

METHOD FOR HAFNIUM POWDER PRODUCTION BY ELECTROLYSIS

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Principle possibility of hafnium metal powder production by electrochemical reduction of hafnium fluorides of various compositions was investigated. Optimum content of hafnium in cathode deposit was determined. Hydrometallurgical processing of cathode deposit using a 10% potassium carbonate solution demonstrated 95% efficiency of hafnium powder extraction. Electrolysis of hafnium fluoride salts in an open-type electrolysis does not make it possible to obtain hafnium metal powder with a low content of interstitial gas impurities and requires iodide refining to remove oxygen and nitrogen. Best process-oriented results were obtained by electrolysis of $\text{HfF}_4\text{-KCl-KF}$ -system.

INTRODUCTION

Incidental extraction of hafnium in the production of nuclear-pure zirconium in the world is realized using various technologies, the choice expediency of which is determined both by the requirements for the equipment availability, and the quality of the metal and its price. In industry, hafnium is obtained in the form of a sponge during the magnesium-thermal reduction of hafnium chloride or an ingot during the calcium-thermal reduction of hafnium fluoride. The process of hafnium electrolytic powder obtaining from a chloride electrolyte was studied for the first time in the paper [1].

Electrolytic hafnium powder was used for the first time for the production of nuclear-grade iodide hafnium rods in the USA in 1951 by the vapor deposition of hafnium tetraiodide onto the molybdenum wire [2]. In the organization of the zirconium nuclear-grade production in Ukraine, the extraction-fluoride technology for obtaining high-purity zirconium salts of zirconium and hafnium was used [3], so the use of hafnium fluoride salts, HfF_4 , K_2HfF_6 and K_3HfF_7 , not hafnium fluoride, in the electrolysis process was of practical interest.

Chloride-fluoride electrolytes for the electrolysis process were first used in the USA during the anodic refinement of a hafnium sponge obtained by the Kroll method [4]. According to [5], electrolytic cleaning of hafnium scrap from the melt to obtain a hafnium powder significantly reduces its cost value compared with the iodide process.

Data of the first papers on the production of hafnium powder from a mixture of fluorides and alkali metals are presented in paper [6].

Systematic studies of electrochemical reactions taking place during the electrolysis of salt melts containing hafnium were carried out at the Institute of Electrochemistry of the Ural Branch of the USSR Academy of Sciences by M.V. Smirnov and co-authors [7, 8].

The use of hafnium tetrafluoride (TFH) powder as a raw material for the production of hafnium powder by electrolysis was not only of scientific but also of practical interest. The quality of the metallic hafnium powder obtained by the electrolysis of molten salts depends on the quality of the initial hafnium fluoride, the industrial technique of which was to be developed.

There are anhydrous and aqueous methods for the fluorination of oxides, which have been studied with the example of REM oxides. The method of anhydrous gas fluorination of oxides (for example, REM oxides) was first tested in the USA [9]. This method concerns the reaction of gas and solid, the time and temperature of the process, providing the completeness of fluorination, reached 8 hours and 700° .

The aim of this work was to study the processes of electrolytic production of hafnium powder and its extraction from cathode deposit.

DESCRIPTION OF FULL-SCALE EXPERIMENT

To carry out the process of electrolysis, a deep TFH purification was required. It must be purified from retained gas impurities and has an optimal grain content. For this to be done, it was subjected to vacuum sublimation refining using a semi-industrial installation of C-500 type. The sublimator is a cylindrical glass, the inner surface of which acts as a condenser and is made of X18H10T alloy. A rod heater was installed with a block-package of plates fixed on it with a rough hafnium tetrafluoride in the central axis of the sublimator [11].

the principle of sublimator operation was as follows:

- when the residual pressure in the device is not more than 0.1 mm Hg, heating of the heater is switched on;
- hafnium tetrafluoride at a temperature of $T = 760^\circ\text{C}$ is sublimated from the plates and condensed on the condenser;
- the device is filled with purified argon;
- after cooling to 40°C it is disassembled to discharge the sublimate and the residue from the plates.

The production of TFH, applicable to the electrolysis process, required the creation of the device for grinding its sublimated crystals, 5 mm in size, to a particle size of less than 1.0 mm, in an argon atmosphere, without air access.

