

OBTAINING HIGH-PURITY ZINC FOR RARE EVENT DETECTORS

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A comprehensive process of zinc distillation refining was investigated, which includes the stages such as oxidizing refining, zinc purification of volatile and nonvolatile impurities by vacuum distillation from a crucible on a hot condenser, and filtration of the distillate. Special attention was given to the study of oxidizing refining and the efficiency of applying this method in a comprehensive Zn purification scheme. A thermodynamic analysis of the oxidation reactions of Zn and present in it impurities Cd, Pb, Fe, Cu, Tl, Ni, Sn, As, Sb, etc., during melting in an argon atmosphere, as well as during distillation of zinc in a vacuum, was performed. The strength of impurity oxides in zinc was estimated by the absolute value of the change in Gibbs free energy during melting of the metal in an argon atmosphere and distillation in the vacuum of 0.5 Pa. Experimental results of the application of the complex process for obtaining high purity ($> 5N$) zinc are presented.

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INTRODUCTION

Many outstanding problems in fundamental physics are related to rare event processes, so called because they actually have a low probability of occurrence (double beta decay and other rare types of nuclear decay), or due to the particles involved, such as neutrinos, hypothetical axions, and dark matter particles (WIMPs – weakly interacting massive particles), have an extremely low cross section for interacting with matter. To register rare events, an important aspect is the arrangement of experimental conditions that ensure an extremely low (ideally zeroth) background and the creation of detectors having extremely high sensitivity. That is why experimental facilities must be located deep underground or underwater (to reduce the impact of cosmic radiation), and the detector material and immediate surroundings must be particularly radiation-pure (to reduce the level of natural radioactivity). To make new highly sensitive detectors, crystals are very often used as cryogenic bolometers [1]. Cryogenic bolometric techniques [2] are one of the most promising experimental approaches in detecting rare events due to excellent energy resolution, recording efficiency, and flexibility in the use of the absorber. A cryogenic bolometer consists of an absorbing material cooled to very low temperature (< 100 mK) and a thermometer able to measure the temperature rise with the tiny energy deposit caused by the interaction of particles with the absorber. But the drawback of the bolometric method is that it cannot discriminate between different particles which release the same amount of energy in the absorber. However, if the absorbing material is also a scintillator, the use of a second readout channel and simultaneous measurement of bolometric and scintillation signals allows different types of particles to be discriminated by changing the ratio of light to heat. It contributes to significant reduction in background to very low level.

Zinc-bearing crystals are widely used in rare-event physics as room-temperature ZnWO_4 scintillators

[3–5], low-temperature ZnSe calorimeters in the CUPID-0 experiment [6], ZnMoO_4 in the LUMINEU facility [7], or CdZnTe semiconductor detectors in the COBRA collaboration [8]. Using elementally purified zinc (> 99.999 wt.%) with its high radioactive purity, it was possible to establish the most stringent lower limits of half-lives for such decay modes of ^{64}Zn as two-neutrino electron capture with positron emission $\varepsilon\beta^+$ and neutrinoless double electron capture $0\nu2\varepsilon$, which are $T_{1/2}^{2\nu\varepsilon\beta^+} > 2.7 \cdot 10^{21}$ years and $T_{1/2}^{0\nu2\varepsilon} > 2.6 \cdot 10^{21}$ years, respectively [9].

In addition to radiation purity, scintillation bolometers also have high requirements on chemical elements. Owing to chemical impurities, point defects can act as traps for both phonons involved in the development and propagation of the bolometric signal and free carriers involved in the scintillation process. So, the content of impurity elements Fe, Cr, V, Ni, As, Cu, Mo, Si, and S, which affect the scintillation characteristics of crystals, should be less than 1 ppm [1, 9–11].

The extreme degree of purification in a process carried out in multiphase systems is usually performed in quasi-equilibrium modes that can be described in terms of thermodynamics. In this regard, it is possible to construct a thermodynamic model of the metal purification process during distillation. Such a model for the zinc refining process is considered in [12]. On the basis of the material balance conditions, the authors proposed an expression that connects the impurity concentration in the melt with their content in the surface layer of the condensate, as well as a purification criterion α which is equal to the ratio of the average concentration of the impurity in the condensate to its concentration in the initial substance.

The model presented in [12] permits to study the behavior of impurities having volatile forms in the Zn-ZnO system. The main result of the calculations is the following: impurities Mg, Ca, Ba remain in the concentrate in the form of non-volatile oxides. Both forms of As (element and oxide those) have high vapor pressure and, according to the calculations, As

evaporates during the process. Sb and Bi do not interact with ZnO and remain in the element form.

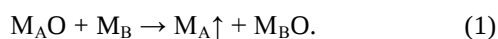
The purpose of this work is to study and analyze the thermodynamic reactions of impurity oxidation during the melting and distillation of zinc, and to investigate the comprehensive distillation method for producing high-purity zinc (> 99.999 wt.%) to create the zinc-containing rare event detectors.

