

UDC 546.832:621.357

*A.P. Mukhachev*<sup>a</sup>, *V.G. Nefedov*<sup>b</sup>, *D.O. Yelatontsev*<sup>a, c</sup>, *O.A. Kharytonova*<sup>c</sup>**ANALYSIS OF THE TECHNOLOGY OF ELECTROCHEMICAL PRODUCTION OF HAFNIUM**<sup>a</sup> Institute of Geotechnical Mechanics named by N. Poljakov, National Academy of Sciences of Ukraine, Dnipro, Ukraine<sup>b</sup> Ukrainian State University of Chemical Technology, Dnipro, Ukraine<sup>c</sup> Dnipro State Technical University, Kamianske, Ukraine

The paper analyzes promising industrial processes for obtaining electrolytic hafnium powder. It is shown that extraction and iodide refining are the main processes used to purify hafnium from impurities, achieving both reactor-grade and high purity. The conducted studies have demonstrated the possibility of creating an alternative, more economical, and environmentally safe technology for hafnium recovery, compared to the current magnesium-thermal method. Production of reactor hafnium by electrolysis from molten electrolyte  $K_2HfF_6-KCl-KF$  is possible due to obtaining hafnium oxynitrate salt of nuclear purity and the creation of a hermetic electrolyzer. It is shown that the process of electrolysis leads to the accumulation of potassium fluoride in the electrolyte and requires its periodic draining with deterioration of technological indicators associated with increased recycling of the electrolyte. It was found that along with hafnium, metallic potassium is released on the cathode, which additionally worsens the technical and economic indicators of production. Sealing the electrolyzer makes it possible to create an overpressure of anode gas and determine its quantitative and chemical composition. Processing hafnium cathode sludge with potassium carbonate solution preserves the potassium cycle in the system and eliminates the effluents generated by ammonium carbonate.

**Keywords:** electrolysis, hafnium, electrolyzer, chloride-fluoride melt, cathode precipitate.**DOI:** 10.32434/0321-4095-2024-154-3-113-121**Introduction**

The applications of hafnium depend on its physical, chemical and mechanical properties, as well as on the purity of the metal, which is determined by the purity of the starting salts used to produce it. Historically, sodium and magnesium thermal methods of producing hafnium powder as a neutron-absorbing material were the first processes, which was determined by the availability of raw materials, hafnium salts, primarily chloride ( $HfCl_4$ ) and potassium fluorohafnate ( $K_2HfF_6$ ) [1].

Hafnium salts were not of high purity due to technological shortcomings in the processes of their production using toxic chlorine. The powders fabricated from these salts were not pure enough and contained

gas impurities (O and N) that did not allow for the production of ductile metal. The powders were purified to international ASTM standards by a low-yield iodide refining process in a vacuum to produce volatile hafnium iodide and its decomposition on a molybdenum or hafnium filament at temperatures up to 1700°C. The hafnium was produced in the form of compact bars and melted by vacuum arc method into larger ingots for further processing [2].

The iodide method reduced the oxygen content to less than 0.03%, nitrogen to less than 0.005%, and carbon to less than 0.01%. The metal had a purity of 99.8% with a zirconium content of  $\leq 4.5\%$ . This was caused by the technical level of the extraction technology for separating zirconium and hafnium. In

© A.P. Mukhachev, V.G. Nefedov, D.O. Yelatontsev, O.A. Kharytonova, 2024

This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

fact, this metal was an alloy and could not be used in reactor construction, as it formed zirconium hydrides that were less stable than hafnium hydride when irradiated, leading to the destruction of products. For use in nuclear engineering, the zirconium content in hafnium should not exceed 0.5%.

The electrolytic method of producing hafnium powder from the  $\text{HfCl}_4\text{-NaCl-KCl}$  electrolyte was first implemented in Ukraine at the Vilnohirsk Mining and Metallurgical Plant in an open electrolyzer. The electrolytic hafnium powder was subjected to iodide refining as it was contaminated with gas impurities (O and N). Hafnium in the form of a 10 mm diameter wire was expensive and met the needs of scientific research only. Electrolytic hafnium powder was fused with nickel (5 wt.%) and used as a ligature to produce heat-resistant alloys applied to aircraft engine turbine blades.

In the US, UK and France, hafnium chloride became the basis for magnesium-thermal reduction of sponge and its iodide refining, which required the creation of by-products of chlorine and magnesium. The production of hafnium powder by electrolysis from an electrolyte based on  $\text{K}_2\text{HfF}_6$  eliminates the need for these industries [3].

The use of hafnium can be divided into two areas: nuclear and physical. The first area is related to the nuclear properties of hafnium as an absorber of thermal and fast neutrons [4]. The second is related to the emission properties of hafnium having a low electron yield energy, which is important for radio engineering.

As an absorbing material in thermal neutron reactors, hafnium is used in the form of a tube, plate, rod or wire. Iwasaki and Konashi [5] showed that it can be used in fast neutron reactors in the form of hafnium hydride powder.