The processes of “wet” TFH production, K_3HfF_7 and K_2HfF_6 were studied along with dry process of TPH obtaining. Pilot batches of these products were used to study the technological features of the hafnium electrolysis process in molten salts.

The chemical composition of hafnium compounds, powder of metal hafnium obtained by electrolysis of its fluorides and iodide hafnium is shown in Tabl. 1. For

the preparation of electrolyte, potassium chloride of the "r" State Standard 4234-69 grade was used. Its chemical composition after drying is indicated in Tabl. 2.

Table 1

No	Product name	Impurity contain, % (weight)*								
		Fe	Al	Si	Ni	Cr	Zr	N	O	C
1	Hafnium dioxide	0.004	0.003	0.002	0.001	0.002	0.48	–	–	–
2	Hafnium tetrafluoride	0.17	0.010	0.010	0.004	0.001	–	–	–	–
3	Potassium hexafluorophanate	0.004	0.008	0.012	0.002	0.001	–	–	–	–
4	Potassium heptafluorophanate	0.004	0.006	0.016	0.001	0.0003	–	–	–	–
5	Metallic hafnium Powder after electrolysis	0.021	0.006	0.002	0.002	0.005	0.54	0.14	0.25	0.1
6	Iodide hafnium State Standard 22517-77	0.04	0.005	0.005	0.05	0.003	0.8	0.005	0.02	0.01

Table 2

Contain, wt.%						
KCl	Si	Fe	Cr	Al	Ni	W
	$2.26 \cdot 10^{-3}$	$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$	$4.0 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$	0.05

The electrolyzer was supplied with direct current from an individual source. Melting of the electrolyte to the working level required 36 hours in order to make its composition consistent with the specified one. The volume of molten electrolyte in the bath was 14 liters. The protective layer of the skull between the electrolyzer wall and the molten salt formed as a result of electrolyte crystallization on cooling the wall with water had a resistance of 50...60 ohms and reliably protected the bath from corrosion. The cylinder, made of X18N10T, was used as the cathode and EG-0 graphite product was used as the anode.

RESULTS AND ITS DISCUSSION

The experimental density of HfF_4 was equal to 6.92 g/cm^3 , the specific surface (according to the BET method) was less than $0.1 \text{ m}^2/\text{g}$.

The size of the TFH powder ranged from 10 to $560 \mu\text{m}$, with a minimum particle radius of $3.9 \mu\text{m}$, a maximum radius – of $1200 \mu\text{m}$, and a specific surface – of $213 \text{ cm}^2/\text{g}$. In the process of hydrofluorination of hafnium oxide, the hafnium fluoride particles become coarsened, and its specific surface area decreases by more than 2 orders of magnitude compared with hafnium oxide.

In the process of sublimation, coarsening of the TFH powder also occurred, that made it possible to improve its quality by reducing the amount of retained gas impurities. The electrolysis process was carried out at the parameters shown in Tabl. 3.

The process of hafnium electrolysis in the presence of various salts can be described by the following equations:



The time of single electrolysis was 1 hour, the current density at the cathode was $2...3 \text{ A/cm}^2$. The results of the electrolysis process of hafnium fluorides in a chloride-fluoride melt are given in Table 3. The average content of hafnium in the cathode deposit varies significantly depending on the electrolyte temperature. It rises from 25 to 45% with the temperature rising from 680 to $850 \text{ }^\circ\text{C}$. In the process of electrolysis, cathode deposit is formed on the cathode in the form of a "pear".

Individual "pears", obtained at $850 \text{ }^\circ\text{C}$, contained 60% or more of hafnium. Metallic potassium deposition on the cathode causes its appearance in the cathode deposit, the processing of which must take into account the results of potassium and water interaction with hydrogen evolution.

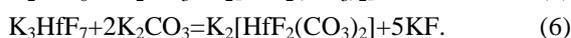
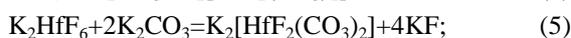
TFH electrolysis occurred evenly, without side effects. The cathode deposit was firmly bonded to the cathode after completion of electrolysis.

