nos	First stage of fluorination				1st condensation	Second stage of fluorination			2nd condensation		Output of $\frac{WF_6, kg/h}{\text{Total length of fluorators, mm}}$
	ø reactor, mm $\frac{\text{(Number of tiers)}}{\text{Boat length, mm}}$		Tempe-rature, °C $\frac{\text{1 section}}{\text{2 section}}$	Flow rate $\frac{F_2, \frac{mole}{h}}{\propto_{F_2}, \text{parts}}$	Volume of input mixture, mole/h $\frac{(N_{WF_6}^{01k})}{m_{WF_6}, kg/h}$	$\frac{\text{Ø reactor, mm (Number of tiers)}}{\text{Boat length, mm}}$	$\frac{\text{Volume of input mixture, mole/h}}{\text{Temperature, }^\circ\text{C}}$	$\propto_{F_2}^{S}$, Parts	Volume of input mixture $\frac{mole/h}{m_{WF_6}, \frac{kg}{h}}$	Mass of outgoing gases, g/h $(\frac{F_2}{WF_6})$	
	1 section	2 section									
1	$\frac{200\ (2)}{1400^{x1}}$	$\frac{200(2)}{1400}$	$\frac{300}{300}$	$\frac{2.0}{0.891}$	$\frac{21.4\ (0.73)}{2.38}$	$\frac{200\ (2)}{2960}$	$\frac{13.4}{350}$	0.9994	$\frac{9.6}{2.85}$	$\frac{0.14}{1.46}$	$\frac{5.23}{5760}$
2	$\frac{200\ (3)}{1200^{x2}}$	$\frac{200\ (3)}{1000}$	$\frac{300}{350}$	$\frac{2.0}{0.960}$	$\frac{18.9\ (0.89)}{4.20}$	$\frac{200\ (3)}{630}$	$\frac{4.8}{350}$	0.9982	$\frac{3.4}{1.03}$	$\frac{0.14}{1.46}$	$\frac{5.23}{2830}$
3	$\frac{300\ (4)}{1400^{x3}}$	—	$\frac{300}{-}$	$\frac{2.5}{0.888}$	$\frac{26.9\ (0.72)}{2.88}$	$\frac{300\ (4)}{1350}$	$\frac{17.2}{350}$	0.9995	$\frac{12.3}{3.65}$	$\frac{0.14}{1.46}$	$\frac{6.53}{2750}$
4	$\frac{360\ (5)}{1400^{x4}}$	—	$\frac{300}{-}$	$\frac{3.0}{0.922}$	$\frac{30.4\ (0.80)}{4.80}$	$\frac{300\ (4)}{1090}$	$\frac{14.3}{350}$	0.9994	$\frac{10.2}{3.03}$	$\frac{0.14}{1.46}$	$\frac{7.83}{2490}$
5	$\frac{200\ (3)}{1400^{xx5}}$	$\frac{200\ (3)}{1400}$	$\frac{300}{350}$	$\frac{3.0}{0.939}$	$\frac{29.6\ (0.84)}{5.44}$	$\frac{200\ (3)}{1665}$	$\frac{11.3}{350}$	0.9992	$\frac{8.05}{2.39}$	$\frac{0.14}{1.46}$	$\frac{7.83}{4465}$
6	$\frac{300\ (4)}{1100^{xx6}}$	$\frac{300\ (4)}{800}$	$\frac{300}{350}$	$\frac{3.75}{0.952}$	$\frac{36.1\ (0.87)}{7.44}$	$\frac{300\ (4)}{820}$	$\frac{11.1}{350}$	0.9992	$\frac{7.92}{2.36}$	$\frac{0.14}{1.46}$	$\frac{9.80}{2720}$
7	$\frac{360\ (5)}{1000^{xx7}}$	$\frac{360\ (5)}{600}$	$\frac{300}{350}$	$\frac{4.5}{0.951}$	$\frac{43.4\ (0.87)}{8.88}$	$\frac{360\ (5)}{653}$	$\frac{13.5}{350}$	0.9994	$\frac{9.7}{2.86}$	$\frac{0.14}{1.46}$	$\frac{11.74}{2253}$

Notes: x – without increase of outer surface of reactor. xx – with increase of outer surface of reactor.

x1 **1st tier**: 2 boats of (wide x long = 150 x 700 mm**). 2nd tier:** 1 boat of 180 x 700 mm in second half of reactor.