Hafnium powder fabricated by electrolysis is a cleaner product for producing cheap hydride than metallothermal powder or sponge [6]. The high melting point of hafnium (2227°C) determines its use as an alloying component in the metallurgy of heat-resistant alloys for aviation and space applications. All areas of application of high-purity hafnium are science-intensive, which determines the prospects for a more efficient electrochemical technology for its production [7].

Electrolytic hafnium powder of reactor purity, obtained from chemically pure hafnium salts in the electrolyte  $\text{K}_2\text{HfF}_6\text{-KCl}$  and  $\text{HfF}_4\text{-KCl}$ , was first produced at the Pridneprovsky Chemical Plant (Ukraine) in an open electrolyzer. The salts  $\text{K}_2\text{HfF}_6$  and  $\text{HfF}_4$  were obtained from hafnium oxide with a zirconium content of less than 0.5% and transition

metal impurities of less than  $1 \cdot 10^{-2}\%$  [8]. The studies confirmed the possibility of obtaining hafnium powder from salt melt by electrolysis.

Wu et al. [9] studied the cathodic mechanism of reduction of  $\text{Hf}^{4+}$  ions in a molten salt system based on  $\text{K}_2\text{HfF}_6$ . It was shown that large hafnium dendrites are formed in the chloride-fluoride melt. The introduction of sodium ions into the electrolyte increases its electrical conductivity and current efficiency, but complicates the technology of cathode sludge and electrolyte processing, as it leads to the generation of waste containing NaF. Studies [10,11] have been devoted to the electrolysis of hafnium chlorides in the  $\text{NaCl-KCl}$  electrolyte, but the high elasticity of  $\text{HfCl}_4$  vapor complicates the electrolysis process.

The anode process that causes anode destruction in a chloride-fluoride electrolyte was described in ref. [12]. The small amount of data in the literature on anodic processes in hafnium electrolysis is explained by the fact that their analysis is possible only in a continuously operating closed electrolyzer without air access.

Vutova et al. [13] reported the features of the cathodic processes, including the electrorefining of hafnium from metal scrap containing impurities that need to be removed. Despite a long period of research on the hafnium electrolysis process, there is no information on its industrial implementation in the literature.

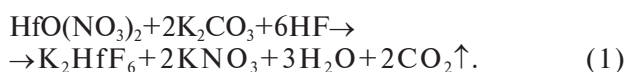
This study aimed to investigate the process of hafnium electrolysis from a molten electrolyte of the composition  $\text{K}_2\text{HfF}_6\text{-KCl-KF}$  in a sealed electrolyzer; establish and analyze the technological parameters that determine the technical and economic indicators of the process; develop reasonable stoichiometric reaction equations; and assess the quality of cathode powder.

### **Experimental**

#### *Procedure for obtaining the initial hafnium salt*

Potassium fluorohafnate  $\text{K}_2\text{HfF}_6$  for electrolysis was prepared from a solution of hafnium oxynitrate, bypassing the stage of obtaining  $\text{HfO}_2$ . The method of reagent injection, specific consumption rates, and process time were determined when obtaining the prototype powder samples.

A hafnium nitrate solution with a concentration of 100–200 g/dm<sup>3</sup> and an acidity of 600 g/dm<sup>3</sup>  $\text{HNO}_3$  was treated with dry  $\text{K}_2\text{CO}_3$  and 40% HF solution in a stoichiometric ratio to achieve pH 4 according to reaction (1):



As a result of reaction (1), crystals  $K_2HfF_6$  were obtained. After washing and drying, the crystals had the following chemical composition (%): Hf 47.9, Zr 0.19, F 30.5, Ni 0.003, Fe 0.01, Al 0.003, and  $SiO_2$  0.03. The content of zirconium with respect to the sum of metals was 0.4%.

#### *Methodology of the pilot experiment*

To conduct pilot studies and determine the optimal technological parameters, 10 kA hermetic electrolyzers were used (Fig. 1), which consisted of a closed water-cooled bath of X18H10T steel (analogue of AISI 321), anodes of graphite of the EG-0 grade, and cathodes of X18H10T steel. The KCl electrolyte was melted using an alternating current supplied to the graphite electrodes. The KCl melt was cooled by water through caissons welded to the bath body and walls. The integrity of the garnish was controlled by measuring the resistance of at least 50 ohms. The current density was from 2 to 3 A/cm<sup>2</sup>. The main parameters of electrolysis are given elsewhere [14].

