

PURE HAFNIUM FOR NUCLEAR POWER

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The processes of producing reactor-grade hafnium are investigated. It is shown that the electron beam melting method is effective for purification of hafnium from metallic impurities. The use of deoxidizing additives makes it possible to purify hafnium from oxygen, and carrying out a vacuum-thermal treatment of the initial charge provides the necessary nitrogen content.

INTRODUCTION

In WWER reactors as in similar reactors PWR the clustered assemblies of control rods of reactor control and safety system serve as reactor control. The clustered assemblies can be operated as automatic control of reactor power and as emergency protection. Boron carbide powder (B_4C) with a natural content of the ^{10}B isotope use in control rods as neutron absorbent material. The neutron absorbing material is sealed in a tube of stainless steel.

Rather small term the service of the control rods of WWER-1000 (2 years as automatic and 5 years as the emergency protection) is connected both with significant embrittlement of the steel cladding 06X18H10T and a swelling of the absorber due to the reaction $^{10}B + ^1n \rightarrow ^7Li + ^4He$ ((n, α) -reaction). ^{10}B isotope undergoes an (k, α) -reaction that depletes the ^{10}B isotope. At a burnup of the ^{10}B isotope more than 40% the appreciable yield of free helium occurs and swelling of boron carbide particles and its force effect on cladding is beginning to affect.

Hafnium absorbs neutrons, but does not disintegrate like ^{10}B isotope. It can absorb several neutrons before losing its absorption cross section. So it doesn't “burn out” quickly [1]. Hafnium is (n, γ) -absorber, and can simultaneously perform functions the neutron absorber and structural material in control rods.

New absorber elements designs have been developed with combined use of hafnium and boron carbide [2]. In Fig. 1 shows one of the absorber element options with increased physical efficiency and service life when using hafnium as an absorbing and structural material.

Pure hafnium has a complex of physical-chemical and mechanical properties that allow using it for the production of control rods intended for long term maintenance-free operation of nuclear reactors. The cross-section of thermal neutron absorption of hafnium is slowly reduced when operating in the conditions of irradiation due to isotopic composition of natural hafnium [1]. According to preliminary estimates service life of hafnium rods can be extended to 15 years or more due to the peculiarities of hafnium isotopes transmutation in the neutron flux.

The relative physical efficiency of hafnium in respect to the core of WWER-1000 is $\sim 80\%$ of the efficiency of boron carbide.

According to foreign and domestic researchers hafnium is an ideal material for control rods in pressurized water reactors and can be successfully used as absorber rods of WWER-1000 reactors.

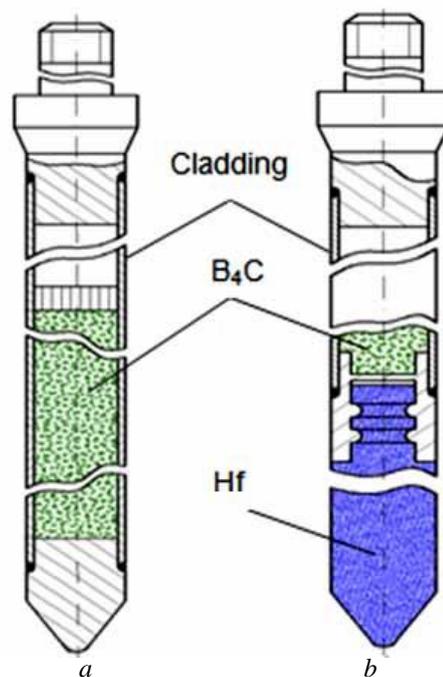


Fig. 1. Absorber elements with boron carbide (a) and combined (n, α) – (n, γ) -absorber (b)

In Ukraine the technology for producing of hafnium including hydrometallurgical stage (the production of pure hafnium tetrafluoride – HfF_4) and metallurgical stage (calcium thermal reduction of hafnium tetrafluoride and subsequent electron-beam melting (EBM)) is developed. This technology allows getting a metal with low content of undesirable impurities influencing the metal plasticity, its corrosive and radiation properties. However in some cases there is also some local nonuniformity in content nitrogen, iron, oxygen and silicon.

