SECTION 1
PURE MATERIALS AND VACUUM TECHNOLOGIES

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OBTAINING AND APPLICATION OF SOME HIGH-PURE METALS

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The results of systematic research on the complex refining of some chemical-activity and rare metals, and some applications of these are represented. Methods of melting, crystallisation, distillation and electrotransport in high vacuum and different combinations of these methods were mainly used for the refining of metals. Complex refining based on the use of complementary physical-chemical, physical methods and wide use ultrahigh vacuum technology, achieves the highest degrees of purification and obtaining metals in its purest form.

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INTRODUCTION

In recent years, the market demand for high-purity metals has continued to expand. High-purity metals are widely used in modern technology and the national economy: nuclear power, electronic, aerospace, medicine, defence, and military industries, as well as in fundamental scientific research. The fields of application of high-purity rare metals are constantly expanding. The development trend of modern science and technology requires high-purity or ultra-high-purity of metals, because some important characteristics of metals are affected by the type and amount of impurities in the matrix, and some characteristics are even masked by trace elements. Therefore, existing methods of refining metals are being improved all the time and new ones are being developed.

This article systematically summarises the relevant research on the production of high-purity metals and presents some areas of their application. For obtaining pure metals at different stages of refining use various chemical and physical-chemical methods, but usually the refining process completes physical methods – distillation, zone recrystallization, electrotransport, and various combinations thereof. These methods are based mainly on physical processes: evaporation and condensation, crystallisation, diffusion and electromigration, etc. The advantages of these methods over the other are associated with the ability to achieve high purity and obtain the final product in a compact form, including single crystals with a perfect crystal structure [1].

On the basis of studies of the behaviour some impurity or groups of impurities during the refining of metals by various physical methods in NSC KIPT were developed and implemented highly efficient methods of refining metals:

– methods based on distillation processes, including the condensation of steam on the column with a temperature gradient in a closed volume, heating and distillation of metal one refining cycle and their combination in a certain order;

– melting and zone recrystallization in ultra-high vacuum and controlled (active) environments using electron beam heating;

– zone melting in combination with electrotransport;

– various combinations of the above listed methods.

Complex refining based on the use of complementary physical-chemical, physical methods and wide use ultrahigh vacuum technology, achieves the highest degrees of purification and obtaining metals in its purest form. This approach to the problem of especially pure metals developed and widely used in NSC KIPT NAS of Ukraine. Methods of obtaining ultrapure metals are continuously improved in order to increase purification efficiency, productivity and cost reduction.

Further progress in the deep purification of metals connected with the search for the most rational complex schemes of refining, with the prevention of interaction residual gases and construction materials of installations with refining metals.

The developed methods and technologies for refining of metals found a practical application in the industry for the production of Be, Nb, Ta, Zr, and many alloys with special physical-mechanical properties (heat resistant, refractory, reactor, superconducting, etc.). These technologies are based on the extensive use of vacuum technology and studied regularities of behaviour of impurities in metals. Thanks to this research NSC KIPT became one of the founders of a new direction – vacuum metallurgy [1].

Below are the results of experimental physical methods refining some metals, which are important components for the production of new materials for modern science and industry.

MATERIALS AND METHODS

Electron-beam melting (EBM), zone melting, electrotransport and distillation methods were used for obtaining pure metals.

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 [1, 2]. In the spectrum of the residual gas in installation were absent heavy hydrocarbons. Refining of metals is carried out in vacuum $(1…5) \cdot 10^{-5}$ Pa. Refining is conducted in the regime: heating → melting → excerpt of metal in molten state → crystallisation → pulling ingot.

Zone melting (recrystallization) with an electron-beam heating is carried out, as a rule, in installations with combined pumping systems [1, 3]. Diffusion pumps are equipped with sorption and condensation traps. Sorption, cryogenic and ion-sorption pumps which are used to give "oil-free" ultrahigh vacuum. Crucibleless electron-beam zone melting (ZM) is carried out in vacuum $1 \cdot 10^{-6}…1 \cdot 10^{-5}$ Pa. There are two purification mechanisms during the vacuum zone melting: zone recrystallization (distribution of impurities along the length of the ingot) and evaporation of impurities. An optimal zone melting speed and a number of zone refining times make the zone purification efficiency higher.

One method for deep refining of metal is a vacuum distillation. An interest in the distillation is due to the fact that this method allows to achieve a high degree of purification of metals with a high yield of good product, and it is environmentally friendly. The difference in vapour pressure of each metal at different temperatures is the basic principle of impure metal vacuum distillation [1]. In this process the impure metal is heated in a retort above its boiling point so that it can form vapours. The impurities do not vaporise and hence they are separated. The vapours of the pure metal are then condensed and separated in a receiver (condenser) leaving the impurities behind. The distillation process can involve condensation in a heated tube (column), the temperature of which was graduated from the bottom to the top. The impurities that are volatilized with base metal pass to the cooler end of the condenser and the purest metal was collected in a zone of the condenser which has temperature of metal condensation.

Electrotransport is used for deep refining of metals in solid and liquid states. By the concept of electrotransport (electromigration or electric field transport) it is the range of phenomena associated with the direction of movement of the solution components in solid or liquid metals under the action of direct electric current. When an electric field is applied, one of the solution components is moved toward the anode, the others – to the cathode. The electrotransport is used mainly for high purity metal production in small amounts and especially in the cases where other purification methods are not effective [4].

Choice of pumping system for different methods of refining was determined mainly by degree of interaction metals in refining conditions with residual gases of the vacuum environment.

For research of refining processes different degrees of purity were used in initial metals and obtained by various methods: powders, rods, bars, granules, wires etc.

The impurities concentration in metal samples has been determined by the Laser Mass Spectrometry measurements on EMAL-2 mass-spectrometer with a laser-plasma ion source. The limiting sensitivity of the analysis method for the metal impurities was $\sim 10^{-5}...10^{-6}$ at. %.

The use of the LECO TC-600 gas analyzer made it possible to determine the content of nitrogen and oxygen in the samples with an accuracy of $5 \cdot 10^{-8}$ at.%. The device was calibrated with certified LECO samples.