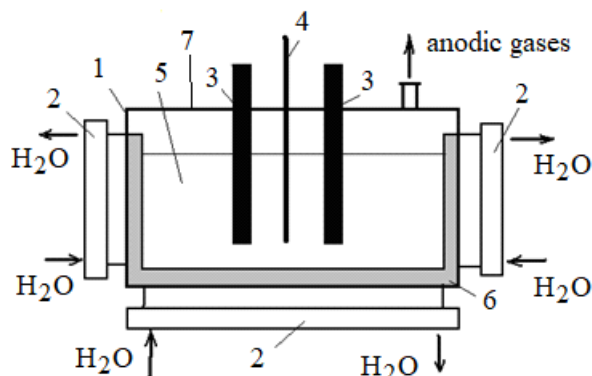


Fig. 1. Schematic diagram of a sealed electrolyzer for the production of hafnium powder: 1 – body; 2 – caissons; 3 – anodes; 4 – cathode; 5 – molten electrolyte; 6 – garnish; 7 – cover

After surfacing the electrolyte in a bath of a given height, the dosage of  $K_2HfF_6$  was added to obtain a hafnium concentration in the electrolyte of at least 4%. The electrolyzers reached the working electrolyte composition within two days. The electrolyte was analyzed for the content of  $K_2HfF_6$ , KCl and KF every 6 hours. The composition of the anode gases in the closed electrolysis mode in an electrolyzer with a load of 10 kA was determined by the chromatographic method. Chlorine in the anode gas was captured with lime milk. The quality of the gas purification from chlorine was controlled by gas sampling. The cathode precipitate (CP) was processed according to the scheme described elsewhere [14] and its chemical composition was analyzed according to standard methods [15].

During the experiment, the specific rates of reagents, yield and quality of hafnium powder were determined. The processing of the cathode sludge resulted in the production of two types of powders (closed and open electrolysis mode), the separation of  $K_2HfF_6$  crystals, and the separation of KCl and KF salts. Potassium fluoride was used as a reagent to obtain  $K_2HfF_6$ , partially replacing 40% hydrofluoric acid. The salt solution was evaporated until KCl crystals precipitated, which were returned to the electrolysis process.

Anode gas is a by-product that is a mixture of chlorine and the sum of CFCs 11-14 (freons F-11, F-12, F-13, and F-14) in the presence of oxygenated carbon compounds and water vapor within 5%. Analysis of literature data showed the possibility of replacing lime milk used for chlorine sanitization in the production of electrolytic zirconium with a 20% NaOH solution to obtain a commercial product, sodium hypochlorite grade A, which is part of the «Bilizna» bleaching agent. This prevents the formation of chloride industrial wastewater and makes the technological scheme closed. CFC recycling schemes are known, which allows their use to produce by-products such as fluoroplastic and CFCs.

#### *Results and discussion*

*Analysis of the operation of an industrial electrolyzer for the production of hafnium with a current load of 10 kA*

It is known that hafnium, like zirconium, is precipitated under diffusion control, i.e., the amount of electricity and the amount of product obtained is proportional to the concentration of the substance in the electrolyte. The concentration of  $K_2HfF_6$  was increased to 20.7%, KF to 26%, and KCl to 53.3% after the process reached the operating mode. It was found that the electrolysis process of the  $K_2HfF_6$ –KCl electrolyte proceeded with an increase in the concentration of KF. As a result of the electrochemical decomposition of  $K_2HfF_6$  over two days, the KF content increased from 2.8% to 26%. At the same time, the KCl concentration decreased from 90.8% to 53–55%. Subsequently, the required electrolyte composition was adjusted by changing the ratio of  $K_2HfF_6$  to KCl. The hafnium concentration was increased after 48 h of the process to reduce the open electrolysis time and increase the process performance.

All the salts were in the melt in a dislocated state, so the concentration of  $K^+$  ions,  $Cl^-$ ,  $F^-$ ,  $[HfF_6]^{2-}$  was 46.7%, 27%, 8.5%, and 16%, respectively.

The data characterizing the operation of an industrial electrolyzer with a current load of 10 kA are shown in Table 1.

Table 1  
Data characterizing the operation of an industrial electrolyzer with a current load of 10 kA

Parameter	Value
Current strength, A	10000
Hafnium productivity, kg/day	200
Average current efficiency, %	50–55
Voltage, V	10–15
Anode current density, A/cm <sup>2</sup>	0.2–0.3
Cathodic current density, A/cm <sup>2</sup>	3.0
Extraction of hafnium from K <sub>2</sub> HfF <sub>6</sub> into cathode precipitate, %	88.6
Yield of hafnium from cathode precipitate, washed powder, %	74.5
Electrolyte temperature, °C	750–800
Machine time factor	0.85
Composition of the electrolyte supply:	
K <sub>2</sub> HfF <sub>6</sub>	by calculation
KCl	by calculation
Composition of the cathode deposit, %:	
Hf	45
K <sub>2</sub> HfF <sub>6</sub>	9.5
KCl	8.0
KF	14
C (powder)	2.0
Composition of anode gases, %:	
chlorine	50–60
freons	40–50

Based on industrial tests, specific consumption rates of reagents and raw materials were determined (Table 2).

Let's determine the current efficiency of hafnium based on the performance of the electrolyzer.

The amount of electricity that passed through the electrolyzer per day can be found as:

$$Q_{\Sigma} = I\tau K = 10000 \cdot 24 \cdot 0.85 = 204000 \text{ A}\cdot\text{h.} \quad (2)$$

where  $Q_{\Sigma}$  is the amount of electricity;  $I$  is the current load;  $\tau$  is the electrolysis duration;  $K$  is the coefficient of machine time.

