

PACS: 81.20.Ym

ELECTROTRANSPORT AS A WAY OF METALS DEEP PURIFICATION**G.P. Kovtun**

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Received January 14, 2014*

The basic mechanisms of impurity ions migration in the liquid and solid metals under the influence of direct electric current have been stated. The estimations for the ultimate distribution of impurity elements in metals at application of direct current have been presented. It has been shown that the separation of interstitial impurities (oxygen, nitrogen, hydrogen and carbon) is achieved most effectively in solid metals during electrotransport. Particular attention was focused on the process of refining metals by zone recrystallization under electrostatic field. It was established experimentally that the impurity flow arising owing to electrotransport prevails over the flow due to the effect of zone recrystallization, and effective distribution coefficients of impurity elements may decrease, increase, or change sign, depending on the direction of the field. A new method for deep refining of refractory metals by zone melting under electric field was proposed. Prospects to use electrotransport for the refinement of metals have been discussed.

KEYWORDS: electrotransport, basic laws, refining of metals, zone melting under electric field

ЕЛЕКТРОПЕРЕНОС ЯК СПОСІБ РАФІНУВАННЯ МЕТАЛІВ**Г.П. Ковтун**

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Викладено основні механізми міграції домішкових іонів в твердих і рідких металах під впливом постійного електричного струму. Наведено оцінки для граничного розподілу домішкових елементів у металах при пропусканні постійного електричного струму. Показано, що в твердих металах у процесі електропереносу найбільш ефективно досягається розділення домішок проникнення (кисню, азоту, водню і вуглецю). Особливу увагу приділено процесу рафінування металів зонною перекристалізацією в постійному електричному полі. Експериментально встановлено, що домішковий потік, що виникає внаслідок електропереносу, переважає над потоком за рахунок ефекту зонної перекристалізації, а ефективні коефіцієнти розподілу домішкових елементів можуть зменшуватися, збільшуватися або міняти знак в залежності від напрямку поля. Запропоновано новий спосіб глибокого рафінування тугоплавких металів зонної плавкою в електричному полі. Обговорено перспективи використання електропереносу для рафінування металів.

КЛЮЧОВІ СЛОВА: електроперенос, основні закономірності, рафінування металів, зонна плавка в електричному полі

ЭЛЕКТРОПЕРЕНОС КАК СПОСОБ ГЛУБОКОГО РАФИНИРОВАНИЯ МЕТАЛЛОВ**Г.П. Ковтун**

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Изложены основные механизмы миграции примесных ионов в твердых и жидких металлах под влиянием постоянного электрического тока. Приведены оценки для предельного распределения примесных элементов в металлах при пропускании постоянного электрического тока. Показано, что в твердых металлах в процессе электропереноса наиболее эффективно достигается разделение примесей внедрения (кислорода, азота, водорода и углерода). Особое внимание уделено процессу рафинирования металлов зонной перекристаллизацией в постоянном электрическом поле. Экспериментально установлено, что примесный поток, возникающий вследствие электропереноса, преобладает над потоком за счет эффекта зонной перекристаллизации и эффективные коэффициенты распределения примесных элементов в зависимости от направления поля могут уменьшаться, увеличиваться или менять знак. Предложен новый способ глубокого рафинирования тугоплавких металлов зонной плавкой в электрическом поле. Обсуждены перспективы использования электропереноса для рафинирования металлов.

КЛЮЧЕВЫЕ СЛОВА: электроперенос, основные закономерности, рафинирование металлов, зонная плавка в электрическом поле

An electrotransport takes a certain place among various methods of deep refining metals. By the concept of electrotransport (electrodifusion, 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. Removal of these impurities by other methods is difficult. Recent studies have shown that the degree of separation of impurity elements during zone recrystallization of metals increases significantly if it is carried out under an electric field and it opens up new opportunities for deep purification of metals. 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.

The aim of this paper is describing the main achievements in the field of deep cleaning of metals using electrotransport and the determination of its opportunities for future use.

THE MAIN LAWS OF REFINING METALS BY ELECTROTRANSPORT

Theoretical postulates of refining metals under electric field effect were considered in a number of books and articles, both in the solid and liquid phases [1-12].

Application of direct electric current to metal sample leads to moving both the matrix ions and impurity ones in a certain direction. The description of the ions motion is based on the proportionality of ion drift velocity v to the external force F acting on the ion:

$$v = UF, \quad (1)$$

where U is the ion mobility. External force F , acting on an ion, is the sum of the force F_z exerted by the electric field and the force F_n due to the scattering of conduction electrons by the ion («electronic wind»), i.e. $F = F_z + F_n$. The force acting on the ion by the electric field is expressed as:

$$F_z = zE, \quad (2)$$

where z is the ion charge; E is the electric field strength.

The strength of «electron wind» F_n is calculated based on quantum representations, according to which the interaction of ions with the conduction electrons is considered as elastic scattering of electrons by the ion [1]:

$$F_n = |e|nI\sigma E, \quad (3)$$

where e is the electron charge; n is the concentration of conduction ion; I is the mean free pass of electron; σ is the cross-section for scattering of electrons.

The total force acting on the impurity ion in a metal:

$$F = (z - |e|nI\sigma) = z_{eff}E, \quad (4)$$

where $z_{eff} = z - |e|nI\sigma$ is the effective ion charge.

Besides the «electronic wind», the existence of «hole wind» is possible also in the presence of mixed electron-hole conductivity. And then

$$z_{eff} = z - |e|n_-I_- \sigma_- + |e|n_+I_+ \sigma_+, \quad (5)$$

where the indices (-) and (+) refer to electrons and holes, respectively.

Depending on the sign of z_{eff} , the resultant force can be directed to the cathode ($z_{eff} > 0$), to the anode ($z_{eff} < 0$) or to be equal to zero ($z_{eff} = 0$).

