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METALLURGY OF RARE AND NOBLE METALS

Short Fluoride Cycle in Tungsten Technology

Yu. M. Korolev[a, *] **and A. N. Timofeev**[b]

[a] *Scientific and Technical Association Powder Metallurgy, Moscow, Russia*
[b] *AO Kompozit, Korolev, Russia*
**e-mail: stapm@mail.ru*

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Abstract—It is found that when a tungsten anode is electrochemically dissolved in a acidic fluorides of alkali metals (K,Na)H_2F_3 and hydrogen fluoride at a temperature of $t \sim 37°C$, the resulting atomic fluorine reacts completely with tungsten to form WF_6. The latter dissolves in the melt, forming complex compounds $(K,Na)_2WF_8$ and (K,Na)WF_7, which is accompanied by an increase in the melting point of the electrolyte. The addition of up to 23 mol % LiF and saturation of the electrolyte by WF_6 lowered its melting temperature below 18°C, which, in an electrochemical process at a temperature of 35–40°C and an anode current density of 0.3–0.5 A/cm^2, made it possible to obtain simultaneously gaseous WF_6 at the anode and H_2 at the cathode. During the gas-phase deposition of tungsten, dense layers are formed from the resulting gaseous mixture with a stoichiometric ratio of components at a temperature of 550–600°C, and the resulting HF is captured by an electrolyte and used to produce a mixture of $WF_6 + H_2$, ensuring the circulation of reagents and the absence of stored waste. Based on the results, a short fluoride cycle in tungsten technology is presented. It uses two operations: the electrochemical synthesis of a gaseous mixture of $WF_6 + H_2$ in an electrolyzer with a filling anode made of fragments of metal tungsten and the reduction of WF_6 by hydrogen with capture the resulting HF, allowing one to reduce the chain of technological devices in the cycle by almost 2 times with a significant reduction in production costs. The hardware and technological scheme of the production chain for the environmentally friendly production of tungsten products with a capacity of ~48.5 t/year, which can be replicated and modified to produce the necessary products, is presented.

Keywords: tungsten, fluorine, fluorination, tungsten hexafluoride, hydrogen, reduction, hydrogen fluoride, complex alkali metal fluorides, electrochemical dissolution, reagent cycle, ecological safety, tungsten products, productivity, energy consumption, cost

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INTRODUCTION

The most promising direction in modernizing tungsten production is the use of fluoride processing [1–3], which is based on three chemical processes carried out at atmospheric pressure:

(i) the electrochemical decomposition of HF in the (K,Na)HF_2 + HF melt at temperature t = 40–50°C with the separate release of fluorine and hydrogen:

$$2HF_{\text{liquid}} = F_{2\,\text{gas}} + H_{2\,\text{gas}};$$

(ii) the fluorination of tungsten powder or waste with fluorine at t = 300–400°C with condensation of the formed tungsten hexafluoride (WF_6) at t = 2.5–3.0°C:

$$W_{\text{sol}} + 3F_{2\,\text{gas}} = WF_{6\,\text{gas}};$$

(iii) the reduction of gaseous WF_6 hydrogen at the stoichiometric ratio of the components on the substrate surface with t = 580–600°C:

$$WF_{6\,\text{gas}} + 3H_{2\,\text{gas}} = W_{\text{sol}} + 6HF_{\text{gas}},$$

ensuring the production of dense tungsten products of a given shape.

The interconnections between these processes are shown in Fig. 1.

The hardware and technological scheme for the industrial implementation of the described cycle is shown in Fig. 2 [1], which shows the designs of the used devices, the technological parameters, and gas flows that ensure the environmental safety of the process.

