

Article

On the Problem of the Distillation Separation of Secondary Alloys of Magnesium with Zinc and Magnesium with Cadmium

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Abstract: An alternative to the existing method of processing secondary magnesium raw materials by remelting in a salt furnace can be distillation separation into volatile metals (Mg, Zn and Cd), low-volatile metals (Al, Mn and Zr) and rare earth elements. The separation of metals may be tracked based on phase diagrams where the field boundaries of the vapor–liquid equilibrium are plotted. Due to the fact that Mg, Zn and Cd have comparable saturated vapor pressures, the possibility of the distillation separation of Mg–Zn and Mg–Cd systems using full state diagrams including the melt–vapor phase transition boundaries were determined in this work. The boundaries of these systems were calculated based on the partial values of saturated vapor, determined by the boiling point method, and presented in the form of temperature–concentration dependencies with the indicated boundaries. The field boundaries were calculated ($L + V$) at atmospheric pressure (101.33 kPa) and in vacuum (1.33 kPa and 0.7 kPa,) supposing the implementation of the process. The possibility of the separate extraction of zinc and cadmium from magnesium was considered using complete phase diagrams including the boundaries of the melt–steam phase transition. When considering the boundaries of the vapor–liquid equilibrium in the binary systems Mg–Zn and Mg–Cd, it was established that it is impossible to separate metals in one “evaporation–condensation” cycle in a vacuum of 1.33 and 0.7 kPa. The problem is caused by the small size of the fields ($L + V$) at the temperature, which suggests processes of the re-evaporation of the condensate from the previous distillation stage. The separation of zinc and cadmium from liquid alloys with magnesium under equilibrium conditions requires several repetitions of the condensate distillation process. In non-equilibrium conditions, the real processes will require a larger number of conversions. This implies the expediency of the joint evaporation of magnesium with zinc and cadmium and the use of condensate for additional charging to liquid magnesium, and the remainder of the distillation, where volatile metals such as Al, Mn, Zr and rare earth elements will be concentrated, should be directed to the preparation of ligatures for special magnesium-based alloys.

Keywords: vapor pressure; phase diagram; vapor–liquid equilibrium; field boundaries; vacuum



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1. Introduction

The low density and sufficiently high strength of magnesium and magnesium alloys have resulted in an increase in their use in various fields, such as the automotive, aerospace and biomedical industries, and the emergence of a large amount of research aimed at studying and improving physical, chemical, mechanical, structural and corrosion properties [1–8]. This fact, in turn, has led to an increase in the interest among the scientific community in the development of new approaches to the processing of magnesium alloys alloyed with various elements [9–12]. Since a predominant number of magnesium-based alloys contain zinc and a small amount of cadmium, this is reflected in scientific publications, particularly [13–17]. The expansion of the scope of application of magnesium and

magnesium alloys entails an increase in the amount of returnable scrap, which is parts made of magnesium alloys that have exhausted their resource, as well as waste generated during the processing of products and semi-finished products [18].

To date, the secondary magnesium scrap corresponding to the magnesium alloy has been remelted in crucible furnaces and poured into ingots. Most scrap containing non-ferrous, ferrous and rare metals is melted down in a salt furnace and then added to raw liquid magnesium in the manufacture of standard alloys. The issue of selling such alloys resulted in the search for other processing techniques.

The authors [18] considered and proposed the following methods of scrap and waste processing: the sorting and separate remelting of scrap and waste containing zinc and magnesium; the remelting of a material with a high zinc content for the production of technical-grade tread alloys with a Zn content of 2–4 mass. %; the purification of alloys from copper, silicon and zinc; the development of new alloys with a high content of Zn, Cu and Si; the use of secondary alloys for the de-sulfurization or modification of cast iron and the use of secondary alloys in the production of aluminum and zinc alloys containing magnesium as an alloying element.

The distillation of these metals in vacuum may be another developed method for the processing of secondary raw materials containing Mg and Zn in some Cd alloys. The high vapor pressure of these metals, relative to Al, Cu, Mn, Si and Zr at moderate temperatures (700–900 °C), allows Mg, Zn and Cd to be isolated into the vapor phase and further into the condensate. However, comparable values of the saturated vapor pressure of Mg, Zn and Cd do not allow for evaluating the possibility of the distillation separation of magnesium-based condensate into components with a high content of zinc and cadmium without additional studies.

The opinion about the possibility or impossibility of the separation of molten systems into components follows from state diagrams including the boundaries of the vapor–liquid equilibrium. Such state diagrams may be constructed on the basis of the thermodynamic functions of the formation and evaporation of solutions, particularly the vapor pressure values of the components that make up the diagram. In this regard, we studied the double diagrams of Mg–Zn and Mg–Cd.