x2 **1st tier:** 2 boats of 150 x 700 mm . **2nd tier:** Boat width is increased from 75 to 180 mm along the length of 350 mm, further 180 mm.
3rd tier: beginning of boat is 500 mm from inlet F_2, its width is increased from 40 to 150 mm along the length of 500 mm, further 150 mm .

x3	**1st tier:** 2 boats of 220 x 700 mm. **2nd tier:** Boat width is increased from 135 to 260 mm along the length of 470 mm, further 260 mm. **3rd tier:** beginning of boat is 500 mm from inlet F_2, its width is increased from 50 to 260 mm along the length of 200 mm, further 260 mm. **4th tier:** beginning of boat is 800 mm from inlet F_2, its width is 220 mm and length is 600 mm.
x4	**1st tier:** 2 boats of 260 x 700 mm. **2nd tier:** Boat width is increased from 160 to 320 mm along the length of 400 mm, further 320 mm. **3rd tier:** beginning of boat is 500 mm from inlet F_2, its width is increased from 100 to 350 mm along the length of 250 mm, further 350 mm. **4th tier:** beginning of boat is 800 mm from inlet F_2, its width is 320 mm and length is 600 mm. **5th tier:** beginning of boat is 900 mm from inlet F_2, its width is 260 mm and length is 500 mm.
xx5	**1st tier:** 2 boats of 150 x 700 mm . **2nd tier:** Boat width is increased from 70 to 180 mm along the length of 600 mm, further 180 mm. **3rd tier:** beginning of boat is 650 mm from inlet F_2, its width is increased from 20 to 150 mm along the length of 350 mm, further 150 mm.
xx6	**1st tier:** 2 boats of 220 x 550 mm. **2nd tier:** 2 boats of 260 x 550 mm. **3rd tier:** Boat width is increased from 60 to 260 mm along the length of 300 mm, further 260 mm. **4th tier:** beginning of boat is 400 mm from inlet F_2, its width is increased from 80 to 220 mm along the length of 200 mm, further 220 mm.
xx7	**1st tier:** 2 boats of 260 x 500 mm. **2nd tier:** 2 boats of 320 x500 mm. **3rd tier:** Boat width is increased from 70 to 350 mm along the length of 400mm, further 350mm. **4th tier:** beginning of boat is 400mm from inlet F_2, its width is increased from 50 to 320mm along the length of 200mm, further 320mm. **5th tier:** beginning of boat is 600 mm from inlet F_2, its width is increased from 50 to 260 mm along the length of 200 mm, further 260 mm.

The same fluorination process optimization with using at the first stage fluorination of the reactors ø 300 of mm with boats in 4 tiers and ø 360 mm with boats in 5 tiers showed (Table 2, rows 3 and 4) the opportunity of increasing the fluorine flow rate up to 2.5 and 3.0 kg/h and increase in the process productivity up to 6.63 and 7.83 kg/h at the same ecological characteristics [7].

The further intensification of the process is possible in case of increase of the first reactor wall heat-away surface where the main quantity of the fluorination reaction heat evolves. In the elementary alternative, this purpose is attained by pipe thread cutting over the outer wall surface of reactor that allows increasing heat-away from the reactor wall into the nearby environment ~1.5 times and accordingly to raise fluorine flow rate. The process optimization results according to the described technique [7] are given in Table 2, rows 5–7. The obtained results show that for reaching the same ecological characteristics it is necessary to increase the total fluorator length. As a result, the process productivity increases to 7.83, 9.80 and 11.74 kg/h for reactors of ø 200, ø 300 and ø 360 mm respectively.

The experiences of WF_6 production show that for keeping the reaction surfase during the whole process, a third part of powder loading should be unused. Based on the above, the fluorinationve cycle time does not exceed 30, 44, and 49 h respectively for reactors of ø 200, ø 300, and ø 360 mm without increase outer surface [7], and 20, 30, and 32 h for reactors with the increased heat-away surface. Then an additional charge of the first reactor is required. Additional charge of the second sections of the first stage fluorination reactors is required more rarely three times as compared with the first one. Additional charge of the second stage fluorination reactors is to carry out more rarely 9–12 times [7].

If after finishing one cycle of fluorination, one connects already a prepared reactor and pours off periodically WF_6 from the condensers into mobile vessels for sending it to reduction, then the process becomes continuous, and for 8000 h per year its productivity amounts to 63, 78, and 94 t/year for the fluorators of ø 200, ø 300, and ø 360 mm with increased heat-away surface.

