

# SECTION 1

## PURE MATERIALS AND VACUUM TECHNOLOGIES

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### TO THE ISSUE OF THE ULTIMATE PURIFICATION OF METALS

G.P. Kovtun<sup>1,2</sup>, D.A. Solopikhin<sup>1</sup>, A.P. Shcherban<sup>1</sup>

<sup>1</sup>National Science Center “Kharkov Institute of Physics and Technology”, Kharkiv, Ukraine;

<sup>2</sup>V.N. Karazin Kharkiv National University, Kharkiv, Ukraine

E-mail: [gkovtun@kipt.kharkov.ua](mailto:gkovtun@kipt.kharkov.ua)

The paper considers issues related to the ultimate content of impurity elements in metals in the processes of their refining by evaporation and distillation in vacuum, zone recrystallization and electromigration. It is shown that at all refining methods, with an increase in the number of refining cycles and the duration of the process, a “saturation effect” arises, associated with the achievement of the ultimate concentrations of impurity elements in refined metals. The reasons for the impossibility to produce absolutely pure metals have been discussed.

In a high-purity state, metals acquire qualitatively new, previously unknown properties, what cause their widespread use both for fundamental research and for practical purposes. There are various methods for deep refining of metals, which are continuously being expanded and improved [1–5, 8, 9]. In the purest chemical elements (silicon, germanium, gallium, mercury), the content of the total impurity elements is around the  $10^{-6}$  at.%, and a number of individual impurities –  $10^{-7} \dots 10^{-9}$  at.% [6].

An increase in purity is associated with an increase in material costs which grow nonlinearly in the area of ultimate cleaning [7]. Therefore, issues almost always arise, which related to the determination of the ultimate content of impurity elements in the processes of metal refining, the possibility of assessing this content, and the establishment of external factors affecting the content of impurities. These and other issues are considered in the article concerned refining metals by the methods of evaporation and distillation in vacuum, directed crystallization and electromigration.

The simple way to remove volatile impurities from a metal is to evaporate them in a vacuum. The time dependence of the distillation rate of highly volatile impurities in a binary alloy was considered in [1]. The main conclusions from this consideration are as follows. First, the content of the volatile component during vacuum distillation decreases exponentially with time, and, second, the complete distillation of the volatile impurity in a finite time ( $t \rightarrow \infty$ ) from the alloy is impossible.

With an increase in the number of refining cycles or the duration of the process, the purity of metals, as a rule, increases, but at the same time, for all methods, the so-called “saturation effect” is observed, that is, the achievement of the ultimate content of an impurity element.

The issue remains undecided, namely can the concentration of the volatile component reach an ultimate value during evaporation and will not change further with an increase in the distillation time?

In the case of a binary alloy consisting of the main nonvolatile component *A* and an impurity volatile component *B*, the total equilibrium pressure of the melt ( $P_{tot}$ ) according to Dalton's law will be equal to the sum of the partial pressures of components *A* and *B*.

$P_{tot} = P_A + P_B$ , where  $P_A$  and  $P_B$  – are the equilibrium partial pressures of components *A* and *B*.

According to Raoult's law, the equilibrium partial pressures for real systems are expressed by the ratios:

$$p_A = \gamma_A p_A^0 N_A \quad \text{and} \quad p_B = \gamma_B p_B^0 N_B,$$

where  $\gamma_A$  and  $\gamma_B$  are the activity coefficients;  $p_A^0$  and  $p_B^0$  are equilibrium vapor pressures of pure components *A* and *B*;  $N_A$  and  $N_B$  are mole fractions, respectively, for components *A* and *B*.

