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Thermodynamics of Evaporation of Liquid Magnesium - Tin Alloys

Volodin V.N., Trebukhov S.A., Mukangaliyeva A.O., *Linnik X.A., Nitsenko A.V., Burabayeva N.M.

Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty, Kazakhstan

** Corresponding author email: x.linnik@satbayev.university*

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ABSTRACT

Based on the values of the partial pressures of magnesium above dimagnesium stannide and melts with tin, determined by the boiling point method (isobaric and isothermal variants, respectively) and tin, calculated by numerical integration of the Gibbs - Duhem equation in accordance with known expressions, the thermodynamic functions were determined: changes in entropy, enthalpy, and free energy of evaporation. Methods to determine the vapor pressure of isobaric and isothermal variants of the boiling point method and calculate thermodynamic values are described. The dependences of the values of partial vapor pressure of magnesium and tin were determined, based on which the energy functions were determined. The measurement error was 7.07%. Data on the change in evaporation entropies are presented graphically. An increase in the partial entropies of evaporation of magnesium and tin was noted with a decrease in their content in the alloy (each) to less than 20 at. %. Extremes are noted: a maximum for magnesium and a minimum for tin at a concentration corresponding to the stoichiometric composition of dimagnesium stannide (60 at. % Mg). The latter indicates the presence of a dissociating compound in the liquid phase that affects evaporation. The values of the change in enthalpy and Gibbs free energy of evaporation are tabulated. It was established that the values of partial and integral enthalpies and Gibbs free energy of vaporization monotonically increase from Mg to Sn in accordance with second-degree dependencies on the concentration of components in the alloy and linearly (Gibbs energy) with temperature. The very small change in the integral value of the free energy of evaporation of magnesium (0.03 ± 0.002 kJ/mol) at 1373 K (1100 °C) indicates a practical coincidence with the boiling point of magnesium. The energy functions of evaporation of magnesium-tin melts will supplement the thermodynamic database and can be used for thermal engineering calculations in the design of distillation processes and apparatus.

Keywords: magnesium, tin, dimagnesium stannide, thermodynamics, entropy, enthalpy, Gibbs energy.

Information about authors:

Volodin Valeriy Nikolaevich
Doctor of Technical Sciences, Professor, Chief Researcher of the Vacuum Processes Laboratory of the Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, 050010, Shevchenko str., 29/133, Almaty, Kazakhstan. Email: volodinv_n@mail.ru; ORCID ID: https://orcid.org/0000-0003-0116-1423

Trebukhov Sergey Anatolyevich
Candidate of Technical Sciences, Professor, Leading Researcher of the Laboratory of Vacuum Processes, Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, 050010, Shevchenko str., 29/133, Almaty, Kazakhstan. Email: s.trebukhov@satbayev.university; ORCID ID: https://orcid.org/0000-0001-9708-0307

Mukangaliyeva Arailym Omirzakkyzy
Master of Technical Sciences, Engineer of the Laboratory of Titanium and Rare Refractory Metals, Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, 050010, Shevchenko str. 29/133, Almaty, Kazakhstan. Email: a.mukangaliyeva@satbayev.university; ORCID ID: https://orcid.org/0000-0001-7032-1764

Linnik Xeniya Alexandrovna
Master of Technical Sciences, Junior Researcher of the Vacuum Processes Laboratory of the Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, 050010, Shevchenko str., 29/133, Almaty, Kazakhstan. Email: x.linnik@satbayev.university, xenija_linnik@mail.ru; ORCID ID: https://orcid.org/0000-0002-0683-1409

Nitsenko Alina Vladimirovna
Candidate of Technical Sciences, Head of the Vacuum Processes Laboratory of the Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, 050010, Shevchenko str., 29/133, Almaty, Kazakhstan. Email: alina.nitsenko@gmail.com; ORCID ID: https://orcid.org/0000-0001-6753-0936

Burabayeva Nurila Muratovna
Candidate of Technical Sciences, Senior Researcher of the Vacuum Processes Laboratory of the Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, 050010, Shevchenko str. 29/133, Almaty, Kazakhstan. Email: nuri_eng@mail.ru; ORCID ID: https://orcid.org/0000-0003-2183-2239

Introduction

Magnesium and its alloys are widely used in various industries [[1], [2], [3], [4], [5], [6], [7], [8]]. In recent years, researchers have paid great attention to the production of biodegradable magnesium alloys that have a minimal negative impact on the human body.