Preparation of the apparatus for fluorination involves its purging by nitrogen, which then is displaced by a mixture of fluorine and WF_6, passes through the whole processing chain and goes out from the second condenser as a mixture with 57 mole % WF_6. For collection of WF_6, which releases together with nitrogen, it is expedient to supply the gases from the second to third condenser (K3, Fig. 2) of 4–6 liters in volume, being cooled to the temperature of -78 °C by solid CO_2 where the equilibrium WF_6 pressure decreases to 0.06 kPa [12], providing practically full condensation of WF_6 supplied in it. However, such impurities as SiF_4, SF_6, PF_3 and others, which have boiling temperature above -78 °C, are condensed at this tempera-ture. The obtained condensate should not be mixed with purer product condensed at the temperature of 2.5–3 °C. It should be distilled with WF_6 condensation at the temperature of 2.5–3 °C . The gaseous product coming out after such distillation is to be hydrolyzed and sent to chemical conversion.

Reduction of tungsten hexafluoride by hydrogen

Tungsten hexafluoride having boiling temperature of 17.2 °C [12] evaporates, mixes with hydrogen, and is reduced to metal at the temperature of 500–600 °C. Traditionally, the process was realized under an excess of hydrogen that makes difficulties in gathering of newly formed HF and unused WF_6. At the stoichiometric relationship of H_2 and WF_6 after the effective interacting of the components, the produced gas mixture contains mainly HF, which is condensed practically in full [4].

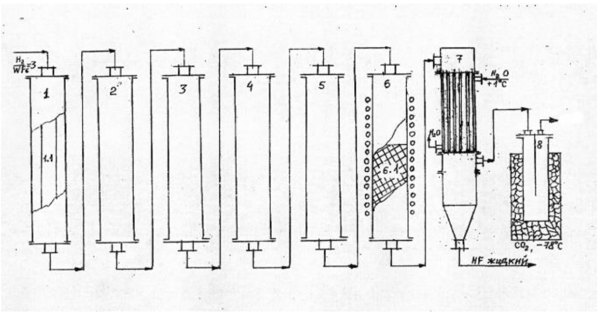

Figure 3: Processing chain of WF_6 reduction by hydrogen. 1–5 purpose-oriented deposition apparatuses; 1.1 – substrate; 6 – WF_6 post reduction apparatus; 6.1 – tungsten «tangle wire»; 7 – condenser at +1 °C; 8 – condenser at temperature of – 78 °C.

According to Fig. 3, gas mixture of WF_6 and H_2 is supplied into the first reaction chamber (1) where deposition of the main tungsten weight as a product or semi-product (purpose-oriented deposition) takes place on the heated surface of the corresponding substrate. For the purpose of increasing the completeness of component use, the gas mixture is supplied into the second (2), and then into the third (3), the fourth (4), and the fifth reaction chambers where also the purpose-oriented deposition of tungsten takes place. In some cases the increase in the number of chambers is useful.

Quantitative interrelation between the parameters and the main result – completeness of WF_6 ($\propto_{WF_6}$) reduction for five apparatuses is described by the equation [8,17]:

$$\propto_{WF_6}^5 = \frac{0{,}0000433\ (K_t^1\,\Pi^1\,\ell^1 + K_t^2\,\Pi^2\,\ell^2 + K_t^3\,\Pi^3\,\ell^3 + K_t^4\,\Pi^4\,\ell^4 + K_t^5\,\Pi^5\,\ell^5)}{q^0 + 0{,}0000433\ (K_t^1\,\Pi^1\,\ell^1 + K_t^2\,\Pi^2\,\ell^2 + K_t^3\,\Pi^3\,\ell^3 + K_t^4\,\Pi^4\,\ell^4 + K_t^5\,\Pi^5\,\ell^5)} \qquad (7)$$

where (K_t^1, Π^1, ℓ^1), (K_t^2, Π^2, ℓ^2), (K_t^3, Π^3, ℓ^3), (K_t^4, Π^4, ℓ^4), (K_t^5, Π^5, ℓ^5) are the process rate constants, perimeters and lengths of the reaction surface for 1,2,3,4 & 5 apparatuses; q^0 is the initial gas mixture flow rate (mole/h). Values of K_t for the most used temperatures are given in Table 3 [4].