In an electrochemical reactor (ECR), the electrolysis of the (K,Na)HF_2 + HF melt is carried out. Hydrogen fluoride under the influence of direct electric current at t = 40–50°C and voltage 10–12 V decomposes into hydrogen released at the steel cathode and fluorine released at the carbon anode. Fluorine enters the fluorination of tungsten loaded into boats placed in cylindrical reactors (∅360 mm and 1 m long) made of nickel. The resulting tungsten hexafluoride (WF_6) condenses in liquid form at t = 2.5–

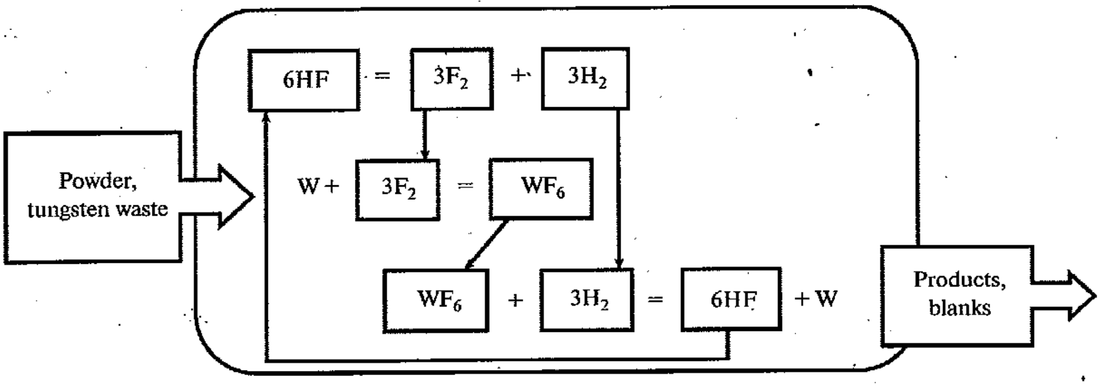

Fig. 1. Environmentally friendly fluoride scheme for producing dense tungsten products from powder and metal waste [1].