Consumption of the amount of electricity to obtain 200 kg/day of hafnium can be calculated in the following way:

$$Q_{\text{Hf}} = m/k = 200000/1.67 = 119760 \text{ A}\cdot\text{h.} \quad (3)$$

From here, we can get the current efficiency (CE) of hafnium:

$$CE_{\text{Hf}} = Q_{\text{Hf}}/Q_{\Sigma} = 119760/204000 = 0.59. \quad (4)$$

Since only a part of the electricity is spent on

the hafnium release, the rest goes to the release of potassium. Hence the current efficiency of potassium can be determined as:

$$CE_{\text{K}} = 1 - CE_{\text{Hf}} = 0.41. \quad (5)$$

The amount of potassium required to ensure the cathodic process will be:

$$m_{\text{K}} = k_{\text{K}} Q_{\text{K}} CE_{\text{K}} = 1.45 \cdot 204000 \cdot 0.41 = 122165 \text{ g} \\ \text{or } 3132 \text{ moles,} \quad (6)$$

where  $k_{\text{K}}$  is the electrochemical equivalent of potassium.

200 kg of hafnium metal contains 11.205 moles of this metal. Potassium fluorohafnate contains twice as many moles of potassium, i.e.  $N_{\text{K}(\text{K}_2\text{HfF}_6)} = 2241$  mol. Then, to balance the cathodic process in terms of potassium, extra KCl must be introduced into the electrolyte:

$$N_{\text{KCl}} = N_{\text{K}\Sigma} - N_{\text{K}(\text{K}_2\text{HfF}_6)} = 3132 - 2241 = 891 \text{ mol.} \quad (7)$$

To compile the stoichiometric equation, let's determine the molar ratio of K<sub>2</sub>HfF<sub>6</sub> to KCl:

$$M_{\text{K}_2\text{HfF}_6}/M_{\text{KCl}} = 1120.5/891 = 1.26. \quad (8)$$

This corresponds to a mass ratio of 5:4. Therefore, 5 moles of K<sub>2</sub>HfF<sub>6</sub> and 4 moles of KCl are required to ensure the cathodic process. To restore the indicated amounts of hafnium and potassium in moles, 5·4+4=24 Faradays of electricity are required.

#### Anodic processes

In early work on the electrolysis of chloride-fluoride melts, it was believed that only chlorine was released at the anode. This was because the standard potential of fluorine is +2.85 V, and that of chlorine is +1.36 V. In subsequent works by Delimarskyi et al., the possibility of interaction of fluorine with a carbon anode was shown, which results in the formation of freons of the CCl<sub>x</sub>F<sub>4-x</sub> type through the C<sub>x</sub>F<sub>y</sub> interaction, where  $x \approx 3.9-4.8$ . The reaction of the interaction of fluorine with carbon is accompanied by a significant release of energy, therefore, as a result of depolarization, the potential of fluorine decreases to 0.9, which is lower than the release potential of chlorine equal to 1.2 V at a temperature of 700°C. A chemical transformation is described by the following reaction:



The CF-compounds form a dense inert, non-conductive film on the surface of the graphite anode,

Table 2

**Specific consumption rates of reagents and raw materials for the production of hafnium hydroxide, fluorohafnate and electrolytic hafnium powder**

Input stream	Value	Unit	Output stream	Value	Unit
<b>Hf(OH)<sub>4</sub></b>					
Raw materials (semi-products):			Product:		
– hafnium nitrate solution from the extraction area	7.2	m <sup>3</sup>	– Hf(OH) <sub>4</sub>	1000	kg
Materials:			Industrial wastewater	99.2	m <sup>3</sup>
– NaOH technical	1.8	t			
Energy resources:					
– electricity	139.7	kWh			
– condensation	92.2	t			
– compressed air	205.3	m <sup>3</sup>			
<b>K<sub>2</sub>HfF<sub>6</sub></b>					
Raw materials (semi-products):			Product:		
– Hf(OH) <sub>4</sub>	1428.8	kg	– K <sub>2</sub> HfF <sub>6</sub>	1000	kg
Materials:			Industrial wastewater	15.6	m <sup>3</sup>
– KCl	1.5	t			
– HF	0.6	T			
– CaO solution	8.1	m <sup>3</sup>			
– NH <sub>3</sub> 25%	0.3	t			
Energy resources:					
– electricity	128.2	kWh			
– steam	1.8	Gcal			
– condensation	4.8	t			
– compressed air	2.3	m <sup>3</sup>			
– recycled water	206.7	m <sup>3</sup>			
<b>Electrolytic hafnium powder</b>					
Raw materials:			Product:		
– K <sub>2</sub> HfF <sub>6</sub>	4460	kg	– electrolytic hafnium powder	1000	kg
			hafnium turnovers:		
			– solid	680	kg
			– solutions (pulp)	19.2	m <sup>3</sup>
Materials:			Waste:		
– KCl 98%	1.2	T	Industrial wastewater	62.6	m <sup>3</sup>
– Ar	350	Kg			
– NaC	800	kg			
– NH <sub>3</sub> 25%	0.8	t			
– H <sub>2</sub> SO <sub>4</sub> technical	0.12	t			
– CaO solution	28	m <sup>3</sup>			
Energy resources:					
– electricity	73000	kWh			
– steam	4.5	Gcal			
– condensation	3.8	t			
– compressed air	29400	m <sup>3</sup>			
– recycled water	8820	m <sup>3</sup>			
– household water	50	m <sup>3</sup>			

as a result of which, under certain conditions of electrolysis, an anodic effect is possible with the formation of mainly carbon fluoride (CF<sub>4</sub>), which leads to the destruction of the anode.