The magnitude of effective charge z_{eff} can be determined from the expression [8]:

$$z_{eff} = \frac{U}{D} \cdot \frac{kT}{e}. \quad (6)$$

Here D is the ion self-diffusion coefficient, T is the temperature, k is the Boltzmann constant.

The value of the impurity ion mobility is dependent on the properties of system and the temperature. In general, the relative mobility of ions is determined by the expression [7]: $\Delta U = (v_1 - v_2)/E$, where v_1 and v_2 are the movement speeds of the impurity ions and a main component, respectively. In the case of dilute solutions the speed of solvent movement v_2 is actually equal to zero, and the expression for the impurity ion mobility becomes:

$$U = \frac{v_1}{E}. \quad (7)$$

Quantitative characterization of the refining process during electrotransport follows from the relationship between the rate of motion of the impurity under the electric field and its reverse motion because of diffusion due to the

appearance of a concentration gradient. The equations of material flow generated by the electric field are used to describe this process. In the case of electrotransport in the rod the flow equation has the form [7]:

$$I = -D \frac{dC}{dx} + UCE, \tag{8}$$

where C is the impurity concentration at a distance x from beginning of the sample.

When electric field applying for sufficiently long time, the first term of flow characterizing diffusion and a second one caused by the presence of electric field balance each other out, giving a zero stream and hence maximally achievable degree of purification (Fig. 1). If t_0 - start time corresponding to the initial concentration C_0 , and the duration of electrotransport $t_1 < t_2 < t_\infty$, then the considerable refinement is observed in the left part of the rod. Maximum purification is achieved at the electrotransport duration, when there comes an equilibrium state according to the equation (8).

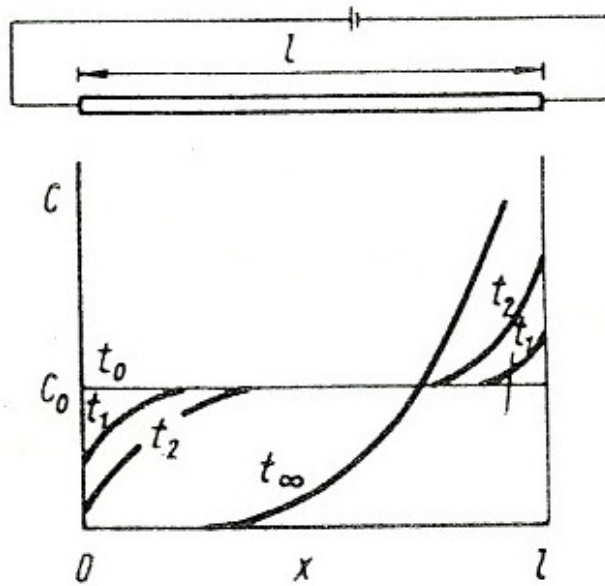


Fig.1. Impurity distribution along the sample length under applied DC current for various time periods, t.

The degree of purification is estimated by the ratio C_t/C_0 from the expression

$$C_t/C_0 = \frac{2}{C_0 L} \int_0^{L/2} C(x, t) dx. \tag{9}$$

In this expression C_t is the average concentration in that half of the sample, where the less impurity remains after the time t; C_0 is the initial concentration; $C(x, t)$ - the impurity concentration depending on the distance at the time t; L is the rod length. The joint solutions of the equations (8) and (9) allow obtaining approximate expressions for calculating the distribution of impurities concentrations along the length of the rod, depending on the electrotransport parameters.

Assuming U, E, and D do not depend on the concentration and position in the rod, Verhoeven [7] proposed an expression for the average impurity concentration in the pure part of the rod in dependence on time:

$$\frac{C_{m(t)}}{C_0} = 2 \left[\frac{1 - e^{-s/2}}{1 - e^{-s}} - \sum_{n=1}^{\infty} C_n e^{-s/4} \sin\left(\frac{n\pi}{2}\right) e^{-\lambda_n t} \right], \tag{10}$$

where $C_n = \frac{32n\pi s [1 - (-1)^n e^{s/2}]}{(s^2 + 4n^2\pi^2)^2}$; $\lambda_n = (n^2\pi^2 + \frac{s^2}{4}) \frac{D}{L^2}$; $s = -\frac{U}{D} EL$; $C_{m(t)}$ is the average concentration of

impurity in the purified part of the rod; C_0 is the initial concentration of impurity; L is the length of the rod; E is the electric field; U is the mobility of impurity ion; D is the diffusion coefficient of impurity ion.

Although the above equation does not allow determining explicitly how different variables affect the cleaning process, it is used to calculate the minimum impurity concentrations achieved by the electrotransport. In particular, the Table 1 shows the calculated values of the relative changes in the concentrations of carbon C_m/C_0 for some metals, made for the first half of rod with length of 10 cm by the field $E = 0.2$ V/cm and different time of electrotransport [7].

It can be seen from Table 1 that the full separation of metals from the carbon impurity at $U/D > 12$ occurs after 5 days. Since the degree of refinement is directly proportional to the ratio U/D then it has to increase with decreasing temperature. However, as the temperature decreases, the diffusion coefficient decreases and therefore increases the time required to achieve the deep purification.

Table 1.

The average relative concentration of carbon C_m/C_0 (C_m - the average concentration of carbon for the first half of rod, C_0 - the initial concentration of carbon) in metals after electrotransport, calculated at different times [7]

System	T, °C	U/D, B ⁻¹	C _m /C ₀		
			1 day	5 days	∞
Th-C	1675	19	4.5·10 ⁻³	1.1·10 ⁻⁸	1.1·10 ⁻⁸
Fe-C	1400	44	4.2·10 ⁻⁴	1.5·10 ⁻¹⁹	1.5·10 ⁻¹⁹
Ni-C	1400	12	7.3·10 ⁻¹	6.5·10 ⁻²	1.2·10 ⁻⁵
Ta-C	2600	52	4.9·10 ⁻²³	4.9·10 ⁻²³	3.9·10 ⁻²³
W-C	2800	5.7	7.5·10 ⁻¹	1.4·10 ⁻¹	6.7·10 ⁻³

The equation (10) was also used to evaluate the efficiency of vanadium purification of interstitial impurities [10]. Impurity concentration was calculated in a clean part at a distance of 2 cm from the end of the sample having total length of 20 cm. With electrotransport temperature of 1650°C, the process duration of 200 h, and the electric field of 0.27 V/cm, the content of oxygen impurity in the vanadium can be reduced by 3·10³ times, N - by 2·10⁶ times and carbon - by 1·10⁷ times.

