SECTION 1
PURE MATERIALS AND VACUUM TECHNOLOGIES

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HIGH-PURITY METALS: PURIFICATION METHODS AND APPLICATIONS

***M.M. Pylypenko*[1,2]**
[1]National Science Center "Kharkiv Institute of Physics and Technology", Kharkiv, Ukraine;
[2]V.N. Karazin Kharkiv National University, Kharkiv, Ukraine
E-mail: mpylypenko@kipt.kharkov.ua

Producing of high-purity metals is a challenging task due to the complexity of several process methodologies, characterization and unique process equipment required which are not readily available. The high-purity metals have been produced for use in the fields of electronics, nuclear energy, aerospace and basic research. The purification 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 have achieved the highest degrees of purification and obtaining metals in its purest form. Description of these techniques as applied to various metals is included in this article along with the results of research on the purification of some chemical-activity, refractory and fusible metals.

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INTRODUCTION

High-purity metals are crucial materials for research and development, and production of advanced materials technologies, which generally require optimum properties, performance, quality and efficiency.

High-purity of the metals is required in the fields of electronics, nuclear energy, aerospace and basic research. The stringent and ever-increasing purity materials' requirements have brought in a variety of improved and refined methods to deal with the demands.

High levels of impurity and gases in steels and alloys significantly reduce their mechanical, corrosion and radiation properties and, therefore, limit their use in operating and designing reactors. Use of high-purity metals as initial components of new structural materials will provide desired properties in the resulting products [1, 2].

The demands for ever-increasing purity of metals stem for their use in sophisticated and high performance modern devices, producing new of the structural and functional materials with improved operational properties. All this has generated and developed rapidly improved and refined methods for achieving high-purity of materials.

Any material is considered to be pure, if its physical properties determined by the atomic-crystalline structure and intrinsic defect, but not by the dissolved or substitutional impurities [3]. The purity is generally represented in terms of percentage (%), for example 99.9% means 3N (3 Nines) or it contains 0.1% of impurities or 1000 parts per million (ppm).

For achieving high purification of metals, methods at different stages of refining various chemical and physico-chemical methods are use. Usually refining process is completed by physical methods such as distillation in vacuum, melting in high vacuum, zone recrystallization, electrotransport (solid state electro-migration) and various combinations thereof. These methods are mainly physical processes: evaporation and condensation, crystallization, diffusion and electro-migration, etc. The advantages of these methods over the others are the ability to yield high-purity material and the final product is obtained in a compact form, including single crystals with a perfect crystal structure.

Various physical methods have been developed based on the nature of an impurity or groups of impurities during the refining of metals by National Science Center "Kharkiv Institute of Physics and Technology" (NSC KIPT). Highly efficient methods of refining metals include:

- 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 methods.

Comprehensive refining, based on the use of complementary physico-chemical, physical methods and implementation of controlled environments in wide use of ultra-high vacuum technology, achieves the highest degrees of clearing and obtaining large amount of metal in its purest form. Methods of obtaining ultra-pure metals are continuously improved in order to increase purification efficiency, productivity and cost reduction [4].

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 material of installations with metal.

The developed methods and technologies for refining of metals on a laboratory scale were transferred for industrial production of Be, Nb, Ta, Zr, etc. 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 behavior of impurities in metals during refining process.

This article covers details of physical methods of refining applied for obtaining of a variety of high-purity metals and discusses specific experimental achievements and practical aspects.

1. THE IMPURITIES IN METALS AND PRINCIPLE OF REFINING

Materials get additional stability by virtue of presence of the chemical impurities. This stability is partly due to chemical bonding. Hence materials tend to get contaminated. Thermodynamically addition of impurities to a high-purity material reduces the free energy. Statistically, the stability of materials due to the presence of impurities can be explained in terms of configuration entropy, which is the portion of a system's entropy that is related to the position of its constituent particles rather than to their velocity or momentum. It is physically related to the number of ways by arranging all the particles of the system while maintaining some overall set of specified system properties, such as energy. Entropy is also a measure of energy distribution through a system. As energy becomes more dispersed or evenly distributed the possibility that energy being used for mechanical work is decreased i.e entropy is increased. Natural processes (in this case contamination by impurity) always increase towards increase in disorder [5].

Variation of configuration entropy of materials is equivalent to the variation of the macroscopic entropy of thermodynamic systems, defined as

$$dS = \delta Q/T, \qquad (1)$$

where δQ is the heat exchanged between the system and the surrounding media, and T is temperature.

The configurational entropy is related to the number of possible configurations by Boltzmann's entropy formula

$$S = k_B \ln W, \qquad (2)$$

where k_B is the Boltzmann's constant, which is equal to $1.3806 \cdot 10^{-23}$ J/K and W is the number of available microstates in a macrostate (ensemble of systems) given by

$$W = N! / (N\text{-}n)!\, n!, \qquad (3)$$

where N is the number of matrix atoms and n is that of impurity. It refers to total number probabilities that a system can be in states n with probabilities.

In statistical mechanics, Boltzmann expressed entropy that can also be expressed as

$$S = k \ln P, \qquad (4)$$

where P is the probability or the number of possible ways a system can be arranged to yield a specific state. Hence, increase in P by addition of impurity leads to a state of greater stability.

Following Stirling's approximation expressed in logarithmic form ($\ln n! = n \ln n - n$). The change in entropy can be written as

$$S = k\,[N \ln N - (N\text{-}n) \ln (N\text{-}n) - n \ln n]. \qquad (5)$$

This formula gives the stability of a material due to addition of impurity. This means that configurational entropy increases as logarithm of W. For example, one mole of a solid contains 10^{23} atoms. If a small quantity of impurity element gets mixed randomly, it will end up with an extremely large number of distinguishable configurations and an appreciable amount of configurational entropy.