A number of researchers have been studying the Mg–Zn system. Publications [19,20] show the results of classical studies and the determination of redundant functions at 923 K (650 °C). The thermodynamic and kinetic factors of the formation of vitreous alloys, including $\text{Mg}_{70}\text{Zn}_{30}$, are considered in [21]. The authors [22] calculated the excess entropy based on the system of solid spheres, which amounted to an insignificant negative value indicating a strong tendency of an association between different atoms. The latter is confirmed by the authors [23].

In [24], the binary compounds of magnesium and zinc were determined by the calorimetric method in the range from temperatures close to absolute zero (2 K) to high temperatures (300 K), represented by linear dependencies.

In [25], new values of the enthalpy of formation of intermediate phases in the Mg–Zn system at 298 K were presented using the calorimetry of the dissolution of a drop in a liquid tin solvent at 665 K (392 °C). In addition, the heat content of MgZn_2 was measured at a high temperature to determine the change in the enthalpy of its formation.

The authors [26] determined the thermophysical properties (electrical conductivity, thermal conductivity and thermoelectric power) of binary magnesium–zinc melts in the range of melting temperatures up to 1200 K (927 °C).

A critical evaluation of the data and thermodynamic modeling using quasi-chemical representations of the magnesium–zinc system to construct a triple Mg–Sn–Zn system was performed in [27] and was in good agreement with the available experimental data.

Considerable attention was also paid to the study of the magnesium–cadmium system. Early studies [28–31] are devoted to the physical and chemical research of hard alloys and compounds. The authors [32] calculated the phase boundaries in the entire range of concentrations of the magnesium–cadmium system. In [33], the authors investigated the

evaporation patterns of some alloys, including magnesium–cadmium alloys, and established, experimentally or extrapolatively, the temperatures from which the compositions of the initial alloys and condensates begin to equalize. For the Mg–Cd system, the indicated temperature is 2200 ± 200 °C. The latter is unlikely, since the boiling points of elemental magnesium and cadmium at atmospheric pressure are found to be equal to 1107 °C and 766 °C [34], respectively.

The authors [35] investigated the structure of liquid magnesium–cadmium alloys using X-ray diffractometry.

The excess thermodynamic functions of the melts of the system under consideration at the melting temperature of magnesium 923 K (650 °C) are given only in the publication [19] and are reproduced in the monograph [20].

More recent studies [36,37] are devoted to modeling the properties of the Mg–Cd system. In [36], a modified cluster/node approximation was used for the phenomenological calculation of the phase diagram and thermodynamic properties of cadmium–magnesium alloys. The authors [37], using Maclurin’s four-parameter model based on infinite series, estimated the values of the excess Gibbs mixing free energy, Gibbs mixing free energy, activity coefficients, activity, entropy and enthalpy of mixing at 923 K. A good agreement with the experimental values was established.

The analysis of the results of research devoted to Mg–Zn and Mg–Cd systems showed the absence of data on the boundaries of the vapor–liquid equilibrium in these systems.

In this regard, we have conducted studies to determine the boundaries of the liquid–vapor phase transition in Mg–Zn and Mg–Cd systems based on experimentally determined values of the vapor pressure of metals composing melts. The results of the research are presented in this article.

2. Materials and Methods

2.1. Method of Calculating the Boundaries of the Liquid–Vapor Phase Transition

The construction of the boundaries of the liquid–vapor phase transition of molten systems is complicated by the high boiling points of solutions and the difficulty of determining the concentration of components in the vapor phase and the equilibrium with the alloy, as well as the problem of the instrumental design of ebulliometric measurements.

Methods for calculating the equilibrium composition of steam in binary systems under isothermal conditions can be divided into two groups. The first group includes methods consisting in the numerical integration of one of the forms of the Gibbs–Duhem equation, while the second group includes methods based on the use of interpolation equations to describe the dependence of activity coefficients, partial pressures of components or excess Gibbs energy on the composition of the solution.

We calculated the boundaries of the melt and vapor coexistence fields based on the partial pressure values of the saturated vapor of the alloy components. With regard to the absence of the boiling process of liquid metal solutions due to the high density of the metals forming them, the boiling point was determined to be equal to the temperature at which the sum of the partial pressures of the metal vapor composing the system, in accordance with Dalton’s law, is equal to atmospheric (0.1 MPa) or other pressure corresponding to the conditions of vacuum technology.