The impurities contained in hafnium influence on its properties. In particular this applies to the interstitial impurities, especially oxygen and nitrogen. The data on the effect of oxygen content on the mechanical properties of hafnium are given in Table 1 and Fig. 2 [3].

Table 1
The data of mechanical researches of hafnium with different oxygen content

Oxygen content, wt. %	σ_B , MPa	$\sigma_{0.2}$, MPa	δ , %
0.005	440.0	290.0	36.0
0.010	445.0	305.0	34.5
0.030	487.0	355.0	30.0
0.045	520.0	370.0	27.5

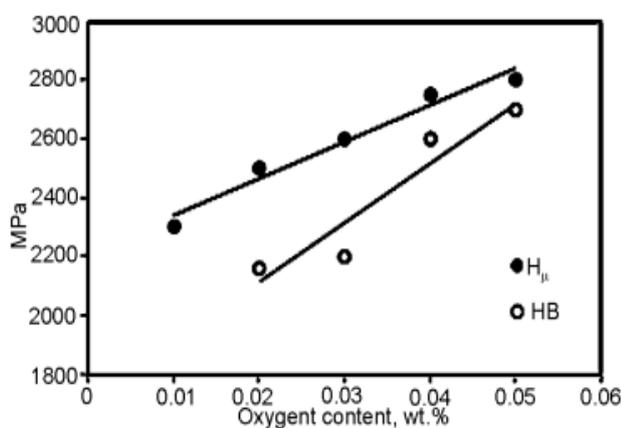


Fig. 2. The values of microhardness (H_μ) and Brinell hardness (HB) for hafnium with different oxygen content

The physical-mechanical properties of hafnium significantly affected by the presence of impurities, so to improve the quality of hafnium was carried out complex of research works on improving processes of producing hafnium of nuclear grade.

REFINING OF HAFNIUM BY ELECTRON-BEAM MELTING

Refining of hafnium is carried out by method of EBM. EBM of metals is performed on an ultra-high vacuum installation. For pumping of installation used two hetero-ion pumps with a pumping speed of 5000 l/s each, and a titanium sublimation pump. Application of such a system of vacuum pumping allows to get an ultimate vacuum in the installation $1.7 \cdot 10^{-6}$ Pa. In the spectrum of the residual gas in installation were absent heavy hydrocarbons. Refining of metals was carried out in vacuum $(1...5) \cdot 10^{-5}$ Pa. Refining was conducted in the regime: heating \Rightarrow melting \Rightarrow excerpt of metal in molten state \Rightarrow crystallization \Rightarrow pulling ingot. The starting material was hafnium, obtained by the method of calcium-thermal recovery of hafnium tetrafluoride. The experiments of refining of hafnium by EBM showed that an increase in power density melting not only accelerates the process of refining of hafnium

metal impurities, but also comes the refining from of oxygen due to its deletion in the form of monoxide HfO. This process is known as distillation deoxidation.

Temperature, evaporation surface and melting time affect the change in the concentration of impurities in the process of EBM. The time dependence of the concentration of an impurity in a liquid metal at a given temperature is described by the equation

$$\frac{V}{S} \lg \frac{C_i^0}{C_i} = k_{evap} \tau, \quad (1)$$

where V – the volume of liquid metal; S – the surface of the liquid metal from which the evaporation of impurities; C_i^0 – the initial concentration of the impurity; C_i – final impurity concentration; k_{evap} – evaporation rate constant; τ – the time required to change the concentration of the impurity.

The evaporation rate constant is defined as

$$k_{evap} = \frac{a \cdot P_i^0 \cdot \gamma}{\rho_{Hf}} \left[\frac{M_{Hf}^2}{2\pi \cdot R \cdot T \cdot M_i} \right]^{1/2}, \quad (2)$$

where a and $\gamma \approx 1$; P_i^0 – vapor pressure of the impurity; ρ_{Hf} – the melt density; M_i , M_{Hf} – molecular weight of the impurity and the base metal; R – the gas constant; T is the temperature of the base metal.