Along with the expansion of the range of magnesium-based alloys, problems have arisen with the processing of the wide variety of waste and secondary raw materials based on it. However, to date, no rational technology has been developed for the processing of biodegradable magnesium secondary raw materials containing tin, silver, and other metals, as well as defective products. One promising method to process such alloys may be vacuum distillation, with magnesium being transferred to the vapor phase and impurities being concentrated in the still bottom. However, no data on the energy characteristics of the evaporation of liquid magnesium–tin alloys have been found. In this regard, there is a need to determine the thermodynamic characteristics of Mg – Sn melt evaporation, which are necessary to calculate the energy costs of the distillation process. This can be done on the basis of experimental studies to determine the saturated vapor pressure values of the components that make up the system.

Magnesium and tin form alloys with unlimited solubility in the liquid state and the presence of a congruent melting compound Mg_2Sn at 778 °C [[9], [10]].

Quite a few papers [[11], [12], [13], [14], [15], [16], [17], [18], [19], [20]] are devoted to the study of the thermodynamic properties of magnesium–tin system melts. In studies [[11], [12]], using the method of electromotive forces of concentration chains, the thermodynamic functions of the system at temperatures of 650 °C and 800 °C were determined over the entire range of liquid alloy concentrations, and large negative deviations from ideal behavior were found. In paper [13], the saturated vapor pressure of magnesium, the thermodynamic functions of liquid alloys, and the liquidus lines of the phase diagram were determined using the isopyestic method at 990 and 1290 K.

The authors of [[14], [15]] determined the thermodynamic functions, thermal stability, and other physical properties of the Mg_2Sn condensed phase.

In the study [16], the partial pressure of saturated magnesium vapor for alloys containing 10–60 at. % Sn was determined using the boiling point method at temperatures of 1154–1385 K (881–1112 °C).

In papers [[17], [18]], data from previous studies were introduced into a double system model using a modified quasi-chemical model, which allowed for very good agreement with published experimental data.

Excess thermodynamic functions and activity coefficients, based on which the saturated vapor pressure can be determined for magnesium-tin alloy components at a temperature of 1073 K (800 °C), are given in publications [[19], [20]].

Other studies have investigated the physical properties and structure of magnesium alloys containing tin [[21], [22], [23]], as well as the effect of alloying additives on them [24]. No other information on vapor pressures, thermodynamic properties, or the thermodynamics of evaporation of the Mg – Sn system has been found in available sources.

This paper aims to determine the partial and integral thermodynamic functions of evaporation of the molten magnesium – tin system.

Materials, research methods, and calculations

Materials. The determination of the thermodynamic functions of evaporation of magnesium–tin alloys is based on the pressure values of the metals that make up the system.

Alloys containing 85.44, 73.18, 60.00, 47.12, and 32.81 at. % (58.18, 35.85, 23.50, 15.43, and 09 wt. %) tin were prepared for experiments to determine the saturated vapor pressure of the components.

To prepare the alloys, tin (99.99 wt. %) and double-distilled magnesium with a content of 99.99 wt.% of the main element were used for the preparation of alloys. The alloy was prepared in an alundum crucible placed in a steel retort at an argon pressure of 500 kPa and a temperature of 800–1100 °C, depending on the composition. Increased pressure was used to prevent magnesium evaporation. The initial components in the crucible were heated to the specified temperature, held for 5 hours, and then cooled by immersion in water.