The composition of the vapor phase ($y_1, y_2 = 1 - y_1$) for a solution of a certain composition ($x_1, x_2 = 1 - x_1$) at the boiling point was determined based on the Clapeyron–Mendeleyev equation, $P_i V = n_i RT$, which implies the following:

$$y_1(y_2)[\text{mole fraction}] = n_1(n_2)/(n_1 + n_2) = \bar{p}_1(\bar{p}_2)/(\bar{p}_1 + \bar{p}_2)$$

where x_1 and x_2 are the number of moles of the first and second metals in the alloy; n_1 and n_2 are the number of moles of the first and second metals in the vapor phase and p_1 and p_2 are the partial pressures of the saturated vapor of the first and second components.

When assessing the decrease in pressure within one atmosphere at the temperature of the phase transitions of the condensed phase, the following was assumed. The authors [38]

studied the cadmium–thallium state diagram with an increase in pressure to 2.6 GPa and found that the effect of pressure on the eutectic temperature can be described by the following equation: $t\ (^{\circ}\text{C}) = 203.5 + 49.72P - 2.351P^2$, where P is the pressure in GPa. Here, when the pressure changes by 0.1 MPa, which corresponds to atmospheric pressure, the decrease will be $5 \times 10^{-3}\ ^{\circ}\text{C}$.

According to the same authors, when the pressure increases to 4 GPa, the liquidus temperature of the Cd alloy is 80. The % Pb varies depending on $t\ (^{\circ}\text{C}) = 266.7 + 56.45P - 2.68P^2$. If the pressure changes with the transition to vacuum, the temperature will change by $5.6 \times 10^{-3}\ ^{\circ}\text{C}$. This means that low pressures have practically no effect on the temperature of the phase transitions of condensed systems and were not taken into account when constructing diagrams in vacuum.

The results of the definitions and calculations performed in this way are set out below.

2.2. Method for Determining the Values of Saturated Metal Vapor Pressure

When estimating the vapor pressure values of magnesium, zinc and cadmium [34], their significant values at relatively low temperatures and comparability should be noted. This means that in the state of equilibrium, both magnesium and zinc will be present in the vapor phase in comparable quantities. The boiling point method based on a sharp increase in the evaporation rate of a volatile component or the sum of volatile components near the equalization of the pressure of saturated metal vapor (or the sum of metals) and a given pressure of an inert gas should be considered the most acceptable way to determine the values of vapor pressure. The boiling point method and the device for its implementation are described in detail in our research [39].

Due to the fact that the saturated vapor pressures of magnesium, zinc and cadmium are comparable in magnitude, the content of metals in the vapor phase is determined by the static method beforehand and at the same temperature, and the partial pressure values of the saturated vapor of each of the metals are determined by the product of the total pressure determined by the boiling point method for the fraction of each metal in the vapor.

The vapor composition was determined using a quartz glass vessel shown in Figure 1.

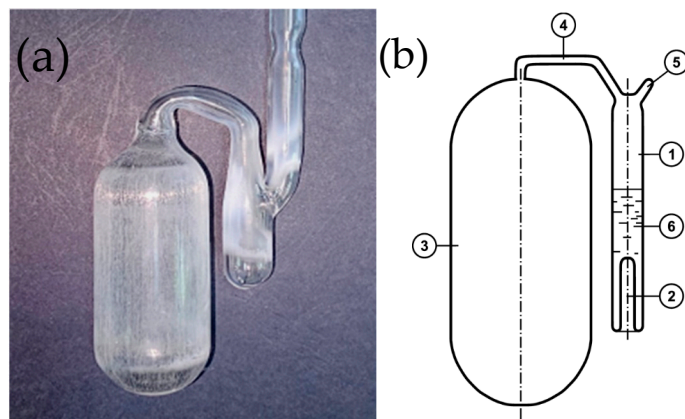


Figure 1. Real photo (a) and diagram (b) of a vessel for determining the composition of steam using the static method: 1—alloy ampoule; 2—thermocouple socket; 3—steam ampoule; 4—capillary; 5—extension for alloy application; 6—alloy.

The vessel consists of two ampoules: a small one to accommodate the alloy suspension and a large one for the vapor phase equilibrium with the alloy, which are connected by a capillary. The time for achieving equilibrium is pre-set. The method of conducting experiments was as follows. A suspension of the test alloy was loaded into the alloy ampoule through the filling extension. The vessel was washed three times with argon and pumped to a pressure of 1 Pa, and then the extension was soldered off. The vessel prepared in this way was placed in the isothermal zone of the furnace heated to the temperature of

the experiment and kept for 24 h. After the exposure time, the vessel was removed and tempered into water. The ampoule for the vapor phase was cut off. The steam condensate in it was dissolved in nitric acid. The number of elements in the nitric acid solution was determined by the chemical method on an atomic absorption spectrophotometer.