Using equations (1) and (2), the final impurity concentration was calculated by setting the initial concentration and the time was determined for which the impurity concentration decreases to a predetermined value, i.e. melting parameters [3]. The diameter of the mold and the volume of the metal are constant values for the EBM process in this installation. The values of T and τ characterize the power of the electron beam and the melting rate.

The time during which the concentration of impurities in hafnium at a certain power (temperature) decreases to a value of $1 \cdot 10^{-4}$ wt.% was calculated. The expose time of metal in the molten state was estimated from the equation $\tau = a + b \ln C_0$, where C_0 – the impurity concentration, a and b – the coefficients dependent on the melt temperature, the type and concentration of impurities. Such calculations were performed for the impurities of iron, aluminum, copper, nickel, titanium, silicon, chromium, etc. As an example, Fig. 3 shows the results of calculating the change in the concentration of iron and titanium in hafnium from the exposure time in the molten state at various temperatures. Calculations also showed that the purification of hafnium from silicon is difficult by EBM, and removal of the more volatile impurities is reduced in a series of Zn > Be > Mn > Cr > Cu > Al > Fe > V > Co > Ni > Si [3].

The obtained parameters were used to optimize the EBM of hafnium in laboratory and experimental industrial conditions. After two successive EBM was obtained hafnium with purity ≥ 99.95 wt.%. Its chemical composition is follows: $N_2 - 1.0 \cdot 10^{-3}$;

Al – $1.0 \cdot 10^{-3}$; W < $1.0 \cdot 10^{-3}$; Fe – $5.0 \cdot 10^{-3}$; O₂ – $1.0 \cdot 10^{-2}$; Si – $3.5 \cdot 10^{-3}$; Mn < $1.0 \cdot 10^{-4}$; Cu – $2.0 \cdot 10^{-4}$; Ni < $1.0 \cdot 10^{-3}$; Nb < $2.0 \cdot 10^{-3}$; C – $5.0 \cdot 10^{-3}$; F < $1.0 \cdot 10^{-3}$; Cr – $2.0 \cdot 10^{-4}$ wt.% [3]. Such a metal on the content of impurities can successfully be used as a structural material of the active core of nuclear reactors on thermal neutrons [3–7].

The necessary degree of hafnium purification from metal impurities is achieved during 2–3 EBM.