1. THEORETICAL AND EXPERIMENTAL RESEARCH

An analysis of the literature on the experimental use of oxidizing refining for zinc showed that the application of this technique in the distillation refining scheme has been investigated to some extent.

The authors of [12, 13] used vacuum distillation in the presence of basic metal oxide for deep purification of zinc. An oriented crystallization process was carried out at the final stage. Analysis of the purity of the purified material showed that the proposed method ensures its purity of no worse than 99.99999 wt.%.

The authors of [14] presented an original installation for multistage vacuum distillation of Cd, Zn, and Te. A feature of this method is the use of an oxide film on the metal surface, which is formed during the melting of Zn (Cd, Te) due to the natural oxygen content in metals. The oxide film serves as a good collector of impurity oxides formed due to their higher sensitivity to oxygen compared to the basic metal as a result of the exchange reaction:



In equation (1), M_A and M_B are elements of the main and impurity components, respectively ($M_B = \text{Li, Na, K, Ca, Mg, Al, Au, Ag, In, etc.}$).

Since impurity oxides are in practice non-volatile (the vapor pressure of the metal P_M exceeds the vapor pressure of the oxide P_{MO} by several orders of magnitude), and the separation coefficients $\alpha = P_M/P_{MO} \gg 1$, they are captured by the oxide film M_AO , i.e. in our case ZnO. The total content of impurities in the initial Zn is $1.3 \cdot 10^{-4}$ wt.%. After three stages of purification, the content of these impurities decreased by 170 times. The results obtained prove the high efficiency of the studied zinc purification method.

It would be appropriate to note here the recent paper [15] which describes a combined method for deep purification of Zn, Cd, and Te developed by the authors, which make it possible obtaining high-purity materials in an installation with a vertical arrangement of crucible. The method includes the following processes: filtration refining of the metal melt with the possibility of its vacuum degassing and additional purification through the oxide layer; first distillation with the possibility of using getter additives in the melt and using getter filters; degassing of the melt with the removal of volatile impurities on a condenser under low vacuum conditions; second distillation and pouring of the metal into the necessary ingots.

The authors of [15] developed and manufactured a pilot model of the installation which was used to carry out the experimental processes of deep purification of

metals using the proposed method. Physical experiments were performed, that makes it possible obtaining Zn of the purity above 99.9999 wt.% on 30 main residual impurities with a final product yield at least 55 wt.%.

The oxidizing refining method is carried out using the installation for refining metals in vacuum [16] developed in the Scientific-Researching Laboratory of Physics of Zirconium and Technologies of Pure Metals of the Institute of Solid-State Physics of Materials Science and Technologies of the NSC KIPT. In subsequent applications of this approach [9, 10, 17, 18], the thermodynamics of impurity oxidation reactions during zinc melting and distillation, as well as the efficiency of oxidative refining of Zn, were not investigated, which were studied in this work.

1.1. THERMODYNAMIC ANALYSIS OF IMPURITY OXIDATION REACTIONS DURING ZINC MELTDOWN AND DISTILLATION

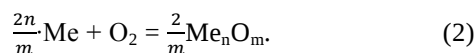
A thermodynamic analysis of the oxidation reactions of Zn and the impurities present in it was performed in the presented paper. Chemically active to oxygen impurities in zinc, their content analyzed in our work, are the following: Pb, Cd, Fe, Cu, Sn, As, Al, Bi, Ni, Sb, Mg, Si, Mn. The efficiency of removing metal impurities from zinc in the form of oxides can be assessed by the values of oxide compounds strength in certain ranges of change in temperature and pressure of the surrounding gas environment. The main characteristic of the strength or stability of metal oxides MeO is their oxygen potential or the change (decrease) in the Gibbs free energy ΔG°_{MeO} during the formation of oxide compounds. To assess the stability of metal impurity oxides in molten zinc under atmospheric pressure, the change in standard Gibbs energy ΔG°_{MeO} can be used. Since zinc distillation in vacuum can be carried out at the temperature greater than $0.6T_{boil}^{Zn}$, where T_{boil}^{Zn} is the zinc boiling point which is approximately 1180 K, the operating temperature range starts from $T = 700$ K and riches up to 1000 K. Within this interval, for the formation of zinc oxide ZnO under normal conditions, the temperature dependence of the decrease in standard energy per mole of oxygen has the form:

$$\Delta G^\circ_{ZnO} = -987332 + 407.96 \cdot T \quad [19],$$

or according to data from another source

$$\Delta G^\circ_{ZnO} = -910012 + 375.22 \cdot T \quad [20].$$

Similarly, using reference data, ΔG° is determined for the formation of stable impurity oxides in zinc, namely: Al_2O_3 , As_2O_3 , Cu_2O , CdO , Bi_2O_3 , Fe_2O_3 , MgO , MnO , NiO , Sb_2O_3 , SiO_2 , SnO_2 , TiO , Tl_2O_3 . To compare the oxygen potentials of the specified impurity oxides with each other, the changes in ΔG°_{MeO} were determined per mole of oxygen, i.e. for reactions that generally proceed according to the equation:



Here m and n are indices (coefficients) representing the ratio of the atom valences in the compounds.