The purity level of some metals was detected by the values of residual resistivity ratio measurements. Residual resistivity ratio or residual resistance ratio (RRR) is defined as the ratio of a metal's electrical resistance at room temperature to that at 0 K, which is usually replaced by liquid helium temperature (4.2 K). It is the one of the common indexes for characterising the quality of metal, including purity and structural characteristics. The RRR measurements were performed applying a DC-method, and the resistance of the sample was obtained by a standard 4-point measurement.

The structure of the metal samples has been investigated by a metallographic method. The thin sections were prepared by electro-polishing method, and further were examined by optical microscopes at different magnifications. The microhardness of those samples was measured by PMT-3 apparatus.

RESULTS AND DISCUSSION

Iron and nickel

Iron and nickel are elements which are necessary components to produce new alloys for advanced nuclear energy of present and future. We know that high levels of impurities and gases in steels and alloys significantly reduce their mechanical, corrosion and radiation properties and, therefore, limit their application for the operating and designing nuclear reactors. New structural materials must be pure. Use of high-purity metals as initial components of new structural materials will provide desired properties in the resulting products [5–7].

Steel is one of the main structural materials for nuclear reactors. Given the complex conditions of operation of various parts and units of nuclear and thermonuclear reactors, increased requirements are set for steels and alloys. Harmful impurities in structural materials significantly affect the strength, corrosion and radiation properties. It is known that the presences of phosphorus, copper, sulphur, lead, bismuth and arsenic in steels greatly affect the low temperature radiation embrittlement of steels. The negative role of these impurities is the formation of grain boundary segregations and the reduction of grain boundary energy. As a result, conditions for the formation and development of grain-boundary cracks, the main cause of the low temperature radiation embrittlement, are facilitated [8]. The use of pure iron and pure metals as alloying components of steels will make it possible to reduce the content of harmful impurities in steels.

Nickel alloys have good technological, corrosion and radiation properties, which allows them to be considered as promising structural materials for core of fast reactors, thermonuclear reactors and reactors that

use molten metals and salts as a coolant. Various nickel based alloys are manufactured: structural, heat-resistant, corrosion-resistant and other types of alloys. The impurities in nickel have a significant effect on its structure and properties. Particularly harmful impurities in nickel are sulphur, oxygen, carbon, and some metals that form nickel fusible eutectics (Pb, Se, Bi). Such impurities like lead, tin, antimony, and sulphur have harmful effects on the heat-resistant properties of nickel alloys. These fusible impurities are usually located along the grain boundaries and have a negative effect on nickel structural materials in the operating temperature range (600…900 °C) [9].

The study of the Fe refining process was carried out by the EBM method in a vacuum at various oxygen partial pressures. Preliminary experiments have found that the oxygen partial pressure of $2 \cdot 10^{-4}$ mm Hg is optimal for removal of carbon. The partial pressure of CO was significantly increased in the spectrum of residual gases during melting with additives oxygen, indicating that there is intensive purification of Fe from carbon on the reaction of formation of carbon monoxide gas.

The EBM of Fe in vacuum decreases the content carbon to 0.015 and oxygen to 0.001 wt.%. Subsequent remelting in vacuum does not give any perceptible change in the content of oxygen and carbon. It should be noted that in the EBM process good purification takes place from nitrogen and hydrogen. Increasing the partial pressure of oxygen during EBM leads to a more intensive purification of the iron from carbon. The first remelting decreases carbon content up to 0.005 wt.%, there is a decrease of oxygen content up to 0.0008 wt.% too. The second remelting reduces the carbon content to 0.003 wt.%, but happens to be a slight increase of the oxygen content in Fe. Therefore, the third remelting of Fe in vacuum with an increased partial pressure of oxygen is undesirable.

The oxygen environment was also useful for refining Fe from Si, although the EBM in a vacuum practically does not reduce the Si content. When the iron's melting point vapour pressure of Si is low therefore the evaporation of Si at vacuum melting does not occur. Carrying out three consecutive EBM in oxygen leads to a substantial reduction of the Si content in the Fe to 0.02 wt.%, obviously, due to the formation of gaseous compound SiO, because SiO_2 has low volatility. Substantial reduction of content of Cu, Sn and Mn also occurs, but content of Ni and Cr in the iron after EBM is practically not changed. The value of the Brinell hardness for the initial samples of Armco-iron was 830 MPa, after refining – 624 MPa.

The impurity contents in carbonyl iron after EBM are given in Table 1, which shows that the impurities of Co and Ni are most difficult to remove from iron during EBM in vacuum. The value of the Brinell hardness for samples of carbonyl iron after EBM was 558 MPa.

To further reduce the content of impurities the distillation method has been applied. Impurity content in Fe after distillation (bottom of distillation column, T = 1500 °C) are shown in Table 1. The distillation of carbonyl Fe remelted by EBM makes it possible to obtain the metal of the purity more than 99.98 wt.%. The purity level of iron is largely determined by the content of Ni and Co [10].

Double EBM in a high vacuum of initial electrolytic Ni with purity 99.987 wt.%, allowed to obtain metal with purity 99.994 wt.%. The refining resulted in reduction of Fe, Co, P, Al, Mg while the concentration of As, Zn, Se, Cl decreased significantly [11]. Purification of Ni by EBM from metallic and interstitial impurities has been experimentally demonstrated. The impurity contents in Ni after EBM are shown in Table 2. Purification of Ni by EBM from metallic impurities and interstitial impurities has been experimentally demonstrated.

Table 1

Content of impurities in carbonyl iron

Impurity	Content of impurities $\cdot 10^3$, wt.%		
	Initial	After EBM	After distillation
Mn	120	2	0.1
Al	20	10	0.3
Cu	150	10	4
Co	17	17	8
Ni	150	100	20
Si	200	50	2
C	50	10	1
O	30	20	2
N	6	3	<1

It is known that the content of oxygen in Ni up to 0.24% has little effect on its ductility, however, it is a harmful impurity, since when oxygen-containing nickel is heated in a reducing atmosphere, cracks form along the grain boundaries and it becomes brittle [12]. Electron beam remelting of Ni leads to reduction of the content of interstitial impurities – O, N, C up to 0.0005, 0.00006, and 0.002 wt.%, respectively. Such interstitial impurities content has practically no effect on the properties of Ni. This is confirmed by studies of the hardness of nickel.