Since W can never be less than one, configurational entropy is either zero or positive. It is zero for an absolutely pure material consisting of the same kind of atoms on all its sites or for perfectly ordered solid like an ultra high pure compound with absolutely no impurity at zero K temperature when available as a single crystal. As the temperature increases the atoms begin to vibrate. The average energy per mode is called thermal energy and is equal to kT, where T is temperature in Kelvin and k is Boltzman's constant. For one mole of atoms thermal energy becomes $NkT = RT$, where R is the universal gas constant. Hence, it is practically impossible to have an absolutely pure material without any structural defects in it above zero Kelvin.

As naturally available material is always impure, it is necessary to adopt purification processes to remove impurities in it. The purification method to be adopted depends upon the nature of matrix material as well as the nature of the impurity. There is no universal single process that can be adopted for all the materials. In literature, varieties of processes are reported. It is the wisdom of the individual to select a right process for their specific applications. Materials with higher purity have very strong tendency to pickup impurities to remain in lower free energy state. In a refining process, we are generally concerned with removal of one or more constituents from a material that contains a number of impurities. This can be illustrated by considering a simple case of an impurity B present in a metal A. The partial molar free energy of formation of solution of B in A, can be given by

$$\Delta G_B = RT \ln a_B, \qquad (6)$$

where a_B is the activity of B in metal A.

When we consider purification of the metal, the activity (a_B) of the component B in A, tends to be zero. In such a case, ΔG_B tends to $-\infty$, indicating the formation of solution of B in A is thermodynamically highly favorable. In other words, to remove the impurity B when $a_B \rightarrow 0$ an enormous amount of work will be necessary.

In the process of their extraction, materials invariably pick up impurities present in the various sources, primary or secondary, from which they are extracted. The presence of foreign elements is an inevitable and unavoidable consequence in the metal extraction process. It must be emphasized that the word

impurity can have different meanings in different situations. The presence of an element, *A*, may be regarded as an impurity in a metal *B*; the same element *A* in metal *C* may not be regarded to the same extent. Its presence may, rather, be desirable instead of an unwanted impurity. Thus, for example, the presence of a minor amount of boron in steel is considered desirable and it is intentionally added to bring about certain improvements in the properties of steel when called for. Its presence, however, in uranium used as nuclear fuel is not tolerated [5].

2. PURIFICATION METHODS

Techniques of metal refining and purification rely on the differences in physico-chemical properties of the base metal and the impurities. In order to reach the desired high-purity, a sequence of purification steps is required. These steps fundamentally apply in the form of chemical, electrochemical and physical methods. The refining process is usually completed by physical methods.

The purification physical methods based on main properties are assembled in Fig. 1.

Different types of impurities can be categorized into chemical (chemical imperfections) and physical (physical imperfections) impurities. Chemical imperfections are the foreign substances present as interstitials or substitutionals or solid solutions in the base material. Because of their small size the interstitials such as H, N, O, and C, are difficult to remove and special efforts are required for their removal to obtain base material in high-purity. New concepts and methodologies are evolving and more efficient processes are being developed for producing special high-purity materials.

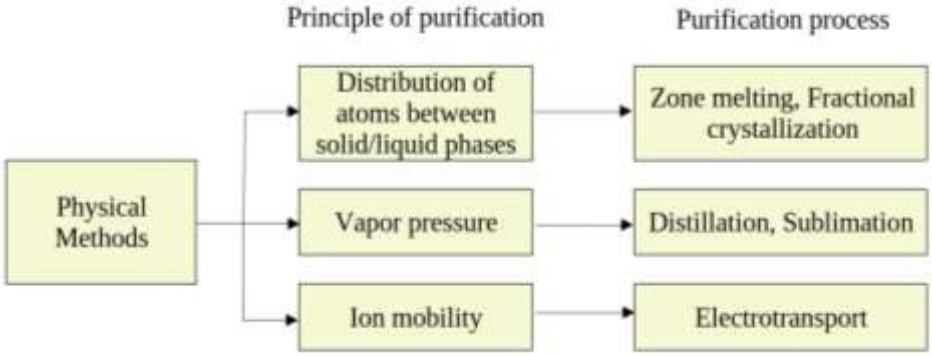

Fig. 1. The purification physical methods based on main properties

There is no one way to achieve purification of material. Physico-chemical processes utilize the difference in chemical, physical and electrochemical behaviour of concerned impurities present in the host and refined products. In the periodic table, no element is so unique that no other element will response similarly to a given treatment.

Preparation of pure materials, though seem simple, envisages having a basic knowledge of origin, type and extent of impurities in the starting material (normally a commercial grade) then working out schemes for purifications which may warrant combining or multistaging processes.

2.1. ELECTRON BEAM MELTING

Refining by electron beam melting (EBM) involves melting under high vacuum and casting in a water cooled copper crucible. Removal of impurities takes place due to degassing, evaporation, distillation and chemical reaction. High-purity refractory metals are invariably produced by this method. Residence time of the feeding and in casting pool governs the extent of purification. High level of purification is possible during EBM refining as the vacuum above the molten liquid pool is several order higher compared to that of vacuum in Vacuum Arc Remelting (VAR) or Vacuum Induction Melting (VIM) or any other melting techniques due to continuous retraction of the cast ingot in the EBM process.

In electron beam melting by virtue of high vacuum, purification takes place due to distillation of volatile impurities and degassing of gaseous impurities as per the following equations.