The gaseous medium pressure P in the quasi-closed volume of the distillatory device is determined by the vapors of the metal being refined. This pressure in a steady distillation process is equalized with the residual pressure in the chamber of the vacuum unit. Thus, to assess the effect of vacuum on the stability of oxides, it is necessary to introduce a value that takes into account the transition of the metal or its oxide into the gaseous state. For the case where the activity of MeO is 1 and the boiling point of the metal is lower at atmospheric pressure than the boiling point of the oxide, the change in Gibbs energy upon formation of the metal oxide according to reaction (2) is given by the formula [20]:

$$\Delta G_{\text{MeO}}^0 - \frac{2n}{m} RT \cdot \ln(P/1.03 \cdot 10^5), \quad (3)$$

where ΔG_{MeO}^0 – change in standard Gibbs energy during the formation of oxidizing compounds; P – pressure of the gas environment, Pa; T – temperature, K; R – universal gas constant, J/(mol·K).

If the boiling point of metals is higher at the atmospheric pressure than the boiling point of the corresponding oxides, for example, such as PbO , SnO_2 , SiO_2 , Al_2O_3 etc., then in the general case for reaction (2) the change in Gibbs energy upon formation of metal oxide is of the form:

$$\Delta G_{\text{MeO}}^0(P, T) = \Delta G_{\text{MeO}}^0 + \frac{2}{m} RT \cdot \ln(P/1.013 \cdot 10^5). \quad (4)$$

The dependences for $\Delta G_{\text{ZnO}}(P, T)$, calculated by formula (3) at $T > 1180$ K, were extrapolated to the temperature range of 700...1000 K. During intensive evaporation of Zn in vacuum, its atoms can capture and drag along impurity oxides Me_nO_m . At the same time, to calculate $\Delta G(P, T)$ during the formation of Me_nO_m in a vacuum, $\Delta G_{\text{MeO}_m}(T)$ can be used in the temperature range the impurity metal is in a liquid or gaseous state, and if necessary, the obtained dependences may be extrapolated to the temperature interval under study. A more detailed description of the model used to calculate the dependences of the change in Gibbs free energy ΔG on temperature and pressure during the formation of impurity oxides in the liquid and vapor phases is given in [21] using the example of oxidizing refining during tellurium distillation.

Calculations of $\Delta G^0(T)$ and $\Delta G(P, T)$ were performed for the formation of base metal oxide (ZnO) and impurity oxides in the liquid and gaseous phases according to formulas (3) and (4). The graphs of the obtained dependences are shown in Figs. 1 and 2.

Analysis of the obtained dependences of the change in the Gibbs potential during the formation of ZnO and oxides of impurities Pb, Cd, Fe, Cu, Sn, As, Al, Sb, Si, Mg, Mn in the liquid phase of zinc during melting in the argon atmosphere shows the following. Impurities Mn, Si, Al, Mg which the change in the Gibbs potential ΔG_{MeO} of oxide formation is higher by absolute value, will deoxidize the oxides, releasing Zn and the elements As, Sn, Fe, Cd, Sb, Pb, Cu from their less stable oxides.

Resistant oxides are removed by filtering the molten zinc. Nonvolatile impurities (Sn, Fe, Sb, Pb, Cu), entering to the melt at the deoxidation, are removed during the distillation process. Volatile impurities Cd and As (Table 1) will pass to the condensate during distillation, but due to the application of a hot condenser, their content in the condensate is reduced by removing them from the volume of the distilling unit.

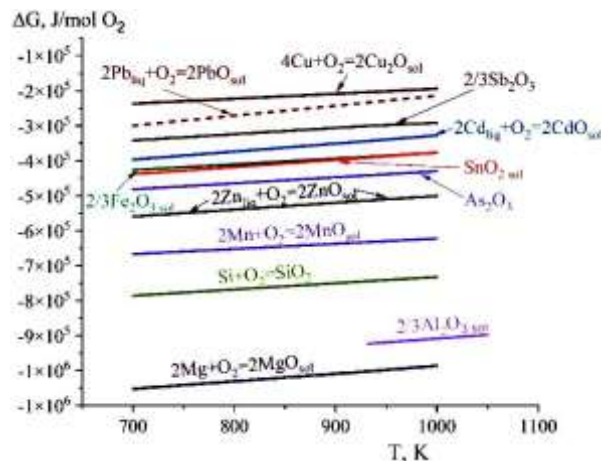


Fig. 1. Change in Gibbs potential at the formation of ZnO and impurity oxides Pb, Cd, Fe, Cu, Sn, As, Al, Sb, Si, Mg, Mn in the liquid phase of zinc during melting in argon atmosphere