According to the given data, the following mechanism of freon formation is proposed. At the first stage, a two-stage oxidation of carbon occurs

with the formation of CFCI by reaction (10), which is a precursor for the formation of CFCs by reactions (11)–(15), which consumes 2 Faradays of electricity:



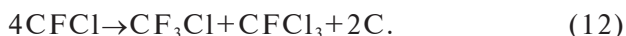
CFCI enters into disproportionation reactions

with the formation of the following freons:

– freon-12:



– freon-13 and freon-11:



Freon-14 can be formed by the following reactions:

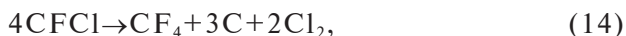
– from freon-13 and CFCl:



– from freon-12:



– from CFCl:



– from CF:



The formation of freon-12 freon-13, freon-11 freon-14 consumes 4, 8, 8 and 6 Faradays of electricity, respectively, whereas both reactions (14) and (15) consume 8 Faradays. It can be assumed that the reaction (13) of obtaining freon-14 is more preferential, because it requires the participation of a smaller amount of electricity. However, a significant part of freon-13 is consumed.

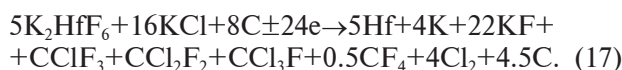
The main condition for writing the reaction equation for obtaining hafnium is the same amount of electricity passing through the electrodes, in this case, 24 Faradays. The percentage ratio of freons in the anode gas is unknown. As a first approximation, the formation of freons according to reactions (11), (12) and (15) is taken as follows:  $0.5\text{CF}_4:\text{CF}_3\text{Cl}:\text{CF}_2\text{Cl}_2:\text{CFCl}_3=0.5:1:1:1$ .  $4+4+4+4=16$  Faradays of electricity is spent on the formation. At the same time, 3.5 moles of carbon are consumed, one mole of chlorine is additionally formed, and 4.5 moles of graphite dust are released into the electrolyte. The total consumption of graphite anode is 8 moles.

Since 24 Faradays of electricity are involved in the cathodic processes, the release of chlorine remains 8 Faradays. One mole of chlorine consumes 2 Faradays of electricity in the following reaction:



That is, 5 mol of chlorine is released at the electrodes in total. 6 chlorine atoms or 3 moles are spent on the formation of freons. Thus, the total amount of chlorine involved in the anodic process is 7 moles or 14 atoms. This means that 10 moles of KCl must be added to the 4 moles of KCl that provide cathodic processes. Another 2 mol of KCl is required for the balance of fluorine and chlorine: a total of 16 mol of KCl.

The performed calculations allow writing the following stoichiometric reaction equation:



Let's analyze equation (17):

– the balance is reconciled in terms of the amount of electricity on the right and left sides of the equation;

– the ratio of chlorine to freons is 4.0 to 3.5 moles, respectively, that corresponds to the values given in Table 1 (50–60% to 40–50%, respectively);

– KF appears in the electrolyte, the presence of which is noted in Table 2.

All this allows us to consider the proposed equation quite adequately describes the processes taking place in the electrolyzer.

The amount of potassium fluorohafnate, which contains 200 kg of hafnium, is determined by the following proportion with molecular masses:

$$m_{\text{K}_2\text{HfF}_6} = (M_{\text{K}_2\text{HfF}_6} / M_{\text{Hf}}) \cdot 200 = 415 \text{ kg}. \quad (18)$$

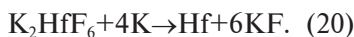
Taking into account that the degree of extraction of hafnium from the salt is 88.6%, the total requirement of potassium hexafluoride is approximately 469 kg. If we assume that the degree of use of potassium chloride is approximately equal to 88.6%, then it is possible to determine its required amount from equation (15) by proportion:

$$m_{\text{KCl}} = (5M_{\text{K}_2\text{HfF}_6} / 16M_{\text{KCl}}) \cdot 469 = 728 \text{ kg}. \quad (19)$$

Feeding of the electrolyzer with salts is carried out separately, which allows for maintaining a constant content of hafnium in the electrolyte by adjusting the ratio of  $\text{K}_2\text{HfF}_6$  and KCl supplied.