The distillation method is based on the difference in the compositions of shared liquid mixture and steam formed therefrom. This difference is estimated by the value of relative volatility α of separable component (separation coefficient).

Under dynamic conditions, the separation coefficient determine by the evaporation rates of the matrix metal and impurities [4, 6]:

$$\alpha_i = \frac{P_i^0 N_i \gamma_i}{P_A^0 N_A \gamma_A} \sqrt{\frac{M_A}{M_i}}, \quad (7)$$

where P_i^0 and P_A^0 saturated vapor pressures of impurity *i* and matrix metal *A;* N_i and N_A molecular fractions of impurity *i* and matrix metal *A;* γ_i and γ_A represent the activity coefficients of impurity *i* and matrix metal *A;* M_A and M_i represent the atomic masses of the matrix metal and impurities, respectively.

The minimum concentration of impurity in the refined material can be determined from the conditions: α=1; N_i+N_A=1.

The degree of purification of the matrix metal from impurities by evaporation into a vacuum during EBM is characterized by the purification coefficient (α)

$$\alpha = \frac{P_i^0 \gamma_i}{P_A^0} \sqrt{\frac{M_A}{M_i}}. \quad (8)$$

The equation directly relating the degree of purification of metal from impurities to the weight loss of the matrix metal is [7]:

$$\lg\frac{C}{C_0} = (\alpha - 1)\lg\frac{W_A}{W_A^0}, \quad (9)$$

where C_0 and C are the concentration of the impurity before and after evaporation; W_A^0 and W_A are the weight of the matrix metal before and after evaporation.

The degassing is governed by Sievert's law: $C_i = const\sqrt{p_i}$ i.e. the solubility of diatomic gas in metals C_i is directly proportional to the square root of the partial pressure of gas p_i over the metal [4].

The dissolution of gases in metal is governed by:

$$1/2\ A_2(g) = [A]_{metal}, \quad (10)$$

where A stands for gas, which may be hydrogen / nitrogen.

The main advantage of electron beam purification is effective separation of impurities due to high power density, use of water-cooled crucible, high pumping of gaseous products, continuous removal of impurities and thereby disturbing the equilibria. In addition to this, melting and casting rate can be controlled in a wide range allowing optimum purification. Pure refractory and chemical active metals like Ta, Nb, Zr, V, Hf, etc. and their alloys are being produced by the EBM method.

2.2. ZONE MELTING

Zone melting (zone recrystallization) or floating zone process are similar methods of purifying metals, in which a narrow region of a crystal is melted, and this molten zone is moved along the crystal. The molten region melts impure solid at its forward edge and leaves a wake of purer material solidified behind it as it moves through the ingot. The principle of zone refining is based on the different solubility of impurities in the liquid and solid phases of the base material. An important characteristic in the process description is the impurity distribution coefficient is k, which is the ratio of the impurity concentration in the solid phase C_S to the concentration in the melt C_L [8]:

$$k = C_S / C_L. \quad (11)$$

The numerical value of the parameter k depends on several factors: the nature of the phase diagram formed by the main component and the impurity, the solidification conditions, the movement velocity of the molten zone, the intensity of mixing, etc. If $k < 1$ the solidifying material becomes cleaner and the melt is saturated with the impurity.

It is distinguish between the concepts of equilibrium distribution coefficient k_0 and effective distribution coefficient k_e. The equilibrium coefficient k_0 is usually determined from the "base-impurity" state diagrams or by the ratio of the maximum solubility of an impurity to its concentration at the point of invariant transformation. However, with such estimation methods, k_0 values can be calculated only in the case of a significant concentration of impurities in the base material.

When carrying out the zone refining process, it is necessary that the rate of crystallization be greater than the diffusion rate of the impurity in the solid phase of the base material, but also does not exceed some optimal value. In this case, the moving crystallization front repels the dissolved impurity faster than it can evenly distribute in the melt, and an impurity-enriched region called the diffusion layer appears before the crystallization front. The width of the diffusion layer depends on the diffusion ability of the impurity, the viscosity of the melt, the nature of the fluid motion, and the rate of crystallization.

Therefore, the main characteristic of the zone impurity separation is effective distribution coefficient k_e, which can be expressed by the Burton-Prim-Slichter formula [4]:

$$k_e = \frac{1}{1+\left(\frac{1}{k_0}-1\right)exp\left(\frac{-v\delta}{D}\right)}, \quad (12)$$

where v is zone speed; δ is the diffusion layer thickness, and D is the diffusion coefficient of the impurity in the liquid. Ratio $v\delta/D$ is called as the reduced rate of crystallization (dimensionless quantity). For most metals the value of the diffusion coefficient D is $5\cdot10^{-5}$ cm^2/s approximately. The width of the diffusion layer in the case of conservative melt mixing in the zone is $\delta \approx 0.01$ cm. Therefore, the ratio $\delta/D \approx 200$ s/cm.

In zone melting only a part of the solid is molten. Local heating using resistance or induction furnaces, electron or laser beams, among others, can be applied. The heat source is moved relative to the axis of the cylindrical solid. The technique of containerless zone melting, also termed the floating-zone method, can be used advantageously if the liquid zone is short enough to be held by surface tension. The intactness or stabilization of the floating zone length is a crucial exercise of the operation as it depends on surface tension and the density of the melt. The use of floating zone melting is extended for obtaining high-purity refractory metals [9].