A more simple expression was proposed in [11] giving the value of the impurity concentration at the point x along the rod in time $t \rightarrow \infty$:

$$\ln \frac{C(x, \infty)}{C_0} = \ln \frac{UEL}{D} - \frac{UEx}{D} \quad (11)$$

In this equation, C_0 and $C(x, \infty)$ - the initial and maximum allowable concentration of impurities at an arbitrary point x of cleaning rod with length of L; E is the electric field; U is the electric mobility; D is the diffusion coefficient of impurity. In the steady state at infinite time of refining the ratio of impurity concentration at the ends of the sample is equal to e^s , where the dimensionless parameter $s=UEL/D$. Thus, the degree of purification can be enhanced by the using of longer sample, increasing of electric field, and optimizing the relationship U/D. In practice, the actual values of relative changes of impurity elements at cathode and anode are much smaller than calculated ones. This discrepancy may be due to several reasons: pollution from the electrodes or the environment during electrotransport, nonuniform temperature distribution along the sample, decreasing the mobility of impurities resulting from their capture by vacancies, etc.

THE REFINEMENT OF METALS IN THE SOLID PHASE BY ELECTROTRANSPORT

For the purposes of refinement, the metals samples are used in the form of rods, wires, strips, which are connected through the holders to the current feedthroughs built in the walls of the working chamber (Fig. 2).

Direct electric current, applied to the sample, heats it to the desired temperature and performs a redistribution of the impurities, as shown in Fig. 1. Depending on the metal vapor pressure, the refining process is carried out in a high vacuum or in an environment of high-purity inert gas.

The electrotransport in solid phase has been used most widely for deep refinement of rare earth metals (REM). Practically all of REM (Y, Sc, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Lu) were subjected to refining by this method [11-21]. 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.

The samples in the form of rods by length of 8-20 cm and diameter of 4-6 mm were commonly used to REM. A certain problem is the sample holders which can contaminate the sample being refined. Different approaches are used to solve this problem. One of them is the removal of sample contaminated areas and continuation of the refining process. The second approach is the use of specimen holders of high-purity refractory metals. For example, the authors Of [18] concluded that it would be better for the REM to use a holder made of tantalum at the cathode and one made of zirconium – at the anode.

Achievement of maximal degree of purification at lower time requires carrying out the electrotransport process at

high temperatures close to the melting point. However, this approach is not always possible for many REM due to their high volatility. For example, for La, Ce, Pr having a low vapor pressure of ($\sim 10^{-9}$ - 10^{-4} Pa) at the melting point, the electrotransport can be carried out in vacuum for several hundreds of hours to achieve theoretical redistribution of impurities. Refinement of Nd, Gd, Tb, Lu, Y, having a higher vapor pressure of ($\sim 10^{-3}$ – 10 Pa) at the melting point, by the electrotransport is possible only at low temperatures in a vacuum. Refinement of Sc, Er, Ho, Dy, Yb, Sm, Tm, relating to the volatile REM (vapor pressure ≥ 100 Pa at the melting temperature) is possible only under an inert gas.

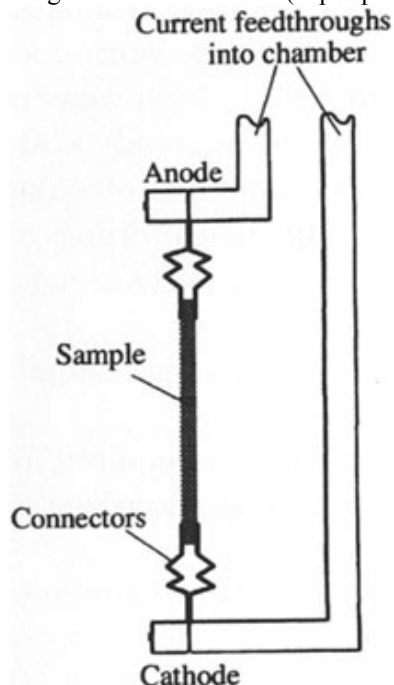


Fig. 2. Schematic diagram of refining metals by the electrotransport in solid phase.

Refining process of REM by the electrotransport method proceeds very long and refinement objects have a high chemical activity. Therefore, it is necessary that the working environment in the chamber was ultrapure, regardless of whether a high vacuum is created in chamber or working environment forms by predetermined pressure of inert gas. In any case, the vacuum system should provide a residual pressure of 10^{-8} Pa and below and the inert gas should maintain high level of purity during the refining process. Elimination of REM contamination can be minimized by pre-high-temperature heating of the working chamber and refining samples under ultrahigh vacuum.

When refining REM by the electrotransport, the emphasis was made mainly on the removal of impurities of oxygen, nitrogen, hydrogen, carbon, i.e. those impurities, separation of which from these metals by other methods is difficult because of the large negative values of formation free energies of oxides, nitrides, carbides, and hydrides. Typically, all the interstitial impurities in REM have a high mobility, effective charge $Z_{\text{eff}} < 0$ and migrate to the anode part of the sample. High mobility is typical for many of substitution impurities in REM. Therefore, electrotransport can be an effective way to separate the REM not only from O, N, C, H, but also from such impurities as Fe, Ni, Al, Ag, Cu, etc. There is a certain correlation between the rate of migration of substitutional impurities and their atomic size. It should be noted that electrotransport method is effective only for the dissolved impurities. Therefore impurities, which do not form solid solutions, must be removed by other methods before the formation of solid solutions.