*Possible side reactions in the electrolyzer*

In the case of an insufficient amount of  $\text{K}_2\text{HfF}_6$  in the electrolyte, reactions (10) and (11) are possible, which increase the specific consumption of electricity. Potassium metal can reduce hafnium hexafluorohafnate due to the formation of the complex ion  $[\text{HfF}_6]^{2-}$  at 750°C:



The resulting hafnium powder is finely dispersed and has a size of 10–20  $\mu\text{m}$ . Reaction (20) leads to an increase in the yield of hafnium in the cathode deposit and an increase in the concentration of KF in the electrolyte. Since potassium metal has a density approximately 3 times less than the density of the electrolyte, it floats to the surface of the electrolyte, simultaneously interacting with chlorine and hexafluorohafnate according to reactions (21) and (20), respectively.



Formed potassium chloride reacted anew:



Fine-dispersed hafnium powder during the processing of CP is released together with carbon powder and is sent to chemical separation and purification. One cannot also deny the possibility of fluorinating the powder formed by the reaction:



The process described by reaction (22) also reduces the hafnium current efficiency.

#### *Cathode deposit processing*

CP is a mixture of hafnium powder, KCl, KF,  $\text{K}_2\text{HfF}_6$  salts, as well as finely dispersed carbon and potassium. Short circuits of closed and open mode are processed according to the same, but autonomous schemes, preventing their mixing. The technical conditions for the content of impurities are met only by the powder of the closed mode (Table 3).

The open-circuit powder, with a yield of up to 20% with respect to the total powder volume, contains a high content of oxygen and nitrogen and is directed for purification by iodide refining to produce hafnium rods with a diameter of 10 mm. This increases the cost of powder production by 15%. Both products (conditioned powder and iodide bar) are sent for vacuum arc or electron beam remelting to produce a functional billet.

The use of potassium carbonate solution (potash)

to wash KCl, KF and  $\text{K}_2\text{HfF}_6$  salts from the powder is technically more feasible than ammonium carbonate, as it eliminates the generation of unprocessed wastewater. Potash makes it possible to preserve the potassium cycle and obtain a virtually waste-free process. The presence of the mixture of KF and KCl salts in the solution after the separation of  $\text{K}_2\text{HfF}_6$  crystals allows them to be successfully separated due to the difference in water solubility at 20°C and 90°C.

Recycling of the drained electrolyte allows for the simultaneous production of a concentrated KF solution to replace hydrofluoric acid, thus paying off the costs of increased electricity consumption and closing the technological cycle. The industrial scheme of hafnium KF processing, similar to zirconium, can be implemented on pulsation columns with a distribution nozzle, which will reduce the specific consumption of energy resources and the yield of powder for chemical processing [15].

#### **Conclusions**

1. The fabrication of hafnium powder in hermetic electrolyzers with a current load of 10 kA from the electrolyte  $\text{K}_2\text{HfF}_6$ –KCl–KF was studied for the first time.

2. The current efficiencies of the cathode and anode processes were analyzed. It was shown that the low (55%) hafnium current efficiency is associated with the side processes of oxidation-reduction of potassium, chlorine and fluorine.

3. Based on the calculations of electrode reactions, stoichiometric equations of reactions occurring in the electrolyzer at a temperature of 750°C and a given ratio of  $\text{K}_2\text{HfF}_6$  to KCl were proposed.

4. The estimated capacity of the 10 kA electrolyzer for hafnium powder was 40 tons per year.

5. The evolution of chlorine in the anode gas requires processing to obtain commercial products (sodium hypochlorite, hydrochloric acid or liquid chlorine).

6. Processing of cathode sludge using potassium carbonate allows creating a closed cycle for potassium chloride and then using the resulting KF to produce  $\text{K}_2\text{HfF}_6$  in the processing of metal turnovers.

7. The electrolytic method of hafnium production from the electrolyte  $\text{K}_2\text{HfF}_6$ –KCl–KF allows for a waste-free process flowsheet and ensures the reactor purity of the metal.

Table 3

**Characteristics of hafnium powder produced in open and closed electrolyzers**

Component	Concentration (wt.%)		Iodine refining	Technical specifications 48-4-176-85
	open mode	closed mode		
N <sub>2</sub>	0.5	0.003–0.004	<0.003	≤0.005
O <sub>2</sub>	<1.0	0.03–0.05	<0.02	≤0.05

