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IODIDE HAFNIUM. RECEIPT, COMPOSITION, PROPERTIES AND APPLICATION IN MATERIALS OF REGULATING UNITS OF NUCLEAR REACTORS

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The role of hafnium purity in the receipt of the plates for the cassette tapes of automatic regulation and compensation in WWER-440 reactors is shown. The use of high-purity (iodide) hafnium in the charge composition for ingot smelting by vacuum-arc remelting makes it possible to increase the yield at the subsequent stages of deformation and to obtain the required properties of the plates.

Metallic hafnium is used in nuclear power because of the unique absorbing nuclear-physical characteristics, high strength and plasticity, processability, corrosion and radiation resistance [1-3]. It is used mainly in the form of automatic regulation and compensation cassette plates in WWER-440 reactors [4] for the cancellation of the local bursts of neutron fluxes, and also in research reactors in Russia and China.

In the CIS, metallic hafnium for nuclear power is prepared by methods of calciumthermic (Ukraine, Dniprodzerzhynsk, SSPE "Zirconium") and electrolytic reduction (Russia, Glazov, JSC ChMP) of potassium tetrafluoride [5-7] and hexafluorozirconate [8], respectively. The most pure hafnium is produced by iodide refining [9, 10]. In industrial conditions iodide hafnium is produced from melting and deformation processes wastes and nonstandard electrolytic powder [11].

Iodide refining process provides a deep purification from impurities and allows to produce the metal in a compact form, reducing its activity to the influence of external factors. The advantage of iodide refining process is that it allows to process various metal wastes generated at manufacturing products, and at the same to obtain high-purity metals in the form of compact bars, convenient for subsequent processing [11]. In industrial conditions hafnium iodide refining process is carried out in metal shelving type devices, made of chromium-nickel alloys, in particular, from alloy CN78T grade [12]. The deposition is performed on four hafnium filaments in the form of round or rectangular cross section studs consistently interconnected. Appearance of iodide hafnium bars is shown in Fig. 1. The chemical composition of iodide hafnium corresponds to the HFI-1 grade according to GOST 22517-77.

The sum of 16 defined therein impurities does not exceed 0.05%, including nitrogen < 0.002, hydrogen < 0.0008, O < 0.007, carbon <0.006%.
Microhardness of iodide hafnium bars is in the range 1760…1930 MPa (179…197 kgf/mm^2) [11, 13].

The scheme and the equipment of iodide refining of metal hafnium wastes and turns are introduced into production in JSC ChMP. Industrial production of iodide hafnium which can be enhanced with a growth of demand and the availability of required quantity of raw material is mastered. The software for the automated conducting of hafnium iodide refining process is developed. The software has been tested in laboratory conditions on the stand model in JSC VNIIHT consisting of the computer, the real-time controller with input and output modules, previously used for software adjustment for automation of zirconium iodide refining process [14].

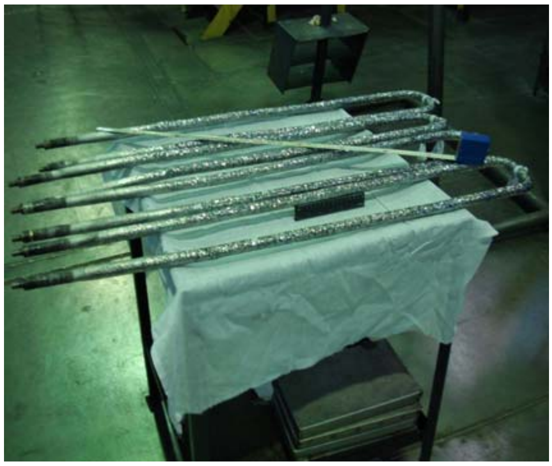

Fig. 1. Iodide hafnium bars produced from melting and deformation processes wastes

The receipt process of the ARC WWER-440 cassettes plates was developed by JSC VNIINM named after A.A. Bochvar [4]. The ingots of calciumthermic hafnium (CTH), produced by SSPE "Zirconium" (Fig. 2), have been used as an initial material at the first stage in 2005. Due to the unevenness of the chemical composition and high hardness of initial metal the yield from an ingot in plates didn't exceed 20…30%. To eliminate this disadvantage, by analogy with the production of zirconium it was recommended to enter iodide hafnium (IH) into the charge of vacuum arc remelting (VAR).