If purity of Ni increases then the value of the hardness decreases, for the initial nickel and after two EBM, the value of Brunel hardness (HB) is 1690 MPa and 800…900 MPa, respectively. Microhardness values also decrease for Ni after refining. For the initial Ni the value of the microhardness H_μ is 1610 MPa, and for Ni after two EBM – 1100…1270 MPa, which indicates an increase in the purity of the metal.

Studies of the Ni microstructure showed that the structure of nickel after EBM is significantly different from the structure of the initial metal. The nature of the grain structure of the samples after EBM is as follows: in the central part of the ingot there are large equiaxed grains ~ 3.2 mm in size, in the peripheral part – small, elongated ~ 0.13 mm in size. There are accumulations of impurities along the grain boundaries in nickel after the first remelting, and the grain boundaries are clean after the second remelting, there are no accumulations of impurities along them, and the number of inclusions significantly decreased, indicating that efficiency of refining nickel by method EBM.

Higher purity Ni was obtained by zone melting. The use of this method made it possible to obtain samples of

a single-crystal nickel with a diameter of 10...14 mm and a length of up to 150 mm. The degree of purification and the nature of the distribution of impurities in Ni single crystals obtained after applying 10 times of zone passes at a zone movement velocity of 4 mm/min are presented in Table 3. The data in Table show that there are two purification mechanisms: zone recrystallization (distribution of impurities along the length of the ingot) and evaporation of impurities. The RRR value of Ni increases more than 14 times after applying the ZM. To achieve a desirable purity level many zone passes should have occurred. Studies of the microstructure of Ni single crystals have shown that nickel is characterised by stepwise growth of single crystals. The microhardness values of the obtained Ni single crystals were studied depending on the degree of purity (see Table 3). The data on microhardness and RRR values of Ni single crystals indicate a significant increase in the purity of the metal in the process of refining by ZM. Studies have shown a significant improvement in the quality of the metal after refining.

Table 2

The content of impurities in Ni, wt.%

Impurity	Initial	After 2 EBM	Impurity	Initial	After 2 EBM	Impurity	Initial	After 2 EBM
Al	0.00009	0.00006	Pb	0.00007	0.00007	Zn	0.0041	0.0008
As	0.00004	0.00001	Mg	0.00005	0.00004	Sn	0.00005	0.00005
Cd	0.00005	0.00005	Co	0.0026	0.0009	Si	0.00003	0.00003
Fe	0.002	0.0017	Bi	0.00004	0.00004	Cu	0.0017	0.0017
P	0.0001	0.00007	Cl	0.0005	0.0002	Se	0.0014	0.00027

Table 3

Results of nickel refining by ZM

Properties	Initial	Single crystal after ZM		
		the beginning of the rod	the middle of the rod	the end of the rod
RRR	70	1000	750	300
H_μ, MPa	1760	950	1010	–

Vanadium and titanium

Vanadium alloys are considered as a promising candidate structural material for fusion and fast-fission reactor applications because of their attractive properties such as superior high temperature thermal and physical properties, good resistance against neutron irradiation and low neutron activation level. It is well known that increased levels of interstitial impurities such as C, N, O would result in loss of workability, weldability and irradiation resistance [13, 14]. On the other hand, increased levels of undesirable elements such as Co, Nb, Ag, Mo, Al, Na, Ni, Cu, Fe etc. would dominate the activation level of vanadium alloys which would substantially influence not only the recycling aspects of used reactor materials but also the waste management aspects of them. The required impurity levels for hands-on recycling of the low-activity vanadium alloys are around the magnitude concentrations of 0.01, 0.1, 0.01, 10, 0.5, and 30 wppm, respectively, for the elements Co, Nb, Ag, Mo, Cu, Ni, and Al based on the neutron irradiation fluence of 15 (MW·year)/m^2 [13].

The low background experiments for search of rare decays are performed in underground laboratories well-shielded from external factors using low background detectors and samples with high chemical and radioactive purity. Vanadium with the lowest concentration of natural (^{40}K, ^{232}Th, and ^{238}U), as well as anthropogenic (^{90}Sr, ^{137}Cs) radionuclides satisfy all the requirements of low background experiment for search of rare decay of ^{50}V and required level of experiment sensitivity [2].

Impurities increase the strength of Ti, also greatly reduces its ductility, but interstitial impurities such as H, O, N, and C have the strongest negative action on properties of titanium. Ti entirely loses its ability to plastic deformation and becomes brittle if it contains 0.003, 0.02, and 0.7 wt.% hydrogen, nitrogen and oxygen, respectively. Under neutron irradiation the embrittlement of Ti alloys increases with increasing contents of O, N, and H in the alloy.

Vanadium and titanium are important components for the production of low-activity alloys for nuclear power. The activation level of these alloys will be depending on impurity contents in alloys. So obtaining high-purity components (V and Ti) for low-activity alloys is relevant today.

The initial materials used for research: rods of technical V, electrolytic vanadium VEL-1 and V, which was received by iodide refining. Studies have shown that carrying out EBM of electrolytic vanadium reduces the metallic impurities for example, Cr concentration was reduced by two orders of magnitude, as well as K concentration was reduced by about 75 times [15]; although almost no reduction in silicon was noted. Carrying out electron beam melting of V in vacuum $5\cdot10^{-4}$ Pa allowed to increase the purity of metal up to 99.95 wt.%. The impurity contents in V after EBM are given in Table 4 [15].

Carrying out ZM can effectively remove impurities of Al, Fe, Ni, Cu and Cr. Si is slightly removed while impurities of refractory metals (W, Mo, Ta and Nb) accumulated during long recrystallization of V [16].