## REFERENCES

1. *Tricot R.* The metallurgy and functional properties of hafnium // *J. Nucl. Mater.* – 1992. – Vol.189. – No. 3. – P.277-288.
2. *Negodin D.A., Khar'kovskii D.N.* Development in the production of hafnium wire conforming to ASTM B737 standard // *Metallurgist.* – 2021. – Vol.64. – No. 9-10. – P.974-983.
3. *Mukhachov A., Kharitonova O., Terentieva O.* Hafnium oxide as efficient material for a new generation dielectric // *Acta Phys. Pol. A.* – 2018. – Vol.133. – No. 4. – P.778-780.
4. *Application of hafnium hydride control rod to large sodium cooled fast breeder reactor* / Ikeda K., Moriwaki H., Ohkubo Y., Iwasaki T., Konashi K. // *Nucl. Eng. Design.* – 2014. – Vol.278. – P.97-107.
5. *Iwasaki T., Konashi K.* Development of hydride absorber for fast reactor—application of hafnium hydride to control rod of large fast reactor // *J. Nucl. Sci. Technol.* – 2009. – Vol.46. – No. 8. – P.874-882.
6. *Production of nuclear grade zirconium: a review* / Xu L., Xiao Y., Van Sandwijk A., Xu Q., Yang Y. // *J. Nucl. Mater.* – 2015. – Vol.466. – P.21-28.
7. *Domestic and international present status and utilization of hafnium resource* / Bo Y., Liu X., Li Y.G., Cai Z.Y. // *Appl. Mech. Mater.* – 2013. – Vol.423-426. – P.679-684.
8. *Korovin Yu.F.* Zero-waste technology of nuclear-pure zirconium // *Coll. Res. Pap. Natl. Mining Univ.* – 2014. – Vol.44. – P.152-161.
9. *Electrochemistry of Hf(IV) in NaCl–KCl–NaF–K<sub>2</sub>HfF<sub>6</sub> molten salts* / Wu Y.K., Yan G.Q., Chen S., Wang L.J. // *Int. J. Miner. Metall. Mater.* – 2020. – Vol.27. – P.1644-1649.
10. *Electrochemical reduction behavior of Hf(IV) in molten NaCl–KCl–K<sub>2</sub>HfCl<sub>6</sub> system* / Liu X., Wu Y.K., Chen S., Song B., Wang L.J. // *Rare Met.* – 2016. – Vol.35. – P.655-660.
11. *Electrochemical reduction of hafnium tetrachloride in molten NaCl–KCl* / Poinso J.Y., Bouvet S., Ozil P., Poinet J.C., Bouteillon J. // *J. Electrochem. Soc.* – 1993. – Vol.140. – P.1315-1320.
12. *Kuznetsov S.A., Kuznetsova S.V.* Hafnium in molten salts: electrochemistry, chemistry, electrodeposition // *ECS Proc. Vol.* – 2002. – Vol. 2002-19. – P. 622-639.
13. *Study of the possibility of recycling of technogenic hafnium during electron beam refining* / Vutova K., Stefanova V., Markov M., Vassileva V. // *Materials.* – 2022. – Vol.15. – Art. No. 8518.
14. *Mukhachov A.P., Kharytonova E.A.* Method for hafnium powder production by electrolysis // *Probl. At. Sci. Technol.* – 2018. – Vol.113. – No. 1. – P.203-207.
15. *Mukhachov A.P., Kharytonova O.A.* Development of process for producing zirconium powder of nuclear purity // *Metallofiz. Noveishie Tekhnol.* – 2020. – Vol.42. – No. 11. – P.1525-1535.

## АНАЛІЗ ТЕХНОЛОГІЇ ЕЛЕКТРОХІМІЧНОГО ОДЕРЖАННЯ ГАФНІЮ

*А.П. Мухачев, В.Г. Неведов, Д.О. Єлатонтсев, О.А. Харитонова*

У роботі виконано аналіз перспективних промислових процесів одержання електролітичного порошку гафнію. Показано, що основними афінажними процесами його очищення від домішок до реакторної та особливо високої частоти залишаються екстракція та йодидне рафінування. Здійснені дослідження показали можливість створення альтернативної, більш економічної та екологічно безпечнішої технології відновлення гафнію, ніж чинна магнієтермічна. Одержання реакторного гафнію методом електролізу з розплавленого електроліту K<sub>2</sub>HfF<sub>6</sub>–KCl–KF стало можливим завдяки одержанню солі оксинітрату гафнію ядерної чистоти та створенню герметичного електролізера. Показано, що процес електролізу призводить до накопичення в електроліті фториду калію і вимагає періодичного його зливу з погіршенням технологічних показників, пов'язаних з підвищенням рециклінгом електроліту. Виявлено, що поряд з гафнієм, на катоді виділяється металевий калій, який додатково погіршує техніко-економічні показники виробництва. Герметизація електролізера дає змогу створити надлишковий тиск анодного газу і визначити його кількісний і хімічний склад. Переробка катодного осаду гафнію за допомогою розчину карбонату калію дозволяє зберегти калієвий цикл у системі та ліквідувати стоки, що утворюються під час використання карбонату амонію.