According to the data on the mass amount of magnesium and zinc (or cadmium) in the condensate, the molar ratio of the elements in the pair was calculated.

The amount of zinc in the steam (the rest is magnesium) was determined at the experimental temperatures (973–1173 K) and assumed to be average. The amount of cadmium in the steam (the rest is magnesium) was determined at the experimental temperatures (923–1023 K) and assumed to be average. The dependence of the concentration of zinc in the vapor phase on the composition of alloys in the Mg–Zn system is shown in Figure 2, and the concentration of cadmium in the Mg–Cd system is shown in Figure 3, along with the partial pressures of the saturated vapor of the first and second components.

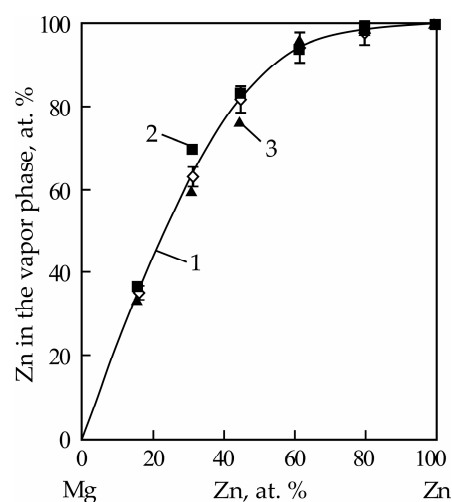


Figure 2. The dependence of the zinc content in the steam on the composition of the alloy: 1—approximation of the average value; 2—at a temperature of 973 K; 3—1173 K.

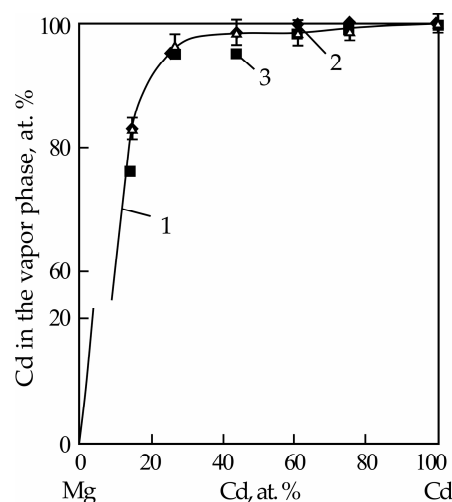


Figure 3. The dependence of the cadmium content in the steam on the composition of the alloy: 1—approximation of the average value; 2—at a temperature of 923 K; 3—1023 K.

The determination of the partial pressures of the components for magnesium alloys with zinc and cadmium is presented by the example of the Mg–Zn system.

To determine the partial pressure of zinc vapor ($\bar{p}_{Zn}$), we multiplied the value of the total pressure for the Mg–Zn alloy (p^{tot}), determined by the boiling point method, by the

proportion of zinc in the vapor phase (Y_{Zn}): $\bar{p}_{Zn} = p^{tot} \times Y_{Zn}$ or $\ln \bar{p}_{Zn} = \ln p^{tot} + \ln Y_{Zn}$. Further, in accordance with the definition of thermodynamic functions, we found the activity coefficient $\gamma_{Zn} = \frac{\bar{p}_{Zn}}{p_{Zn}^0 \times a_{Zn} \times x_{Zn}}$ or $\ln \gamma_{Zn} = \ln \bar{p}_{Zn} - \ln p_{Zn}^0 - \ln x_{Zn}$, where p_{Zn}^0 is the vapor pressure for elemental zinc and x_{Zn} is the atomic fraction of zinc in the alloy.

The magnesium activity coefficient (γ_{Mg}) was calculated by the numerical integration of the Gibbs–Duhem equation using an auxiliary function $\alpha_{Zn} = \ln \gamma_{Zn} / x_{Mg}^2$ proposed by Darken [40], which, after transformation [41] and substitution into the equation $\ln \gamma_{Mg} =$

$$- \int_{\ln \gamma_{Zn} \text{ at } x_{Mg}=1}^{\ln \gamma_{Zn} \text{ at } x_{Mg}} \frac{x_{Zn}}{x_{Mg}} d \ln \gamma_{Zn}, \text{ binds } \ln \gamma_{Zn} \text{ and } \ln \gamma_{Mg} \text{ in the form of an expression convenient for numerical integration: } \ln \gamma_{Mg} = - \frac{\ln \gamma_{Zn} \times x_{Zn} \times x_{Mg}}{x_{Mg}^2} + \int_{x_{Zn}=0}^{x_{Zn}} \frac{\ln \gamma_{Zn}}{(1 - x_{Zn})^2} dx_{Zn},$$

where x_{Mg} is the atomic fraction of magnesium in the alloy equal to $x_{Mg} = 1 - x_{Zn}$.