A good degree of purification from easily volatile metal impurities is achieved at high speeds of zone movement. The carrying out one or two passes of the zone refining at a speed of 16 or 8 mm/min leads to a significant decrease in the impurity content for which the saturated vapor pressure p_0 at the melting point of the base metal is high enough. In the case of zirconium at its melting temperature T_m = 2125 K metals such as Al, Ca, Cu, Fe, Mn, Ni, Si, Ti, Cr, etc. are characterized by the value of $p_0 > 1\cdot10^{-1}$ Pa. The saturated vapor pressure of zirconium at this temperature is $2.6\cdot10^{-3}$ Pa [10].

To obtain high-purity refractory metals samples, the vertical crucibleless zone melting method of round rods in vacuum $1\cdot10^{-4}$ Pa with electron beam heating was chosen. The method is described in sufficient detail in [11]. The advantages of this technique include: the ability to grow single crystals of refractory metals and alloys with a melting point of over 2000 K; absence of crucible; the creation of a narrow heating region by focusing an electron beam; high specific power concentration. The purification process included the

heating of the initial billet with the purpose of degassing and carrying out the refining stages by zone melting at different rates (16 to 1 mm/min). The samples were obtained in the form of cylindrical rods 100…300 mm long, with a cross section of 8...10 mm.

2.3. ELECTROTRANSPORT

An electrotransport takes a certain place among various methods of deep refining metals. By the concept of electrotransport (electrodiffusion, electrical migration) it is meant 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 (DC). When electric field applying, ones of the solution components are moved toward the anode, the others – to the cathode. Power efficiency of the electrotransport is low and to achieve significant degree of metals purification it is required large current densities and significant times. 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. However, as a method of metals deep cleaning, the electrotransport has its advantages: the method is relatively simple in the equipment design, you can use small amounts of source metal for the refining process, and, very importantly, the method makes it possible to achieve very deep cleaning of metal. Electrotransport is most prevalent method mainly to remove impurities of oxygen, nitrogen, hydrogen, carbon from almost all the rare earth metals (Y, La, Ce, Tb, Lu, Nd, etc.) and from a large refractory group (W, Mo, Ta, Nb, V, Hf, Zr, etc.) in a solid state [12]. Removal of these impurities by other methods is difficult.

It has a basic difference that the redistribution of impurities is taking place within one phase rather than partitioning between two phases (like zone refining). The apparatus comprises of a vacuum chamber, a mechanism to hold the specimen ingot, provision for high direct current supply and arrangement for adequate cooling of the electrical leads. Typically current densities in the range of $10^3...10^5$ A·cm^{-2} are applied in this process. This call for smaller cross section of the subject material is used. The samples in the form of rods by length of 8...20 cm and diameter of 4...6 mm were commonly used.

The electrotransport in solid phase has been used most widely for deep refinement of rare earth metals. Practically all of rare earth metals were subjected to refining by this method [13]. Apparently, this was due to the need of producing high-purity metals samples to determine their true properties, in particular, the different nuclear constants. Electrotransport method allowed them to produce small quantities of samples of high-purity metals sufficient for research.

Some reactive refractory metals (Ta, Nb, Mo, V, Zr, Hf and several others) [14] also were subjected to refining by electrotransport. The degree of separation of the impurity elements mainly depends on the current density and the process time.

In spite of the advances on deep cleaning of many metals involving electric field, it should be noted that as a method of refining metals the electrotransport has been developed still insufficiently in the scientific and technological terms.

To further understand the mechanisms of the electric field effect it is important to determine the correlation between the physicochemical properties of refined metal as well as impurity element and the main electrotransport parameters: migration rate of impurity ion and the direction of its movement. Performing similar research will help to determine the character of the redistribution of impurity elements in the metal under the influence of electric field and increase the efficiency of electrotransport for refining metals.

Effect of electric field on the migration of impurity ions is known a comparatively long time, but the use of this method for refining metals is not widespread compared with other refining methods. This is mainly due to the long duration of the refining process and its low productivity. Promising way is the use of electric field during zone recrystallization of metals. Such combination allows you to increase the degree of metals refining, reduce the refining time and, if necessary, to eliminate the heterogeneity of impurity elements in the ingot.

2.4. ZONE MELTING IN AN ELECTRIC FIELD

Electrotransport phenomenon in liquid metals can be used to improve the efficiency of zone purification. Electrotransport of impurity ions in liquid metals is mainly governed by the same laws as in solid ones. Unlike conventional zone recrystallization of metals, during zone melting in an electric field **(**ZMEF) the direct electric current of certain strength is applied to refining sample. Migration of impurity ions under an electric field occurs in the liquid zone, although not excluded that appreciable electrotransport of impurities can be observed in the rest (solid) part of the sample at high current densities and long duration of process.

It is assumed in the theory of zone recrystallization that there is the diffusion layer of thickness δ, enriched (or depleted) by impurities in a liquid at the boundary to the solid phase. If you apply a direct electric current to the interface, then the effect of electrotransport within the fixed boundary layer contributes to the overall flow of impurities.

In the absence of electric field the effective distribution coefficient is described by the expression (7). If DC which creates movement of ions dissolved at the interface and applies to the interface, the equation (12) takes the form

$$k'_e = \frac{1+v'/v}{1+\left[\frac{1}{k_0}\left(1+\frac{v'}{v}\right)-1\right]exp\left[\frac{-v\delta}{D}\left(1+\frac{v'}{v}\right)\right]}. \qquad (13)$$

In this equation, notation k_0, D, δ, v are the same as in equation (12); $v' = \Delta UE$ is the speed of impurity ions motion; E is the electric field; ΔU is the difference between mobility of ions and impurity ions of the refined metal.