Table 5 compares the effectiveness of purification of technical purity V rods by methods of EBM and zone melting. The data in Table 5 show that ZM is a more effective method for purification of V samples than EBM. Si content in a technical metal is high, and it is the limiting impurity for the ZM process.

Table 4

The impurity contents in V after EBM, ppm

Metal	Al	Fe	Si	Cu	Cr	Na	K	Mn	Ni	Cl	P	O
Initial	120	70	17	100	850	3	130	1.5	8	42	70	590…800
After EBM	11	10	17	18	7	0.4	1.7	0.11	5	4	0.5	160…200

Table 5

The content of impurities in the technical vanadium after EBM and ZM

Type of metal	Content of impurities, ppm						
	Fe	Cr	Cu	Mo	Si	Mg	Al
Initial	1000	30	5	60	1500	16	200
After EBM in vacuum $5\cdot10^{-4}$ Pa	200	<30	2.4	40	1500	5	20
After ZM in vacuum $2\cdot10^{-5}$ Pa	17	<30	<1.4	20	1300	<0.5	<10

The most pure V was obtained using a method of electrotransport or electromigration on wire samples obtained from metal after double EBM of electrolytic powder vanadium. Studies have shown that interstitial impurities are migrated to the cathode side of the V sample when passing a constant electric current of high density, i.e. effective charge of these impurities is positive. From the numerical calculations of solution of the equation for electrotransport follows that at 1650°C for 200 h at a current density of approximately $5\cdot10^3$ A/sm^2 electrotransport will result in a significant reduction in oxygen, nitrogen and carbon. It is experimentally shown that under the above conditions the RRR values of V samples after purification by electrotransport increases from 50 up to 1600. The high purity V obtained by electrotransport with the value of RRR = 1200 has purity more than 99.99% wt.%.

Analysis results indicate that for a higher degree of purification of V it is necessary to use a combination of different refining methods which would remove impurities such as Si, refractory metals, C, N, O from vanadium. Vacuum distillation of V, which can reduce silicon content in the metal more than ten times as well as impurities of refractory metals, is worth exploring.

Titanium ingots with diameter of 150 mm and purity 99.99 wt.% are produced by method EBM using sponge TG-90. Impurity content in the Ti after EBM is given in Table 6. Analysis of the results of experimental melting of titanium sponge TG-90 showed that the hydrogen content of Ti after EBM decreased by 4.5 times compared to the initial concentration and the concentration of O and N was significantly decreased. Impurity content in the obtained Ti ingots is much less than required by the standards for titanium.

Table 6

Impurity content in Ti, ppm

Type of metal	Al	V	Fe	Si	Ni	O	N	H
Initial sponge TG-90	100	3	500	100	400	400	200	72
After EBM	7	1.5	400	5	50	70	15	16

More pure Ti was obtained after EBM of the initial titanium, which was received by iodide refining (iodide titanium). Impurity contents in the iodide titanium after two electron-beams remelting are: Al – $8.0\cdot10^{-1}$; P – 1.0; S – 8.0; K – $6.0\cdot10^{-1}$; Ca – 2.0; V – 3.0; Cr – 3.0; Mn < $9.0\cdot10^{-1}$; Fe – 15; Ni – 50; Cu – 3.0; Zn – 2.0; As – 8.0; Sn < 8.0 ppm. It should be noted that EBM of Ti favourably affects the vacuum conditions of the installation due to the good getter abilities of layers of titanium deposited on the chamber walls due to evaporation at EBM [7]. The physical substantiation and experimental study of the Ti refining by crucibleless electron beam zone melting method in vacuum were carried out. Calculations of the equilibrium, limiting and effective distribution coefficients for impurity elements in the base metal were carried out. The elemental composition, microstructure and microhardness of the samples have been investigated. The refining of Ti was studied experimentally, and samples with a purity of 99.92 wt.% were received. The total content of impurities was reduced by a factor of 1.5 (from 0.12 to 0.08 wt.%). The concentration of interstitial impurities was significantly reduced (oxygen – by 1.3; carbon – by 2; nitrogen – by 2.5 times) [17].

Ti refining by zone recrystallization method in an electric field made it possible to significantly reduce the content of both metallic and gas-forming impurities. The oxygen concentration was reduced by 2.2 (from 0.033 to 0.015 wt.%), carbon by 3.3 (from 0.01 to 0.003 wt.%), nitrogen by 22 times (from 0.009 to 0.0004 wt.%). The purity of the obtained samples was characterised by a value of 99.95 wt.% by Ti content. The total amount of impurities had been reduced by a factor of 2.4 (from 0.12 to 0.05 wt.%) [18].

Investigation of regularities refining of V and Ti allowed reaching a higher level of purity metals by applying methods of EBM, zone recrystallization and electrotransport in vacuum. Suggested methods for obtaining high-purity metals have created the necessary prerequisites for their use in improving existing and producing new structural materials.

Zirconium, hafnium, niobium

Zirconium, hafnium, niobium are widely used in nuclear power, space technology, chemical industry, and electronics. The possibility of using these metals in various fields of technology largely depends on their purity.

The basic material for the active zones of such reactors are zirconium-based alloys, which have an optimal combination of nuclear, corrosion, mechanical, thermal and other physicochemical characteristics. An improvement of Zr materials will increase the efficiency of existing power units, increase the depth of fuel burnup, extend the design life, ensure operational reliability and safety [19, 20]. The interstitial and metallic impurities (O, C, Si, P, Mg, K, Ca, Cl, F, Ni, H, etc.) have a negative effect on the structure and properties of Zr even in small amounts [21, 22]. This can lead to a change in mechanical and corrosion characteristics, as well as to changes in deformation and heat treatment modes. Therefore, experimenters are always interested in obtaining high-purity metal samples. The study of the characteristics of such samples makes it possible to more correctly assess the physical and mechanical properties associated with an own nature of metals.

