SECTION 1

PURE MATERIALS AND THE VACUUM TECHNOLOGIES

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HIGH PURE ZIRCONIUM

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The results of investigations of zirconium refining processes by methods of electron-beam melting and zone recrystallization using high-vacuum technology are presented. It is shown that the applied methods of zirconium refining allow to effectively reduce the content of impurities. Investigation of the properties of the obtained samples of high-purity zirconium and the dependence of these properties on the content of impurities allowed to reveal new features of high-purity zirconium.

INTRODUCTION

Pure metals are widely used in important areas of new technology and the national economy: nuclear power engineering, microelectronics, space technology, medicine, as well as fundamental research. The need for high-purity metals for science is determined by the need to establish their true properties. With an increase in the purity of metals, not only their known properties change, but also new, previously masked by the presence of impurities.

Optimum combination of nuclear, corrosion, mechanical, thermal and other physical and chemical properties [1–3] make zirconium one of the best materials for core of light water nuclear reactors with a working temperature of the coolant to 350…400 °C. However, impurities in zirconium alloys significantly affect their structure and properties. The presence in zirconium in C, Si, P, Mg, K, Ca, O, Na, Cl, F, Ni, H, especially in complex content, have a negative impact. Even very small additives effectively affect the physico-mechanical and physicochemical properties of zirconium, which may cause a change in the mechanical and corrosion properties of zirconium alloys, as well as changes in optimal modes of deformation and heat treatment [4–6]. In addition, the influence of the total content of impurities on the properties of zirconium alloys is also possible. It is also necessary to limit the content of materials with a high neutron absorption coefficient, in particular hafnium (less than 0.01 wt.%) in zirconium, which is explained by the need to ensure the efficiency of the operation of the nuclear reactor. In order to meet the increasing requirements for zirconium alloys of nuclear reactors, it is necessary to reduce the concentration of these impurities to the minimum values.

High-purity zirconium is required both for the creation of new structural materials with given properties, and for studies on the detection of new properties inherent in high-purity zirconium.

Technical zirconium is mainly produced by the metal-thermal reduction of dioxide (ZrO_2), the reduction of chloride ($ZrCl_4$) by magnesium (sodium), or the electrolysis of halides in the melt of alkali metal chlorides. The content of the main component in technical zirconium is approximately 99.0…99.8%, with the main impurities are, %: O $(5…30)·10^{-2}$; C ~ $5·10^{2}$; N $(1…10)·10^{-3}$; Hf, Fe, Ni ~ 10^{-2}; A1, Cr, Cu, Ti, Co ~10^{-3} [1–3, 7]. The composition of such a metal does not meet the requirements of modern technology and requires additional refinement. In particular, zirconium for nuclear reactors should contain a small amount of impurities with a large absorption of thermal neutrons, as well as impurities that reduce its technological plasticity and corrosion resistance (interstitial impurities and a number of metallic impurities) [7–10].

Usually methods of vacuum smelting, transport reactions, etc. are used for additional purification of technical zirconium. Deep purification of this metal requires the use of a complex of methods, including chemical refining at the stage of obtaining zirconium salts and physical methods [3, 7, 9, 11].

Getting zirconium of high purity is very complicated by its high chemical activity in relation to interstitial impurities. The purity that is achieved is determined not only by the efficiency of the purification method, but also by the amount of impurities which absorbed by the metal during the refining process.

The development of new and improved existing zirconium alloys is impossible without a deep study of the processes of obtaining high purity zirconium. In this regard, it is necessary to study the patterns of behavior of impurities in the process of obtaining high-purity zirconium by physical methods and study the influence of the purity of the metal on its properties.

The conducted research was aimed at physically substantiating and experimentally investigating the behavior of impurities in the process of zirconium refining by physical methods and determining the effect of zirconium purity on its properties.

To achieve this goal the following tasks were solved: calculate and experimentally investigate the behavior of impurities in the process of zirconium refining by electron-beam melting (EBM) and zone recrystallization in high vacuum; obtain high purity zirconium and investigate the effect of zirconium purity on its properties.

MATERIALS AND METHODS

For the refining of zirconium were used: melting and zone recrystallization in an ultra-high vacuum with the use of electronic heating and a combination of some methods.