In applying of the electric field the value of the effective distribution coefficient (equation (13)) depends, mainly, on the passage of two processes: 1) the displacement of impurities (with $k_0 < 1$) by advancing crystallization front (which is proportional to zone

melting speed *v*, the difference *1* - k_0 and the impurity concentration); 2) flow that caused by electrotransport due to different mobility of main component ion and impurity ion (proportional to *v'* and impurity concentration). The efficiency of refining at ZMEF increases when the direction of the processes is the same.

Improvement of purification by by ZMEF method compared with the floating-zone melting may result from combined action of several factors: electrotransport in stationary diffusion layer; improving conditions of zone refining by reducing the thickness of the diffusion layer; Peltier effect leading to change in k_e for impurities.

The method of zone recrystallization in an electric field was used for refining tungsten, beryllium, molybdenum, ruthenium, rhenium, osmium, niobium, yttrium, cerium, lanthanum, and other metals [4]. For many metals redistribution of impurities caused by electrotransport prevails over impurity displacement flow due to the effect of zone recrystallization. Thus, when conducting experiments on refractory metals W, Mo, Re, Ru, Os, it was found that most impurity elements have the effective ion charge Z* < 0 and migrate towards the anode.

2.5. VACUUM DISTILLATION

Vacuum distillation is considered to be the effective method for metal purification due to reducing reaction temperature and effectively reducing the adverse effects of the gas. It has been widely used in the field of metallurgical purification.

Different metals have different saturated vapor pressures when the same temperature is set under airtight conditions. Vacuum distillation uses this principle to separate the matrix metal and impurities. In the vacuum heating environment, the impurities with high saturated vapor pressure first volatilize into the gas phase, and then the vapor becomes solid crystals under the condensation and adheres to the wall of the condenser. Impurities with relatively low vapor pressure will remain in the crucible at the bottom of the vacuum distillation equipment. Matrix metal achieves purification in this way. Vacuum distillation has the advantages of a short process, high efficiency, and environmental protection. It has been widely used in alloy separation and secondary resource recovery.

Different metals have different saturated vapor pressures when the same temperature is set under airtight conditions. According to this principle, it is possible to preliminarily judge whether impurities can be separated from the matrix metal in the vacuum purification experiments of metals. The impurities with saturated vapor pressures higher than the matrix metal enter the gas phase earlier. In contrast, impurities with low saturated vapor pressure remain in the melt and finally remain in the crucible residue to achieve separation.

The separation coefficient (α) is used to express the degree of separation of impurities in the vacuum distillation process [4].

The separation coefficient in molecular evaporation in vacuum, when molecules evaporate and condense without interacting with each other and residual gases

$$\alpha = \frac{P_{\mathrm{A}}^{0}\gamma_{\mathrm{A}}}{P_{\mathrm{B}}^{0}\gamma_{\mathrm{B}}}\sqrt{\frac{M_{\mathrm{B}}}{M_{\mathrm{A}}}}, \qquad (14)$$

where P^0_A and P^0_B saturated vapor pressures of pure components *A* and *B*; γ_A and γ_B represent the activity coefficients of components *A* and *B*; M_A and M_B represent the atomic masses of the components *A* and *B*, respectively.

In the case of a dilute ideal solution, when $\gamma_A = \gamma_B$, the separation coefficient during molecular evaporation is determined

$$\alpha = \frac{P_{\mathrm{A}}^{0}}{P_{\mathrm{B}}^{0}}\sqrt{\frac{M_{\mathrm{B}}}{M_{\mathrm{A}}}}. \qquad (15)$$

Based on the magnitude of the separation coefficients of impurities in the matrix metal in the temperature range from the melting point to the boiling point, impurity elements can be divided into highly volatile (α < 1) and low-volatile (α > 1) impurities. When the separation coefficient α is close to 1, the distribution of impurities in the gas and liquid phase is equivalent, so it is difficult to separate the impurities by vacuum distillation. Based on the separation coefficient of the impurities, the farther the separation coefficient is from 1, the easier it is to separate the impurities from the matrix metal.

Refinement of fusible metals (Ga, Cd, Zn, Te, Pb, In, etc.) to the purity level > (6N) have been realized by distillation. This method and it combining with vacuum heat treatment and filtration in a single cycle allows to achieve a high degree of purification of metals with a high yield of good product [15–17]. Production this high pure metals need for synthesis of semiconducting compounds and generation heterostructures to be applied in the fields of microelectronics, optoelectronics, microwave electronics.

3. APPLICATIONS THE PHYSICAL METHODS

High-purity materials are mainly associated with their applications in microelectronics, space engineering, atomic energy, medicine and basic science research. Most radical ways of enhancing the efficiency of materials purification is to employ refinement techniques with different mechanisms of impurity separation. Many of the processes begin with chemical, physico-chemical and end up with processes like vacuum distillation, electron-beam melting, electrotransport and zone refining. The final purity is invariably achieved by growing single crystals with perfect lattice structures. For research of physical and chemical refining processes was used metals, differing in initial degree of purity and methods of preparation. Purification methods for some metals with their analysis data carried out in Department of Pure Metals, Physics of Metals and Technologies of New Materials NSC KIPT are discussed below.

3.1. REFINING OF METALS BY THE EBM METHOD

An ultra-high vacuum installation was used for produced the pure refractory and chemical active metals by the EBM method. Hetero-ion pumps with a pumping speed of 5000 l/s and a titanium sublimation pump used for pumping of the installation. Application of such a system of vacuum pumping allows to get an ultimate vacuum in the installation $1.7 \cdot 10^{-6}$ Pa [4]. 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 ⇒ metal in molten state ⇒ crystallization ⇒ pulling ingot.

Niobium after calcium-aluminum-thermal recovery as initial material was used for purification by EBM method. Results of consecutive electron beam melts of niobium are summarized in Table 1. 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.%.