Table 3: Values of K_t for the most used temperatures [4]

Temperature, °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

Using equation (7), the completeness of reduction of WF_6 can be calculated for one ($\propto_{WF_6}^1$), two ($\propto_{WF_6}^2$), three ($\propto_{WF_6}^3$), four ($\propto_{WF_6}^4$), and five ($\propto_{WF_6}^5$) chambers. Based on the obtained data, a fraction of WF_6 reduced in each chamber is determined. Similarly the calculation is carried out for greater number of apparatuses. The process productivity (M, kg/h) is calculated with equation:

$$M = 0.046 q^0 \propto_{WF_6} \qquad (8)$$

To reach more complete interrelation of WF_6 and H_2, the gas mixture is supplied into WF_6 post reduction apparatus [6, Fig. 3], the working area of which is heated to the temperature of 800 °C [8,17]. The present work considers two versions of the post reduction apparatus:

1st version. The cylinder of inner diameter ø 200 mm and length of heating area 1200 mm. Its inner volume holds 3 kg of 0.05 mm tungsten «tangle-wire» scrap, which has surface of $12.5*10^6$ mm^2.

2nd version. The cylinder of inner diameter ø 300 mm and length of heating area 1200 mm. Its inner volume holds 6 kg of similar tungsten «tangle-wire» scrap, which has surface of $25*10^6$ mm^2. The calculation of ($\propto_{WF_6}^{sum}$) for the whole system is carried out by the following formula:

$$\propto_{WF_6}^{sum} = \frac{0{,}0000433\ (K_t^1\ \Pi^1\ \ell^1 + K_t^2\ \Pi^2\ \ell^2 + K_t^3\ \Pi^3\ \ell^3 + K_t^4\ \Pi^4\ \ell^4 + K_t^5\ \Pi^5\ \ell^5 + K_t^x\ \Pi^x\ \ell^x)}{q^0 + 0{,}0000433\ (K_t^1\ \Pi^1\ \ell^1 + K_t^2\ \Pi^2\ \ell^2 + K_t^3\ \Pi^3\ \ell^3 + K_t^4\ \Pi^4\ \ell^4 + K_t^5\ \Pi^5\ \ell^5 + K_t^x\ \Pi^x\ \ell^x)} \quad (9)$$

where K_t^x = 42 is the mean value designed for the temperature of 800 °C and a range of ($\propto_{WF_6}$) alteration from 0.8 to 0.99; $\Pi^x \ell^x$ is the reaction surface area in the post reduction apparatus, which is summarized from the apparatus wall surface and the surface of tungsten «tangle-wire» placed into the apparatus.

The stoichiometric composition gas mixture application at the atmospheric pressure allows using, at purpose-oriented deposition of tungsten of required quality, the temperature of 580–600 °C (2, Fig. 3), ensuring the maximum productivity of the process. Considering that in enriching the gas mixture by hydrogen fluoride, the range of admissible temperatures extends, it is expedient to maintain in the first apparatus of purpose-oriented deposition the average temperature of 580 °C, and in the next apparatuses – 600 °C [8]. The parameters and results of WF_6 reduction process by hydrogen at various equipment and technological solutions are given in Table 4 for location in each apparatus of the reaction surface with sizes of $\Pi\ell$ = 615,240 mm^2.

For synchronization of WF_6 production and its reduction processes, the initial gas mixture flow rates are selected, which allow supplying to the reduction the whole hydrogen, which has been produced in the electrolytic cell simultaneously with fluorine.

As follows from Table 4, comparatively low completeness of purpose-oriented use of WF_6 (63.8–79.9 %) is reached in one reaction chamber, and 19.9–35.9 % of tungsten, being precipitated in the post reduction apparatus, turn into waste and are recycled to fluorination. It can be justified in case of individual item production. In using two chambers, the completeness of the purpose-oriented use of WF_6 is increased up to 79.4–89.6 %, and the amount of waste recycled to fluorination is run down to 10.1–14.6 % [8].

In the mass production, it is necessary to use 3–5 successively-connected apparatuses with periodic replacement of the apparatus where deposition is completed. In this case the completeness of the purpose-oriented use of WF_6 amounts to 90–94 %, and 6.7–9.7 % are recycled to fluorination. Total completeness of WF_6 reduction can reach 99.58–99.79 %.

If the deposition surface is less, the process results decrease, and it is necessary to increase the number of the apparatuses of the purpose-oriented deposition, and if the deposition surface is increased it is possible to decrease their number. The reaction surface ($\Pi\ell$) can be increased when a substrate of greater size or several substrates are arranged in the apparatus.