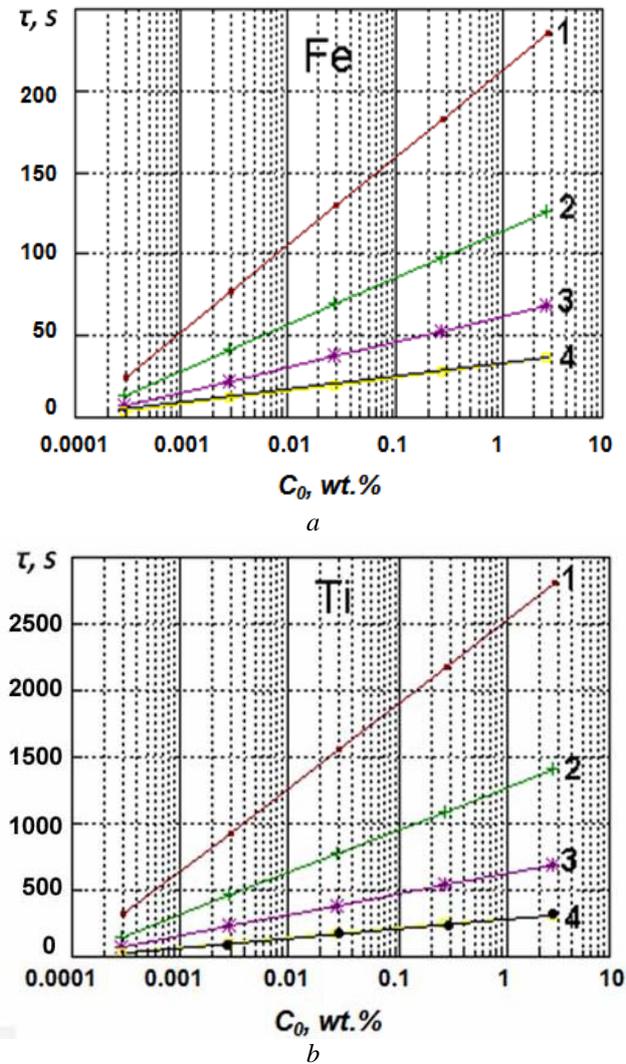


Fig. 3. The change in the concentration of iron (a) and titanium (b) in hafnium from the exposure time in the molten state at a temperature: 1 – 2505; 2 – 2600; 3 – 2700; 4 – 2800 K

PURIFICATION OF HAFNIUM FROM OXYGEN

Great difficulty in obtaining of nuclear grade hafnium is purification from interstitial impurities – nitrogen and oxygen. At high oxygen and nitrogen content in hafnium it is almost impossible to mechanical treatment which greatly limits its application in the form of products for the nuclear power industry (rod, band, tube, wire).

Based on the analysis of literature data and taking into account obtained results of laboratory studies aluminum was chosen as a hafnium deoxidizer [4–6]. The calculation of deoxidizing ability of aluminum

showed that aluminum forms a volatile oxide which then desorbed from the hafnium at EBM by reaction $2AlHf + [O] \rightarrow (Al_2O)_{gas}$. Content of aluminum which was added into hafnium on the reduction melting stage after EBM was $1 \cdot 10^{-2} \dots 3 \cdot 10^{-3}$ Pa. According to the experimental results (Table 2) lower oxygen content is observed already on the reduction stage and significantly – after electron beam melting (Table 3) [2–5]. The oxygen content is decreased almost three times. The aluminum content in all samples of hafnium obtained after electron beam melting was $(2 \dots 3) \cdot 10^{-3}$ wt.% regardless the aluminum were added or no.

Table 2

Oxygen content in hafnium after EBM

Aluminum additive, wt.%	Oxygen content in hafnium, wt.%	
	roughing ingot	after EBM
–	0.15	0.045
–	0.17	0.050
–	0.18	0.055
0.20	0.10	0.035
0.20	0.11	0.030
0.25	0.12	0.030

With increasing purity of hafnium, its hardness decreases from HB = 1900...2200 MPa (oxygen content 0.10...0.18 wt.%) for the initial hafnium, up to 1300...1500 MPa (oxygen content 0.03...0.05 wt.%) for metal after EBM. A decrease in values is also characteristic of microhardness. The microhardness H_{μ} of the initial hafnium is 2900 MPa, and after EBM is 2400 MPa, which indicates an increase in the purity of the metal.

Table 3

Content of impurities in hafnium ingots

Element	Content of impurity, wt.%	
	before EBM	after EBM
Al	0.026...0.25	0.002...0.003
Si	0.02	0.0045
Fe	0.04	0.007
Cu	0.003	0.0002
Ni	0.026	0.001
Ti	0.01	0.001
Nb	0.005	0.005
Ca	0.23	0.0005
Cr	0.003	0.0003

The hafnium ingots with purity of more than 99.94 wt.% were produced in factory conditions using the parameters obtained in laboratory researches. These ingots were produced using addition of aluminum on the reduction melting stage and subsequent EBM. The

content of impurities in the obtained hafnium are as follows: nitrogen – $3.0 \cdot 10^{-3}$; aluminum – $3.0 \cdot 10^{-3}$; tungsten – $1.0 \cdot 10^{-3}$; iron – $3.0 \cdot 10^{-3}$; oxygen – $4.0 \cdot 10^{-2}$; silicon – $3 \cdot 10^{-3}$; manganese – $3.0 \cdot 10^{-4}$; copper – $2.0 \cdot 10^{-3}$; nickel – $3.0 \cdot 10^{-3}$; niobium – $2.0 \cdot 10^{-3}$; carbon – $3.0 \cdot 10^{-3}$; chrome – $1.0 \cdot 10^{-3}$ wt.%. Hafnium produced by using of aluminum additives on the reduction stage after refining by EBM can be successfully used as the structural material of a nuclear reactor core.

