UDC 669.297

PURIFICATION OF HAFNIUM FROM OXYGEN AND NITROGEN

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Received 24.08.2013

Data on the influence content of interstitial impurities on the mechanical properties of hafnium are presented in this work. Investigations the purification of hafnium from oxygen at added of aluminum on the melting reduction stage with subsequent refining electron beam melting were performed. It is shown that vacuum thermal treatment of hafnium tetrafluoride before carrying out melting reduction reduces the nitrogen content in hafnium less than 0.005 wt.%.

Keywords: hafnium, reactor, refining, impurities, properties.

ОЧИСТКА ГАФНИЯ ОТ КИСЛОРОДА И АЗОТА

Н.Н. Пилипенко, А.А. Дробышевская

В работе приведены данные по влиянию содержания примесей внедрения на механические свойства гафния. Выполнены исследования по очистке гафния от кислорода при введении алюминия на стадии восстановительной плавки с последующей рафинирующей электронно-лучевой плавкой. Показано, что вакуум-термическая обработка тетрафторида гафния перед проведением восстановительной плавки обеспечивает снижение содержания азота в гафнии меньше 0,005 мас.%.

Ключевые слова: гафний, реактор, рафинирование, примеси, свойства.

ОЧИСТКА ГАФНІЮ ВІД КИСНЮ ТА АЗОТУ

М.М. Пилипенко, А.О. Дробишевська

В роботі приведені дані щодо впливу вмісту домішок проникнення на механічні властивості гафнію. Виконано дослідження з очищення гафнію від кисню при введенні алюмінію на стадії відновлювальної плавки з подальшою електронно-променевою плавкою. Показано, що вакуум-термічна обробка тетрафториду гафнію перед проведенням відновлювальної плавки забезпечує зниження вмісту азоту в гафнії менше 0,005 мас.%.

Ключові слова: гафній, реактор, рафінування, домішки, властивості.

INTRODUCTION

In WWER reactors as in similar foreign reactors PWR the clustered assemblies of absorber elements of control protection system (CPS) serve as regulators [1]. The clustered assemblies can be operated in automatic control regime of reactor power and in the emergency protection regime. In the standard absorber elements vibrocompacted boron carbide powder (B_4C) with a natural abundance of the ^{10}B isotope used as an absorbent material. Cladding of absorber element diameter of 8.2 mm and a wall thickness of 0.6 mm is made of steel 06X18H10T. Immersion depth in the core of auto regulation rods is from 1500 mm at the beginning of the campaign to 300 mm at the end of the campaign and emergency protection rods during normal operation of the reactor are in the raised position at a distance of 80 – 100 mm from the upper edge of the core. Thus during reactor operation all the rods of control protection system are in non-uniform neutron field resulting in an uneven burnup of the ^{10}B isotope in boron carbide range adjustment of the absorber element. Their lower parts are at greatest irradiation.

Rather small term the service of the standard absorber elements of WWER-1000 (2 years in automatic regime and 5 years in the emergency protection regime) is connected both with significant embrittlement of the steel cladding 06X18H10T and a swelling of the absorber due to the reaction $^{10}B + {}^{1}n \rightarrow {}^{7}Li + {}^{4}He$. At a burnup of the ^{10}B isotope mo-re 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. Containing ^{10}B isotopes (n, α)-absorbers are characterized by relatively low radiation resistance due to the accumulation of large amount of gas products and do not provide the operability in emergency situations related to overheating.

Visible progress in increasing service life the clustered assemblies of CPS can be achieved when using a combined (n,α)-(n,γ)-absorber in the absorber elements of CPS of pressurized water reactors [2, 3]. As a result developed an interest to hafnium relating to the number of (n, γ)-absorbers. Hafnium in the absorber elements of CPS can simultaneously perform functions the neutron absorber and construction material. Fig. 1 shows the absorber elements of various types.