The gas mixture after the post reduction containing mainly HF (t_{boil} = 19.5 °C [11]) with a small content of 0.53–1.05 % wt. WF_6 is supplied to condensation at the temperature of +1 ° with the use of a tubular heat interchanger (7, Fig. 3) made of stainless steel. For practically full condensation of HF and WF_6 the heat interchanger should have 19 or 37 tubes of ø 18–20 mm with the 1-m cooling zone where the gas mixture passes from the top downward. The liquid condensate flows down into the accumulator and should be drained off periodically in mobile vessels for purification of HF from WF_6 and recycling it for fluorine and hydrogen production. About 3–14 g/h HF escape with non-condensing hydrogen. For fuller HF recovery, the gas mixture after condensation at +1 °C is passed through vessel (8) of 4–6 liter in volume cooled by

Table 4: Parameters and results of WF_6 reduction by hydrogen at various equipment and technological solutions

Nos.	$\frac{WF_6 \text{ flow rate, } kg/h}{\text{Initial mixture flow rate, mole/h}}$	Purpose-oriented deposition of tungsten					Post-reduction of WF_6 $\frac{\text{W weight, g/h}}{\text{Part of deposited W, \%}}$	Total completeness of utilization of WF_6 $\frac{\text{parts}}{W \text{ output, t/year}}$	Weight of condensed HF (g/h) at $\frac{+1℃}{-78℃}$	WF_6 content in condensate, wt. %	Yield of gases $\frac{\text{Volume, } l/h}{\text{HF weight, g/h}}$
		1 chamber	2 chambers	3 chambers	4 chambers	5 chambers					
		$\frac{\text{W weight, g/h}}{\propto^1_{WF_6}\text{, parts}}$	$\frac{\text{W weight, g/h}}{\propto^2_{WF_6}\text{, parts}}$	$\frac{\text{W weight, g/h}}{\propto^3_{WF_6}\text{, parts}}$	$\frac{\text{W weight, g/h}}{\propto^4_{WF_6}\text{, parts}}$	$\frac{\text{W weight, g/h}}{\propto^5_{WF_6}\text{, parts}}$					
1	$\frac{5.23}{70.2}$	$\frac{2579}{0.7986}$	$\frac{2895}{0.8965}$	$\frac{3004}{0.9202}$	—	—	$\frac{216.0\,*}{6.7\,*}$	$\frac{0.9972}{24.03}$	$\frac{2098.3}{2.85}$	0.70	$\frac{3.32}{0.020}$
2	$\frac{6.53}{87.6}$	$\frac{3066}{0.7605}$	$\frac{3524}{0.8740}$	$\frac{3687}{0.9145}$	—	—	$\frac{330.9\,*}{8.2\,*}$	$\frac{0.9965}{29.50}$	$\frac{2617.4}{4.42}$	0.87	$\frac{5.16}{0.030}$
3	$\frac{7.83}{105.1}$	$\frac{3510}{0.7260}$	$\frac{4122}{0.8526}$	$\frac{4347}{0.8992}$	—	—	$\frac{467.4\,*}{9.7\,*}$	$\frac{0.9958}{34.78}$	$\frac{3135.6}{6.37}$	1.05	$\frac{7.43}{0.044}$
4	$\frac{7.83}{105.1}$	$\frac{3510.0}{0.7260}$	$\frac{4122.0}{0.8526}$	$\frac{4347.3}{0.8992}$	$\frac{4464.3}{0.9234}$	$\frac{4535.8}{0.9382}$	$\frac{288.5\,**}{5.98\,**}$	$\frac{0.9979}{36.29}$	$\frac{3146.1}{3.25}$	0.53	$\frac{3.79}{0.022}$
5	$\frac{9.80}{131.5}$	$\frac{4109.8}{0.6792}$	$\frac{4974.9}{0.8222}$	$\frac{5306.7}{0.8770}$	$\frac{5482.2}{0.9060}$	$\frac{5590.6}{0.9239}$	$\frac{444.3\,**}{7.36\,**}$	$\frac{0.9973}{44.72}$	$\frac{3932.4}{5.08}$	0.67	$\frac{5.94}{0.036}$
6	$\frac{11.74}{157.6}$	$\frac{4628.6}{0.6385}$	$\frac{5756.3}{0.7941}$	$\frac{6205.6}{0.8561}$	$\frac{6447.1}{0.8894}$	$\frac{6597.9}{0.9102}$	$\frac{627.8\,**}{8.69\,**}$	$\frac{0.9968}{52.78}$	$\frac{4707.6}{7.31}$	0.80	$\frac{8.53}{0.051}$

*First version of post reduction apparatus. ** Second version of post reduction apparatus solid CO_2 to the temperature of -78 °C where HF is additionally condensed and its partial pressure in the gas mixture decreases down to 0.67 kPa [14]. As a result, the volume of non-condensed gas decreases down to 3.3–8.5 l/h and it carries away 20–51 mg/h HF out of the system. In evolving 8.5 l/h of non-condensed gases into the ventilation system of 5,000 m^3/h capacity, HF concentration in the air will reach 0.01 mg/m^3, being significantly lower than the admissible concentration limit 0.5 mg/m^3 [13].