The photo of iodide hafnium bars received earlier in the device H-3 is given in Fig. 3. An electrode for smelting of a hafnium pilot ingot on the basis of double burden (CTH+IH) is shown in Fig. 4. The chemical composition of the electrode components and the EBM and VAR ingots is given in Table 1. It also shows the average results of Brinell hardness (HB) measurements of samples. The ingot hardness after 2 VAR was about a half of HB CTH and IH sum.

Table 1

Chemical composition and hardness of initial iodide and calciumthermic hafnium and EBM and VAR ingots

№	Element	Mass share, %						
		IH bars (№8) HFI-2	EBM ingot (№74)	CTH ingot 2EBM (№78)	IH bars (№13, 16) HFI-1	2 VAR ingot (CTH+IH)		
						Top	Bottom	Side
1	Zirconium + Hafnium	99.76	99.77	>99.88	-	99.86	99.84	99.88
2	Zirconium	0.56	0.54	0.3	0.84; 0.58	0.64	0.49	0.62
3	Nitrogen	<0.003	0.003	0.0049	<0.003	0.0054	0.0047	0.0051
4	Aluminium	<0.003	0.003	0.003	<0.003; 0.0042	0.0024	0.0028	0.0025
5	Hydrogen	-	-	-	-	0.00009	<0.00007	-
6	Tungsten	-	-	-	-	<0.003	<0.003	<0.003
7	Iron	0.0052	0.003	0.0083	0.0073; 0.03	0.012	0.015	0.011
8	Calcium	<0.01	<0.001	<0.01	<0.01	<0.003	<0.003	<0.003
9	Oxygen	0.02	0.03	0.039	0.02; 0.04	0.026	0.017	-
10	Silicon	<0.003	0.004	0.011	0.004; <0.003	0.0091	0.012	0.0098
11	Magnesium	<0.001	<0.003	<0.003	<0.003; <0.001	<0.001	<0.001	<0.001
12	Magnesium	<0.0003	<0.0003	0.0003	<0.0003	<0.0003	<0.0003	<0.0003
13	Copper	-	-	0.001	-	<0.001	<0.001	<0.001
14	Molybdenum	0.155	0.16	0.0038	0.066;0.073	0.042	0.053	0.052
15	Nickel	0.022	0.001	<0.003	0.01;0.038	0.0070	0.015	0.0076
16	Niobium		-	-	-	<0.01	<0.01	<0.01
17	Titanium	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
18	Carbon	0.005	0.005	0.022	0.005	0.012	0.013	0.012
19	Fluorine	-	<0.003	<0.003	-	-	-	-
20	Chromium	<0.003	<0.001	<0.003	0.003	0.0020	0.0017	0.0017
21	Hardness, HB, average			240	135	183	197	185