Some reactive refractory metals (Ta, Nb, Mo, V, Zr, Hf) [22-28] and several others [29-31] also were subjected to refining by electrotransport. The degree of separation of the impurity elements mainly depends on the current density and the time. As an example, Fig. 3 shows the change in the R_{res} (ratio of resistivity at room and helium temperatures) along the length of vanadium samples, depending on the time of electrotransport [23]. Studies have shown that the DC flow in vanadium with density of $5 \cdot 10^3$ A/cm² 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 hours at a current density of $\sim 5 \cdot 10^3$ A/cm² the 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 R_{res} of vanadium increases from 50 to 1600 [23] as a result of the refinement by the electrotransport.

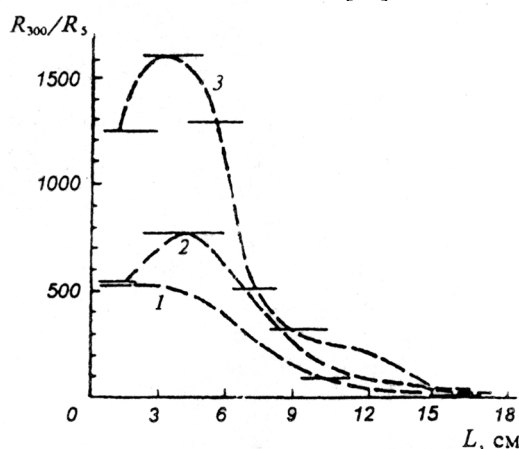


Fig. 3. The change in R_{res} of vanadium along the length L of a sample after electrotransport at $T = 1650^\circ\text{C}$; $j = 2500$ A/cm²; 1 – 100 h, 2 – 200 h, 3 – 400 h.

Researches on refining of vanadium with use of electrotransport were carried out in [22]. The anodic part of the sample had $R_{\text{res}} = 1000 \div 1100$ at a current density of 2150 A/cm² after 220 hours. Prepurified vanadium rod was welded to the anode part of the sample to eliminate the migration of impurities from the cold part. In this case, the anode part of the sample had values $R_{\text{res}} = 1800-2000$, and in isolated case the value was equaled about ~ 2850 . At that the high-purity part of material was one third of the entire length of the sample. A similar scheme has been used for refining zirconium [27]. After exposure during more than 1000 hours at $\sim 1600^\circ\text{C}$ the middle part of the zirconium rod had $R_{\text{res}} = 650$, which is the maximum value for zirconium [27]. At that, all the interstitial impurities (O, N, C, H) in a β -Zr shifted to the anode under the influence of electric field. At the same time the sign of Z_{eff} for interstitial impurities in Nb varies with temperature, $Z_{\text{eff}} > 0$ for interstitial impurities in Mo [25, 26]. For substitutional impurities it is noted a relationship between the sign of Z_{eff} and atomic number of dissolved metal. Table 2 shows the values of R_{res} for a number of metals subjected to refining by the

electrotransport method in solid phase. Basing on the values R_{res} , the purity of metals shown in Table 2 have a higher degree of purity compared to that, achieved by other methods of refining.

Table 2.

High-purity refractory metals and rare earth metals subjected to refining by ET in solid phase, and the known values of

Metal	R_{res} [11-28]																			
	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	V	Zr	Hf	Cr	Th
R_{res}	520	1200	260; 400		250; 400	120	300		340; 405	400	124	90	46		150	1880; 2850	650	15	700	1000

Despite the possibility of deep purification of metals, the electrotransport in the solid phase has disadvantages also. Pollutions of refining metals from the side of electrodes and surrounding atmosphere are observed. The high current densities (up to 10^4 A/cm²) and long times are needed, and the amount producing high-purity metal is small.

REFINING METALS IN LIQUID PHASE BY THE ELECTROTRANSPORT

Electrotransport of impurity ions in liquid metals is mainly governed by the same laws as in solid ones. Current theory of electrotransport in liquid metals considered in the monographs Belashchenko [2,3], Mikhailov [5] and others [7-9]. When current flowing through the liquid metal, the different types of convective mixing (heat, concentration, electrokinetic and magnetohydrodynamic convection) have a strong influence on mass transfer. Convective effects prevent the formation of high impurities gradients in a metal; therefore the problem of their as much as possible complete suppression is set always during refining.

During calculations the presence of convective effects is taken into account by replacement of the molecular diffusion coefficient D_0 by an effective diffusion coefficient $D = D_0 + D_c$, where D_c is the convective diffusion coefficient. It is impossible to get rid of convective phenomena completely, but their effect can be significantly reduced if the electrotransport of liquid metals is implemented in tubes with sufficiently small cross section ($d < 3$ mm).

Theoretical estimates of the limits of liquid metals refinement by electrotransport were attributed usually to specific devices.

The estimates of theoretical limits of liquid metals refinement in the devices that are most favorable for metal purification by the electrotransport method have been made. In particular, such a device may consist of a tube closed at one end and filled with liquid metal, and the other end is inside a container filled with a large quantity of molten metal. In this case, the impurity concentration in the metal at the end of the tube contacting with the reservoir remains essentially constant. The calculated relative changes in the concentration of impurities C_i/C_0 (C_0, C_i - initial and final contents of the impurity element) at the first two centimeters of ten-centimeter-long tube under an electric field of $E = 0.1$ V/cm depending on the time of electrotransport are shown in Table 3 [5].

Table 3.