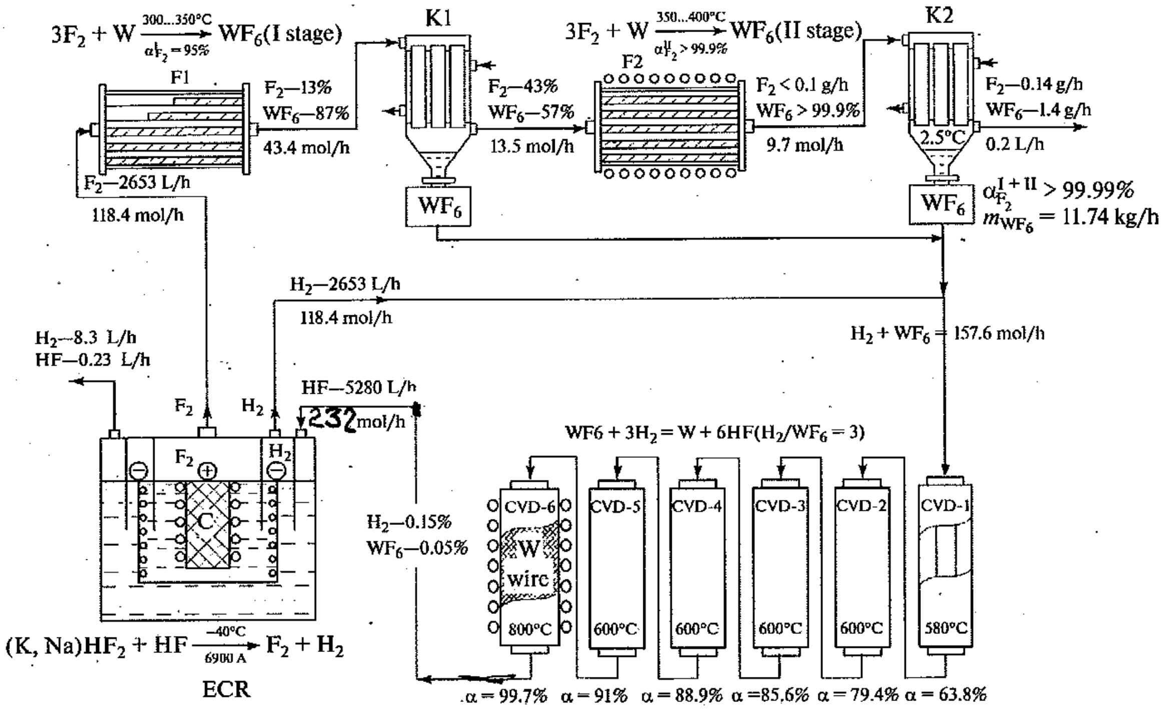

Fig. 2. Apparatus and technological scheme of fluoride conversion in tungsten technology for ftorator with a developed heat-transfer surface, Ø360 mm, with five tiers of boats with tungsten at a fluorine consumption of 4.5 kg/h.

3.0°C in a stainless-steel heat exchanger with 7 pipes Ø80 mm and 800 mm in length. To achieve high efficiency, the fluorination process is carried out in two stages with intermediate condensation WF_6 between them, which ensures minimum emissions of gases into ventilation [1, 4]. Condensed WF_6 is transferred for reduction by hydrogen generated in ECR.

The reduction process of WF_6 with hydrogen on a heated surface is carried out at a stoichiometric ratio of the components [1, 5]. First, there is a targeted deposition of a dense layer of tungsten on substrates of a given shape at t = 580–600°C to obtain the required products, while the gas mixture passes through several series-connected apparatuses until the full use of reagents is ~90%. In order to achieve a more complete reaction of the components, the gas mixture after the targeted deposition of tungsten is sent to the apparatus with a reaction surface temperature of ~800°C, where the completeness of the reaction between components reaches >99%. Hydrogen fluoride (HF) obtained during the reduction is captured and sent to an ECR to obtain fluorine and hydrogen. As a result, a circulation of the used reagents is created [1–3].

The cycle includes metal powder and waste, and finished or semifinished products of dense tungsten come out. The operating cycle does not require the consumption of reagents (only the replenishment of losses is necessary) and does not create stored waste [1].

The continuous operation of the described technological cycle while consuming an electric current of 6900 A in the ECR makes it possible to fluorinate ~58 t/year of tungsten and produce ~48.5 t/year of finished products in compliance with all environmental requirements, while simultaneously expanding the range and improving product quality, as well as reducing its cost [1]. To increase productivity, the chain of technological devices can be replicated and modified for the release of the required products.

The literature describes the production of products from tungsten of both widespread use (rods, plates, pipes, and crucibles) and unique products of various shapes and sizes, which are difficult or impossible to manufacture by existing methods [6–21]. A detailed description of the physicochemical foundations of the discussed processes is presented in the monograph [22].

Despite the obvious advantages of the new technology for the production of tungsten products in comparison with the existing one and the accumulated experience of using similar processes in the production of uranium [23, 24], making decisions about the modernization of existing production facilities is hampered by conservative caution arising from the presence of fluorine in the cycle.

Therefore, this work is aimed at simplifying the described cycle by synthesizing WF_6 on the tungsten anode of the ECR as a result of the interaction of the evolved atomic fluorine with tungsten. In this case, fluorine production, tungsten fluorination, and WF_6 condensation devices are excluded from the cycle.

RESEARCH METHOD

An electrolyzer used for studies is shown in Fig. 3.