Fig. 2. Ingot of calciumthermic hafnium

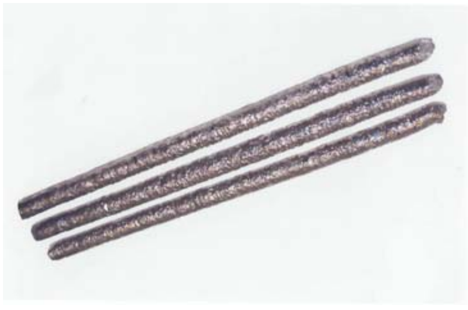

Fig. 3. Hafnium iodide bars HFI-1 grade received in H-3 device

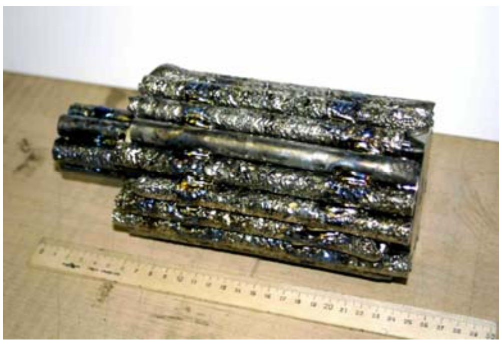

Fig. 4. Double burden (CTH + IH) electrode for VAR

As a result of carrying out R & D at its first stage in 2005 after two VAR of double burden (57% of CTH+43% of IH) in a vacuum-arc furnace (Fig. 5) from an ingot 160 mm in diameter and weighing 22 kg (Fig. 6), after cutting it into rectangular templates 12 mm thick, multiple hot and cold deformation with intermediate etching and annealing pilot plates have been made with dimensions of 150×76,2×0,6 mm for ARC WWER-440 cassettes according to TU 001.369-98 (Fig. 7) and 350×69×2 mm for experienced PEL of JSC «SSC RIAR» SM reactor.

Plates with dimensions of 150×0,6×76 mm were also made from a hafnium ingot melted by electron beam method (EBM) from iodide hafnium HFI-2 grade (see Table 1).

Direct output from the hafnium cast billets to finished plate of ARC WWER-440 averaged 40.4%. 41.4% of hafnium turned into wastes, 15.1% – in etching solutions (Table 2).

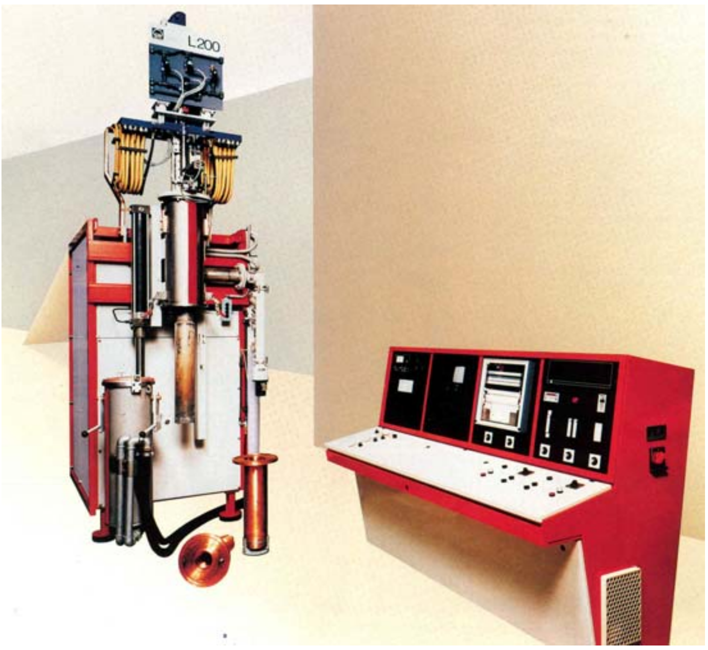

Fig. 5. Vacuum – arc furnace L 200

Fig. 6. Pilot ingot 160 mm in diameter weighing 22 kg smelted from double burden (CTH+IH)

Fig. 7. Plates made of a hafnium ingot smelted from double burden

At present JSC ChMP mastered the industrial production of hafnium electrolytic powder. Hafnium electrolytic powder has 2…3 times higher content of impurities in comparison with iodide metal. Reduction of the impurity's content in electrolytic and waste hafnium is achieved by using refining EBM at the first stage. According to data of work [15] in the EBM process a purification of hafnium from aluminum, boron, iron, oxygen, silicon, titanium and chromium takes place. At the same time the hardness of ingots decreases approximately by 40 HB. Vacuum and arc remelting of two and three component burden leads to an increase of ingots purity at the expense of basis dilution by purer (iodide) metal.