Table 1

Results refining of Nb by EBM

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

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 values of the relative residual resistivity *RRR = R(300 K)/R(4.2 K)* = 2500, which corresponds to the content of a basic element of 99.995 wt.%, excluding tantalum [18].

Powdered ruthenium 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 electron beam melting method in high vacuum. Samples of high-purity ruthenium were obtained by refining the electron beam melting. The multiple electron beam melting 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. 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. The value of the microhardness of ruthenium after electron beam melting is 6420 MPa [19].

Powder and rods with purity of 99.7 wt.% were used for purification of Ta. Vacuum electron beam melting reduces the content of metallic impurities in the tantalum compared to their content in the initial material by few orders of magnitude, and significantly reduces the content of interstitial impurities. Degassing and evaporation of volatile impurities are the main purification processes of tantalum by EBM. The obtained results showed that the product after the EBM process was Ta 99.98 wt.%. These results show that the concentrations of some impurities such as Mo, Fe, Zr, Ni, V, Nb, Cu, and Cr are significantly less than the corresponding initial impurities concentrations (more than 10 times). The impurities that limit the purification of Ta have been also determined, this is W, Re, Os, Nb [20, 21].

Double EBM in a high vacuum of initial electrolytic nickel 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. Purification of nickel by EBM from metallic and interstitial impurities has been experimentally demonstrated. Electron beam remelting of nickel leads to reduction of interstitial impurities – oxygen, nitrogen, carbon up to 0.0005, 0.00006, and 0.002 wt.%, respectively. Such interstitial impurities content has practically no effect on the properties of nickel. If purity of nickel increases then the hardness decreases, for the initial nickel and after two EBM, HB is 1690 and 800...900 MPa, respectively. Studies have shown a significant improvement in the quality of metal after refining [22].

Pure refractory and chemical active metals and other metals like Zr, Hf, Ti, V, Fe, Cu, etc. had also been obtained by the EBM method in high vacuum [21].

3.2. ZONE REFINING AND ELECTROTRANSPORT OF REACTIVE REFRACTORY METALS

Zone melting (recrystallization) with an electron-beam heating is carried out, as a rule, in installations with combined pumping systems [4]. 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 $1 \cdot 10^{-6} \ldots 1 \cdot 10^{-5}$ 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.

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 Zr by using the zone

melting. Table 2 shows the results of measurements of the *RRR* value along the Zr samples length obtained by ZM at a various vacuum. It is seen that impurities accumulates at the starting end of the sample of zone refined metal and a lower vacuum provides obtaining a more pure metal. Increase of the number of zone passes there is an increase in the purity of the metal due to evaporation of impurities and increases the distribution of impurities along the ingot (zonal separation). The holding of six passes of zone in vacuum $6 \cdot 10^{-6}$ 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 $2.0 \cdot 10^{-3}$, $1.7 \cdot 10^{-3}$, and $9.0 \cdot 10^{-3}$ wt.%, respectively, the content of metallic impurities is less than 10^{-5} wt.% [23, 24].

Table 2

RRR along the length of the Zr samples

Zr samples	starting part	middle part	ending part
Initial	40	40	40
After ZM in vacuum $5 \cdot 10^{-6}$ Pa	50	110	130
After ZM in vacuum $2 \cdot 10^{-7}$ Pa	75	150	250

The physical substantiation and experimental study of the Hf refining by cruciblelessl electron beam zone melting method in vacuum were carried out. The zone melting method was most efficiently when several stages of experiments were carried out sequentially, namely:

- zone melting at a big speed (16 or 8 mm/min) to remove highly volatile metallic impurities;
- 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.

All operations were carried out in a vacuum of at least $1 \cdot 10^{-4}$ Pa [25]. 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 Hf refining by the method of zone melting in an electric field (ZMEF) was carried out. The refining of Hf by the ZMEF method was carried out with a variability of connection of direct current (in the direction and against the movement of zone melting). The results of chemical analysis of refined Hf samples indicate an insignificant content of Al, Ca, Cu, Si, Ti, which have been removed during the joint passage of the processes of zone recrystallization and evaporation. The concentration of the iron was significantly reduced at the stages of zone melting (Table 3) [26]. The purity of Hf after the ZMEF was 99.9 wt.% (initial purity – 99.5 wt.%).

The considerable 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 zone melting was carried out in an electric field directed opposite to the zone movement (see Table 3). 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 3

Concentration of impurities in hafnium samples

Materials	Concentration of element, wt. %										
	Zr	O	N	C	Al	Fe	Ca	Cu	Mo	Si	Ti
Hafnium iodide	0.23	0.03	0.003	0.04	0.003	0.007	0.01	0.002	0.07	0.004	0.003
Hf after ZM	0.21	0.02	$4 \cdot 10^{-4}$	0.022	$1 \cdot 10^{-5}$	$4 \cdot 10^{-4}$	$7 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	0.02	$4 \cdot 10^{-5}$	$2 \cdot 10^{-4}$
Hf after ZMEF $\vec{E} \uparrow\uparrow \vec{v}$	0.17	0.013	$8 \cdot 10^{-5}$	0.0021	$<2 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$<3 \cdot 10^{-6}$	$<3 \cdot 10^{-6}$	0.01	$<1 \cdot 10^{-5}$	$<5 \cdot 10^{-5}$
Hf after ZMEF $\vec{E} \uparrow\downarrow \vec{v}$	0.12	0.011	$5 \cdot 10^{-5}$	0.0018	$<2 \cdot 10^{-6}$	$2 \cdot 10^{-4}$	$<3 \cdot 10^{-6}$	$<3 \cdot 10^{-6}$	0.008	$<1 \cdot 10^{-5}$	$<5 \cdot 10^{-5}$

The physical substantiation and experimental study of the process of titanium refining from metal and interstitial impurities during ZM in a direct electric field was carried out. Purification by the ZMEF method was carried out with the simultaneous passage of several physical processes as an evaporation of gas-forming and volatile metallic impurities, zone redistribution of impurities, and migration of impurity ions under the action of an applied direct electric field.