2.3. Preparation of Magnesium Alloys with Zinc and Cadmium

A correct description of the dependence of the vapor pressure values on the composition of the melt requires at least five compositions within the concentration range. To prepare the alloys, 99.99 mass. % magnesium, 99.99 mass. % zinc and 99.995 mass. % cadmium was used. The composition of the prepared alloys is given in Tables 1 and 2.

Table 1. Composition of Mg–Zn system alloys.

Alloy No.	Mg		Zn	
	Atomic Fraction	mass. %	Atomic Fraction	mass. %
1	0.841	66.29	0.159	33.71
2	0.694	45.74	0.306	54.26
3	0.553	31.50	0.447	68.50
4	0.388	19.07	0.612	80.93
5	0.205	8.75	0.795	91.25

Table 2. Composition of Mg–Cd system alloys.

Alloy No.	Mg		Cd	
	Atomic Fraction	mass. %	Atomic Fraction	mass. %
1	0.853	55.59	0.147	44.41
2	0.733	37.25	0.267	62.75
3	0.558	21.48	0.442	78.52
4	0.386	11.96	0.614	88.04
5	0.243	6.48	0.757	93.52

The alloys were prepared by the slow heating of the amounts of metals corresponding to the composition of the alloy in sealed quartz ampoules with pre-evacuated air. Heating was performed at 50–100 °C per hour to 100 °C for the liquidus line, and the melt was kept at this temperature for 12 h, followed by quenching into water.

3. Results and Discussion

3.1. Results of Determining the Partial Pressures of Components for Magnesium Alloys with Zinc and Cadmium

The alloy composition, experimental temperature (T) and total vapor pressure for Mg–Zn alloys, determined experimentally (experimental p^{tot}), the total vapor pressure for Mg–Zn alloys, calculated by approximating the expression (estimated p^{tot}), the zinc fraction in vapor phases (Y_{Zn}), the partial pressure of zinc vapor ($\bar{p}_{Zn}$), the partial pressure of magnesium vapor ($\bar{p}_{Mg}$) and the relative error of the experiments (relative Δ) are given

Table 3. Experimental conditions and partial pressures of zinc and magnesium vapor for liquid alloys of the Mg–Zn system.

Alloy Composition, Atomic Fraction		$T, \text{ K}$	Experimental $p^{tot},$ kPa	Estimated $p^{tot}, \text{ kPa}$	$Y_{Zn},$ fraction	$\bar{p}_{Zn},$ kPa	$\bar{p}_{Mg},$ kPa	Relative $\Delta, \%$
Zn	Mg							
1.0	0	873	1.47	1.46	1.0	1.46	—	+0.55
			1.33					−7.95
			1.60					+9.44
		1073	30.80	30.66	1.0	30.66	—	+0.46
			29.33					−4.34
			32.00					+4.37
0.795	0.205	973	5.33	5.38	0.985	5.36	0.05	−0.98
			5.73					+6.45
			4.80					−10.83
		1173	68.79	67.46	0.985	67.16	0.99	+1.98
			67.33					−0.19
			66.26					−1.77
0.612	0.388	973	3.33	3.43	0.951	3.19	0.16	−2.92
			3.33					−2.92
			3.73					+8.75
		1173	49.93	45.27	0.951	42.14	3.06	−0.75
			46.00					+1.62
			45.06					−0.46
0.447	0.553	973	1.87	2.04	0.884	1.68	0.34	−8.47
			2.27					+11.11
			2.00					−2.10
		1173	29.06	29.04	0.884	23.93	5.81	+0.06
			28.80					−0.83
			29.33					+0.99
0.306	0.694	973	1.47	1.37	0.753	0.87	0.46	+7.69
			1.33					−2.56
			1.33					−2.56
		1173	20.53	20.47	0.753	13.05	7.71	+0.31
			20.00					−2.28
			21.33					+4.22
0.159	0.841	973	1.07	1.08	0.345	0.38	0.65	−0.56
			1.07					−0.56
			1.20					+11.52
		1173	16.00	15.98	0.345	5.61	10.77	+0.13
			15.20					−4.88
			16.93					+5.94
0	1.0	1023	1.73	1.72	0	—	1.72	+0.52
			2.00					+16.12
			1.47					−14.58
		1273	38.00	38.01	0	—	38.01	−0.03
			37.20					−2.13
			38.80					+2.08
Δ _{av.} = 4.02								

Table 4. Experimental conditions and partial pressures of cadmium and magnesium vapor for liquid alloys of the Cd–Mg system.