Hafnium in the form of iodide bars, electrolytic powder and production waste in a various ratio as a part of burden has been used for smelting of the HFE-1 grade ingots according to TU 001.402-2008 and the subsequent production of plates with dimensions of 150×76,2×0,6 mm (drawing 445.01.016) according to TU 001.403-2008 [16, 17]. 7 ingots have been received in total with 160 mm in diameter weighing of 80…100 kg melted from burden of different composition:

- 2 ingots from 100% of waste (a trimming at plates cutting on the finished size);
- 2 ingots from 100% of iodide bars;
- 1 ingot from 100% of hafnium electrolytic powder;
- 2 ingot of triple burden (70% powder, 20% iodide bars, 10% waste).

Table 2

Microhardness of cast (2VAR) and deformed hafnium in initial and annealed conditions

Number	Sample number	State	Microhardness ($H_\Diamond$)	
			MPa	kgf/mm^2
1	4	Cast initial	1880...1930/ average 1900	192…197/ average 194
2	7	Cast initial	2040…2100/ average 2080	208…214/ average 212
3	0	Deformed initial	2550…2630/ average 2600	260…268/ average 265
4	1	Deformed initial	2460…2550/ average 2520	251…260/ average 257
5	3	Deformed annealed	1880…1930/ average 1910	192…197/ average 195
6	4	Deformed annealed	1820…1930/ average 1880	186…197/ average 192

Table 3

Physical and mechanical properties at stretching of plates 2 and 0.6 mm thick

Number	Sample number	Plate size, mm	State	$\sigma_{0,2}$, MPa (kgf/mm^2)	$\sigma_в$, MPa (kgf/mm^2)	δ, %
1	0	350×69×2	Deformed initial	687 (70.0)	775 (79.0)	4.8
2	1	350×69×2	Deformed initial	716 (73.0)	775 (79.0)	5.8
3	3	350×69×2	Deformed annealed	353 (36.0)	530 (54.0)	18.0
4	4	350×69×2	Deformed annealed	368 (37.5)	520 (53.0)	14.0
5	-	150×76×0,6	Deformed annealed	177 (18.0)	530 (54.0)	37.0
TU 001.369-98			Deformed annealed	≥150 (15)	≥400 (40)	≥12

100% iodide rods ingots were manufactured according to the double vacuum arc remelting scheme (VAR-VAR), the rest - according to the refining electron-beam melting - vacuum arc remelting scheme (EBM-VAR). The content intervals of impurity elements in ingots from burden of different composition is given in Table 4. The smallest amount of impurities (excluding accompanying Zr element) is at ingots melted on an iodide basis, then at ingots of triple burden and electrolytic powder and the highest - at reverse metal.

Plates of all ingots are being produced by the same scheme.Production of plates includes hot forging of ingots, machining of the forgings, the subsequent hot and cold rollings with intermediate and finishing annealings of sheets, cutting down of plates in the size and machining. The appearance of a plate is given in Fig. 8.

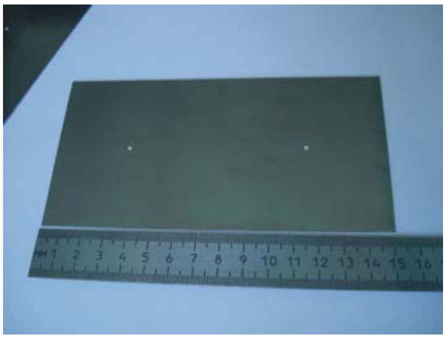

Fig. 8. Appearance of a plate 150×76,2×0,6 mm (drawing 445.01.016)

The manufactured plates pass control on compliance to TU 001.403-2008 requirements (appearance and mechanical properties). The results of mechanical tensile tests, including the units from burden CTH+IH, are shown in Table 5 and Fig. 9.

The properties of plates from all burden types are found to correspond to TU 001.403-2008 requirements. The plates made of iodide hafnium ingots, are characterized by a reduced level of strength properties and high plasticity ($\sigma_в$ = 366.6…385.0 MPa, $\sigma_{0.2}$ = 180.7…188,8 MPa, δ = 42.0…42.7%). The plates from ingots on the electrolytic powder basis have high strength characteristics ($\sigma_в$ = 507.7 MPa, $\sigma_{0.2}$ = 304.1 MPa, δ = 31.0%).