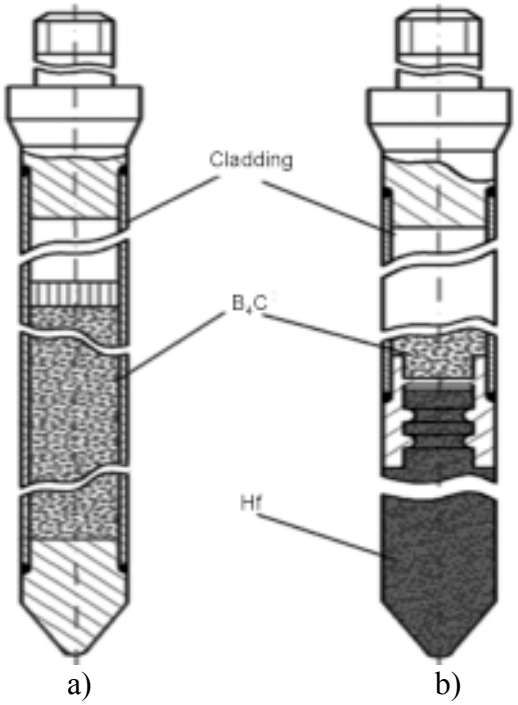

Fig. 1. Absorber elements with boron carbide (a) and combined (n, α)-(n, γ)-absorber (b).

Pure hafnium has a complex of physical-chemical and mechanical properties [4, 5] that allow using it for the production of regulators 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. 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 [2]. The relative physical efficiency of Hf in respect to the core of WWER-1000 is ~80% of the efficiency of boron carbide [6].

According to foreign and domestic researchers [1, 6, 7] hafnium is an ideal material for control rods in pressurized water reactors and can be successfully used as an absorber rods of CPS WWER-1000 reactors.

In Ukraine the technology for obtaining of hafnium including hydrometallurgical repartition (the production of pure hafnium tetrafluoride – HfF_4) and metallurgical repartition (calcium thermal reduction of hafnium tetrafluoride and subsequent electron-beam melting (EBM)) is developed [8]. 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.

On the hafnium properties influence the impurity contained therein. 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 fig. 2 and

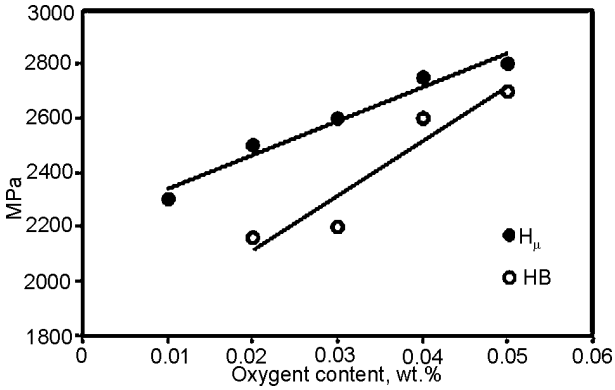

Fig. 2. The values of microhardness H_μ and Brinell hardness HB for hafnium with different oxygen content.

in tabl. 1 [9].

Table 1

The data of mechanical researches of hafnium with different oxygen content

Oxygen content, wt.%	$\sigma_в$, 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

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

PURIFICATION FROM OXYGEN

To remove oxygen from hafnium during EBM was suggested at a stage of reduction melting added into metal a third component which would formed a volatile oxide. This component should have a greater affinity for oxygen than hafnium and its gaseous suboxide should have greater volatility at the melting temperature of hafnium than hafnium monoxide.

Based on the analysis of literature data and taking into account obtained results of laboratory studies aluminum was chosen as a hafnium deoxidizer [10, 11]. The calculation of deoxidizing ability of aluminum showed that aluminum forms a volatile oxide which then desorbed from the hafnium at EBM by reaction $2Al_{Hf} + [O] \rightarrow (Al_2O)_{gas}$. Aluminum was added into hafnium on the reduction melting stage in an amount of 0.2 – 0.25 wt.% and then roughing metal subjected to remelting by electron beam in vacuum $1 \cdot 10^{-2} – 3 \cdot 10^{-3}$ Pa. According to the experimental results (tabl. 2) lower oxygen content is observed already on the reduction stage and significantly – after electron beam melting [10, 11]. The oxygen content is decreased almost three times (from 0.11 – 0.12 to 0.03 – 0.04 wt.%). The aluminum content in all samples of hafnium obtained after electron beam melting was $(2 – 3) \cdot 10^{-3}$ wt.% regardless of the aluminum additives were added or no.