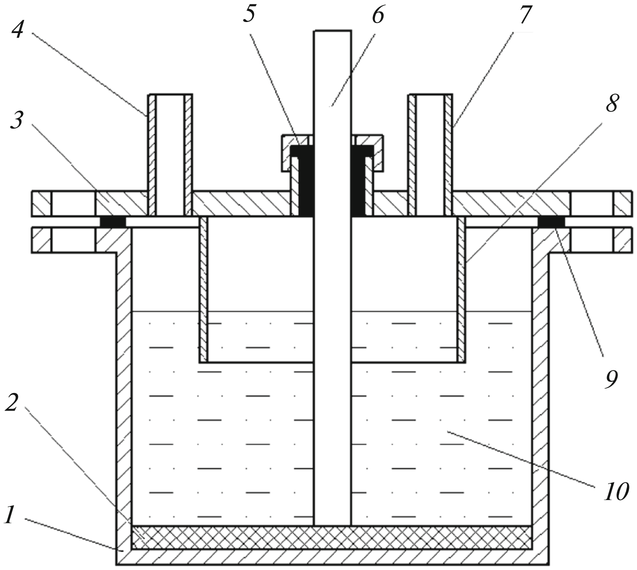

Fig. 3. Electrolyzer for synthesizing a $WF_6 + H_2$ gaseous mixture: (*1*) body, (*2*) bottom electrical insulating gasket, (*3*) cover, (*4*) branch pipe for hydrogen outlet, (*5*) electrically insulating stuffing box, (*6*) tungsten anode, (*7*) branch pipe for WF_6 outlet, (*8*) partition between the cathode and anode spaces, (*9*) gasket, and (*10*) electrolyte.

The electrolyzer body *1*, made of stainless steel in the form of a cylinder ∅100 mm and 100 mm in height, was the cathode of the electrochemical cell. Tungsten rods ∅3.5 or 8 mm, fixed on the cover *3* along the cell axis in the stuffing box *5,* allowing their vertical movement, were used as anode *6*. To prevent a short circuit when the anode was lowered, a gasket *2* from fluoroplastic was placed at the bottom of the electrolyzer. The electrolyte consisted of molten KHF_2, $NaHF_2$, and HF salts. The tightness of the cell was ensured by a gasket *9* from the flouroplastic. Before the start of the process, the electrolyzer was heated by an electric stove and, after the start of electrolysis, the temperature was maintained due to the heat released during the electrolysis. In a number of experiments, air cooling was used to maintain the required temperature.

At the first stage, the completeness of the interaction of atomic fluorine released at the anode with tungsten was determined, since the presence of unreacted fluorine in the WF_6 can cause popping when mixed with hydrogen. In these experiments, a hermetically welded concentric partition *8* was present on the cell cover *3*, the lower edge of which was immersed in the molten electrolyte, providing the separation of the cathode and anode spaces of the electrolyzer. In the case of the incomplete interaction of atomic fluorine with the tungsten anode, gaseous fluorine should be released into the anode space of the electrolyzer and leave it through the branch pipe *7*. To detect fluorine in the anode gas, strips of filtered paper moistened with an aqueous solution of KJ were used. Upon contact between fluorine and KJ, a reaction occurs:

$$2KJ + F_2 = 2KF + J_2,$$

which is accompanied by the characteristic brown staining of the test strip [23]. Multiple tests of the anode gas during electrolysis under various conditions showed the absence of elemental fluorine in it, which indicates the complete interaction of fluorine released at the anode with tungsten, which is accompanied by the formation of WF_6.

However, the resulting WF_6 was not released from the molten electrolyte in a gaseous form, but inter-

Table 1. Parameters and results of electrochemical synthesis of the $WF_6 + H_2$ gaseous mixture with the subsequent reduction of WF_6 to metal