EBM of zirconium 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 $1.7\cdot10^{-6}$ Pa [7]. In the spectrum of the residual gas in installation were absent heavy hydrocarbons. Refining of zirconium is carried out in vacuum $(1\ldots5)\cdot10^{-5}$ Pa. Refining is conducted in the regime: heating ⇒ melting ⇒ excerpt of metal in molten state ⇒ crystallization ⇒ pulling ingot. Zone recrystallization with an electron-beam heating is carried out in installations with combined pumping systems [7]. Diffusion pumps are equipped with sorption and condensation traps; sorption, cryogenic and ion-sorption pumps which are used to give “oil-free” ultrahigh vacuum. Electron-beam zone recrystallization is carried out in vacuum $1\cdot10^{-6}\ldots1\cdot10^{-5}$ Pa. Choice of pumping system for different methods of refining determined mainly by degree of interaction metals in refining conditions with residual gases of the vacuum environment.

The initial materials used for research: zirconium obtained by calcium-thermal recovery of zirconium tetrafluoride (CTZ) and zirconium after iodide refining (IZr).

RESULTS OF ZIRCONIUM REFINING

ELECTRON-BEAM MELTING

One of the main methods of zirconium refining is EBM, which allows to obtain pure metal. The process of EBM consists in the melting of the initial ingot in a vacuum and its further crystallization.

The EBM process of zirconium is characterized by the presence of limiting degrees of purification of more volatile metallic impurities. Calculated minimum achievable concentrations of impurities in zirconium after EBM are given in Tabl. 1 [11]. The calculation of the minimum achievable concentration of impurity was carried out based on the fact that the distribution coefficient is equal to 1, according to the formula:

$$C_{\min}^{Me} = \frac{p_{Zr}^{0}}{\gamma_{Me}\cdot p_{Me}^{0}}\sqrt{\frac{M_{Me}}{M_{Zr}}}, \qquad (1)$$

where p_{Zr}^{0} and p_{Me}^{0} – partial pressure of zirconium vapor and impurity; γ_{Me} – coefficient of activity of the impurity; M_{Zr} and M_{Me} – the molecular masses of the components.

It follows from Tabl. 1 that purification of zirconium from volatile impurities decreases in a series: Zn > Be > Mn > Al > Cr > Cu > V > Fe > Co > Ni > Si. In the process of EBM, it may be difficult to purify zirconium up to the required level from Co, Si, and Ni.

The degree of metal purification can be related to the loss of the weight of the main component [7]:

$$\lg\frac{C}{C_0} = (\alpha-1)\lg\frac{W_{Zr}}{W_{Zr}^{0}}, \qquad (2)$$

where C_0 and C are the initial and final concentrations of the impurity; W_{Zr}^{0} and W_{Zr} – the initial and final weight of the main component; $\alpha = \frac{p_{Me}^{0}\cdot\gamma_{Me}}{p_{Zr}^{0}}\sqrt{\frac{M_{Zr}}{M_{Me}}}$ – the purification factor. Effective purification is possible only when α>>1.

For the study of the behavior of impurities in zirconium during its refining by the method of the EBM, the values included in equation (2) were determined. An estimation of efficiency of purification of zirconium from impurities was carried out by this method.

Table 1

Minimum estimated concentrations of impurities in zirconium

Impurity	Coefficient of activity, γ_{Me}	Concentration, wt.%
Aluminum	0.07	$9.1\cdot10^{-4}$
Beryllium	0.38	$3.9\cdot10^{-5}$
Vanadium	0.72	$1.3\cdot10^{-2}$
Iron	0.052	$4.4\cdot10^{-2}$
Cobalt	0.011	$3.3\cdot10^{-1}$
Silicon	0.0006	1
Manganese	0.18	$1.4\cdot10^{-4}$
Copper	0.088	$4.8\cdot10^{-3}$
Nickel	0.004	0.9
Chrome	0.14	$2.0\cdot10^{-3}$
Zinc	0.025	$1.0\cdot10^{-5}$
Molybdenum, Niobium, Hafnium, Tungsten	–	No purification

The content of impurities, which is expected after the EBM with weight loss of the main element (zirconium) from 1 to 5%, was determined. The analysis of the results of calculations made it possible to draw a conclusion on the efficiency of purification of zirconium from metallic impurities when it was refined by the method of EBM. The generalized results of calculations of the efficiency of purification of zirconium by the method of EBM are given in Tabl. 2. It can be seen that when refining zirconium with this method, the metal impurities Al, Cu, Ti, Be, Fe, Mn, Cr have a purification factor α of more than 250 and are effectively removed from zirconium; impurities Si, Ni, B have α from 1 to 250 and will be removed only if the weight of the base is lost to 2%, and the impurities Hf, Nb, and Mo, having $\alpha < 1$, will accumulate in zirconium, so they need to be removed at earlier stages of purification.