The plates from a triple burden have a high level of tensile properties at a higher elongation value in comparison with a 100% electrolytic powder burden ($\sigma_в$ = 500.3…510.1 MPa, $\sigma_{0.2}$ = 295.1…306.6 MPa, δ = 32.0…33.7%), in this case an important role is played by a type of a material from which waste are received [17].

The following conclusions can be made from the analysis of data in Table 5 and Fig. 9:

1. The main influence on the plates quality characteristics provides a difference in the oxygen, nitrogen and carbon content (Table 4). There is no stability by characteristics of mechanical properties at production of plates from reverse metal.
2. The plates made of iodide hafnium ingots as the most pure metal, are characterized by a reduced level of strength properties and high plasticity that is due to the low content of the above-mentioned impurities.
3. The ingot melted on the basis of electrolytic powder, permitted to receive plates with high strength characteristics, but with the reduced plasticity.
4. Earlier obtained data on properties of plates from an ingot of double burden (57% of CTH + 43% of IH) fully correspond to the determined patterns.

Increase of technical and economic indicators of production demands compulsory involvement of reverse metal in process when outputting products. In this case the maintenance of production characteristics at an optimum level and their stabilization are possible at addition of iodide metal in burden composition when smelting ingots. It is realized in the scheme of receiving ingots on the basis of three-component burden: wastes, electrolytic powder and iodide metal. The limited content of reverse metal doesn't lead to instability of properties, and the use of powder provides a high level of mechanical properties.

Table 4

Mass fractions intervals of impurity elements in ingots from the burden of different composition, %

Element	Burden composition of ingots											
	100 % of waste (2 ingots)			100 % of iodide bars (2 ingots)			100 % of powder (1 ingot)			Triple burden: -70% powder; -20% iodide bars; -10% waste (2 ingots)		
	Min	Max	Average	Min	Max	Average	Min	Max	Average	Min	Max	Average
Zr	0.24	0.31	0.28	0.43	0.52	0.46	0.67	0.68	0.68	0.63	0.67	0.65
N	<0.003	0.0073	0.0042	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
C	0.005	0.0082	0.0069	<0.003	0.0023	0.0021	0.0062	0.0072	0.0067	0.0057	0.0067	0.0061
O	0.018	0.023	0.021	0.01	0.011	0.010	0.015	0.018	0.017	0.017	0.023	0.020
Fe	<0.003	0.0037	0.0033	<0.003	0.005	0.0044	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Si	0.0037	0.0048	0.0044	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Ni	<0.003	0.0073	0.0042	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Ti	<0.003	<0.003	<0.003	<0.003	0.0034	0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Al	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Ca	<0.003	0.0042	0.0033	<0.003	0.003	0.003	0.0057	0.006	0.0059	<0.003	<0.003	<0.003
Mg	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Mn	<0.0003	<0.0003	<0.0003	<0.003	<0.003	<0.003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Cr	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cu	<0.001	0.0012	0.0011	<0.001	0.0013	0.0011	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Nb	0.0063	0.011	0.0087	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Mo	0.0087	0.091	0.0391	<0.003	<0.003	<0.003	<0.003	0.018	0.0105	0.0031	0.013	0.0096
W	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Zr+Hf	99.9	99.8	99.88	99.9	99.9	99.94	99.9	99.9	99.92	99.9	99.9	99.92
Sum of impurities without (Zr+Hf)	–	–	0.1115	–	–	0.0566	–	–	0.0744	–	–	0.0730