The apparatuses of purpose-oriented deposition of tungsten and post reduction of WF_6 should be purged by nitrogen during their cooling. The purge gases are supplied into the condenser that has the temperature of -78 °C. For exclusion of the excess of admissible concentration limit of HF in the ventilation gases, the purge gas flow rate should not exceed 0.36 m^3/h [8].

Condensed HF contains 0.53–1.05 wt.% WF_6, which can be separated with the regulated hydrolysis [4].

In depositing tungsten on a strip or a bar, flat or cylindrical workpieces is produced for the subsequent deformation. Deposition of a tungsten layer of necessary thickness on the surface of copper substrate (with following its dissolution) allows producing various tungsten articles. Unlike the used powder metallurgical techniques, the described method forms pore-free articles and workpieces with finer-grained structure [8]. The reaction chambers for production of cited above workpieces and articles are shown in Fig. 4.

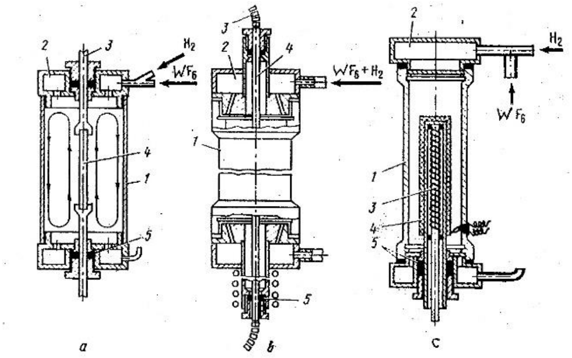

Figure 4: Reaction chambers for production of tungsten strips and bars (a), tubes (b) and crucibles (c). 1 – Body; 2 – Gas-distributing device; 3 – Heater; 4 – Substrate; 5 - Seal

Production of flat workpieces for rolling

To form tungsten flat workpiece, the reaction chamber shown on fig. 4a is used where substrate is heated by passing the current through it. The parameters and the process performances given in Table 4, row 6 are realized during the deposition of a tungsten layer of ~22.75 mm thick on the surface of a strip of 2*260*1000 mm in dimensions. As a result, a flat workpiece of 47.5*307*1000 mm in dimensions and ~280 kg in weight is produced for 41 h, which may be used for manufacture of magnetron sputtering targets. Tungsten deposition of 13 mm thick on four substrates of 2*50*1000 mm in dimensions in a chamber of the parallelepiped geometry allows producing in the course of ~24 h four flat workpieces of 28*76*1000 mm in sizes and ~41 kg in weight each. 10-mm thick tungsten deposition on 10 substrates of 2*40*500 mm in sizes in the reaction chamber having the parallelepiped geomettry (Fig. 5) allows producing flat workpieces of 22*60*500 mm in sizes and ~12,7 kg in weight each for ~18 h. For producing flat workpieces of greater (smaller) dimentions, the process duration is to be increased (decreased).

The uniformity of tungsten deposition along the length of a substrate, when it is heated by passing of the current, is reached because the areas of less section and having greater resistance are heated to higher temperature, thus ensuring higher deposition rate on these areas.

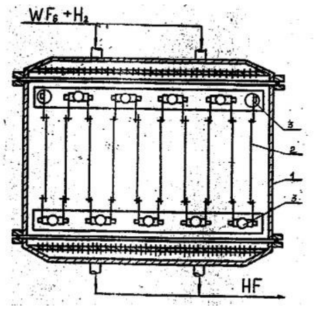

Figure 5: Reaction chamber scheme for production of 10 workpieces. 1 – body; 2 – Substrate; 3 – Current lead.

Tungsten deposition of ~10 mm thick on four substrates of 2*30*500 mm in sizes has been described earlier [16]. Rolling of the produce flat workpieces to 4.5–5 mm thick was carried out in the direction perpendicullar to the substrate rolling direction. The degree of reduction during the first pass reached 35–45 %. On the subsequent passes the degree of reduction varied from 20 to 25 %. The columnar structure characteristic for deposited tungsten fractured in reaching total degree of 60–65 % in reduction.