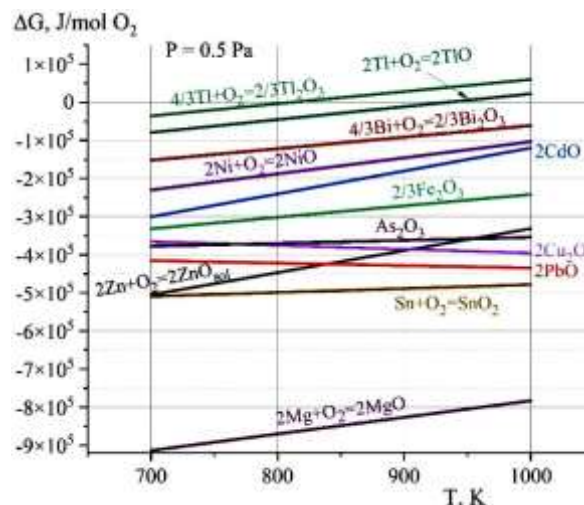


Fig. 2. Change in Gibbs potential during the formation of ZnO and oxides of impurities Fe, Cu, Pb, Tl, Bi, Cd, Ni, As, Sn, Mg during distillation of zinc in vacuum 0.5 Pa

At the distillation temperature, Mg and Sn oxides are more stable than zinc oxide. The remaining oxides of Pb, Ni, Cu, Fe, Cd, As, Bi, Tl have a lower oxygen potential. These oxides are formed at the interface between the liquid and vapor phases and, as a result of low vapor pressure of theirs and their elements (Pb, Cu, Fe, As, Bi, Tl), they will remain in the residue in the crucible during distillation. Volatile As and Cd, both in elemental and oxide form, at the interface between the vapor phase and condensate during zinc distillation, will migrate to the condensate, thus limiting the purity of the refined product. The use of a hot condenser and the proposed filtration of the resulting condensate is a

method of additional zinc purification of these difficult-to-remove impurities.

1.2. COMBINED PROCESS OF ZINC PURIFICATION BY DISTILLATION METHOD

The complex zinc purification process consists of the following main stages: oxidizing refining by filtering the molten initial metal in an argon atmosphere; distillation of zinc in vacuum with condensation on a hot condenser and filtration of the distillate by its melting and casting into mensural ingots. The block diagram of this process is presented in Fig. 3.

The filtration process (oxidizing refining) was carried out in an argon atmosphere after preparation of the initial zinc, analysis of impurity content and loading into the device. Filtration involves percolation of the metal through a small diameter hole in a conical plate. In this case, the metal being refined, which is on the

plate at a temperature above its melting point, flows down on the convex surface through the hole to the crucible. In this procedure, basic metal oxide, non-volatile oxides of metal impurities, and slags remain on the surface of the plate in the form of a film which is then removed out of the subsequent refining process. Removing the oxide film from the surface of the metal melt during distillation leads to an increase in the productivity of the process, but as analyses of the impurity composition have shown, the amount of some impurities in zinc decreases by 2–5 times after filtration. The results of the analysis of the impurity content and the purity of the metal after oxidizing refining are given in Table 1. Fig. 4 shows a photo of a plate with collected contaminants (a) and filtered zinc (b) to illustrate the effect of filtration visually.

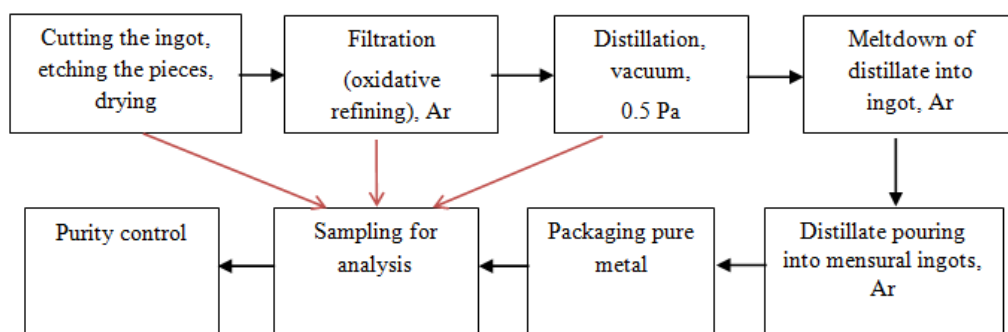


Fig. 3. Block diagram of the complex process of obtaining high-purity zinc by vacuum distillation



Fig. 4. Collected oxide contaminants after filtration of the initial zinc (a) and filtered zinc (b)

After preliminary purification, Zn was distilled in vacuum with condensation of metal vapor on a hot condenser. It leads to additional removal of volatile impurities and oxides from the condensate of metal.