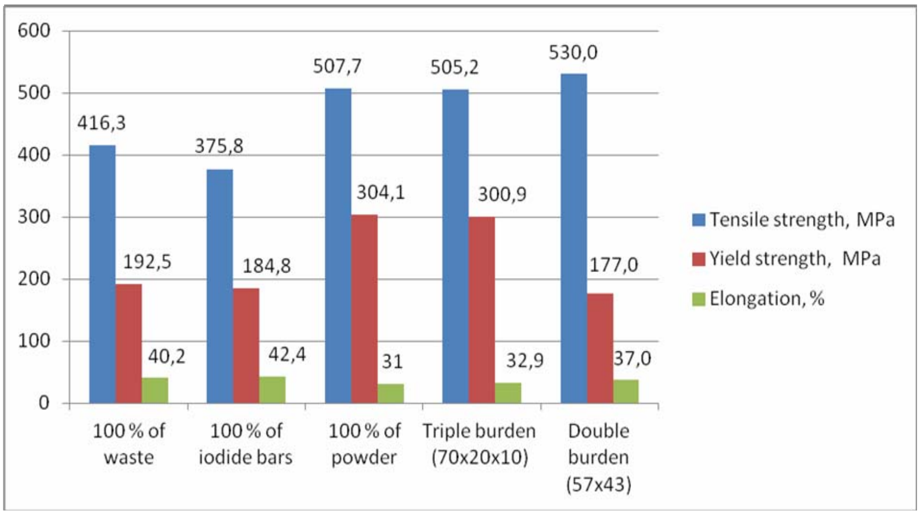

Fig. 9. Mechanical properties of the plates (average data)

Table 5

Mechanical properties of the plates made of ingots from different burden composition

Burden composition	Ingot	Mechanical properties		
		Tensile strength, σ_B, MPa	Yield strength conditional $\sigma_{0,2}$, MPa	Elongation δ, %
100% of waste	№1	342.1	179.0	42.0
	№2	490.5	206.0	38.4
	Average	416.3	192.5	40.2
100% of iodide bars	№1	385.0	180.7	42.7
	№2	366.6	188.8	42.0
	Average	375.8	184.8	42.4
100% of powder	№1	507.7	304.1	31.0
Triple burden: -70% powder; -20% iodide bars; -10% waste	№1	510.1	306.6	32.0
	№2	500.3	295.1	33.7
	Average	505.2	300.9	32.9
Double burden: - 57 % calciumthermic hafnium; - 43 % iodide bars	№1	530	177	37
TU 001.403-2008 requirements		≥ 300	≥ 150	≥ 12

With the purpose to reduce the product's prime cost and increase the yield the scheme of receiving plates from the aggregative hafnium ingots 320 mm in diameter weighing 700…1000 kg is being developed today at JSC ChMP [16].

REFERENCES

1. V.D. Risovany, E.P. Klochkov, V.B. Ponomarenko. *Hafnium in nuclear equipment.* Dimitrovgrad: RIAR, 1993, 143 p.

2. V.D. Risovany, A.V. Zakharov, E.P. Klochkov, et al. *Absorbing materials of management and protection cores of nuclear reactors*. Ulyanovsk: 2012, 442 p.

3. V.D. Risovany, R.V. Azhazha, K.V. Kovtun, et al. Hafnium - material for systems of indemnification of surplus reactivity in nuclear power reactors // *VANT. Series "Physics of Radiation Effects and Radiation Materials Science".* 2013, №2, p. 118-122.

4. A.K. Shikov, O.V. Bocharov, V.M. Arzhakova, et al. Using of Hf in control elements of the nuclear reactors and power units // *Metal Science and Heat Treatment*. 2003, №8, p. 20-23.

5. M.L. Kotsar, V.M. Azhazha, K.A. Lindt, et al. Receipt of pure zirconium and hafnium // *High-Purity Substances*.1992, №4, p. 85-92.

6. K.A. Lindt, Fyodorov, M.L. Kotsar, et al. Production of zirconium and hafnium in the Industrial Association "PCP" for satisfaction of nuclear energy requirements of Ukraine // *VANT. Series "Physics of Radiation Effects and Radiation Materials Science".* 1994, issue 2, 3, p. 114-124.

7. V.V. Shatalov, M.L. Kotsar, V.M. Azhazha, et al. Extraction - calciumthermic technology of hafnium receipt // *VANT. Series "Physics of Radiation Effects and Radiation Materials Science".* 1999, issue 2(77), p. 9-13.