Production of cylindrical workpieces

To produce cylindrical workpieces, tungsten deposition is carried out on a substrate of similar shape in the reaction chamber shown in Fig. 4a. The realization of process parameters and results given in Table 4, row 6 takes place in increasing the bar dia-meter of 1000 mm long from 35 to 63 mm. For this purpose the process takes +28 h. As a result, workpiece of ~60 kg in weight is produced. In locating in the reaction chamber five substrates (Fig. 6) of 1000 mm long and increasing their diameter from 30 to ~48.5 mm, five workpieces of 35.6 kg each are produced in 13.3 hours.

The produced workpieces may be deformed by forging in swaging tools or with radial-swaging machines. To reach the same results in producing workpieces of ø 13.8 mm for rotational swaging, tungsten deposition on 18 rod substrates of ø 8 mm uniformly located in the reaction chamber is recommended. Workpieces of 2.885 kg each can be produced in 5.2 hours. For producing bars of greater (smaller) diameter, the process time is increased (decreased).

The production of bar workpieces is described in [2,17-20]. Rotational swaging of ø 15 mm bars showed the columnar structure of deposited tungsten fractures in reaching the total deformation degree >65 % [20].

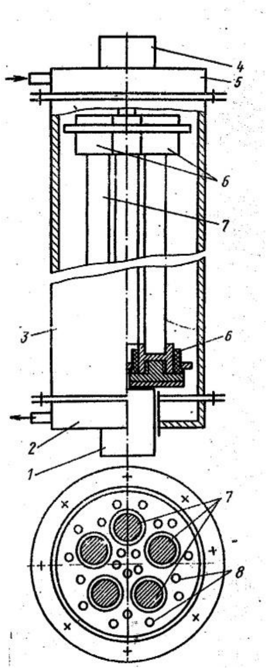

Figure 6: Reaction chamber scheme for production of 5 cylindrical workpieces.1,4 – Current leads; 2,5 – Gas-distributing devices; 3 – Body; 6 – Substrate attachment; 7 – Substrates; 8 – Holes for input (output) of gas mixture.

Production of tungsten tubes

The tube production is carried out by tungsten deposition of demanded thickness on the outer surface of a copper tube with the use of the reaction chamber shown in fig. 4b. After removing the copper substrate, the tungsten tube is produced with the quality of inner surface, which is equivalent to the outer surface of the copper substrate. If necessary, the outer surface of tungsten tube may be machined by the known techniques. The process performances given in Table 4, row 6 are reached during the tungsten deposition of ~6 mm thick on the substrate of ø 190 mm and length of 1000 mm, as well as during the tungsten deposition of 4.2 mm thick on five substrates of ø 35 mm (Fig. 6) or during the deposition of a layer of ~0.9 mm thick on 18 substrates of ø 10 mm of the same length. In the first case, a tube of ø 202*6 mm and ~71 kg in weight is produced for 10.8 h; in the second case, five tubes of ø 43,4*4,2 mm and ~10 kg in weight each are produced for 7.5 h; and in the third case, 18 tubes of ø 11.8*0.9 mm and ~0.6 kg in weight each are produced for 1.6 h. For producing greater wall thickness, the process duration is increased.

The uniformity of tungsten deposition around the substrate diameter is reached by uniform distribution of the gas mixture over the reaction chamber section. The uniformity of tungsten deposition throughout the substrate length is ensured with the use of the convective gas stream arising because of temperature difference of the substrate and the chamber walls (shown in Fig. 4a by arrows). In supplying the initial gas mixture from above with the speed lower the convective gas stream speed, it is diluted with the rising gas stream containing mainly HF and pushed aside into the descending branch of the convective stream. High concentrations of WF_6 and H_2 in the top part of the downward convective stream branch and their low concentration in the upward branch create the conditions for diffusion of reacting components in the direction of the deposition surface, which has the maximum speed above and slows down when moving downwards as a result of the decrease of reagent concentration difference in downward and upward convective stream branches. At the bottom of the chamber the downward and upward convective stream branches have practically identical composition, and the diffusive delivery rate of reagents to the deposition surface is close to zero. Here, the reagents supply rate to the reaction surface is determined by the rising convective stream branch. It drops in moving upward at the expense of reagents for tungsten deposition. The described two ways of reagents delivery to the deposition surface, the intensity of which oppositely varies throughout the chamber height, provide rather uniform tungsten deposition along the length of the substrate. During the deposition process, the gas mixture supplying direction into the reaction chamber may be reversed [22], if necessary. Production of tungsten tubes of various sizes is described in [2, 4, 21, 22].