The chemical properties of Zr and Hf are very similar, but the main applications in reactor construction are not the same due to the different neutron-physical characteristics. Hf is characterised by a high thermal neutron absorption cross section ((105±5) b), which is three orders of magnitude higher than that of Zr. Under radiation exposure, the hafnium absorption cross section decreases very slowly. This is due to the isotopic composition of Hf and the peculiarities of isotope transmutation in the neutron flux. Therefore, it finds application in the manufacture of controls for control and protection systems of reactors. Hf has good mechanical and corrosive properties over a wide temperature range [23].

The physical and mechanical properties of Hf are significantly affected by the presence of impurities, primarily interstitial impurities, especially oxygen and nitrogen. Hf is practically not amenable to mechanical processing at an increased oxygen content, which limits the possibilities of its use in nuclear power engineering. Therefore, in order to improve the quality of Hf, it is necessary to improve the metallurgical processes for obtaining hafnium of nuclear purity, its deformation processing and the study of physical and mechanical properties.

High durability and good corrosion stability (including under high temperatures) allow using niobium as a construction material. Such application is typical for producing components of aircraft, pipes and containers for transporting and storing liquid metals and capsules for radioactive heat-releasing elements. Nb is a common alloying element that allows improving the properties of steels and alloys that contain this element. Nb makes the alloy materials durable, corrosive-resistant and refractory. The considered metal is also applied in producing condensers that serve as important elements in electronics. Niobium condensers are worse than tantalum ones, but they are much cheaper. Nb_3Sn, Nb_3Ge, NbN, and NbTi compounds are used for making super condensers. Such properties are highly-demanded in scientific equipment used for physical experiments. The Nb metal used for superconductor applications requires the value of the RRR > 300, which in turn needs a stringent purity of Nb and allows impurities (substitutional and interstitial) in ppm levels only. High purity Nb is used to fabricate r.f. cavities for the acceleration of electrons.

It is well established that properties of wrought Nb and its alloys depend to a large extent on the purity of the raw material [24]. In particular, Nb and its alloys become brittle if the interstitial impurities such as O, N, H, and C are not kept sufficiently low. Further, the interstitial impurities have a marked adverse effect on room temperature ductility, ductile to brittle transition characteristics, weldability and workability.

Zr and Hf intended for reactor materials should contain no more than 0.05, 0.006, 0.005% oxygen, nitrogen, and carbon, respectively. In addition, the hafnium content should not exceed 0.01% in zirconium. The interstitial elements (oxygen, nitrogen and hydrogen) have a significant influence on the performance of zirconium [25]. On the other hand, Zr and Hf have a high chemical activity with respect to interstitial impurities, which makes it difficult to remove them by vacuum remelting. The content of interstitial impurities and HB values for Zr, Hf, and Nb after various refining methods are given in Table 7. As can be seen from Table 7, oxygen is most weakly removed from Zr, Hf and Nb during vacuum melting, although it most strongly affects the reactor properties of products made from these metals.

A technology was proposed that makes it possible to purify Zr and Hf from oxygen by introducing a deoxidizing component – Al [26–28]. The addition of aluminium to the initial calcium-thermal Zr and Hf at the stage of reduction melting reduces the oxygen content in the metals after electron beam melting to 0.03…0.004%. The aluminium content does not exceed 0.002…0.003%. This technology has been tested under pilot conditions for obtaining Zr and Hf with reduced oxygen content [27].

As a starting material were used Zr, which was produced by iodide refining (iodide Zr), and metal produced by calcium-thermal recovery of zirconium tetrafluoride (CTZr). Impurity contents in CTZr and iodide zirconium after EBM are shown in Table 8 [29, 30].

Experimental results of the ZM of metals showed the existence of two mechanisms of purification – zone recrystallization and evaporation. Therefore, it is possible to obtain higher purity of Zr by using the ZM.

Table 7

The content of interstitial impurities (wt.%) and HB values, MPa for Zr, Hf, and Nb after various refining methods

Metal condition	Zr				Hf				Nb			
	O	N	C	HB	O	N	C	HB	O	N	C	HB
Initial	0.17…0.19	0.005…0.007	0.09…0,12	1800…2100	0.08…0.12	0.005	0.055	2950	0.21	0.04	0.018	–
Vacuum-arc melting	0.17…0.19	0.003…0.006	0.008…0.1	1600…1700	0.07…0.1	0.005	0.0025	2780	0.11	0.025	0.011	520
EBM	0.05…0.1	0.002…0.006	0.005…0.006	1300	0.004…0.005	0.005	0.002	2250	0.005	0.0035	0.005	500
ZM	0.003	0.002	0.009	–	–	–	–	–	0.0025	0.001	0.003	400

Table 8

The content of impurities in Zr after EBM

Impurity	The content of impurities 10^3, wt.%		
	Iodide Zr		CTZr after EBM
	Initial	After EBM	
Cu	4	0.1	0.4
Fe	9	0.8	0.5
Al	4	0.8	0.5
Ni	40	0.6	3.5
Mg	0.4	0.3	
Mn	1.5	0.1	–
Cr	1.3	0.2	0.9
Si	18	4.5	–
Ti	2	0.4	–

Table 9 shows the results of measurements of the RRR value along the Zr samples after ZM in a various vacuum. It is seen that melting at a lower vacuum provides obtaining a more pure metal. With the increase in the number of zone passes there is an increase in the purity of the metal, evaporation of impurities and increase the separation of impurities along the ingot, zonal separation. The holding of six passes of zone in vacuum $6\cdot10^{-6}$ Pa at a movement velocity of zone 1.2 cm/h it is possible to obtain a high-purity zirconium: the RRR value is 250 and the microhardness value is 590 MPa. Contents of oxygen, nitrogen and carbon equal $2.0\cdot10^{-3}$, $1.7\cdot10^{-3}$, and $9.0\cdot10^{-3}$ wt.%, respectively, the content of metallic impurities is less than 10^{-5} wt.% [31, 32].

Table 9

RRR along the length of the Zr samples

Zr samples	The starting part of the ingot	The middle part of the ingot	The ending part of the ingot
Initial	40	40	40
After ZM in vacuum $5\cdot10^{-6}$ Pa	50	110	130
After ZM in vacuum $2\cdot10^{-7}$ Pa	75	150	250

The physical grounds and an experimental study of the efficiency of applying the zone recrystallization method in an electric field for zirconium refining from metal and gas-forming impurities were carried out. The changes in the elemental composition, microhardness, and structure of the obtained ingots were investigated. It is shown that the application of the method can significantly reduce the content of interstitial impurities. The Zr samples with a purity of 99.91 wt.% were obtained [33, 34].