The relative concentration of impurities (C_i/C_0) under electrotransport

System: metal – impurity element	U/D, B ⁻¹	C_i/C_0 at the first two centimeters of the tube			
		1 day	5 days	10 days	∞
Cd-Ni, Co, Ag, Au	23	$9.4 \cdot 10^{-4}$	$2.2 \cdot 10^{-9}$	$2.2 \cdot 10^{-9}$	$2.2 \cdot 10^{-9}$
In-Ni, Co, Te, Ag	14	0.036	$6.9 \cdot 10^{-6}$	$6.9 \cdot 10^{-6}$	$6.9 \cdot 10^{-6}$
Sn-Ni, Co, Ag, Au	12	0.068	$6.4 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$	$2.6 \cdot 10^{-5}$
Pb-Co, Te, Ag, Au	1.9	0.53	0.14	0.053	0.037

It is seen from Table 3 that all dissolved metals at $U/D > 12$ should be well removed after 5 days of electrotransport. However, it is valid under the conditions that there is no convective motion of the melt and no interaction of the refined metal with tube material. In real conditions, the use of long capillary cells proved to be highly effective for deep cleaning of small amounts of a number of liquid metals (e.g., gallium, cadmium, zinc). This process was studied most fully as applied to gallium [4]. The purest gallium ($R_{res} = 100000$) was currently produced just by the method of electrotransport.

The main limitation for the widespread application of electrotransport for refinement of liquid metals is the low productivity (~0.5 g/day for a single cell). You can improve performance if soak the porous medium or a group of capillaries by the liquid metal and apply a large current to a system. Description of the devices for deep cleaning liquid metals by electrotransport is given in [4,32,33].

COMBINATION OF ZONE MELTING WITH ELECTROTRANSPORT (ZMET)

Electrotransport phenomenon in liquid metals can be used to improve the efficiency of zone purification.

Unlike conventional zone recrystallization of metals, during ZMET 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 [34] that there is the diffusion layer of thickness δ , enriched (or depleted) by impurities in a liquid at the boundary to the solid phase (liq - sol). 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.

Character of changes in effective distribution coefficient under the influence of electric field was considered by Pfann and Wagner [35]. In the absence of electric field the effective distribution coefficient is described by the expression [34]

$$K = \frac{1}{1 + \left(\frac{1}{K_0} - 1 \right) \exp\left(-\frac{v\sigma}{D} \right)}, \quad (12)$$

where K_0 is the equilibrium distribution coefficient; D is the impurity diffusion coefficient in a liquid phase; δ is the thickness of diffusion layer in a fluid at the interface; v is the speed of crystallization front. If DC which creates movement of ions dissolved at the interface and applies to the interface (liq - sol), the equation (12) takes the form

$$K = \frac{1 - v'/v}{1 + \left[\frac{1}{K_0} (1 + v'/v) - 1 \right] \exp\left[-\frac{v\sigma}{D} (1 + v'/v) \right]}. \quad (13)$$

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.

As can be seen from equation (13), the effective distribution coefficient is determined mainly by two flows of impurities: one flow leads to ousting of impurities by advancing crystallization front (which is proportional to v , difference $1 - K_0$ and concentration), the other flow is caused by electrotransport (which is proportional to v' and concentration). It may coincide with the first flow or have an opposite direction depending on the direction of the electric field. If $v' > 0$ (flow of impurity ions is directed from the liquid to the boundary), the electric field increases K , if $v' < 0$, the electric field decreases the K . It concerns both to the case $K_0 < 1$, and the case $K_0 > 1$.

Under the influence of an electric field, the effective distribution coefficient K can be changed, that in principle allows obtaining the following results:

- 1) K factor close to unity, can be changed so that it would be significantly different from unity, and thereby the efficiency of the zone melting can be increased;
- 2) impurity elements coefficients of different «sign» ($K > 1$) and ($K < 1$) can be modified so that they will be either greater or less than unity, and this allows to concentrate impurity elements in one end of the ingot;
- 3) the coefficient K can be made close to unity and eliminate segregation of impurities along the ingot.

It should be noted that the derivation of equation (13) does not include a number of other effects at the interface of liq-sol that may affect the magnitude of K , in particular a Peltier effect which is the release (or absorption) of additional heat at the boundary liq-sol. Since electric current applies to the liq-sol and sol-liq boundaries in the liquid zone, the value of Peltier heat is doubled, and an additional temperature gradient, caused by the heating of one phase boundary and cooling of another, is arisen in the liquid phase. Due to this, an additional impurity flow, caused by diffusion under a thermal gradient field, arises in liquid zone and increases or decreases "zone effect" of purification degree in depending on the direction of the electric field [6].

The mechanism of metal purification by ZMET method was studied insufficiently, although the positive influence of the electric field was noted by many researchers. Improvement of purification by ZMET method compared with the conventional floating-zone melting may result from combined action of various factors: electrotransport in stationary diffusion layer; electrotransport in the solid phase; improving conditions of zone refining by reducing the thickness of the diffusion layer as a result of thermal and magnetohydrodynamic convection; Peltier effect leading to change in K for impurities especially at low current densities.

Apparently, one of the first studies on the use of ZPEP was the work on refining tungsten [36]. Results of tungsten purification by ZMET are shown in Fig. 4.

As seen from Fig. 4, application of an electric field improves the refining of tungsten in comparison with zone melting without field. Moreover, a positive purification effect increases with increasing electric field intensity. ZMET was used for refining beryllium [37], molybdenum [38], ruthenium, rhenium [23,39,40] Os [41], niobium [42], yttrium, cerium, lanthanum, [43], and other metals [44-46].

Performed researches made it possible to reveal a number of features of refining by zone melting method combined with electrotransport. First, redistribution of impurities caused by electrotransport prevails over impurity flow due to the effect of zone recrystallization. A similar effect is observed for almost all metals when cleaning them by ZMET. For many refractory metals (W, Mo, Re, Ru, Os), most impurity elements have $Z_{\text{eff}} < 0$ and migrate towards the anode. In most cases, a maximum purification effect is achieved when the electric field is opposite to the direction of floating zone movement. As an example, Fig. 5 shows the results of refining rhenium by ZMET.