Experimental studies have shown that electron-beam melting is a very effective process for refining of zirconium. Impurity contents in iodide zirconium after electron-beam melting are shown in Tabl. 3. In the Table, in addition to the chemical purity of zirconium, which is characterized by the total content of impurities, the value of the residual resistivity ratio *RRR* = *R*(300 K)/*R*(4.2 K) is given.

From Tabl. 3 it can be seen that the use of EBM leads to a decrease in the content of impurities in Zr. The main elements that are not removed from zirconium during the EBM are Hf, C, and Mo. Comparison with the estimated concentrations of impurities carried out by the ratio (2) show that the concentration of Hf, Mo, and Ti in zirconium is well in line with the calculated values. However, the content of other metal impurities exceeds the calculated values, especially for Si, Fe, and Cr.

Table 2

The efficiency of purification of zirconium by the method of EBM

Coefficient α	Efficiency	Impurities
<1	no purification even if the weight of the base is lost to 5%	Hf, Mo, Nb
1…250	significant purification if the weight of the base is lost to 2%	B, Si, Ni
>250	significant purification if the weight of the base is lost <1%	Al, Cu, Ti, Be, Fe, Mn, Cr

The microhardness of the initial iodide zirconium was 1200 MPa, and after the EBM it dropped to 800 MPa. The dual remelting of iodide zirconium in an installation with an oil-free pumping system made it possible to get a zirconium ingot with a hardness of 640 MPa, a purity of 99.99 wt.%.

Favorable refining conditions in combination with optimal technology allow to achieve a significant increase in metallurgical purity of zirconium at the EBM. The generalized results of systematic researches of the process of CTZ and iodide zirconium refining by the method of EBM, obtained by the author [12–14], are characterized by the following data: microhardness of zirconium decreases from 1200 to 800 MPa, there is a significant decrease in the concentration of metal and gas impurities in zirconium, as well as a decrease in the hardness of samples of zirconium. Moreover, the parameters of the purity of the double refining of zirconium by the method of EBM are somewhat better.

Changes in the content of metallic impurities in the CTZ after two EBM are shown in Fig. 1. The content of interstitial impurities in the CTZ varies from 0.18 to 0.12 wt.% after the first EBM and to 0.1 wt.% after the second EBM (Fig. 2,a). Brinell hardness of CTZ decreases from 2250 to 1750 and 1370 MPa after the first and second EBM respectively (see Fig. 2,b). The given data testify to the efficiency of the EBM method when refining zirconium from impurities [12].

Table 3

Impurity contents in iodide zirconium

Impurity	The content of impurities, wt.%	
	Initial	After EBM
Oxygen	0.04	0.008…0.013
Nitrogen	0.006	0.004
Carbon	0.035…0.04	0.025
Hydrogen	0.0045	0.001
Iron	0.025	0.008
Aluminum	0.004	0.003
Copper	0.0065	0.0006
Nickel	0.0065	0.004
Chrome	0.005	0.002
Titanium	0.0023	0.0001
Silicon	0.006	0.005
Niobium	<0.001	<0.001
Hafnium	0.018	0.018
Calcium	0.006	0.0001
Fluorine	0.003	0.0002
Molybdenum	0.005	<0.001
RRR	30	100

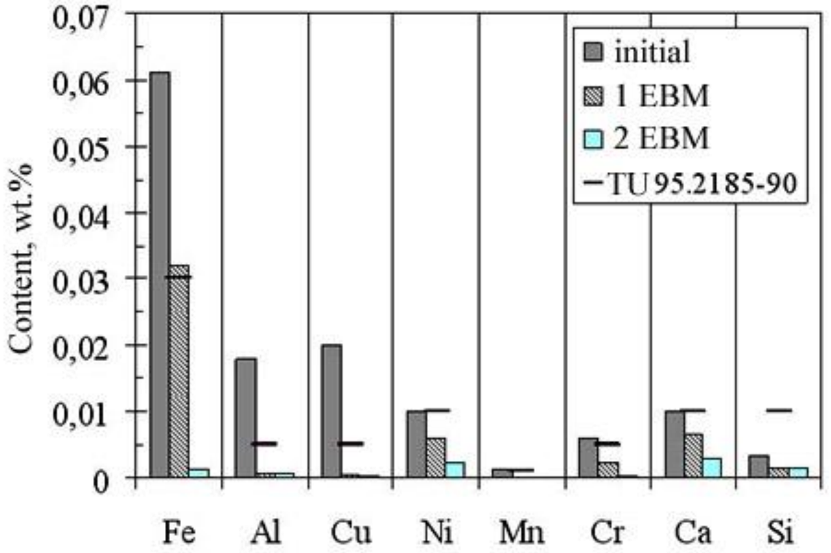
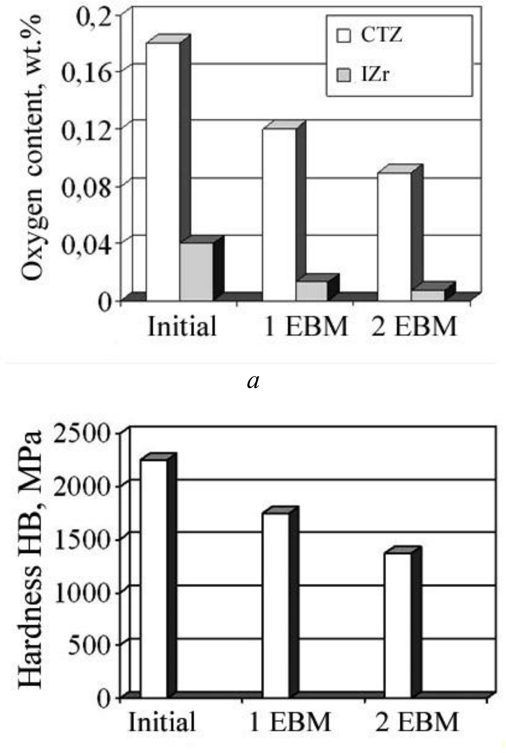