The scheme of device and a detailed description of the metal filtration and distillation process are given in previous papers [9, 16–18].

The availability of volatile and non-volatile impurities in zinc was determined by calculating the values of the ideal impurity separation coefficients α_i during molecular evaporation [22] according to the formula:

$$\alpha_i = \frac{p_{Zn}^0 \sqrt{M_B}}{p_B^0 \sqrt{M_{Zn}}}, \quad (5)$$

where p_{Zn}^0 , p_B^0 – pressure of zinc and impurity B vapor; M_{Zn} , M_B – molecular weight of zinc and impurity B, respectively.

Table 1 shows the values of the ideal impurity separation coefficients α_i during molecular sublimation of zinc in vacuum, calculated by formula (5). The vapor pressure of the elements at given temperatures was taken from [23].

Table 1
Calculated values of ideal impurity separation
coefficients α_i during molecular evaporation of zinc
in vacuum

Impurity	Temperature, K			
	700	800	900	1000
P	$2.9 \cdot 10^{-4}$	—	—	—
S	$6.1 \cdot 10^{-4}$	—	—	—
Fr	$3.7 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$	—	—
Cs	$2.2 \cdot 10^{-3}$	$2.3 \cdot 10^{-2}$	$5.6 \cdot 10^{-2}$	—
Rb	$9.7 \cdot 10^{-3}$	$2.6 \cdot 10^{-2}$	$5.5 \cdot 10^{-2}$	—
Se	$2.7 \cdot 10^{-2}$	$4.1 \cdot 10^{-2}$	$6.9 \cdot 10^{-2}$	—
As	$5.3 \cdot 10^{-2}$	$4.1 \cdot 10^{-2}$	—	—
K	$2.1 \cdot 10^{-2}$	$4.7 \cdot 10^{-2}$	$8.7 \cdot 10^{-2}$	$1.4 \cdot 10^{-1}$
Cd	$9.8 \cdot 10^{-2}$	$1.4 \cdot 10^{-1}$	$1.9 \cdot 10^{-1}$	$2.4 \cdot 10^{-1}$
Zn	1	1	1	1
Te	2.9	2.38	2.4	2.6
Na	7.3	6.4	5.9	5.6
Mg	15	9.1	6.1	4.8
Li	$2.1 \cdot 10^2$	$9.7 \cdot 10^1$	$5.5 \cdot 10^1$	$3.4 \cdot 10^1$
Sr	$5.3 \cdot 10^2$	$4.6 \cdot 10^2$	$1.7 \cdot 10^2$	$1.11 \cdot 10^2$
Ra	$2.4 \cdot 10^4$	$1.1 \cdot 10^3$	$6.0 \cdot 10^2$	$4.1 \cdot 10^2$
Sb	$2.9 \cdot 10^4$	$5.9 \cdot 10^2$	$1.9 \cdot 10^2$	$2.1 \cdot 10^2$
Bi	$7.8 \cdot 10^4$	$2.5 \cdot 10^3$	$1.1 \cdot 10^3$	$5.7 \cdot 10^2$
Ba	$2.6 \cdot 10^6$	$1.8 \cdot 10^5$	$2.2 \cdot 10^3$	$1.2 \cdot 10^3$
Tl	$1.4 \cdot 10^6$	$4.3 \cdot 10^5$	$1.9 \cdot 10^3$	$9.8 \cdot 10^2$
Ca	4.110^3	$1.3 \cdot 10^3$	$1.2 \cdot 10^3$	$4.8 \cdot 10^2$
Pb	$4.5 \cdot 10^6$	$1.0 \cdot 10^5$	$3.5 \cdot 10^4$	$1.4 \cdot 10^4$
In	—	$2.4 \cdot 10^7$	$3.8 \cdot 10^6$	$8.5 \cdot 10^5$
Mn	—	$6.2 \cdot 10^9$	$4.3 \cdot 10^7$	$5.1 \cdot 10^5$

The impurities located above the Zn row are considered to be volatile, and below them they are nonvolatile. In this regard, the process of removing volatile impurities during distillation was carried out on a hot condenser. At the same time, non-volatile impurities remained in the residue of metal in the crucible.

This combination of purification stages significantly increases purification efficiency, productivity of the process, and the yield of a suitable product, which is at least 95% of the initial mass.

The distillation device [16] is made of high-purity dense graphite which is characterized by heat resistance, chemical inertness to zinc, and minimal impurity content. The concentration of impurities in it, such as Si, Fe, Al, Mg, B, Cu, Mn, is 1.0...0.1 ppm. The quasi-closed type distillation device consists of two identical parts: the lower part serves as a crucible, and the upper one is a collector for the condensation of Zn. The volume of the crucible makes it possible loading from 1.8 to 2.3 kg of initial zinc.

2. RESULTS AND DISCUSSION

It should be noted that zinc grade CW00 was chosen for the research of the purification process, as it has the highest purity among the grades of technical purity.