It is seen from the Fig. 5 that the maximum redistribution of impurities along the length of the ingot is achieved, when the electric field is opposite to the movement direction of the floating zone (curve 1). When the directions of electric field coincide with zone movement, the redistribution of impurity elements along the ingot has the opposite

character (curve 3). Table 4 shows the comparative measurement results of ruthenium R_{res} after zone melting without electric field, and under electric fields of different directions relative to the zone movement. It can be seen (Table 4) that the highest degree of purification achieved in that case where zone melting is performed under an electric field whose direction is opposite to the movement zone.

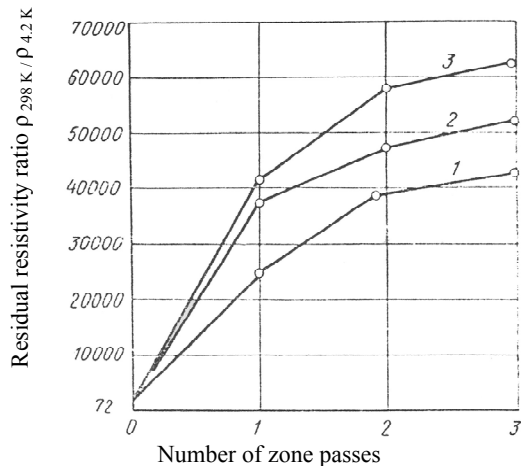


Fig. 4. Changing in R_{res} of tungsten depending on the number of zone's runs through the sample during ZMET [36]. 1 - $E = 0$; 2 - $E = 0.125$ V/cm, 3 - $E = 0.260$ V/cm; zone moving speed is 2.5 mm/min; the directions of field and zone movement are opposite.

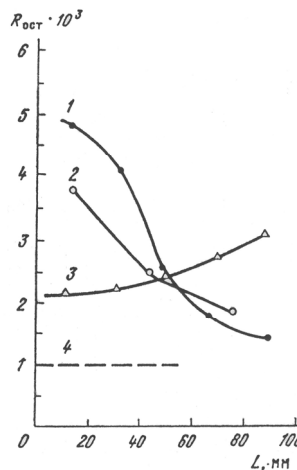


Fig. 5. R_{res} change along the length L of rhenium single crystals after 10 runs of the zone without an electric field and under an electric field of different direction [40]. 1 - ZMET, field is opposite to zone movement; 2 - floating zone melting without a field; 3 - ZMET, field coincides with the direction of zone motion; 4 - melting in vacuum.

Table 4. Effect of the electric field on the degree of Ru purification ($E = 0.15$ V/cm; $I = 1200$ A/cm²; $V = 3$ mm/min)

Kind of process	R_{ocm}		
	Starting part of sample	Middle	End part of sample
Zone melting (10 runs)	1300	1000	900
Zone melting + field $E \uparrow \uparrow V$	1080	1100	1260
Zone melting + field $E \uparrow \downarrow V$	2000	1600	650

Os refining by zone melting in combination with electrotransport eliminates nonmonotonic distribution of impurity elements, which observed in osmium sample during refining by zone melting in the absence of the field (Fig.6).

Apparently, this is primarily due to the change in carbon effective distribution coefficient K which for zone melting without a field has $K > 1$, and for zone melting in combination with electrotransport it acquires value $K < 1$.

For refractory metals most of substitutional impurities have $Z_{eff} < 0$ and migrate towards the anode. However, interstitial impurities (O, N, H, C) can have both positive and negative values of the effective charges and their influence on the process of metals purification in some cases can be decisive. For example, when refining molybdenum by ZMET, then Z_{eff} for carbon and hydrogen has negative values, and for the oxygen and hydrogen – positive ones. According to estimates, the admixture of tungsten in molybdenum also has $Z_{eff} > 0$. As a result, the distribution of impurity elements in molybdenum may vary substantially in dependence on the direction of the field (Fig. 7).

The complicated character of changes in magnitude of R_{res} is observed also in niobium during ZMET [42]. According to the authors of [42] for oxygen and carbon at the melting point of niobium the values of effective charges are near zero, and for nitrogen $Z_{eff} = +1.7$. As a result, the average areas of niobium crystals are the most pure ($R_{res} \sim 2600$), if the directions of electric field and zone movement coincide. The authors also noted that under the influence of electric field the structural perfection of niobium single crystals is improved, too.

Thus, at the refining of metals by ZMET, the character of impurity distribution along the ingot will depend on both direction of the electric field and qualitative and quantitative content of impurities in the source metal.

Investigations of refining Mo, Re, Ru, Os and other metals by means of zone melting and zone melting in combination with electrotransport allowed developing a new way of deep refining of refractory metals, in which the increase of the metals purity is achieved by intensification of evaporation, band separation and electrotransport. Refining process was carried out in two stages. In the first stage, a zone melting in combination with electrotransport was performed at the highest possible current densities and high speeds of liquid zone movement. As a result of

intensive mixing of liquid zone, the effective removal of volatile impurities was achieved due to their evaporation. In the second stage, the refining was carried out for parameters which have been by 5-10 times lower than initial values. In this case, the mechanism of impurities separation along the ingot length is realized most fully due to optimizing the values of K .

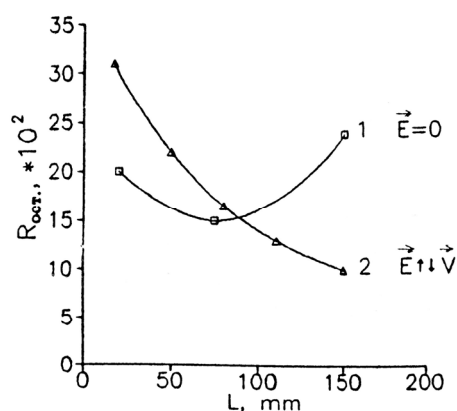


Fig. 6. The change in R_{res} along the length L of osmium specimens
1 - after zone melting, 2 - zone melting in combination with electrotransport [41].