Fig. 1. Changes in the content of metallic impurities in zirconium after two EBM



a

b

Fig. 2. Change in the oxygen content in CTZ and iodide metal (a) and the change in the hardness of Brinell of CTZ (b) depending on the number of melting

Further purification of zirconium can be achieved by using a complex of chemical and physical refining techniques. In particular, in the previous stages, more complete removal of hafnium, nitrogen, carbon, etc. from zirconium is needed. The removal of volatile metallic impurities can be achieved by electron beam melting; it is advisable to add deoxidizing components for the refining of zirconium from oxygen.

ZONE RECRYSTALLIZATION

Of all the refractory metals, zirconium has the least pressure of the saturated vapor at the melting point, which allows it to be subjected to multiple zone recrystallization in a vacuum without noticeable evaporation. Perhaps for this reason, the method of zone melting (recrystallization) is most often used for deep purification of zirconium. The difficulty of zirconium refining by zone smelting is due to the fact that zirconium, unlike most other rare metals, has a hexagonal close-packed lattice (hcp) with large lattice periods and somewhat increased in comparison with the ideal ratio of *c/a.* The solubility of gas impurities in it, especially the oxygen admixture, is elevated; in addition, it does not form volatile oxides, which facilitate the removal of oxygen during the smelting of other refractory rare metals. For this reason, the requirements for purity of the gas environment during refining of zirconium are increasing.

Experimental results of the zone melting of metals showed the existence of two mechanisms of purification – zone recrystallization and evaporation. Therefore, it is possible to obtain higher purity of zirconium by using the zone melting. During the first passes of zone the refining occurs mainly by evaporation of volatile metallic impurities (Fe, Ni, A1, Ti, Cr, Si, etc.), removal of hydrogen and a certain amount of oxygen, carbon and nitrogen. After that, in zirconium, the main impurities are carbon, oxygen and hafnium. Next passes of the zone cause redistribution of impurities (mainly oxygen) along the sample length. Effective distribution coefficient K for metal impurities is less than 1 ($K < 1$); for oxygen, nitrogen and carbon $K > 1$.

Application of zone melting allowed to obtain high degree of purity zirconium. Studies have shown that zone melting in a higher vacuum ensures a more pure metal. With the increase in the number of passes of the zone there is a general increase in the purity of the metal, due to the evaporation of impurities and increase the distribution of impurities along the sample length. The holding of six passes of zone in vacuum $6 \cdot 10^{-6}$ Pa at a speed displacement of zone 1.2 cm/h it is possible to obtain a high-purity zirconium: residual resistivity ratio $RRR = 250$ and the value of microhardness of 590 MPa. Contents of oxygen, nitrogen and carbon equal $2.0 \cdot 10^{-3}$, $1.7 \cdot 10^{-3}$, and $9.0 \cdot 10^{-3}$ wt.%, respectively, the content of metallic impurities is less than 10^{-5} wt.% [15].

INFLUENCE OF ZIRCONIUM PURITY ON ITS PROPERTIES

The study of the effect of metal purity on the microstructure and the mechanical properties of zirconium showed a significant effect of the purity of the metal on the properties.