Production of tungsten crucibles

For production of crucibles, a reaction chamber is used, which is shown in Fig. 4c. Tungsten is deposited on the outer surface of thin-wall copper substrate of the corresponding shape inside of which a heater is located. Described in Table 4 (row 6) the process parameters and performances described in Table 4 (row 6) are realized in depositing tungsten of 12 mm thick on a substrate in diameter of 300 mm and 550 mm long. Every 21.7 h, out of the described process line, a crucible rough workpiece of 143 kg in weight is removed. At next step it is necessary to cut the auxiliary shield, which prevents tungsten deposition on the inner surface of the substrate; and to dissolve the substrate. About 8 % of metal is deposited on the shield, which is returned to the fluorination.

To manufacture crucibles of thicker walls, the process proceeds more longer time. As a result, its performances slightly improve due to the increase of tungsten deposition surface. In manufacturing crucibles of less thick wall, the process duration is reduced.

The uniformity of tungsten deposition is reached as described above.

To produce crucibles with increased thickness of the bottom and the walls adjoining to it, a substrate is located with the bottom downwards and gas mixture is supplied from below. In this variant the convection stream magnifies the reagents delivery rate to the low part of the substrate.

The production of crucibles by reduction of WF_6 by hydrogen is described in [2, 4, 15]. Pore-free tungsten crucibles fabricated according to the described process have more correct and exact configuration of the inner space as well as higher surface smoothness of the inter walls in comparison with porous crucibles, which are produced by powder metallurgy.

Using copper substrates of various shapes and sizes, one can produce unique articles from dense tungsten practically of unlimited dimensions, the manufacture of which with conventional methods is difficult or impossible [5]. The physical-mechanical properties of gas-phase tungsten produced by reduction of WF_6 by hydrogen are given in [2, 5].

Organization of production

For continuous process production it is necessary to provide the systematic replacement of the apparatuses where the relevant process has finished as well as upon pouring off the produced WF_6 (in the fluorination line) and condensed HF (in the reduction line) into auxiliary mobile vessels.

The continuous process with the use of one process line (fluorination and reduction) for 8,000 t/year depending on the fluorator diameter (fluorine flow rate for fluorination) provides the annual tungsten article production rate from 24 to 52.8 t. The process nature allows operating some process lines simultaneously in the automated operation. The apparatuses of post reduction of WF_6 and condensation of HF can be integrated. The staff is necessary for:

- Preparation and replace apparatuses into the process line;
- Withdrawal of articles, semi-products, and waste from the removable apparatuses;
- Pouring-off of HF out of the reduction line and WF_6 out of the fluorination line;
- Additional charge of the fluorators and other operations necessary for provision of continuous operation of each section.

Taking into account that the tungsten deposition occurs at the temperature of 580–600 °C, the power consumption for production of 1 kg tungsten in using the fluoride conversion is 2–2.5 times as small as existing technology based on the powder metallurgy.

Lacking special requirements to tungsten powder allows one to intensify its production and reduce the expenses. As a raw material, one can use a large-size fraction of the tungsten powder («screenings») obtained in the production of tungsten powder for hard alloy metals. Involving other metal waste into the cycle also reduces the production cost.

The WF_6 reduction process parameters and results recommended in Table 4 are dictated by intention to synchronize the volumes of producing fluorine, which is used for fluorination, and hydrogen used for WF_6 reduction. In using hydrogen (partially or completely) received from other sources, there is a possibility of substantial growth of initial gas mixture flow rate and, as consequence, the productivity of WF_6 reduction process [4]. The demanded completeness of WF_6 use is reached as a result of the increase in the number of substrates in the reaction chambers or the number of successively purpose-oriented tungsten deposition apparatuses. In this case it is necessary to have greater number of the fluorination process lines.

The process lines for reduction of WF_6 may contain reaction chambers with various substrates. Corresponding calculations may be executed with the use of the above equations.

Conclusion

Production of various tungsten products with the use of described fluoride cycle ensures the circulation of fluorine-containing products and hydrogen without formation of significant quantities of unused waste. Evolution of dangerous gas products (F_2, HF, WF_6) into the ventilation system is not accompanied by the excess of maximum concentration limit.

The designed apparatuses and process decisions allow us to produce commercially large-sized workpieces of flat and cylindrical shape for deformation as well as tubes, crucibles, and other tungsten articles of various sizes with the productivity of the process line of ~6.6 kg/h (~52.8 t/year).

Unlike the powder metallurgical techniques, dense articles are produced, practically of unlimited sizes with finer-grained structure, thus the power consumption per 1 kg of product falls 2–2.5 times. To increase the production efficiency, it is recommended to operate some process lines simultaneously in the automatic mode. Using of powder without special requirements (waste) additionally reduces the production expenses.

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