The mechanical properties of high purity zirconium and the influence of the impurities of oxygen and nitrogen on the strength and ductility of zirconium have been investigated (Table 10) [31].

Refining of hafnium is carried out by electron-beam melting. The starting material is hafnium, obtained by calcium-thermal recovery of hafnium tetrafluoride. The experiments of refining of hafnium by EBM showed that an increase in power density of melting not only accelerates the process of refining of hafnium from metal impurities, but also the purification from oxygen due to its removal in a monoxide HfO. This process is known as distillation deoxidation.

Table 10

The dependence mechanical properties of Zr on its purity

Total impurity content, wt.%	σ_B, MPa	σ_{02}, MPa	δ, %
$5\cdot10^{-2}$	200	120	28.0
$1\cdot10^{-2}$	130	85	34.0
$5\cdot10^{-3}$	103	25	49.5

Table 11

The content of impurities in Hf after EBM

Impurity	wt.%	Impurity	wt.%
Al	0.001	Ni	<0.001
Si	0.0045	C	0.005
W	<0.001	Ti	0.001
N	0.001	Nb	<0.002
Fe	0.005	F	<0.001
Cu	0.0002	Ca	0.0005
O	0.01	Cr	0.0002
Mn	<0.0001	N	0.003

The calculations of the optimal parameters of the EBM for the refining of Hf from metal impurities are made. The obtained parameters were used to optimise the EBM of Hf. After two successive EBM was obtained Hf with purity ≥99.9 wt.%. Impurities content in this Hf is present in Table 11 [27, 28, 35].

The physical substantiation and experimental study of the Hf refining by crucibleless electron beam ZN method in vacuum were carried out. It was found that for the refining of Hf, the ZN method will be most efficiently applied when several stages of experiments are carried out sequentially, namely: 1) high-temperature heating; 2) ZN at a big speed (16 or 8 mm/min) to remove highly volatile metallic impurities; 3) melting at a low speed (2 or 1 mm/min) for the display of the effect of impurity displacement of together with the movement of the liquid zone; 4) thermal cycling in the temperature range of polymorphic transformation. All operations must be carried out in a vacuum of at least $1\cdot10^{-4}$ Pa [36]. Zone recrystallization made it possible to decrease the oxygen and carbon concentrations (from 0.03 to 0.02 wt. % oxygen, from 0.04 to 0.022 wt. % carbon), zirconium – from 0.23 to 0.065 wt. %.

The study of the possibility of Hf refining by the method of zone melting in an electric field (ZMEF) was also carried out. The refining of Hf by the ZMEF method was carried out with a variability of connection (in the direction and against the movement of ZN). The results of chemical analysis of refined Hf samples indicate an insignificant content of Al, Ca, Cu, Si, Ti, which were removed during the joint passage of the processes of zone recrystallization and evaporation. The concentration of Fe was significantly reduced at the stages of ZN (Table 12) [37]. The purity of Hf after the ZMEF was 99.9 wt.% (initial purity – 99.5 wt.%).

The special attention was paid to the study of the distribution of interstitial impurities in Hf after various stages of melting. The best degree of purification was achieved when ZN was carried out in an electric field directed opposite to the zone movement (See Table 12). The simultaneous passage of refining processes (evaporation of highly volatile impurities in vacuum, zone recrystallization, electrotransport) significantly increased the efficiency of Hf purification from all types of impurities. High-purity hafnium samples with a low content of interstitial impurities were obtained. The oxygen concentration decreased by 2.5 times, carbon – 20 times, nitrogen – 60 times.

Table 12

Results of chemical analysis of hafnium samples

Materials	Concentration of a chemical element, wt.%					
	Zr	O	N	C	Al	Fe
Hafnium iodide	0.23	0.03	0.003	0.04	0.003	0.007
Hf after ZM	0.21	0.02	$4\cdot10^{-4}$	0.022	$1\cdot10^{-5}$	$4\cdot10^{-4}$
Hf ZMEF $\vec{E}\uparrow\uparrow\vec{v}$	0.17	0.013	$8\cdot10^{-5}$	0.0021	$<2\cdot10^{-6}$	$5\cdot10^{-6}$
Hf ZMEF $\vec{E}\uparrow\downarrow\vec{v}$	0.12	0.011	$5\cdot10^{-5}$	0.0018	$<2\cdot10^{-6}$	$2\cdot10^{-4}$

Materials	Concentration of a chemical element, wt.%				
	Ca	Cu	Mo	Si	Ti
Hafnium iodide	0.01	0.002	0.07	0.004	0.003
Hf after ZM	$7\cdot10^{-6}$	$1\cdot10^{-5}$	0.02	$4\cdot10^{-5}$	$2\cdot10^{-4}$
Hf ZMEF $\vec{E}\uparrow\uparrow\vec{v}$	$<3\cdot10^{-6}$	$<3\cdot10^{-6}$	0.01	$<1\cdot10^{-5}$	$<5\cdot10^{-5}$
Hf ZMEF $\vec{E}\uparrow\downarrow\vec{v}$	$<3\cdot10^{-6}$	$<3\cdot10^{-6}$	0.008	$<1\cdot10^{-5}$	$<5\cdot10^{-5}$

The use of an integrated approach, including high-temperature heating, stages of ZN at different rates, and thermal cycling in the range of the polymorphic transformation temperature, made it possible to obtain single-crystal Hf samples. According to X-ray diffraction data, the parameters of the hafnium crystal lattice were determined: $a = (0.31950 \pm 5\cdot10^{-5})$ nm and $c = (0.50542 \pm 5\cdot10^{-5})$ nm (at 298 K), which corresponds to the density $\rho = 13.263$ g/cm^3 and axial ratio $c/a = 1.5819$ [38].