Alloy Composition, Atomic Fraction		T , K	Experimental p^{tot} , kPa	Estimated p^{tot} , kPa	Y_{Zn} , fraction	$\bar{p}_{Zn}$, kPa	$\bar{p}_{Mg}$, kPa	Relative Δ , %
Zn	Mg							
0.757	0.243	773	1.20	1.18	0.985	1.16	3.51×10^{-4}	+1.87
			1.33					+12.90
			1.07					−9.17
		923	15.20	15.49	0.985	15.25	1.69×10^{-2}	−1.85
			14.93					−3.59
			15.60					+0.74
0.614	0.386	823	2.00	2.95	0.983	2.90	3.51×10^{-3}	−2.63
			1.73					−15.77
			2.13					+3.70
		973	20.53	21.01	0.983	20.65	9.76×10^{-2}	−2.28
			21.46					+2.15
			19.73					−6.08
0.442	0.558	873	2.13	2.17	0.977	2.12	2.86×10^{-2}	−1.62
			2.67					+24.46
			1.73					−20.09
		1023	19.20	19.15	0.977	18.72	0.51	+0.27
			19.73					+3.03
			18.66					−2.55
0.267	0.733	923	1.60	1.67	0.865	1.44	0.16	−4.19
			1.73					+3.59
			1.60					−4.19
		1073	13.87	14.08	0.865	12.18	1.97	−1.49
			13.47					−4.33
			14.13					+0.36
0.147	0.853	973	1.60	1.54	0.626	0.97	0.56	+3.76
			1.73					+12.12
			1.33					−13.80
		1123	12.67	12.54	0.626	7.85	5.21	+1.04
			11.73					−6.46
			13.47					+7.42
0	1.0	1023	1.73	1.72	—	—	1.72	+0.52
			2.00					+16.12
			1.47					−14.58
		1273	38.00	38.01	—	—	38.01	−0.03
			37.20					−2.13
			38.80					+2.08
Δ _{av.} = 5.92								

The total experimental error in the Mg–Zn system was defined as the sum of the errors of independent measurements (temperature—1%, weighing 0.1%, pressure—0.5%, approximation of vapor composition data —3.68%, approximation of experimental data—4.02%) and amounted to 9.3%.

For the Mg–Cd system, the total error of experiments in the system was 9.19%. The errors of independent measurements were temperature—1%, weighing—0.1%, pressure—0.5%, approximation of vapor composition data—1.67% and approximation of experimental data—5.92%.

The alloy composition, experimental temperature (*T*) and total vapor pressure for Mg–Cd alloys, determined experimentally (experimental p^{tot}), the total vapor pressure

for Mg–Cd alloys, calculated by approximating the expression (estimated p^{tot}), the zinc fraction in vapor phases (Y_{Cd}), the partial pressure of cadmium vapor ($\bar{p}_{Cd}$), the partial pressure of magnesium vapor ($\bar{p}_{Mg}$) and the relative error of the experiments (relative Δ) are given in Table 4.

The partial vapor pressures of magnesium and zinc over Mg–Zn melts correspond to Equations (1) and (2), and those of magnesium and cadmium over the melts of the Mg–Cd system correspond to dependences (3) and (4):

$$\ln \bar{p}_{Zn} = (13,596x_{Zn}^4 - 37,502x_{Zn}^3 + 35,248x_{Zn}^2 - 11,236x_{Zn} - 14,360) \times T^{-1} - 9.531x_{Zn}^4 + 25.707x_{Zn}^3 - 24.39x_{Zn}^2 + 9.169x_{Zn} + 22.66 + \ln x_{Zn} \quad (1)$$

$$\ln \bar{p}_{Mg} = (13,596x_{Mg}^4 - 35,010x_{Mg}^3 + 29,641x_{Mg}^2 - 9774x_{Mg} - 14,576 + 1138 \ln x_{Mg}) \times T^{-1} - 9.531x_{Mg}^4 + 25.125x_{Mg}^3 - 23.081x_{Mg}^2 + 9.524x_{Mg} + 21.174 + 0.386 \ln x_{Mg} \quad (2)$$

$$\ln \bar{p}_{Mg} = (-7342x_{Mg}^3 + 14,225x_{Mg}^2 - 7540x_{Mg} - 15,466 + 1116 \ln x_{Mg}) \times T^{-1} + 5.263x_{Mg}^4 - 8.325x_{Mg}^3 + 1.954x_{Mg}^2 + 1.438x_{Mg} + 22.881 + 0.578 \ln x_{Mg} \quad (3)$$

$$\ln \bar{p}_{Cd} = (7342x_{Cd}^3 - 18,814x_{Cd}^2 + 16,718x_{Cd} - 17,342) \times T^{-1} + 5.263x_{Cd}^4 - 19.744x_{Cd}^3 + 26.646x_{Cd}^2 - 15.534x_{Cd} + 26.534 + \ln x_{Cd} \quad (4)$$

where x_{Cd} is the atomic fraction of cadmium in the alloy, equal to $x_{Cd} = 1 - x_{Mg}$. We determined the saturated vapor pressure of elemental cadmium introduced into the equation earlier [42].