**Ключові слова:** електроліз, гафній, електролізер, хлоридно-фторидний розплав, катодний осад.

## ANALYSIS OF THE TECHNOLOGY OF ELECTROCHEMICAL PRODUCTION OF HAFNIUM

*A.P. Mukhachev<sup>a,\*</sup>, V.G. Nefedov<sup>b</sup>, D.O. Yelatontsev<sup>a,c</sup>, O.A. Kharytonova<sup>c</sup>*

<sup>a</sup> *Institute of Geotechnical Mechanics named by N. Poljakov, National Academy of Sciences of Ukraine, Dnipro, Ukraine*

<sup>b</sup> *Ukrainian State University of Chemical Technology, Dnipro, Ukraine*

<sup>c</sup> *Dnipro State Technical University, Kamianske, Ukraine*

\* e-mail: map45@ukr.net

The paper analyzes promising industrial processes for obtaining electrolytic hafnium powder. It is shown that extraction and iodide refining are the main processes used to purify hafnium from impurities, achieving both reactor-grade and high purity. The conducted studies have demonstrated the possibility of creating an alternative, more economical, and environmentally safe technology for hafnium recovery, compared to the current magnesium-thermal method. Production of reactor hafnium by electrolysis from molten electrolyte K<sub>2</sub>HfF<sub>6</sub>–KCl–KF is possible due to obtaining hafnium oxynitrate salt of nuclear purity and the creation of a hermetic electrolyzer. It is shown that the process of electrolysis leads to the accumulation of potassium fluoride in the electrolyte and requires its periodic draining with deterioration of technological indicators associated with increased recycling of the electrolyte. It was found that along with hafnium, metallic potassium is released on the cathode, which additionally worsens the technical and economic indicators of production. Sealing the electrolyzer makes it possible to create an overpressure of anode gas and determine its quantitative and chemical composition. Processing hafnium cathode sludge with potassium

Received 16.02.2024



carbonate solution preserves the potassium cycle in the system and eliminates the effluents generated by ammonium carbonate.

**Keywords:** electrolysis; hafnium; electrolyzer; chloride-fluoride melt; cathode precipitate.

#### REFERENCES

1. Tricot R. The metallurgy and functional properties of hafnium. *J Nucl Mater.* 1992; 189: 277-288. doi: 10.1016/0022-3115(92)90382-U.
2. Negodin DA, Khar'kovskii DN. Development in the production of hafnium wire conforming to ASTM B737 standard. *Metallurgist.* 2021; 64: 974-983. doi: 10.1007/s11015-021-01078-0.
3. Mukhachov A, Kharitonova O, Terentjeva O. Hafnium oxide as efficient material for a new generation dielectric. *Acta Phys Pol A.* 2018; 133: 778-780. doi: 10.12693/APhysPolA.133.778.
4. Ikeda K, Moriwaki H, Ohkubo Y, Iwasaki T, Konashi K. Application of hafnium hydride control rod to large sodium cooled fast breeder reactor. *Nucl Eng Design.* 2014; 278: 97-107. doi: 10.1016/j.nucengdes.2014.07.002.
5. Iwasaki T, Konashi K. Development of hydride absorber for fast reactor—application of hafnium hydride to control rod of large fast reactor. *J Nucl Sci Technol.* 2009; 46: 874-882. doi: 10.1080/18811248.2007.9711595.
6. Xu L, Xiao Y, Van Sandwijk A, Xu Q, Yang Y. Production of nuclear grade zirconium: a review. *J Nucl Mater.* 2015; 466: 21-28. doi: 10.1016/j.jnucmat.2015.07.010.
7. Bo Y, Liu X, Li YG, Cai ZY. Domestic and international present status and utilization of hafnium resource. *Appl Mech Mater.* 2013; 423-426: 679-684. doi: 10.4028/www.scientific.net/AMM.423-426.679.
8. Korovin YuF. Zero-waste technology of nuclear-pure zirconium. *Coll Res Paper NMU.* 2014; 44: 152-161.
9. Wu YK, Yan GQ, Chen S, Wang LJ. Electrochemistry of Hf(IV) in NaCl–KCl–NaF–K<sub>2</sub>HfF<sub>6</sub> molten salts. *Int J Miner Metall Mater.* 2020; 27: 1644-1649. doi: 10.1007/s12613-020-2083-3.
10. Liu X, Wu YK, Chen S, Song B, Wang LJ. Electrochemical reduction behavior of Hf(IV) in molten NaCl–KCl–K<sub>2</sub>HfCl<sub>6</sub> system. *Rare Met.* 2016; 35: 655-660. doi: 10.1007/s12598-014-0345-9.
11. Poinso JY, Bouvet S, Ozil P, Poignet JC, Bouteillon J. Electrochemical reduction of hafnium tetrachloride in molten NaCl–KCl. *J Electrochem Soc.* 1993; 140: 1315-1320. doi: 10.1149/1.2220977.
12. Kuznetsov SA, Kuznetsova SV. Hafnium in molten salts: electrochemistry, chemistry, electrodeposition. *ECS Proc Vol.* 2002; 2002-19: 622-639. doi: 10.1149/200219.0622PV.
13. Vutova K, Stefanova V, Markov M, Vassileva V. Study of the possibility of recycling of technogenic hafnium during electron beam refining. *Materials.* 2022; 15: 8518. doi: 10.3390/ma15238518.
14. Mukhachov AP, Kharytonova EA. Method for hafnium powder production by electrolysis. *Probl At Sci Technol.* 2018; 113: 203-207.
15. Mukhachov AP, Kharytonova OA. Development of process for producing zirconium powder of nuclear purity. *Metallofiz Noveishie Tekhnol.* 2020; 42: 1525-1535. doi: 10.15407/mfint.42.11.1525.