Table 2

Oxygen content in hafnium after electron beam melting

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

Using the parameters obtained in laboratory researches in factory conditions the hafnium ingots purity of more than 99.94 wt.% were obtained at the addition of aluminum on the reduction melting stage after EBM with an impurity content: nitrogen – $3.0 \cdot 10^{-3}$ wt.%.; aluminum – $3.0 \cdot 10^{-3}$ wt.%.; tungsten – $1.0 \cdot 10^{-3}$ wt.%.; iron – $3.0 \cdot 10^{-3}$ wt.%.; oxygen – $4.0 \cdot 10^{-2}$ wt.%.; silicon – $3 \cdot 10^{-3}$ wt.%.; manganese – $3.0 \cdot 10^{-4}$ wt.%.; copper – $2.0 \cdot 10^{-3}$ wt.%.; nickel – $3.0 \cdot 10^{-3}$ wt.%.; niobium – $2.0 \cdot 10^{-3}$ wt.%.; carbon – $3.0 \cdot 10^{-3}$ wt.%.; chrome – $1.0 \cdot 10^{-3}$ wt.%. Hafnium obtained by using of aluminum additives on the reduction stage after refining by EBM can be successfully used as the construction material of a nuclear reactor core.

REDUCING THE CONCENTRATION OF NITROGEN IN HAFNIUM

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 [12].

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 $1.3 \cdot 10^{-1} – 1.3 \cdot 10^{-6}$ 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 [13, 14]. Change of the general pressure in the chamber during heating of the unsublimated and sublimed hafnium tetrafluoride is shown in fig. 3. It is noted that amount of the gases desorbed from the sublimated and unsublimated hafnium tetrafluoride is significantly different. From unsublimated hafnium

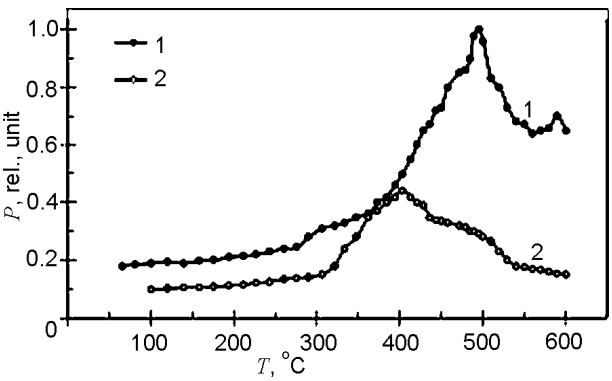

Fig. 3. Change of the total pressure in the chamber during heating of unsublimated (1) and sublimed (2) hafnium tetrafluoride.

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 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 H_2O) (fig. 4). 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.

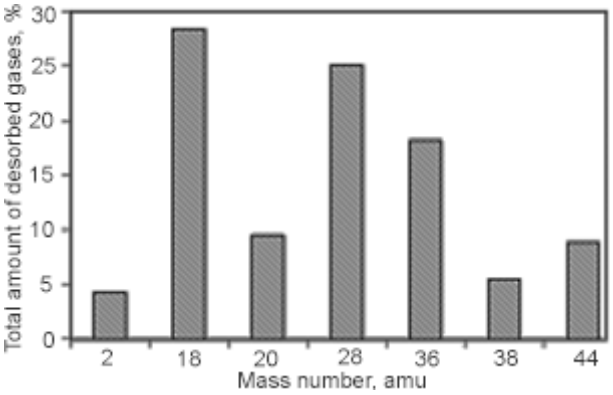

Fig. 4. Percentage of the desorbed gases with different masses from the unsublimated hafnium tetrafluoride in the temperature range 20 – 600 °C.

The results obtained allow to conclude that for reducing the nitrogen content in hafnium when using sublimed 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.%.

CONCLUSION

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 gas 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 electron beam melting 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 obtaining of hafnium with low oxygen and nitrogen content for modern technologies and creating of construction materials for nuclear reactors of the new generation and other responsible applications.

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