The obtained temperature–concentration dependences of the partial pressures of magnesium and zinc for Mg–Zn melts, as well as those of magnesium and cadmium over Mg–Cd solutions, are used to calculate the boundaries of the coexistence of liquid and vapor in these systems.

3.2. Boundaries of the Fields of Liquid and Vapor Coexistence in Mg–Zn and Mg–Cd Systems

The boundaries of the vapor–liquid equilibrium fields ($L + V$) at atmospheric pressure (101.33 kPa) and in vacuum (1.33 kPa and 0.7 kPa) are plotted on the state diagram of condensed phases [43] of the Mg–Zn system. The field ($L + V$ (1.33 kPa)) is shaded for convenience. The complete diagram of the Mg–Zn state, including condensed and vapor phases, is shown in Figure 4.

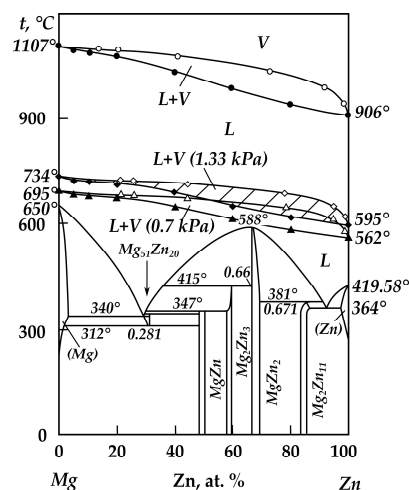


Figure 4. Phase diagram of the magnesium–zinc system.

The analysis of the Mg–Zn diagram shown in Figure 4 shows that a decrease in pressure significantly shifts the temperature of the area of coexistence of liquid and vapor to the liquidus line. A pressure reduction of less than 0.7 kPa is impractical due to the possible precipitation of $MgZn_2$ crystals from the melt.

The distillation separation of liquid magnesium alloys with zinc in one operation is impossible due to the small width of the temperature fields. Currently, industries use alloys of two Mg–Al–Zn–Mn and Mg–Zn–Zr systems where the zinc content is 0.3–0.8 and 4.0–6.0 mass. %, respectively [18]. Table 5 shows the number of distillation operations and the metal content in, first, the condensate of the initial melt with a content of 6 mass. % and, then, the condensate from the previous operation prior to the isolation of zinc into a separate fraction at a pressure of 0.7 kPa.

Table 5. Content of zinc and magnesium in the condensate during the repetition of the condensate distillation process.

Distillation Process:	Zinc and Magnesium Content in Condensate:			
	Zn, at. %	Mg, at. %	Zn, mass. %	Mg, mass. %
1. Initial alloy	2.46	97.54	6.00	94.00
2. Operation 1 condensate	7.89	92.11	18.73	81.27
3. Operation 2 condensate	21.35	78.65	42.20	57.80
4. Operation 3 condensate	47.39	52.61	70.79	29.21
5. Operation 4 condensate	87.13	12.87	94.79	5.21
6. Operation 5 condensate	99.80	0.20	99.93	0.07

We can see that those six cycles of “evaporation–condensation”, or the process of rectification, will be required to isolate zinc in the form of a rough metal. However, the process of rectification in vacuum is accompanied by a significant deterioration in mass transfer. Here, the joint evaporation of magnesium and zinc from secondary raw materials with a concentration of low volatile aluminum, manganese and zirconium is the most expedient. Magnesium with a high zinc content can be charged to liquid magnesium, and the residue can be used for distillation for alloying heat-resistant alloys.

Magnesium alloying with cadmium improves the structure of the magnesium alloy and improves the mechanical characteristics and corrosion resistance [13,14]. The cadmium content in magnesium reaches 2 mass. %. Cadmium is a more volatile component than magnesium. In this regard, the steam and the residue from distillation will be enriched with cadmium and magnesium, respectively. The boundaries of the vapor–liquid equilibrium fields ($L + V$) at atmospheric pressure and in vacuum (1.33 kPa and 0.7 kPa) are plotted on the state diagram of condensed phases [44] of the Mg–Cd system. The field ($L + V$ (1.33 kPa)) is shaded. The complete Mg–Cd state diagram is shown in Figure 5.