Table 2 presents the results of the analysis of the content of impurities in the initial zinc, after filtration and distillation in vacuum. The analysis was performed using high-resolution laser mass spectrometry. The random error of the analysis results is characterized by a relative standard deviation of 0.15...0.30.

Table 2
The content of major impurities in the initial zinc, after filtration
and distillation in vacuum (distillate)

Impurity	Grade, product		
	initial	after filtration	distillate
	impurity, $\times 10^5$ wt. %		
Pb	5	1	0.8
Cd	200	40	14
Fe	3	1	< 0.09
Cu	6	2	< 0.1
Sn	5	2	< 0.6
As	50	10	1
Al	2	1	< 0.03
Bi	3	2	< 0.1
Ni	4	2	< 0.3
Sb	2	1	< 0.1
Zn, wt. %	99.997	99.9994	> 99.9998

Analysis of the results shows that oxidizing refining is quite effective for zinc, and especially for volatile impurities of cadmium and arsenic (by 5 times). These impurities limit the purity of the zinc and they are poorly removed during distillation purification of the metal. More efficient removal of these elements from the condensate is achieved by using a hot condenser. In terms of overall zinc purity, this combined process provides purification efficiency of more than one order

of magnitude, namely from 99.997 wt.% in the initial metal to > 99.9998 wt.% in purified that. Such quality of purified zinc perfectly meets the purity requirements for its use in the processes of growing zinc-bearing scintillation crystals for rare event detectors.

The produced distillate was melted into an ingot and the distillate was filtered and poured into mensural ingots of various diameters for convenience of use,

including in the form of granules [18], in the process of assembling the charge for the synthesis of compounds.

Fig. 5 shows photographs of zinc as initial metal, distillate, ingots, and granules obtained of purified zinc. Zinc obtained by the proposed comprehensive distillation refining method was used to study double β -

decays of the zinc isotope ^{64}Zn [9]. The granules of purified zinc were used to grow Zn^{82}Se crystals enriched with the selenium isotope ^{82}Se to search for neutrinoless double beta decay of the ^{82}Se isotope [10].