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 purity of the samples after the ZMEF method was characterized by a value of 99.95 wt.% by titanium content. The total amount of impurities was reduced by a factor of 2.4 (from 0.12 to 0.05 wt.%). Oxygen concentration has been 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.%) [27].

Float-zone melting in an ultra-high vacuum and controlled environment in combination with electrotransport was used to grow single crystals of high-purity tantalum. Single crystals of tantalum obtained by zone melting 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 volatile $< 10^{-5}$ %, for low-volatile $< 10^{-4}$ %. The 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 were obtained [28, 29]. 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.

The initial materials used for research of vanadium zone melting: rods of technical vanadium and vanadium, which was received by iodide refining. Carrying out zone melting 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 vanadium [30]. The effectiveness of purification of technical vanadium rods by zone melting is more effective method for purification of vanadium samples than EBM. ZM of vanadium is carried out at a speed of 4 cm/hour. Si content in a technical metal is high, and it is the limiting impurity for ZM process.

For the study of ZM process V obtained by iodide method was also used. The distribution of the relative residual resistance *RRR* and microhardness of along the sample such vanadium after one pass of the melt zone is shown in Fig. 2.

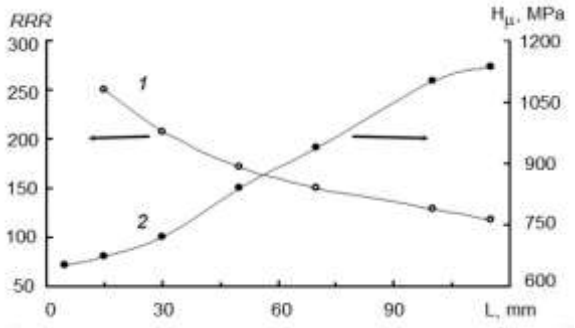

Fig. 2. Distribution of RRR (1) and microhardness (2) along the length of the sample of V after one pass of melt zone

Researches on refining of vanadium with use of electrotransport were carried out. Studies have shown that the degree of separation of the impurity elements mainly depends on the current density and the time. The change in the *RRR* along the length of vanadium samples depends on the time of electrotransport [14]. The DC flow in vanadium forces the interstitial impurities to migrate to the cathode side, i.e. effective charges of these impurities are positive. It follows from calculated estimates that at 1650 °C for 200 h at a current density of $\sim 5 \cdot 10^3$ A/cm^2 the significant reduction of oxygen, nitrogen and carbon, respectively, by $3 \cdot 10^3$, $2 \cdot 10^6$, and $1 \cdot 10^7$ times is expected as a result of refinement by electrotransport. It was shown experimentally that the value *RRR* of vanadium increases from 50 to 1600 [14] as a result of the refinement by the electrotransport. The high-purity V obtained by electrotransport with the value of *RRR* = 1200 has purity more than 99.99% wt.%.

Some reactive refractory metals (Ta, Nb, Mo, V, Zr, Hf) and several others [12] also were subjected to refining by electrotransport.

3.3. DISTILLATION OF FUSIBLE METALS

Cd, Zn, Te, Pb and same others metals are used as initial elements in the preparation of oxides for the production of high-quality low-background scintillation crystals. The main requirements to the content of chemical impurities in initial metals and raw materials for high-quality optical quality scintillators are as follows: Fe, Mg, Mn, Cr, V, Co < 1 ppm; Ni, Cu < 0.2 ppm. Obviously, contamination with radioactive elements: K, Rb, Lu, La, Sm, U, Th should be as low as possible, too. Recently, relatively inexpensive CdZnTe detectors have been created for detecting hard X-rays and γ-radiation. To create CdZnTe detectors with the required properties, requirements are imposed on the purity of the source elements to a value of > 99.9999 %. To achieve such a level of metals purity, new advanced refining techniques should be developed [31].

Research and development of deep refining processes by distillation in vacuum of these metals have been carried out.

One of the main procedures to produce high-purity cadmium and zinc is vacuum distillation. There is a known method of refinement by vacuum distillation with a condensation under temperature gradient on the condenser that is accompanied by the condensing metal re-evaporation. A disadvantage of this method is its low efficiency because condensate of purified metal is spread out on the condenser along the temperature gradient, which requires mechanical separation of the most pure part of the condensate.

A much more effective method is the two-stage distillation by using the distillation device [32]. The first stage includes the distillation of volatile impurities and removing oxide layer from the surface of melted metal. The metal heated up to the melting temperature flows down into the crucible through a hole in a plate. During this procedure, volatile (Se, K, Rb, Cs, Fr, S, P) impurities and volatile oxides of heavy metals are condensed in a main condenser together with about 5 % of the metal being refined. Heavy oxides of impurity metals and slags remain on the plate surface in the form of a thin film.

During the second stage, after changing the main condenser for the additional one, the metal can be purified from heavy volatile impurities (Cu, Fe, Ni, Co, Ag, Pb, TI, Sb, B, Li, Sn, Mn, Ra, Th, U, etc.) by additional distillation. During this stage, approximately 5...10 % of initial metal remains in the crucible. The condensate obtained at this stage is the final refined product.