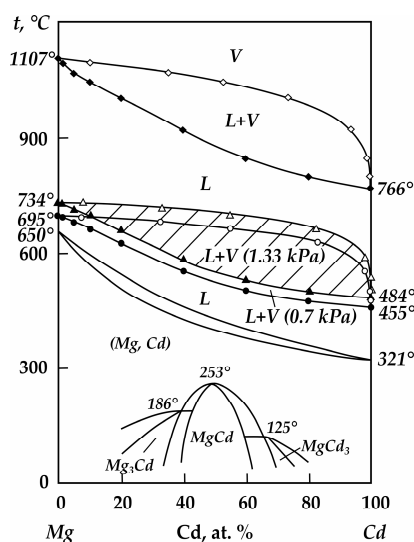


Figure 5. Phase diagram of the magnesium–cadmium system.

The analysis of the Mg–Cd diagram shown in Figure 5 shows that a decrease in pressure significantly shifts the temperature of the area ($L + V$) to the liquidus line. Reducing the pressure to 50 Pa does not complicate the distillation process due to the crystallization process of the alloy, since the vapor pressure of magnesium and cadmium at the melting point is 40 Pa and 17 Pa, respectively.

We have traced the change in the condensate composition during the distillation of magnesium with an initial cadmium content of 2 mass. % (0.44 at. %) at a pressure of 0.7 kPa. The number of distillation operations and the metal content in, first, the condensate of the initial melt and, then, the condensate from the previous operation prior to the separation of cadmium into a separate fraction are given in Table 6.

Table 6. Content of cadmium and magnesium in the condensate during the repetition of the condensate distillation process.

Distillation Process:	Cadmium and Magnesium Content in Condensate:			
	Cd, at. %	Mg, at. %	Cd, mass. %	Mg, mass. %
1. Initial alloy	0.44	99.56	2.00	98.00
2. Operation 1 condensate	3.39	96.61	13.96	86.04
3. Operation 2 condensate	23.24	76.76	58.34	41.66
4. Operation 3 condensate	88.15	11.85	97.18	2.82
5. Operation 4 condensate	99.99	0.01	99.998	0.002

As can be seen from the table, five “evaporation–condensation” cycles will be required to release cadmium as a refined metal. Cadmium preferably passes into the vapor phase. The rectification process is also impractical here. The most acceptable way of processing magnesium scrap with a high cadmium content is the joint evaporation of magnesium and its conversion into a collective condensate, which can be added to raw magnesium, and the residue from distillation is used for the alloying of heat-resistant alloys.

4. Conclusions

Distillation separation into volatile metals such as Mg, Zn and Cd, low volatile metals such as Al, Mn and Zr and rare earth elements may be an alternative to the existing method of processing secondary magnesium raw materials by remelting in a salt furnace. The advantage of this method over existing ones is the absence of the pre-sorting of magnesium scrap. The possibility or impossibility of such a separation of melts into individual metals can be determined based on the boundaries of the vapor–liquid equilibrium on phase diagrams including condensed and vapor phases. Currently, there are additional diagrams for Mg–Zn and Mg–Cd magnesium systems. The construction of such diagrams is possible on the basis of the values of the partial pressures of saturated steam for the melt. In this regard, the authors performed experiments to determine the vapor pressure of metals in these systems using the boiling point method (isothermally). The pressures of saturated vapor of magnesium, zinc and cadmium in dual systems are represented by temperature–concentration dependences. The latter was used to calculate the boundary of the fields of the vapor–liquid equilibrium in binary systems of magnesium with zinc and cadmium. The possibility of the separate extraction of zinc and cadmium from magnesium was considered using complete phase diagrams including the boundaries of the melt–steam phase transition. When considering the boundaries of the vapor–liquid equilibrium in the binary systems Mg–Zn and Mg–Cd, it was established that it is impossible to separate metals in one “evaporation–condensation” cycle in a vacuum of 1.33 and 0.7 kPa. The problem is caused by the small size of the fields ($L + V$) at the temperature, which suggests processes of the re-evaporation of condensate from the previous distillation stage. Based on the state diagram, the isolation of zinc and cadmium by distillation in vacuum under equilibrium conditions requires six and five operations, respectively. In non-equilibrium conditions, the real processes will require a larger number of conversions. This implies the expediency of

the joint evaporation of magnesium with zinc and cadmium, the condensation of steam into a separate product and the use of condensate for additional charging to liquid magnesium, and the remainder of the distillation, where volatile metals such as Al, Mn, Zr and rare earth elements will be concentrated, should be directed to the preparation of ligatures for special magnesium-based alloys.

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