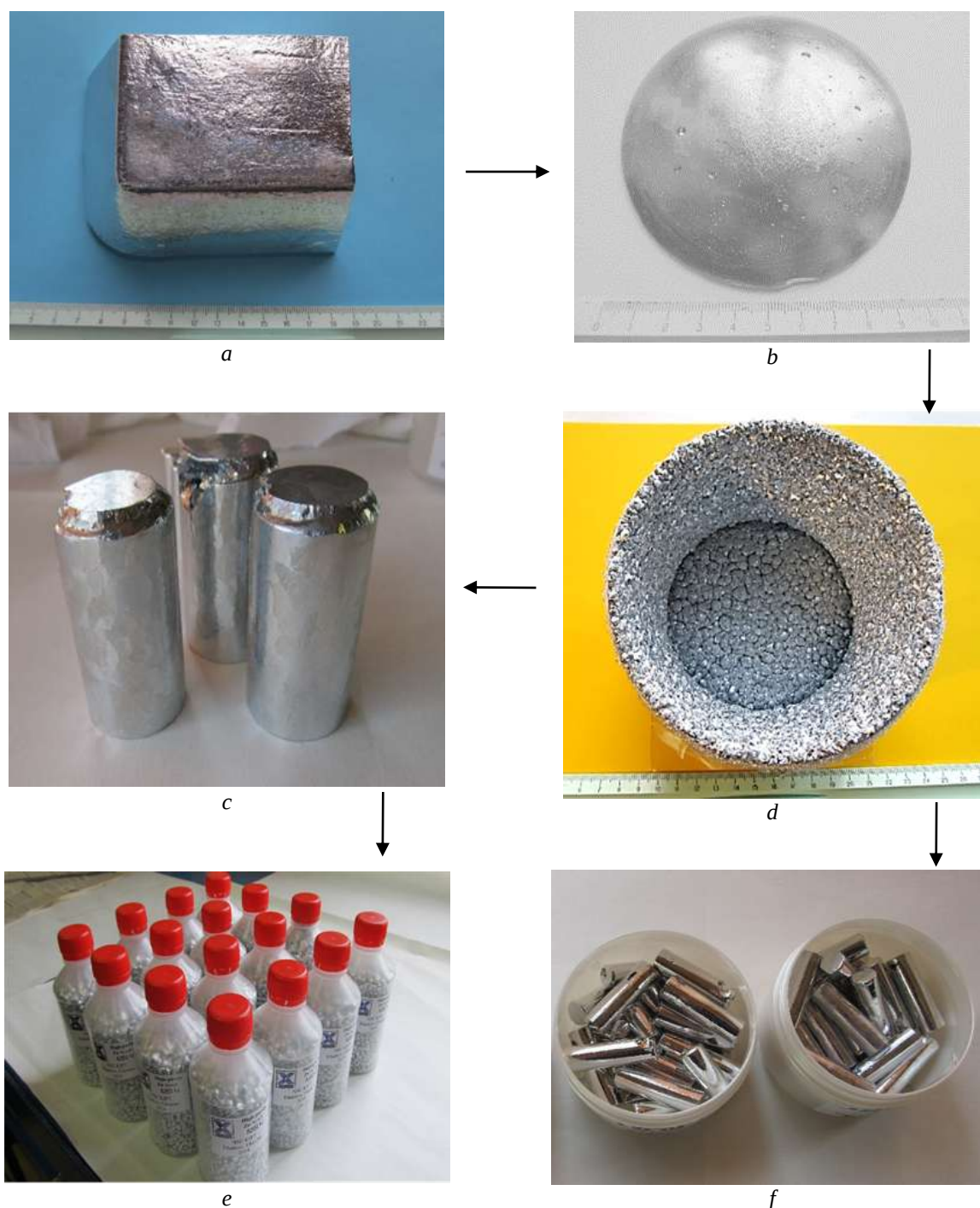


Fig. 5. Photos of zinc before and after purification and of the resulting high-purity zinc products: initial piece of zinc (a); filtered zinc (b); zinc distillate (d) distillate ingots (c, f); zinc granules (e)

CONCLUSIONS

A thermodynamic analysis of the oxidation reactions of impurities during melting in an argon atmosphere and distillation of zinc in vacuum was performed. Stable and unstable impurity oxides have been determined in relation to the main zinc oxide by calculating the change (decrease) in the Gibbs free energy ΔG_{MeO} during the

formation of oxide compounds. Such characteristic makes it possible to determine the behavior of impurity oxides and evaluate the efficiency of oxidizing refining and distillation of zinc in vacuum.

The efficiency of oxidizing refining in the scheme of a comprehensive process of distillation purification of zinc was investigated. The use of this method allows reducing the content of major impurities by 2...5 times,

especially such as Cd and As, which are difficult to remove by distillation.

The results of experimental studies of the complex process of distillation refining of zinc are presented. Studies have shown that the efficiency of such a process is more than an order of magnitude larger (from 99.997 wt.% in the initial to > 99.9998 wt.% in the purified one). The purity of such zinc fully satisfies the requirements for a material to produce rare event detectors.