Table 3

Hafnium fluoride name	Electrolyte contain, % (weight)			Electrolyte temperature t , °C	Quantity of passed, per hour	Weight of loaded fluorine, kg	Weight of loaded, chloride, kg	Metallic hafnium contain in cathode deposit, % (weight)	Current metal output, %
	Hf	F	Cl						
1. Hafnium tetrafluoride	4.2–8.9	7.2–8.2	34.9–40.5	820–850	424	1.2	1.25	43.2	77.0
2. Hafnium tetrafluoride	6.4–10.1	6.1–15.7	22.2–37.4	700–820	4670	11.7	14.62	38.5	73.0
3. Potassium hexafluoride	7.5–12.9	7.5–9.3	–	720–740	440	2.6	1.66	36.2	82.5
4. Potassium heptafluoride	3.7–7.5	8.9–19.0	30.0–38.8	710–780	1150	3.4	0.5	–	–
5. Potassium heptafluorhaphnate	4.1–5.4	14.3–14.7	24.4–26.0	680–720	400	2.1	1.45	25.5	56.0

While electrolysis conducting, melt turbidity was observed on the second day. It was produced by the release of metal potassium. It was also detected at this time in the cathode deposit. The cathode deposit (CD) contained up to 45% of metal hafnium powder that was in the salts of the solidified electrolyte. The powder production is achieved by electrolyte salts leaching in an aqueous solution of potassium carbonate.

When the cathode deposit interacts with the solution of potassium carbonate, the following reactions occur:



CD processing in carbonate medium preserves high quality of hafnium powder. The flow chart for the cathode deposit processing is shown in Figure.

The cathode deposit, cooled under the layer of potassium chloride, was crushed to the size of 1...5 mm, and then successively treated with 10 and 5% of potassium carbonate solution, water and 5% hydrochloric acid solution followed by 4-fold aqueous washing of the powder from the acid.

The ratio S:L of all treatments was 1:3. The washed hafnium powder was dried in air during the day.

The quality of electrolytic and hafnium iodide is shown in Tabl. 1.

The content of metal impurities in fluoride salts is at the same level as the metal powder which indicates that there is no equipment corrosion both during the electrolysis, and during the CD processing.

Electrolysis of potassium pentafluorohaphnate did not allow obtaining the strong CD. It was very loose and slipped off the cathode, so that the hafnium current output was 56%.

The use of potassium carbonate solution to dissolve the hafnium-containing salt of cathode deposit enables to maintain the potassium balance in the system and organize a complete turnover of salts in the technological cycle. In the process of electrolysis, anode gases which contain chlorine and freons are formed, chlorine was entrapped with alkali solution of NaOH according to sanitary standards. The chlorine-free gas containing a mixture of freons was released into the atmosphere.

CONCLUSIONS

On the basis of the experimental results obtained, the optimal technological parameters of the electrolysis processes and cathode deposit processing are determined.

It is preferable to use hafnium tetrafluoride obtained after the extraction process as the starting salt for the production of pure metal hafnium powder.

The use of hafnium tetrafluoride in the electrolyte, instead of potassium fluorhaphnate, makes it possible to exclude the accumulation of potassium fluoride in the electrolyte and its bath drain, which increases the hafnium current output.

The processing of cathode deposit in the solution of potassium carbonate in alkaline medium allows preserving the purity of hafnium powder and organizing potassium closed technological cycle. The optimal hafnium content in the cathode deposit was 40%, with current output of 75...80%.

Hafnium powder obtained in the open process of electrolysis has an increased content of gas impurities, which purification is possible only by iodide refining.

The powder has a low content of metallic impurities at the level of the iodide metal. The use of electric current as a reagent in the electrolysis process of molten salts allows maintaining high purity of hafnium, preventing its loss.