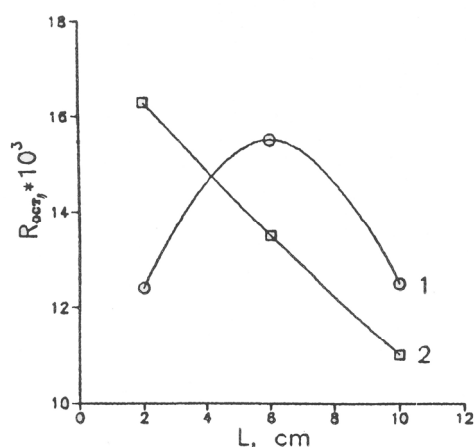


Fig. 7. Change in R_{res} along the length L of molybdenum single crystals after 6 runs of floating zone during ZMET [38];
1 - the field coincides with the direction of zone movement; 2 - the field is opposite to zone movement; zone movement speed is 4.5 mm/min; the field strength is 0.15 V/cm.

As a result, in a series of refining of refractory metals in the most favorable scenario there is a combination of complex of physical refining methods: evaporation, zone separation of impurities, electrotransport. The proposed method not only improves the purity of metals, but also reduce the refining time by 1.5-2 times. Application of this refinement scheme allowed to get high-purity and structurally perfect single crystals W, Mo, Re, Ru, Os, having the magnitude $R_{res} \geq 70000, 30000, 60000, 4500$ and 3000 respectively.

CONCLUSION

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. 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.

REFERENCES

1. Fiks V.B. Ionnaya provodimost' v metallakh i poluprovodnikakh. - M.: Nauka, 1969. - 215s.
2. Belashchenko D.K. Yavleniye perenosa v zhydkikh metallakh i poluprovodnikakh. - M.: Atomizdat, 1973. - 400s.
3. Belashchenko D.K. Issledivaniye rasplavov metodom elektroperenosa. - M.: Atomizdat, 1977. - 88s.
4. Mikhajlov V.A., Bogdanova D.D. Elektroperenos v zhydkikh metallakh. - Novosibirsk: Nauka, 1978. - 224s.
5. Belyayev A.I. Fiziko-khimicheskiye osnovy ochistki metallov i poluprovodnikovyykh materialov. - Metallurgiya, 1973, 224s.
6. Tikhinsky G.Ph., Kovtun G.P., Azhazha V.M. Polucheniye sverkhchistykh redkikh metallov. - M.: Metallurgiya, 1986. - 160s.
7. Verhoeven J.D. Electrotransport as a Means of Purifying Metals // J. Metals. - 1966. - Vol. 18, No.1. - P. 26-31.
8. Lakshman T.S. Electrotransport in metals and alloys // Trans Indian. Inst. Met. - 1975. - Vol. 28. - P. 345-364.
9. Electrotransport and its applications / Ed. V.A. Mikhailov. - Novosibirsk: Nauka, 1982. - P. 144 (in Russian).
10. Heumann T., Dreyer K. Zur Frage der Reinigung fester Metalle mittels Elektrotransport // Z. Metallkunde. - 1977. - Bd. 68, H. 11. - S.729-733.
11. Carlson O.N., Schmidt E.A., Peterson D.T. Purification rare-earth metals be electrotransport // Less-Common Metals. - 1975. - Vol. 39, No.2. - P. 277-286.
12. Fort D. Purification of rare earth metals // Purification Process and Characterization of Ultra High Purity Metals. Series: Springer Series in Materials Processing (Eds.: Waseda, Yoshio, Isshiri, Minora). - 2002. - XIV. - P.145-177.
13. Schmidt F.A, Carlson O.N. Electrotransport of carbon, nitrogen and oxygen in scandium // J. Less-Common Met. - 1976. - Vol. 50, No. 2. - P. 237-244.
14. Carlson O.N., Schmidt F.A. Electrotransport of solutes in rare earth metals // J. Less-Common Met. - 1977. - Vol. 54, No. 1. - P.73-84.