The initial material for EBM was Nb after calcium-aluminium-thermal recovery. Results of consecutive electron beam melts of Nb are summarised in Table 13. The content of metal impurities after two consecutive remelting of niobium by EBM are as follows: Al – 0.004; Fe – 0.0001; Cr < 0.001; Ni < 0.0004; Si – 0.005; Cu – 0.0006; Ca < 0.003 wt.%.

Annealing in active environments (for example, oxygen), and then in an ultra-high vacuum of wire samples of niobium allows to increase the purity of the metal up to the value of the RRR = 2500, which corresponds to the content of a basic element of 99.995 wt.%, excluding tantalum [39].

Table 13

Results refining of niobium

Material	Contents of impurity $\cdot 10^3$, wt.%				RRR	HB, MPa
	C	O	N	H		
Initial	40	210	18	6	–	–
1-t EBM	5	5	3.5	0.5	94	500
2-d EBM	3	4	1.6	<0.5	172	420
3-d EBM	1.4	–	<1	<0.5	450	384

Material of higher purity could be obtained after the refining of niobium by ZM method. The content of impurities in ZM metal with the value of the RRR = 12000 (according to neutron activation analysis) are as follows: Na – $5.0\cdot10^{-5}$; Cs < $1.0\cdot10^{-6}$; Cu < $1.0\cdot10^{-4}$; Ag < $1.0\cdot10^{-4}$; Au < $8.0\cdot10^{-9}$; Rb < $1.0\cdot10^{-5}$; Zn < $1.0\cdot10^{-5}$; Cd < $1.0\cdot10^{-5}$; Ga < $2.0\cdot10^{-8}$; Se < $2.0\cdot10^{-7}$; La < $3.0\cdot10^{-6}$; Eu < $5.0\cdot10^{-8}$; Lu < $1.0\cdot10^{-6}$; Yb < $3.0\cdot10^{-6}$; Dy < $3.0\cdot10^{-7}$; Th < $1.0\cdot10^{-5}$; Hf < $5.0\cdot10^{-6}$; As < $8.0\cdot10^{-7}$; Sb < $8.0\cdot10^{-7}$; Ta – $8.0\cdot10^{-5}$; Cr < $2.0\cdot10^{-5}$; Te < $1.0\cdot10^{-5}$; W – $1.0\cdot10^{-5}$; Mn < $5.0\cdot10^{-8}$; Fe <$5.0\cdot10^{-4}$; Co <$2.0\cdot10^{-6}$; Re – $4.0\cdot10^{-6}$; Ir < $2.0\cdot10^{-7}$; Br < $5.0\cdot10^{-8}$; Ar < $5.0\cdot10^{-6}$ wt.% [1, 3].

High-purity Zr and Nb are mainly intended for the creation of structural reactor materials – fuel cell cladding, channel pipes. High-purity Hf is one of the most promising absorbing materials for thermal reactor controls.

Tantalum and ruthenium

Tantalum features several unique properties that have led to its increasing use in a range of modern industrial applications. The metal's many unique properties – such as high melting point, corrosion resistance, hardness, and resistance to chemical attack – make it ideal for a wide range of industrial applications. Tantalum is used for manufacturing electronics, tools, and other types of industrial equipment.

Tantalum is used for the production of electrical capacitors and resistors, while the ability to hold substantial amounts of charge in a small component has made it possible for electronics manufacturers to miniaturise electrical parts and devices. With over 75% of electronics and components – such as mobile phones, computers, DVD players and video game systems – contain Ta in some format. Tantalum is also well known for its biocompatibility and this makes tantalum ideal for pairing with living tissue in medical implants and prosthetics. Ta and its alloy are used in nuclear reactors, missile parts, chemical processing equipment, heat exchangers, and storage tanks. Impurities in the metal can have an undesirable effect on the properties of the articles formed from the Ta. Decrease of total impurities or increase in purity in tantalum has resulted in the decrease of its hardness [40].

Many new uses are emerging for ruthenium. Most is used in the electronics industry for chip resistors and electrical contacts. Ru alloys also find application in manufacturing of turbines of jet engines. Ru has also applications in therapy. For instance, 106 isotope of ruthenium has application in radiotherapy of malignant cells of the eye. Ru finds application in manufacturing solar cells for production of solar energy. Ru oxide is used in the chemical industry to coat the anodes of electrochemical cells for chlorine production. Ru is also used in catalysts for ammonia and acetic acid production [41].

Ru is one of the elements used for carrying out low-background experiments for recording double β-decay. An increase in the sensitivity of the experiment is directly related to a decrease in the level of the internal background of the samples. The main sources of the internal background in the metal can be α- and β-active isotopes of natural origin. These are ^{40}K, as well as radionuclides of uranium (^{238}U and ^{235}U) and thorium (^{232}Th) series. Therefore, additional purification of Ru from these and other elements is necessary, which should also lead to a decrease in the level of background radionuclides [42].

Powder and rods of Ta with purity of 99.8 wt.% were used for purification. Vacuum electron beam melting reduces metallic impurities in Ta samples and significantly reduces the interstitial impurities ($\times10^{-4}$ wt.%): Al – 3...20; Si – 3...20; Cr <5; Fe – 5...10; Cu < 1; H_2 – 1...6; C – 3...20; N_2 – 1...10; O_2 – 5...50. Main consideration is given for behaviour of metal impurities and interstitial impurities during EBM. Degassing and evaporation of volatile impurities are the main purification processes of tantalum by EBM. The impurities which lower the contents in initial metal will allow obtaining necessary purity of Ta are determined, this is W, Re, Os, Nb [43].