Recently, a new purification method for Cd, Zn and Te from interstitial impurities by vacuum distillation using getter filters was proposed [33]. Effectiveness of getter filters made of Zr (51 wt.%) – Fe (49 wt.%) alloy was demonstrated for purification of zinc from gaseous impurities and carbon: the content of these impurities in the purified metal is one order of magnitude lower than that in the initial metal. At the same time, the content of N, C, O in the distillated metals without the getter have been decreased only by 2–3 times. Analysis of metal samples contamination has shown that application of a Zr-Fe getter filter for Zn distillation provides additional purification by a factor of 2–5. This result was used for further investigations to purify natural and isotope-enriched cadmium and natural zinc.

The high-purity ingots of natural cadmium and zinc, enriched ^{106}Cd and ^{116}Cd have been obtained by using the developed complex refinement method (heating with filtration in combination with distillation through getter filter). This method allows to achieve purified metal concentration exceeding 99.999%, high yield (96%), and low irrecoverable losses (< 1%) of the initial metals [31].

Lead is an excellent material for passive protection in low-background experiments as well as for the production of lead tungstate and molybdate crystals for use as optical waveguides in low-background experiments for registration of rare nuclear decays. Molybdates and tungstates of lead are also the promising scintillators for use at cryogenic temperatures. However, the conventional lead containing a radioactive isotope ^{210}Pb the activity of which can be tens or even thousands of Bq/kg, which is unacceptable to create the low-background scintillation devices. The half-life of ^{210}Pb is 22.3 years. Therefore, a radioactivity of lead, smelted hundreds and thousands of years ago can be very low [34].

Besides a purity of the radioactive scintillation detectors the strict requirements are imposed to content of stable of chemical elements, in particular, to the content of transition metals (Fe, V, Cr, Mn, Ni, Co, etc.) leading to a reduction of optical and scintillation properties of crystals. Their content should not exceed ~ (0.1...1) ppm.

The subject of study was the ancient (archaeological) lead. For deep purification of lead a complex process of refining was used. The first stage – filtration of lead combined with heating to remove surface contaminants and various impurities as well as gas-forming impurities. The second stage – re-condensation of metal into superheated liquid phase to remove the low-volatile and volatile impurity elements [35].

The computational studies of the behavior of impurity elements in the archaeological lead were carried out. Ideal coefficients of impurities separation were determined at the temperatures of distillation and condensation of lead, on the basis of these coefficients the range of low-volatile and volatile impurities was identified during refining of lead by distillation under a vacuum. A complex method for deep purification of ancient lead with condensation of steam into a liquid phase and simultaneous purification from highly volatile and non-volatile impurities in a single refining cycle was developed. The purification efficiency of this method is better by more than two orders of magnitude relative to the initial purity. The high-purity > 99.9996wt. % archaeological lead was obtained suitable for the growing scintillation crystals $PbWO_4$ and $PbMoO_4$ was fabricated. The main impurities in archaeological lead are Cu, Sb, Ag. After refining, their concentration decreases significantly – more than 10–500 times. The content of other impurities in purified lead is below the sensitivity limit of the analysis methods: for Rb, Y, Zr, Nb, Ru, Pt, Au $< 1\cdot10^{-8}$ ppm; for Sc, In, Te $< 1\cdot10^{-7}$ ppm; for Se, Pa $< 1\cdot10^{-6}$ ppm [36].

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 removal of metallic impurities in any metal matrix can be achieved by conventional purification processes such as zone melting, distillation, sublimation, electrotransport, electron beam melting, etc. A combination of purification processes was necessary to increase the efficiency of the removal of impurities and increase the purity of metals.

The electron beam melting method is quite effective for the production of pure refractory and chemically active metals like Ta, Nb, Zr, V, Hf, etc. and their alloys. Decrease of total impurities or increase in purity in these metals has resulted in the improve of its properties. The vertical crucibleless zone melting method of round rods in vacuum with electron beam heating to obtain high-purity refractory metals was chosen. The method of zone refining in an electric field for high melting point metals like Zr, Hf, Ti, V, Nb, Ta, and other metals are very much useful for increase its purity. Some reactive refractory metals were subjected to refining by electrotransport. The degree of separation of the impurity elements mainly have depended on the current density and the process time. Refinement of fusible metals (Ga, Cd, Zn, Te, Pb, In, etc.) to the purity level > 6N have been realized by distillation and new method including heating with filtration in combination with distillation though getter filter. This method provides high purification efficiency, high yield of product and low losses of initial metals.

High-purity metals are crucial building blocks for research and development, and production of advanced materials technologies, which generally require optimum properties, performance, quality and efficiency.

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ВИСОКОЧИСТІ МЕТАЛИ: МЕТОДИ ОЧИЩЕННЯ ТА ЗАСТОСУВАННЯ

М.М. Пилипенко

Виробництво металів високої чистоти є складним завданням через складність технологічних методик, процесів та унікального технологічного обладнання, яке не завжди доступне. Метали високої чистоти виготовляються для використання в електроніці, ядерній енергетиці, аерокосмічній галузі та фундаментальних дослідженнях. Для рафінування металів переважно використовувалися методи очищення плавленням, кристалізацією, дистиляцією та електротранспортом у високому вакуумі, а також різні комбінації цих методів. Комплексне рафінування, засноване на використанні взаємодоповнюючих фізико-хімічних та фізичних методів, дозволило досягти найвищих ступенів очищення та отримання металів у найчистішому вигляді. Опис цих методів, що застосовуються до різних металів, включено до цієї статті разом із результатами досліджень з очищення деяких хімічно активних, тугоплавких та легкоплавких металів.