PURIFICATION OF HAFNIUM FROM NITROGEN

One of the undesirable rigidly limited impurities at obtaining hafnium is nitrogen. Its content in the metal in accordance with the technical conditions should not exceed 0.005 wt.%. Analysis of statistical data about the behavior of nitrogen at obtaining hafnium indicates that nitrogen content in the melting products is always higher of its content in the starting materials [8]. Comparison of the nitrogen content in the starting materials and melting products allows concluding that to 30% of nitrogen adsorbed goes into hafnium from the unsublimated hafnium tetrafluoride. This fact dictates the need for reduce the amount of nitrogen adsorbed by hafnium tetrafluoride. To determine of the character process of gas separation from the sublimated and unsublimated hafnium tetrafluoride experiments were carried out in the temperature range 20...700 °C at a residual pressure $1.3 \cdot 10^{-1} \dots 1.3 \cdot 10^{-6}$ Pa.

Analysis of the residual gases spectra showed that the main gases which desorbed during heating hafnium tetrafluoride are nitrogen, carbon oxide, water vapor, hydrogen fluoride and other gases [3, 9]. Change of the general pressure in the chamber during heating of the unsublimated and sublimed hafnium tetrafluoride is shown in Fig. 4. The nature of the change in total pressure for sublimated and unsublimated hafnium tetrafluoride reflects the mechanisms of gas desorption from hafnium tetrafluoride upon heating. It is noted that amount of the gases desorbed from the sublimated and unsublimated hafnium tetrafluoride is significantly different. From unsublimated hafnium tetrafluoride a greater number of gaseous impurities is desorbed (up to 3 wt.%) than from sublimated (up to 0.5 wt.%). With increasing temperature the maximum on curves of the total pressure change of unsublimated hafnium tetrafluoride is approximately one hundred degree higher than of the sublimated.

The process of gas separation from unsublimated hafnium tetrafluoride is more complex due to the high content of the gas impurities in it and desorption of gas impurities with mass numbers 36 (HfO) and 38 (Hf·H₂O). Fig. 5 shows the percentage composition of the desorbed impurities with different masses from unsublimated hafnium tetrafluoride when heated in vacuum at the temperature range of 20...600 °C. At these temperatures, the main peak of gases separation from unsublimated hafnium tetrafluoride is associated with the desorption of a group of impurities with mass numbers of 20 (Hf), 36 (HfO) и 38 (Hf·H₂O) (hydrogen fluoride in combination with water). After sublimation, the total amount of these impurities in the sublimated product is significantly reduced, and the main peak of

gas separation from sublimated hafnium tetrafluoride is mainly associated with water removal. A comparison of the normalized composition of gases desorbed from unsublimated hafnium tetrafluoride with the composition of gases desorbed from of sublimated hafnium tetrafluoride shows that content of water, nitrogen, carbon oxide and fluorine-containing impurities of the unsublimated products is about 25%. The main gas impurity desorbed from sublimated hafnium tetrafluoride is water.

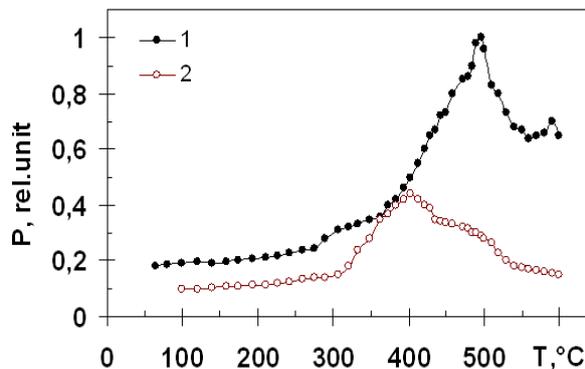


Fig. 4. Change of the total pressure in the chamber during heating of unsublimated (1) and sublimated (2) hafnium tetrafluoride