As the distillation proceeds, the mole fractions of components *A* and *B* will change, and the mole fraction of the volatile component ( $N_B$ ) will change faster. With a change in the molar fractions of components *A* and *B*, their equilibrium partial vapors pressures will also change, which, upon reaching certain (final) concentrations of the components, will be equal to each other, that is,  $P_A = P_B$ . In this case:

$$p_A = \gamma_A p_A^0 N_A^K \quad \text{and} \quad p_B = \gamma_B p_B^0 N_B^K,$$

where  $N_A^K$  and  $N_B^K$  are equilibrium mole fractions of components *A* and *B*, the ratio of which will not be changed with increasing sublimation time.

Achieving equality of the partial vapor pressures of the main and impurity components makes it possible to estimate the final (ultimate) content of the volatile component in the process of distilling the melt.

A number of assumptions can be made for estimated calculations. Let us assume that during the evaporation of a highly volatile impurity, the mass of the main component does not change. In this case, from the equality condition

$$p_A = \gamma_A p_A^0 N_A \quad \text{and} \quad p_B = \gamma_B p_B^0 N_B^K,$$

the final value of the molar fraction of the volatile component has the form:

$$N_B^K = \frac{\gamma_A P_A^0 N_A}{\gamma_B P_B^0}$$

For dilute solutions ( $\gamma_A \rightarrow 1$ ) and taking into account that  $N_A = 1 - N_B^K$ , then

$$N_B^K = \frac{P_A^0}{\gamma_B P_B^0 + P_A^0}$$

For the case of an ideal system ( $\gamma_B \rightarrow 1$ ), the final (ultimate) content of the molar fraction of the volatile component will be determined by the expression

$$N_B^K = \frac{P_A^0}{P_B^0 + P_A^0}$$

In the process of multiple distillation, there will be occur also a change in the partial pressures of the impurity element and the main component. When equality between them is reached, the content of the volatile component will not change either in the melt or in the condensate.

The process is more complex where during the evaporation of a highly volatile component, partial evaporation of the main component also occurs. In this case, we can use the expression to calculate the change in the concentration of alloy components during evaporation [8].

$$\lg \frac{C_B}{C_B^0} = \left[ \frac{\gamma_B P_B^0}{P_B} \cdot \sqrt{\frac{M_A}{M_{Bi}}} - 1 \right] \lg \frac{W}{W_A^0} \quad (1)$$

Here  $C_B^0$  and  $C_B$  are the concentration of a highly volatile impurity, respectively, before and after evaporation,  $M_A$  and  $M_B$  are molecular weights of components A and B,  $W_A^0$  and  $W_A$  are the masses of the main component before and after evaporation. The expression (1) makes it possible to estimate the content of volatile impurity in the melt taking into account the mass loss of the main component.

In the case of directional crystallization of metals, a "saturation effect" is also observed. After multiple passes of the liquid zone, the distribution of impurities along the length of the ingot approaches the steady-state final state which characterizes the maximum attainable separation of impurities [9].

Fig. 1 shows an approximate distribution of the concentration of impurity  $C$  with a distribution coefficient  $K < 1$  after one pass and multiple passes.

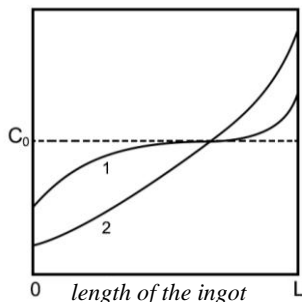


Fig. 1. Distribution of impurity concentration  $C$ , with the distribution coefficient  $K < 1$  along the length of the ingot  $L$ , after one pass (1) and multiple passes (2).  $C_0$  is the concentration of impurities in the charge. The zone moves from left to right

Additional passes make the start section deeper, heighten the end section and shorten the length of the horizontal part of the curve. As a result, all three areas are encompassed by a single, relatively smooth curve. After multiple passes through the zone, the distribution of the impurity approaches to the steady state which characterizes the final, maximum attainable separation of the impurity.

In this case, the convection flow of the impurity, caused by the crystallization action of the zone, meets the equal opposition of the reverse flow due to the accumulation of the impurity in the final section.