1	Formula composition of electrolyte, mol	$2.18(K,Na)WF_7$ $0.27(K,Na)H_2F_3$ $1.0LiHF_2$ $0.78HF$	$2.34(K,Na)WF_7$ $0.11(K,Na)H_2F_3$ $1.0LiHF_2$ $2.79HF$
2	HF content, % mol	18	45
3	Electrolyte saturation WF_6, %	89	95.5
4	Electrolysis temperature, °C	38 ± 4	37 ± 1
5	Voltage, V	7.2 ± 0.5	7.8
6	Electric current strength, A	1.2 ± 0.2	2.0
7	Process time, h	8.0	4.5
8	Anode diameter, mm	3.5	8.0
9	Cathode diameter, mm	100	100
10	Melt height, mm	44	48
	Current density, A/cm^2:		
11	anode	0.51	0.34
12	cathodic	<0.01	<0.01
13	Reduction temperature, °C	570 ± 4	550 ± 5
14	Weight loss of electrolyte, g (per process/per 1 h)	13.9/1.7	20.7/4.6
15	Mass of the deposited tungsten, g (per process)	2.8	3.4
16	Received WF_6 mass, g (per process/per 1 h)	16.0/2.0	15.0/3.3
17	Share WF_6, % (in the melt/in the gas phase)	72/28	54/46
18	Evaporated HF mass, g (per process/per 1 h)	9.5/1.2	13.8/3.0

acted with potassium and sodium fluorides, forming complex compounds according to the reactions [25–27]

$$KF + WF_6 = KWF_7,$$

$$NaF + WF_6 = NaWF_7.$$

Evidently, the evolution of gaseous WF_6 is possible only after the conversion of the bulk of potassium and sodium fluorides into a complex compound $(K,Na)WF_7$, but this increases the melting point of the electrolyte.

Therefore, further studies were carried out using an electrolyte based on $(0.5KF + 0.5NaF)HF$ with the addition of LiF, which lowers the melting point of the electrolyte and increases its electrical conductivity [28, 29]. The electrolyte was additionally replenished with hydrogen fluoride. Then, electrolysis was performed to form WF_6, and then complex compounds KWF_7 and $NaWF_7$. After the repeated repetition of the these procedures, an electrolyte containing 2.45 mol (K,Na)F [30.8 mol %] + 1.0 mol LiF [12.6 mol %] + 2.18 mol WF_6 [27.4 mol %] + 2.32 mol HF [29.2 mol %] was obtained. Its formula composition is shown in Table 1 (row 1, left column). An electric current passed through the electrolyte at a temperature of 18°C, which indicates the presence of a liquid phase in it; i.e., its melting point is below 18°C. This electrolyte was used in an experiment on the electrochemical synthesis of a gaseous mixture $WF_6 + H_2$ with the subsequent reduction of WF_6 to metal, which was carried out on the installation schematically shown in Fig. 4.

The gas mixture from the electrolyser *1* by pipeline *2* entered inside the copper tube *3* (∅6 × 1 mm, length 700 mm), heated externally by an electric oven *4* with a heating zone length of 250 mm. The temperature was measured with a thermocouple attached to the outside of the tube. The reduction of WF_6 with hydrogen occurred on the inner surface of the copper tube and was accompanied by the deposition of a layer of metallic tungsten *5* on it.

After that, the electrolyte was additionally saturated with WF_6 to the formula composition shown in Table 1 (row 1, right column), and was again used for the electrochemical synthesis of the $WF_6 + H_2$ mixture with the subsequent reduction of WF_6 to metal. The main parameters and results of electrochemical synthesis of gaseous mixture $WF_6 + H_2$ with subsequent