In the study of microstructure, it was found that the structure of pure zirconium (RRR ~100) consists of relatively large grains, the size of which is 5…10 mm. With a decrease in the purity of zirconium, the size of the grains decreases, and in the case of technical purity metal (RRR ~7) after annealing the grain size was 0.5…2.0 mm. The microstructure of zirconium with $RRR = 30$ is shown in Fig. 3. In all investigated samples, irrespective of purity, two types of inclusion were found: needles, located mainly on the borders of the grains, and rounded inside the grains. With the increase of zirconium purity, the inclusions diminish from 0.5…1.0 to 0.2 μm, as well as their number decreases.

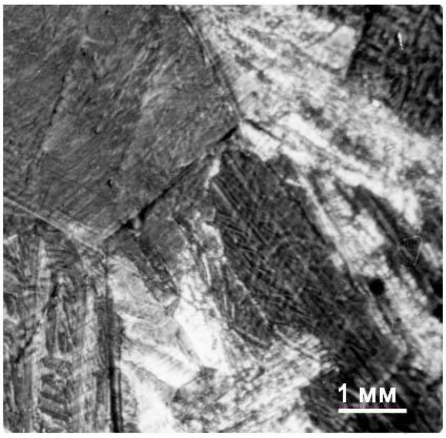


Fig. 3. Microstructure of zirconium with RRR = 30

The mechanical properties of high purity zirconium and the effect of purity on the characteristics of strength and ductility of zirconium were investigated [15, 16]. Increasing the purity of zirconium leads to a decrease in the values of the ultimate strength and increase the plasticity (Tabl. 4). The microhardness (H_μ) of such samples is also reduced. The properties of metals, in particular the amount of microhardness, depend to a large extent on the content of impurities. The dependence of the change in the value of the microhardness of zirconium on the oxygen content is shown in Fig. 4. It is seen that the value of the value of microhardness of zirconium depends on the concentration of oxygen in the metal. Therefore, according to the value of microhardness, it is possible to determine the purity of the metal.

Table 4

Mechanical properties of zirconium of different purity

Relative residual resistivity *RRR*	Ultimate tensile strength σ_B, MPa	Yield strength $\sigma_{0.2}$, MPa	Elongation δ, %
7	400…470	280…320	18.0
30	200	120	28.0
100	130	85	34.0
200	105	25	49.5

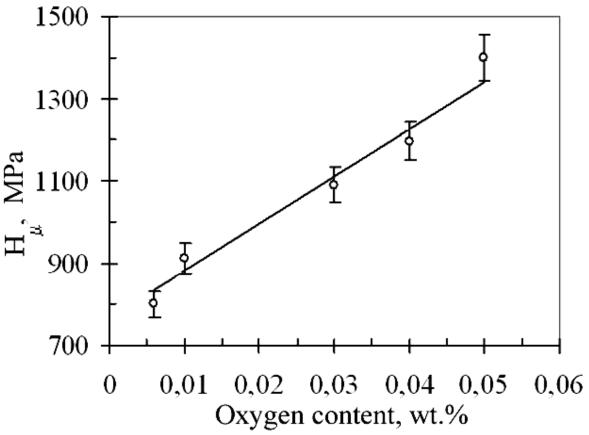


Fig. 4. Dependence of microhardness of zirconium on the oxygen content

CONCLUSIONS

The behavior of metallic impurities and interstitial impurities during electron beam melting and zone recrystallization in high vacuum were investigated. Zirconium of high purity was obtained and the influence of zirconium purity on its properties was investigated. The peculiarities of zirconium properties are determined depending on the content of impurities.

Thus, studies have shown that EBM and zone recrystallization in high-vacuum allow to effectively reduce the content of impurities in zirconium and to obtain high-purity zirconium.

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ВЫСОКОЧИСТЫЙ ЦИРКОНИЙ

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Изложены результаты исследований процессов рафинирования циркония методами электронно-лучевой плавки и зонной перекристаллизации с применением высоковакуумной техники. Показано, что применяемые методы рафинирования циркония позволяют эффективно снизить содержание примесей. Исследования свойств полученных образцов высокочистого циркония и зависимости этих свойств от содержания примесей позволили выявить новые особенности высокочистого циркония.

ВИСОКОЧИСТИЙ ЦИРКОНІЙ

М.М. Пилипенко

Викладено результати досліджень процесів рафінування цирконію методами електронно-променевої плавки та зонної перекристалізації із застосуванням високовакуумної техніки. Показано, що ці методи рафінування цирконію дозволяють ефективно знизити вміст домішок. Дослідження властивостей отриманих зразків високочистого цирконію і залежності цих властивостей від вмісту домішок дозволили виявити нові особливості високочистого цирконію.