A similar (final) distribution of impurities is observed in the process of refining metals using the method of electromigration – the movement of ions of impurity elements in solid or liquid metals under the applied a constant electric field [5]. The movement of the impurity ion is carried out under the action of the force  $F = Z_{eff} \cdot E$ , where  $Z_{eff}$  is the effective charge of the ion;  $E$  is the electric field strength.

The quantitative characteristic of the refining process during electromigration follows from the relationship between the speed of movement of the impurity under the applied electric field and its reverse movement in consequence of diffusion caused by the appearance of a concentration gradient.

To describe this process, one uses the equation of the matter flow ( $I$ ) generated by an electric field [5].

$$I = -D \frac{dC}{dx} + UCE, \quad (2)$$

where  $C$  is the impurity concentration at a distance  $x$  from the beginning of the sample;  $D$  is a self-diffusion coefficient of impurity ion;  $U$  – ion mobility;  $E$  is the electric field strength.

For a sufficiently long time of electric field application, the first term of the flux, characterizing the reverse diffusion, and the second term, due to the action of the electric field, balance each other, giving zero flux and, consequently, the maximum achievable degree of purification (Fig. 2).

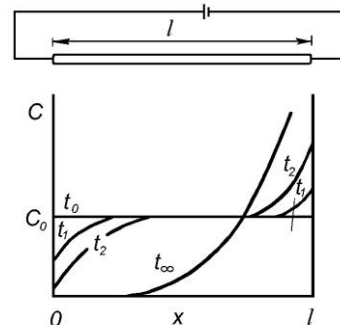


Fig. 2. Distribution of impurities along the length of the sample  $L$  under the influence of a direct current for different periods of time  $t$

The "saturation effect" is inherent in other methods of deep cleaning of metals. In this regard, the question is natural – is it possible to obtain an absolutely pure substance? In our opinion, it is impossible.

The "saturation effect" at the refining of metals is conditioned by the mechanisms of separation of

impurity elements, or rather, their limiting ability in deep refining of metals.

On the other hand, the impossibility to obtain an absolutely pure substance is associated with technical difficulties due to contamination of the substance to be purified by construction materials and the environment.

The impossibility to obtain an absolutely pure substance is, apparently, of a fundamental nature. The realization of any process in the system is associated with a decrease in the Gibbs energy. The basic Gibbs energy equation is  $G = H - TS$ , where  $H$  – enthalpy;  $S$  – entropy,  $T$  – temperature. The process in the system is possible at  $\Delta G < 0$ . The achievement of absolutely pure substance in the process of refining metals can be considered as an approximation to the state of matter with zero entropy, which is impossible in principle.

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### К ВОПРОСУ О ПРЕДЕЛЬНОЙ ОЧИСТКЕ МЕТАЛЛОВ

*Г.П. Ковтун, Д.А. Солопихин, А.П. Щербань*

Рассмотрены вопросы, связанные с предельным содержанием примесных элементов в металлах в процессах их рафинирования, методами испарения и дистилляции в вакууме, зонной перекристаллизации и электропереноса. Показано, что при всех методах рафинирования с увеличением числа циклов рафинирования и длительности процесса возникает «эффект насыщения», связанный с достижением предельных концентраций примесных элементов в рафинированных металлах. Обсуждены причины невозможности получения абсолютно чистых металлов.

### ДО ПИТАННЯ ПРО ГРАНИЧНЕ ОЧИЩЕННЯ МЕТАЛІВ

*Г.П. Ковтун, Д.О. Солопихін, О.П. Щербань*

Розглянуті питання, пов'язані з граничним вмістом домішкових елементів у металах у процесах їх рафінування, методами випаровування та дистиляції у вакуумі, зонної перекристалізації та електроперенесення. Показано, що при всіх методах рафінування зі збільшенням числа циклів рафінування та тривалості процесу виникає «ефект насичення», пов'язаний з досягненням граничних концентрацій домішкових елементів у рафінованих металах. Обговорено причини неможливості одержання абсолютно чистих металів.