REFERENCES

1. I. Dafinei, S. Nagorny, S. Pirro, et al. Production of ^{82}Se enriched zinc selenide (ZnSe) crystals for the study of neutrinoless double beta decay // *Journal of Crystal Growth*. 2017, v. 475, p. 158-170; <https://doi.org/10.1016/j.jcrysgro.2017.06.013>
2. L. Gironi. Scintillating bolometers for Double Beta Decay search // *Nucl. Instrum. Meth. A*. 2010, v. 617, p. 478; <https://doi.org/10.1016/j.nima.2009.10.080>
3. A.S. Barabash, P. Belli, R. Bernabei, et al. Low background scintillators to investigate rare processes // *J. Instrum.* 2020, v. 15, issue 07, C07037; <https://doi.org/10.1088/1748-0221/15/07/c07037>
4. A.S. Barabash, P. Belli, R. Bernabei et al. Improvement of radiopurity level of enriched $^{116}\text{CdWO}_4$ and ZnWO_4 crystal scintillators by recrystallization // *Nucl. Instrum. Meth. Phys. Res. Section A: Accel. Spectrom. Detect. Assoc. Equip.* 2016, v. 833, p. 77; <https://doi.org/10.1016/j.nima.2016.07.025>
5. P. Belli, R. Bernabei, Yu.A. Borovlev, et al. New development of radiopure ZnWO_4 crystal scintillators // *Nucl. Instrum. Meth. Phys. Res. Section A: Accel. Spectrom. Detect. Assoc. Equip.* 2019, v. 935, p. 89; <https://doi.org/10.1016/j.nima.2019.05.014>
6. O. Azzolini, M.T. Barrera, J.W. Beeman, et al. CUPID: the first array of enriched scintillating bolometers for $0\nu\beta\beta$ decay investigations // *Eur. Phys. J. C*. 2018, v. 78, issue 5, p. 428; <https://doi.org/10.1140/epjc/s10052-018-5896-8>
7. E. Armengaud, C. Augier, A.S. Barabash, et al. Development of ^{100}Mo – containing scintillating bolometers for a high-sensitivity neutrinoless double-beta decay search // *Eur. Phys. J. C*. 2017, v. 77, issue 11, p.785; <https://doi.org/10.1140/epjc/s10052-017-5343-2>
8. J. Ebert, M. Fritts, D. Gehre, et al. Results of a search for neutrinoless double- β decay using the COBRA demonstrator // *Phys. Rev. C*. 2016, v. 94, issue 2, p. 024603; <https://doi.org/10.1103/PhysRevC.94.024603>
9. F. Bellini, M. Beretta, L. Cardani, et al. Search for double β -decay modes of ^{64}Zn using purified zinc // *Eur. Phys. J. C*. 2021, v 81, issue 106; <https://doi.org/10.1140/epjc/s10052-021-08918-y>
10. G.P. Kovtun, A.P. Shcherban, D.A. Solopikhin, et al. High-pure zinc for growing Zn^{82}Se scintillation crystals // *PAST*. 2020, N 1(125), p. 12-16.
11. А.П. Щербань. Получение высокочистых металлов для производства низкофоновых сцинтилляционных детекторов редких событий // *ВАИТ. Серия «Вакуум, чистые материалы, сверхпроводники»*. 2011, №6(19), с. 3-10.
12. I.R. Schelpakova, V.I. Kosyakov, S.V. Kovalevski, and V.A. Shestakov. The use of evaporation in vacuum for purification and analysis of zinc // *Materials res. bull.* 1998, v. 33, N 2, p. 173-181.
13. S.V. Kovalevsky and I.R. Shelpakova. High-Purity Zinc, Cadmium, Tellurium, Indium and Gallium: Preparation and Analysis // *Chemistry for Sustainable Development*. 2000, v. 8, p. 85-87.
14. M.D. Pavlyuk, V.M. Kanevskii, and Yu.M. Ivanov. Production of High-Purity Cd, Zn, and Te by Multistage Vacuum Distillation // *Zhurnal neorganicheskoi khimii*. 2013, v. 58, N 8, p. 1082-1085 (in Russian).
15. В.Н. Абрютин, Е.В. Давыдова, М.А. Егоров, И.И. Марончук, Д.Д. Саникович. Глубокая очистка теллура, цинка и кадмия для применения в электронике // *Известия вузов. Материалы электронной техники*. 2022, т. 25, №2, с. 164-174; DOI: 10.17073/1609-3577-2022-2-164-174
16. Г.П. Ковтун, О.П. Щербань. Пристрій для рафінування металів у вакуумі: Деклараційний патент на корисну модель №1246. Україна, 2002. Бюл. № 5.
17. Г.П. Ковтун, А.П. Щербань, В.Д. Вирич. Получение цинка высокой чистоты сочетанием дистилляционного и кристаллизационного методов рафинирования // *Вісник Харківського національного університету. Серія фізична «Ядра, частинки, поля»*. 2004, №619, в. 1/23/, с. 95-104.
18. Г.П. Ковтун, А.П. Щербань, Ю.В. Горбенко, Д.А. Солопихин, В.Д. Вирич, Л.А. Пироженко. Получение высокочистых гранулированных металлов кадмия, цинка и свинца // *Технология и конструирование в электронной аппаратуре*. 2017, №1-2, с. 55-60; https://old.tkea.com.ua/tkea/2017/1-2_2017/st_09.htm
19. Е.А. Казачков. *Расчеты по теории металлургических процессов*. М.: «Металлургия», 1988, 288 с.
20. И.С. Куликов. *Термодинамика оксидов: Справочник*. М.: «Металлургия», 1986, 344 с.
21. О.П. Shcherban, D.O. Solopikhin, O.I. Kondrik. Purification of tellurium by a complex refining method // *Polish journal of science*. 2024, v. 1, N 80, p. 39-47; <https://doi.org/10.5281/zenodo.14176578>
22. В.А. Пазухин, А.Я. Фишер. *Разделение и рафинирование металлов в вакууме*. М.: «Металлургия», 1969, 204 с.; <https://i.twirpx.link/file/2733104>
23. А.Н. Несмеянов. *Давление пара химических элементов*. М.: Изд-во АН СССР, 1961, 396 с.; <https://i.twirpx.link/file/788045>

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ОТРИМАННЯ ЦИНКУ ВИСОКОЇ ЧИСТОТИ ДЛЯ ДЕТЕКТОРІВ РІДКІСНИХ ПОДІЙ

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Досліджено комплексний процес дистиляційного рафінування цинку, який включає такі етапи, як окисне рафінування, очистку цинку від важколетких і легколетких домішок шляхом перегонки у вакуумі з тигля на гарячий конденсатор і фільтрацію дистиляту. Особливу увагу приділено дослідженню окисного рафінування і ефективності застосування цього прийому в комплексній схемі очистки Zn. Виконано термодинамічний аналіз реакцій окиснення Zn і присутніх у ньому домішок Cd, Pb, Fe, Cu, Tl, Ni, Sn, As, Sb та ін. при розплавленні в атмосфері аргону, а також при дистиляції цинку у вакуумі. По абсолютній величині зміни вільної енергії Гіббса оцінено міцності оксидів домішок у цинку при розплавленні металу в атмосфері аргону і при дистиляції у вакуумі 0,5 Па. Наведено експериментальні результати застосування комплексного процесу для отримання цинку високої ($> 5N$) чистоти.