15. Jordan R.G., Jones D.W. The purification of rare earth metals. Solid state electrotransport processing of terbium // *J. Less-Common Met.* – 1975. – Vol. 42, No. 1. – P. 101-110.
16. Muirhead C.M., Jones D.W. The purification of rare earth metals. Solid state electrotransport processing of praseodymium // *J. Less-Common Met.* – 1976. – Vol. 50, No. 1. – P. 73-83.
17. Volkov V.T., Nikiforova T.V., Ionov A.M., Pustovit A.N., Sikharulidse G.G. Preparation of purity yttrium single by electrotransport. // *J. Less-Common Met.* - 1981. - Vol. 79, No. 2. - P. 199-205.
18. Nikiforova T.V., Volkov V.T. The effect of purity and the materials used for adapters on the purification yttrium by solid state electrotransport // *J. Less-Common Met.* – 1986. – Vol. 115, No. 1. – P. 91-95.
19. Ionov A.M., Volkov V.T., Nikiforova T.V. Behaviour of interstitial impurities on the surface of yttrium during solid state electrotransport: Auger studies // *Journal of Alloys and Compounds.* – 1995, No. 223. – P. 91-96.
20. Fort D., Pechrsky V.k., Gschneidner K.A. Solid state electrotransport purification of dysprosium // *Journal of Alloys and Compounds.* – 1995, No. 226. – P. 190-196.
21. Isshiki M. Purification of rare earth metals // *Vacuum.* – 1996. – Vol. 47, No. 6-8. – P. 885-887.
22. Carlson O.N., Schmidt F.A., Alexander D.G. Electrotransport Purification and Some Characterization Studies of Vanadium Metal // *Metall. Trans.* – 1972. – Vol. 3, No. 5. – P. 1249-1254.
23. Azhazha V.M., Kovtun G.Ph., Tikhinsky G.Ph. Polucheniye i metallofizika osobo chistyykh metallov // *Metallofizika i novejskiye tehnologii.* – 2000. – Vol. 22. – S. 21-35.
24. Schmidt F.A., Carlson O.N. Electrotransport of carbon in niobium and tantalum // *J. Less-Common Met.* – 1972. – Vol. 26. – P.247-253.
25. Fromm E., Kirchheim R., Mathuni J. Change of electrotransport-direction with increasing temperature in the niobium-oxygen system // *J. Less-Common Met.* – 1975. – Vol. 43, No. 1. – P. 211-215.
26. Schmidt F.A., Carlson O.N. Electrotransport of carbon in molybdenum and uranium // *Metallurgical Transaction.* – 1976. – Vol.7, No.1. – P. 127-132.
27. Zee R.H., Carpenter G.J.C., Schmidt F.A. Purification of zirconium by electrotransport processing // *Scripta Metallurgica.* – 1984. – Vol. 18, No. 5. – P. 489-493.
28. Kekesi T., Isshiki M. Principles of Metal Purification and Purity Evaluation // In book “Purification Process and Characterization of Ultra High Purity Metals”. Series: Springer Series in Materials Processing (Eds.: Waseda, Yoshio, Isshiki, Minoru). – 2002. – XIV. – P. 39-69.
29. Carlson O.N., Weins W.N., Schmidt F.A. Diffusion and electrotransport of metallic solutes in thorium metal // *Trans. of American Nuclear Society.* – 1977. – Vol. 27. – P. 286-287.
30. Okafor I.C. Diffusion and electrotransport of some transition element in β -thorium // *Acta Metallurgica.* – 1987. – Vol. 35, No.3. – P. 759-764.
31. Kuroda K., Matsuyama K., Kato K., Fujisawa T., Yamauchi C. Influence of precipitation of graphite and precipitated cementite solid state electrotransport of carbon in γ -iron // *J. Japan Institute of Metals.* – 1996. – Vol. 60, No.5. – P. 446-451.
32. Lopatina E.A., Belashchenko D.K., Krutovsky E.P., Gushchina E.I. Elektroprenos pripesey redkikh metallov v zhydkom galii // *Izvestiya Akademii Nauk SSSR, Metally.* – 1977. – No.2. – S. 112-117.
33. Mikhailov V.A., Shchukin L.I., Drakin S.I. et al. Konvektivnoye peremeshyvaniye pri elektroprenose v rasplavlennykh provolochnykh obraztsakh indiya i galliya, uderzhivayemykh oksudnoy plynkoy // *Izvestiya Akademii Nauk SSSR, Metally.* – 1985. – No. 4. – S. 42-45.
34. Pfann V. Zonnaya plavka. – M.: Mir, 1970. – 361s.
35. Pfann V.G., Wagner R.S. In the book *Zone melting* ed. Vigdorovich V.N. – M.: Metallurgiya, 1966. – P. 95-109 (in Russian).
36. Hay D.R., Scala E. Zone-Rifining Tungsten in the Presence of a Superimposed Direct Current // *Trans. Met. Sos. AIME.* – 1965. – Vol. 233, No.6. – P. 1153-1155.
37. Grinyuk V.N., Papirov I.I., Tikhinsky G.Ph., Dyakov I.G. // *Izvestiya AN SSSR, Metally.* – 1967. – No. 4. – S. 77-84.
38. Kovtun G.P., Elensky V.A., Shcherban' A.P., Tomskaya L.A., Voronina L.N., Kramskaya T.A. Rafinirovaniye molibdena zonnou plavkoi v elektricheskom pole // *Voprosy atomnoi nauki i tekhniki. Ser. "Obshchaya i yadernaya fizika".* – 1984. – Vyp. 1 (26). – S. 55-57.
39. Azhazha V.M., Kovtun G.P., Elensky V.A., Volkenshtein N.V., Startsev V.E., Cherepanov V.I. Temperaturnaya zavisimost' elektrosoprotivleniya monokristallov ruteniya vysokoi chistoty, poluchennykh zonnou plavkoi v elektricheskom pole // *FMM.* – 1976. – T. 41. – Vyp. 4. – S. 888-890.
40. Zelensky V.Ph., Tikhinsky G.Ph., Azhazha V.M. Polucheniye ocobochistyykh redkikh i redkozemel'nykh metallov i nekotorye ikh svoistva // *Vysokochistye veshchestva.* – 1994. – No. 3. – S. 66-75.
41. Kovtun G.P., Elensky V.A., Tomskaya L.A., Karlina Z.G., Saenko E.M. Polucheniye monokristallov osmiya i nekotorye ikh svoistva // *Vysokochistye i monokrystallicheskie materialy.* – M.: Nauka. – 1987. – S. 61-67.
42. Malang E.U., Oglesby C. S., Siegrist T., Bucher E. Purification and single growth of niobium by combined zone refining and electrotransport // *Physica B.* – 1995. – No. 204. – P. 363-366.
43. Azhazha V.M., Vyugov P.N., Lavrinenko S.D., Pavlov V.S., Pylipenko N.N., Tikhinsky G.Ph. Rafinirovaniye redkozemel'nykh metallov fizicheskimi metodami // *Vysokochistye veshchestva.* – 1993. – No. 2. – S. 5-12.
44. Murphy J.E., Wong M.M. Purification of yttrium by zone refining and filed freezing // *J. Less-Common Met.* – 1975. – Vol. 40, No. 1. – P. 65-77.
45. King C.A., Brown S.V. The combination of electrotransport and zone refining techniques for the growth and purification of metallic crystals // *Review of Scientific Instruments.* – 1992. – Vol. 63, No. 5. – P. 3185-3187.
46. Dost S., Liu Y.C., Haas J., Roszmann J., Grenier S., Audet N. Effect of applied electric current on impurity transport in zone refining // *Crystal Growth.* – 2007. – No. 307. – P. 211-218.