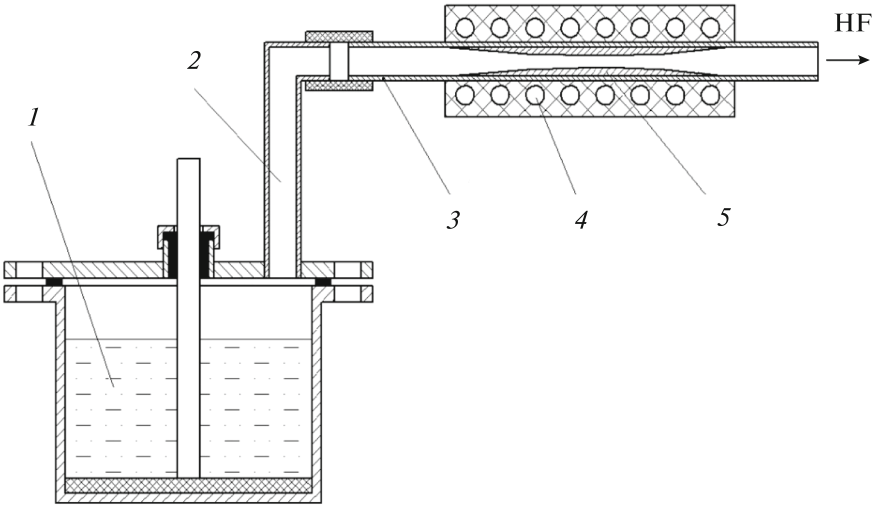

Fig. 4. Installation for electrochemical synthesis of a $WF_6 + H_2$ gaseous mixture with subsequent reduction of WF_6 hydrogen to metal: (*1*) electrolyzer, (*2*) pipeline, (*3*) copper tube-substrate, (*4*) electric oven, and (*5*) layer of deposited tungsten.

reduction of the obtained WF_6 hydrogen to metal are given in the table.

DISCUSSION

As follows from Table 1, the electrochemical dissolution of the tungsten anode in the melt of complex fluorides of alkali metals and hydrogen fluoride is accompanied by the release of gaseous WF_6 and H_2 from the melt, which then interact at $t = 550–570°C$ with the release of metallic tungsten. After cutting a copper substrate with a tungsten deposit into lengths and dissolving copper in nitric acid, tungsten tubes 4 mm in diameter and 20 mm in length with a wall thickness of 0.1–0.3 mm were obtained. A measurement of the density of the sediment and its X-ray phase studies have shown that it is pure tungsten with a density close to theoretical.

With a degree of electrolyte saturation with tungsten hexafluoride equal to 89%, only 28% of the formed WF_6 passes into the gas phase and, with an increase in the degree of electrolyte saturation to 95.5%, the share of WF_6 passing into the gas phase increases to 46%. It follows from this that, upon the full saturation of the electrolyte, all the WF_6 that formed together with hydrogen will leave the melt. In the gas phase, there will be a constant ratio of $H_2/Wf_6 = 3$, which is necessary for the efficient and environmentally friendly implementation of the reduction process [5].

Simultaneously with the formation of H_2 and WF_6, the evaporation of "free" HF occurs in the electrochemical reactor (Table 1, line *18*), the intensity of which, according to Raoult's law, is proportional to its content in the electrolyte (line *2*). This does not create insurmountable difficulties for the industrial implementation of the process, since the evaporated HF passes through the reduction apparatus, mixes with the HF, and is absorbed by the electrolyte. The presence of an increased content of HF in the gas mixture during the reduction of WF_6 with hydrogen leads to a decrease in the deposition rate of tungsten due to a decrease in the concentration of the reacting components, but at the same time allows to increase the process temperature (without deteriorating the quality of the deposited tungsten), which leads to an increase in the deposition rate of tungsten.

During saturation of the WF_6 electrolyte, its electrochemical synthesis was carried out at a temperature of ~32°C and the content of free HF was equal to ~1%. In this case, the HF evaporation rate was <0.1 g/h. Increasing the anode diameter up to 30 mm and the height of the molten electrolyte up to 72 mm with its full saturation and anode current density of ~0.3 A/cm^2 allows on to receive ~17 g/h (0.057 mol/h) WF_6 and 0.171 mol/h H_2 at the same evaporation rate of HF ~ 0.1 g/h (0.005 mol/h). The resulting gas mixture contains, mol %, Wf_6 (24.5), H_2 (73.5), and HF (2.0), which is the desired result. This gives grounds to recommend the following electrolyte composition (mol %) for practical use: $KWF_7(38) + NaWF_7(38) + LiHF_2(22) + HF(2)$. The density of such electrolyte is ~3 g/cm^3.