8. M.G. Shtutsa, A.V. Alexandrov, R.F. Bekmansurov, et al. Use of iodide metal for smelting of industrial zirconium and hafnium ingots // *Thesis of report. International conference "High-purity metals: receipt, applications, properties", 15-18 November 2011*. Kharkov, 2011, p. 24.

9. A.V. Yelyutin, N.D. Denisova, A.P. Baskova, et al. Behavior of impurities in the process of zirconium and titanium iodide refining // *Scientific works of GIREDMET.* M.: GIREDMET, 1980, v. 96, p. 63-69.

10. A.I. Yevstyukhin, G.A. Leontyev, M.L. Kotsar, et al. Clarification from impurities in the process of iodide refining of hafnium and its alloys with nickel // *Constructional materials in atomic engineering*: Collection of scientific works / MIFI. M.: Energoatomizdat, 1987, p. 15-24.

11. M.L. Kotsar, A.V. Alexandrov, M.G. Shtutsa, et al. Production of high-purity titanium, zirconium and hafnium by the iodide refining method under industrial conditions // *Inorganic materials*. 2010, v. 46, №3, p. 332-340.

12. A.V. Alexandrov, M.G. Shtutsa, M.L. Kotsar, et al. Apparatus for iodide refining of hafnium. Patent RF, No. 2353687, MPK C22B34/14, C22B9/00 // *Inventions. Utility models*. 2009, №12, p. 866.

13. M.L. Kotsar, A.V. Alexandrov, S.G. Akhtonov, et al. High-purity titanium, zirconium and hafnium in nuclear-power engineering. // *Atomic Energy.* 2011, v. 111, issue 2, p. 72-77.

14. S.A. Lavrikov, M.L. Kotsar, A.A. Chernyshev, et al. Development of experimental bench for iodide zirconium refining of automatization process, on the

basis of industrial furnace SKB-5025 (СКБ-5025) // *Non-ferrous Metals.* 2013, №2, p. 82-87.

15. N.K. Filatova, O.V. Bocharov, V.M. Arzhakova, et al. Hafnium refinement by electron beam remelting // VANT. Series "Materials Science and New Materials". 2012, №1, p. 210-218.

16. D.A. Negodin, E.V. Ilyenko, A.M. Kobyzev, et al. Commercial production of metal hafnium and hafnium-based products // *VANT. Series "Physics of Radiation Effects and Radiation Materials Science".* 2012. №2, p. 97-101.

17. M.L. Kotsar, A.O. Lapidus, A.V. Alexandrov, et al. High-purity hafnium. Receipt and application in the materials of regulation bodies of nuclear reactors // *Thesis of report. X Russian conference on reactor materials science, 27-31 May 2013.* Dimitrovgrad, 2013, p. 152-154.

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ЙОДИДНЫЙ ГАФНИЙ. ПОЛУЧЕНИЕ, СОСТАВ, СВОЙСТВА И ПРИМЕНЕНИЕ В МАТЕРИАЛАХ ОРГАНОВ РЕГУЛИРОВАНИЯ ЯДЕРНЫХ РЕАКТОРОВ

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Показана роль чистоты гафния при получении пластин для кассет автоматического регулирования и компенсации в ВВЭР-440. Использование высокочистого (йодидного) гафния в составе шихты для выплавки слитков методом вакуумно-дугового переплава позволяет повысить выход годного материала на последующих деформационных стадиях и получить необходимые свойства пластин.

ЙОДИДНИЙ ГАФНІЙ. ОТРИМАННЯ, СКЛАД, ВЛАСТИВОСТІ І ЗАСТОСУВАННЯ В МАТЕРІАЛАХ ОРГАНІВ РЕГУЛЮВАННЯ ЯДЕРНИХ РЕАКТОРІВ

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Показано роль чистоти гафнію при отриманні пластин для касет автоматичного регулювання та компенсації ВВЕР-440. Використання високочистого (йодидного) гафнію в складі шихти для виплавки злитків методом вакуумно-дугового переплаву дозволяє підвищити вихід придатного матеріалу на наступних деформаційних стадіях і отримати необхідні властивості пластин.