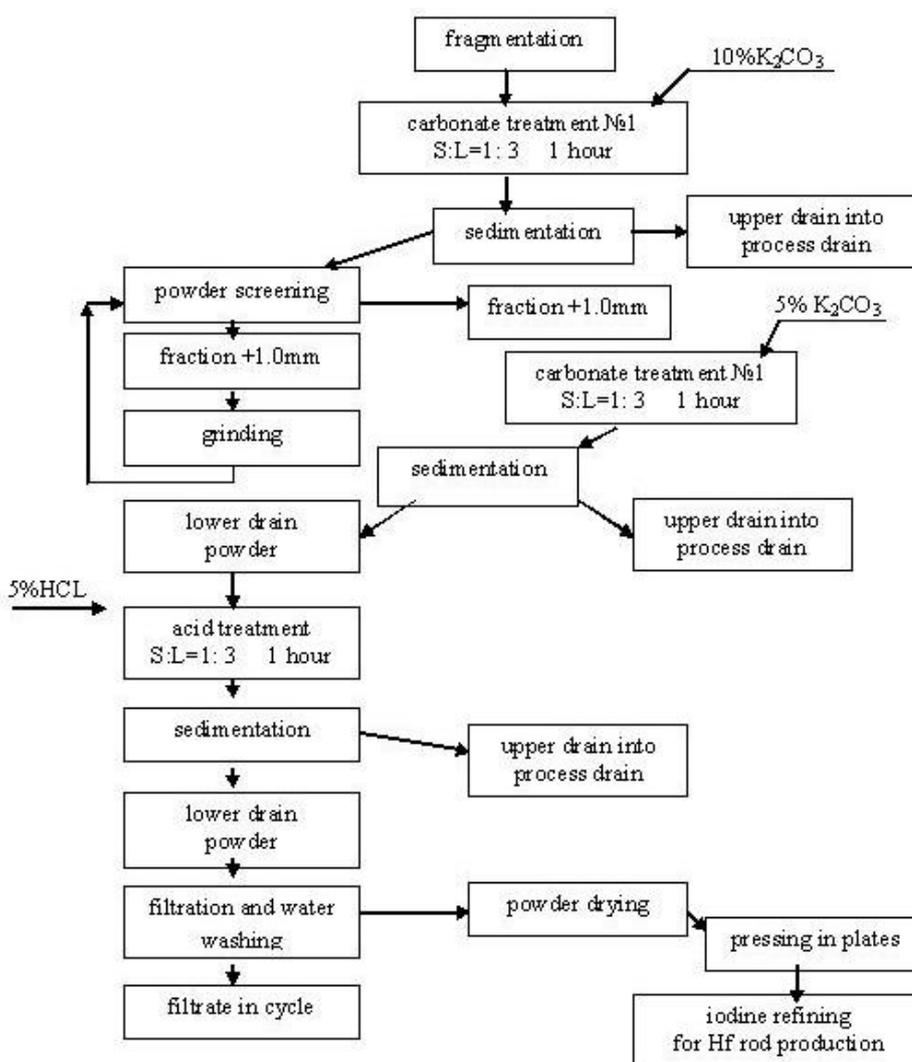


Fig. 1. Flow chart for hafnium cathode deposit processing

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ЭЛЕКТРОЛИТИЧЕСКИЙ МЕТОД ПОЛУЧЕНИЯ ПОРОШКА ГАФНИЯ ЯДЕРНОЙ ЧИСТОТЫ

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Изучена принципиальная возможность получения порошка металлического гафния методом электрохимического восстановления фторидов гафния различного состава. Определено оптимальное содержание гафния в катодном осадке. Гидрометаллургическая переработка катодного осадка с применением 10% раствора поташа показала эффективность извлечения порошка гафния со степенью 95%. Открытый электролиз фторидных солей гафния не позволяет получить порошок металлического гафния с низким содержанием газовых примесей внедрения, порошок требует йодидного рафинирования для очистки от кислорода и азота. Наилучшие технологические результаты получены при электролизе системы $\text{HfF}_4\text{-KCl-KF}$.

ЕЛЕКТРОЛІТИЧНИЙ МЕТОД ОТРИМАННЯ ПОРОШКУ ГАФНІЮ ЯДЕРНОЇ ЧИСТОТИ

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Вивчена принципова можливість отримання порошку металевого гафнію методом електрохімічного відновлення фторидів гафнію різного складу. Визначено оптимальний зміст гафнію в катодному осаді. Гідрометалургійна переробка катодного осаду із застосуванням 10% розчину поташу показала ефективність вилучення порошку гафнію зі ступенем 95%. Відкритий електроліз фторидних солей гафнію не дозволяє отримати порошок металевого гафнію з низьким змістом газових домішок впровадження, порошок вимагає йодидне рафінування для очищення від кисню та азоту. Найкращі технологічні результати отримані при електролізі системи $\text{HfF}_4\text{-KCl-KF}$.