For the industrial implementation of the described process, it is advisable to use an electrolyzer with a filling anode, shown in Fig. 5 [30], which is a cone made of metal tungsten fragments 3–30 mm in size obtained by grinding waste or specially prepared for this. Such an anode has a large tungsten dissolution surface and a lower probability of passivation by bubbles of the evolved gas.

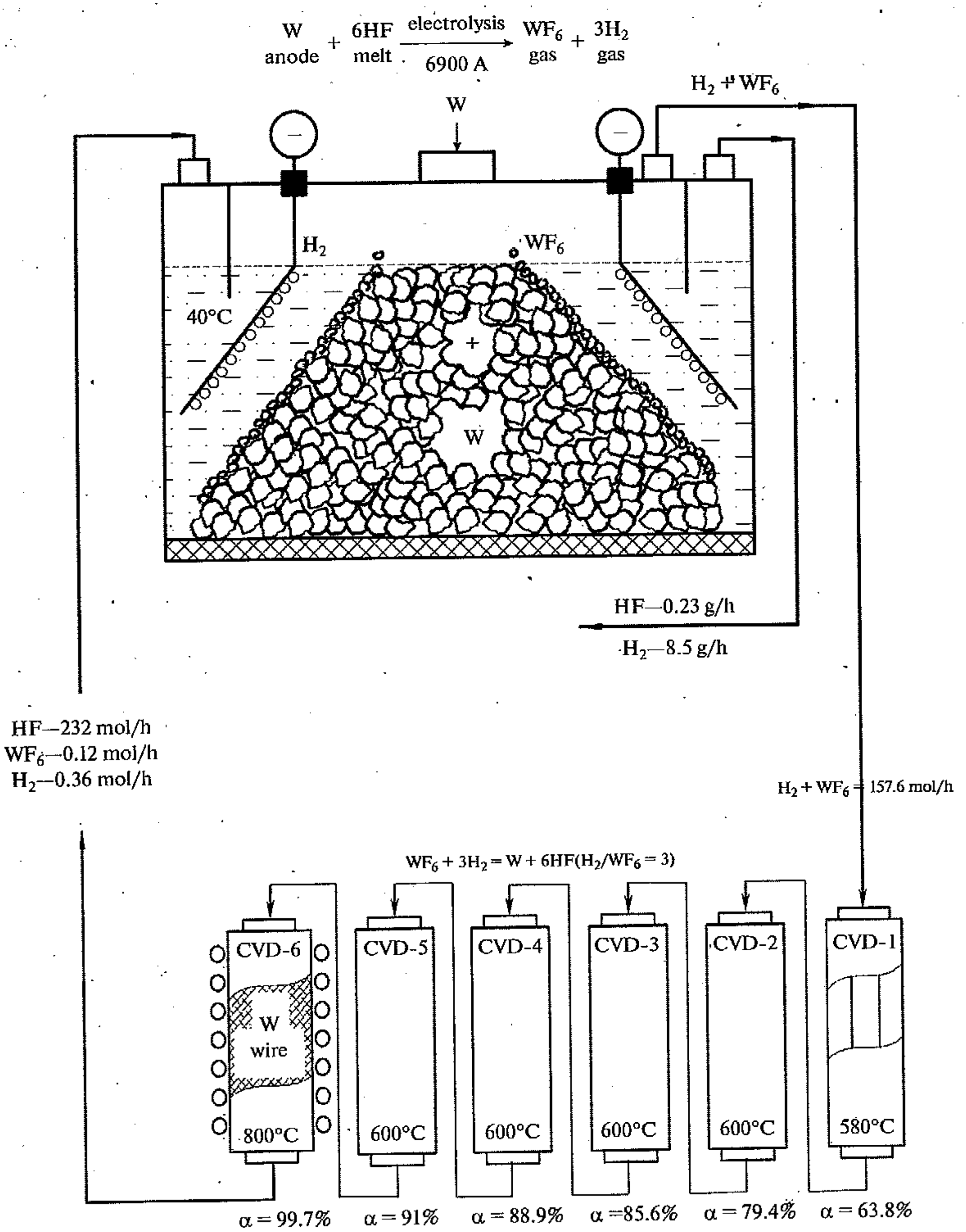

Fig. 5. Apparatus and technological scheme of a short fluoride cycle in tungsten technology with a capacity reaching 6.6 kg/h.