Experimental results of tantalum refining by the ZM method from various starting materials (powder and rod) are given in Table 14. These data confirm the existence of two purification mechanisms: zone recrystallization (distribution of impurities along the length of the ingot) and evaporation of impurities. For example, the content of copper in the beginning part of the ingot is $1\cdot10^{-5}$, and in the end part it is $1\cdot10^{-4}$ wt.%, silicon $7\cdot10^{-5}$ and $5\cdot10^{-4}$ wt.%, respectively. Table 14 also clearly shows the influence of the movement velocity of the molten zone during the refining of tantalum by this method on the distribution of impurities in the ingot. Elemental analysis of the obtained samples showed that the main impurity elements that hinder the purity of tantalum are niobium (the content after ZM is $8\cdot10^{-2}$ wt.%), tungsten ($4\cdot10^{-3}$ wt.%), carbon ($4\cdot10^{-1}$ wt.%), and oxygen (< $3\cdot10^{-3}$ wt.%) [44].

Table 14

Distribution of RRR along the length of the Ta ingots after ZM

Metal	RRR				Parameters of ZM
	Initial	beginning of the samples	middle of the samples	end of the samples	
Rod	9	100	98	70	n=5, f=12
	9	160	154	140	n=5, f=4
Powder	–	109	115	110	n=5, f=12
	–	173	154	114	n=5, f=12; n=1, f=4

n – number of zone passes, f – zone movement velocity, mm/min.

The efficiency of ZM increases in case of its combination with the method of electrotransport. In this case, the effective distribution coefficient changes due to additional electrodiffusion flows, and an increase in the degree of purification of metals is achieved as a result of the electromigration of impurities. As a result of ZM with electrotransport, carried out under cryogenic pumping conditions, there was a redistribution of impurities along the length of the samples. For example, the carbon concentration was 0.002 and $5\cdot10^{-4}$ wt.%, iron $0.7\cdot10^{-4}$ and $<0.1\cdot10^{-4}$ wt.%, niobium 0.015 and 0.004 wt.% in the cathode and anode parts of the samples. Studies have shown that electrotransport achieves the distribution of impurity elements (niobium, carbon and oxygen) which limit the purification of tantalum by ZM; therefore, the combination of ZM with electrotransport provides a higher degree of refining [45].

Float-zone melting in an ultra-high vacuum and controlled environment in combination with electrotransport was used to improve purity of tantalum to grow single crystals. Single crystals of tantalum obtained by ZM in a controlled environment of oxygen had 99,999 wt.%. The content of metallic impurities in the resulting tantalum is below the sensitivity of analysis methods: for easily volatile $<10^{-5}$ %, for hardly volatile $<10^{-4}$ %. Zone refining were gave oriented single crystals of Ta with diameter 7…10 mm and length 150…180 mm and disorientation elements of substructure <0.01° and the microhardness value of 750 MPa [44–46].

Zone recrystallization in a rarefied oxygen medium and in combination with electrotransport is an effective process that makes it possible to obtain single-crystal samples of tantalum of a high degree of purity and high structural perfection.

Powdered ruthenium (Ru) with a purity of 99.85 wt.% was used as the starting material for refining. Purification of the initial ruthenium was carried out by the EBM method in high vacuum. Samples of high purity ruthenium were obtained by refining this method. The content of the main impurity elements in the ruthenium samples before and after the EBM is given in Table 15. The multiple EBM method made it possible to obtain ruthenium with a purity of > 99.99 wt.%, primarily due to purification from interstitial impurities and most metal impurities, including potassium. When compared with the impurity composition of the original metal, the high efficiency of using this method for refining ruthenium is confirmed. As can be seen from Table 15, as a result of refining, all the analysed impurities are purified by an average of two to three orders of magnitude, including potassium – by more than 50 times.

Table 15

The content of impurities in Ru samples, wt.%

Element	B	C	N	O	F	Na	Al
Initial Ru	0.00004	0.12	0.0001	0.004	0.00001	0.00006	0.00004
After EBM	<0.00002	0.005	0.00008	0.0006	<0.000003	0.000005	0.000001

Element	Si	P	Cl	K	Ca	Mn	Fe
Initial Ru	0.0005	0.00002	0.0002	0.0008	0.0003	0.00003	0.004
After EBM	0.00003	<0.000003	<0.000005	0.000015	0.00002	<0.000008	0.0003

Element	Ni	Co	Cu	Ga	W	Re	Os
Initial Ru	0.0002	0.0003	0.001	0.0002	0.012	0.007	0.002
After EBM	0.00005	<0.000009	0.0004	<0.00002	0.0005	0.0008	<0.001

The resulting ruthenium ingots meet the requirements for the material necessary for carrying out low-background experiments for recording double β-decay of ruthenium. The value of the microhardness of ruthenium after electron beam melting is 6420 MPa [42].

CONCLUSIONS

The purification techniques mainly depend on the physical and chemical properties of the base metal and impurities present in the respective host material matrix. The high purity levels of metals can be achieved by conventional purification processes such as zone melting, electron beam melting, distillation,

electrotransport, high vacuum annealing, etc. Zone refining and electron beam melting for high melting point metals and chemically active metals: tantalum, niobium, vanadium, zirconium, titanium, and hafnium are very much useful. Combinations of purification processes are necessary to improve the efficiency of metal purification from impurities. Ultra-high purity metals are crucial materials for fundamental scientific research and development, and production of advanced materials technologies, which generally require optimum properties, performance, quality and efficiency.

For example, further development of nuclear power is largely dependent on the development of advanced structural materials for new generation reactors and improving materials operated nuclear power plants through the use of high-purity metals as starting components and the use of new technologies of their production, which will provide extension of service life, reliability and safety of structural elements of nuclear reactors. Application of pure and high-purity metals as initial materials for components of construction NPP largely determines the further development of nuclear energy.

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ОТРИМАННЯ ТА ЗАСТОСУВАННЯ ДЕЯКИХ ВИСОКОЧИСТИХ МЕТАЛІВ

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Представлено результати систематичних досліджень з комплексного рафінування деяких хімічно активних і рідкісних металів та їх застосування. Для рафінування металів в основному використовувалися методи плавлення, кристалізації, дистиляції та електропереносу у високому вакуумі та різні комбінації цих методів. Комплексне рафінування, засноване на використанні взаємодоповнюючих один одного фізико-хімічних і фізичних методів та широкому застосуванні техніки надвисокого вакууму, дозволяє досягти найвищих ступенів очищення та отримання металів у найчистішому вигляді.