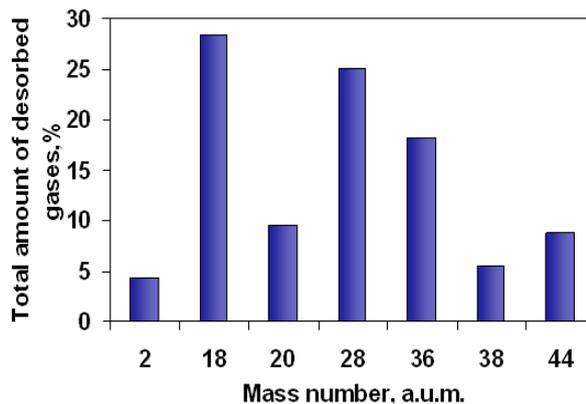


Fig. 5. Percentage of the desorbed gases with different masses from the unsublimated hafnium tetrafluoride in the temperature range 20...600 °C

To obtain hafnium tetrafluoride with a low content of adsorbed nitrogen, it is necessary to heat it in vacuum, and for a more complete removal of gas products from hafnium tetrafluoride, exposure is required at the temperature of their maximum removal.

The results obtained allow concluding that for reducing the nitrogen content in hafnium when using sublimated hafnium tetrafluoride the preliminary operation of vacuum thermal treatment in the temperature range 300...600 °C is desirable and for unsublimated hafnium tetrafluoride is necessarily.

Efficiency the use of vacuum thermal treatment was shown in practice during the laboratory melting. Nitrogen content in the obtained hafnium ingots without the use of vacuum thermal treatment of hafnium tetrafluoride was varied in the range 0.005...0.019 wt.%. After vacuum thermal treatment the

nitrogen content in alloys does not exceed 0.005 wt.% [3].

CONCLUSIONS

The results of studies on the hafnium refining presented in this paper show that the developed methods of refining are highly effective for reducing the amount of impurities. It is shown that the EBM method is effective for purification of hafnium from metallic impurities. The use of aluminum as a deoxidizing component on the reduction melting stage of hafnium results in essential decrease the oxygen content in the metal (to 0.03...0.04 wt.%) on the EBM stage. Carrying out of vacuum thermal treatment of hafnium tetrafluoride before the reduction melting in the temperature range of 300...600 °C provides a nitrogen content in the metal less than 0.005 wt.%. Thus the research results of refining hafnium allow carrying out the scientific approach to producing of hafnium with low oxygen and nitrogen content for modern technologies and creating of structural materials for nuclear reactors of the new generation and other responsible applications.

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ЧИСТЫЙ ГАФНИЙ ДЛЯ ЯДЕРНОЙ ЭНЕРГЕТИКИ

Н.Н. Пилипенко, А.А. Дробышевская, Ю.С. Стадник, Ю.А. Ступак

Исследованы процессы получения гафния реакторной чистоты. Показано, что метод электронно-лучевой плавки эффективен для очистки гафния от металлических примесей. Применение раскисляющих добавок позволяет очистить гафний от кислорода, а проведение вакуумно-термической обработки исходной шихты обеспечивает необходимое содержание азота.

ЧИСТИЙ ГАФНІЙ ДЛЯ ЯДЕРНОЇ ЕНЕРГЕТИКИ

М.М. Пилипенко, А.О. Дробішевська, Ю.С. Стаднік, Ю.О. Ступак

Досліджено процеси отримання гафнію реакторної чистоти. Показано, що метод електронно-променевої плавки ефективний для очищення гафнію від металевих домішок. Застосування добавок, що розкислюють, дозволяє очистити гафній від кисню, а проведення вакуумно-термічної обробки вихідної шихти забезпечує необхідний вміст азоту.