For synthesizing the gas mixture in the amount required according to Fig. 2, the filling anode should have a cone base of Ø1.2 m, a height of ~0.6 m, and a mass of ~2.2 t. The dimensions of the electrolyzer should be Ø1.5 m and height ~0.9 m (excluding the device for the additional loading of tungsten); the mass of the electrolyte in it is ~3 t. Similar to that shown in Fig. 2, in the electrolyzer between the cathode and the body, it is necessary to provide a gas duct for the passage of the gas mixture after the additional reduction of WF_6 with hydrogen to recovery the formed HF and unreacted WF_6. The hardware-technological scheme of a short fluoride cycle in tungsten technology with the same productivity as in Fig. 2 is shown in Fig. 5. It consists of electrochemical synthesis of a gaseous mixture of $WF_6 + H_2$ stoichiometric composition as a result of the dissolution of a filling tungsten anode in a melt containing (mol %): $KWF_7(38) + NaWF_7(38) + LiHF_2(22) + HF(2)$, and gas-phase deposition from the resulting mixture of semifinished products and finished products from dense tungsten. The resulting HF is returned to the electrolyzer for the synthesis of WF_6 and H_2. That is, like in Fig. 2, the reagents used are circulated; environmental standards hold true; and a small amount (<1 g/h) of harmful substances enters the ventilation, which cannot lead to an excess of the MPC in the outgoing gases [31].

In the event of emergencies, the process is practically safe for operators, because, when the power supply of the electrolyzer is turned off, the release of WF_6 stops.

To purge the reduction apparatus before and after the tungsten deposition processes, hydrogen is used from balloons (additional source), which is then expediently sent to the WF_6 additional reduction apparatus. This helps increase the completeness of WF_6 reduction, but at the same time increases the flow of hydrogen leaving the electrolyzer and carrying away HF and WF_6. Therefore, the gases leaving the electrolyzer gas duct after the absorption of HF and WF_6 must be sent to a ~10 L condenser cooled by "dry ice" (solid CO_2) to a temperature of –78°C. The equilibrium vapor pressure of HF and WF_6 at this temperature is equal to 0.6 and 0.06 kPa, respectively [26, 28], which ensures their almost complete condensation. Their release into ventilation (<1 g/h) cannot lead to an excess of the MPC. The product condensed at this temperature must be evaporated and sent to the WF_6 additional reduction apparatus simultaneously with hydrogen after purging the apparatus for target deposition of tungsten.

Capturing HF and WF_6 from gases directed to the ventilation can also be carried out by sorption on granular NaF at $t = 60–70$°C. The resulting product can be used for planned electrolyte replacement.

CONCLUSIONS

The electrochemical dissolution of a tungsten anode in a melt of complex fluorides of alkali metals and hydrogen fluoride makes it possible to synthesize on an industrial scale a gaseous mixture of $WF_6 + H_2$ with stoichiometric composition, intended for the production of semifinished and finished products from dense tungsten, which gives the possibility of excluding from the previously described fluoride cycle in tungsten technology (Fig. 2) [1] the production of fluorine, devices for tungsten fluorination, and the condensation of the resulting WF_6. As a result, the chain of technological devices is reduced almost 2 times, which, accordingly, reduces the investment in the creation of production, as well as costs and depreciation deductions in the cost of production.

Considering that the described technological cycle is based on relatively low-temperature processes (≤800°C), the direct consumption of electricity for the production of 1 kg of deposited tungsten is 18–20 kWh, which is significantly less than the existing technology based on powder metallurgy methods [1–3]. The involvement of metal waste in the cycle also reduces the cost of production.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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