An alloy with a content of 60.0 at. % Mg and 40.0 at. % Sn corresponds to the composition of the intermetallic compound Mg_2Sn – dimagnesium stannide. Analysis of the phase composition of the obtained sample, performed on a Bruker D8 Advance diffractometer with copper radiation

$\lambda_{k\alpha}$ = 0.154051 nm with a graphite monochromator, showed the presence of 97.8 % Mg_2Sn and 2.8 % Sn.

There is no information on the evaporation or decomposition of Mg_2Sn. In the case of congruent evaporation of the compound, the system should be considered as two quasi-binary systems: Sn–Mg_2Sn and Mg_2Sn–Mg with corresponding thermodynamic characteristics.

Determination of vapor pressure and vapor composition of Mg_2Sn. In this regard, the pressure and composition of the Mg_2Sn vapor were first determined. The boiling point method (isobaric variant) was used to determine the vapor pressure. The experiments were carried out on a continuous weighing setup, which is described in detail in [25]. The determination procedure was as follows. A sample of the Mg_2Sn alloy was placed in a quartz crucible and suspended on scales in a quartz retort filled with argon. Then, by throttling the inlet of the vacuum pump, the pressure specified by the experimental conditions was set and the crucible was lowered into the shaft furnace. The crucible with the sample was placed in a predefined isothermal zone of the furnace. After that, the furnace was heated at a constant rate. At the same time, the mass loss (Δm) and the corresponding temperature in the system were recorded. The temperature at which a sharp increase in the rate of mass loss was observed at a given pressure was considered equal to the vapor pressure of dimagnesium stannide or its decomposition components.

The composition of the vapor was judged by the composition of the condensate after the evaporation of Mg_2Sn in a vacuum at a temperature of 850 °C and a pressure of 0.67 kPa in a horizontal retort furnace.

Determination of the vapor pressure of magnesium over its alloys with tin. The saturated vapor pressures of magnesium and tin differ by several orders of magnitude – at the boiling point of magnesium (1373 K), the saturated vapor pressure of tin is 0.1 Pa [26]. In this regard, the isothermal boiling point method was chosen to determine the values of magnesium vapor pressure above its alloys with tin. The experiments were performed on a setup described in paper [25].

The determination method was as follows. A sample of the alloy was placed in a crucible, which was suspended in a retort outside the heating zone. The retort was evacuated twice using a vacuum pump and then filled with argon. After this, the lower part of the retort was placed in the isothermal zone of a preheated electric furnace. The retort was heated under an overpressure of 2–5 kPa with an open inert gas supply system to suppress the evaporation of components and compensate for the pressure increase in the retort due to gas expansion during heating. Once the sample reached the target temperature, argon evacuation from the retort volume was initiated while maintaining a constant sample temperature (isothermal mode). At the same time, the loss of the sample in mass and the change in pressure were simultaneously recorded. The pressure at which a sharp increase in the evaporation rate (weight loss) was observed was considered to be equal to the pressure of magnesium vapor above the alloy.

The values of the partial pressures of saturated magnesium vapor of alloys of the same concentration at different temperatures were described by the equation: $\ln\bar{p}_{Mg} = B + A \times T^{-1}$, then the dependence of each of the coefficients *A* and *B* was determined as a function of the magnesium concentration in the initial alloy. As a result, the temperature-concentration dependence of the magnesium vapor pressure $\ln\bar{p}_{Mg} = f(T, x_{Mg})$ was obtained.

The partial pressure of tin vapor above the magnesium–tin alloy was determined as: $\bar{p}_{Sn} = p^o_{Sn} \times a_{Sn} = p^o_{Sn} \times \gamma_{Sn} \times x_{Sn}$, where p^o_{Sn} is the saturated vapor pressure above elemental tin; a_{Sn} is the activity of tin in the alloy; γ_{Sn} is the activity coefficient of tin; x_{Sn} is the concentration of tin in the alloy, equal to $x_{Sn} = 1 - x_{Mg}$. Here x_{Mg} is the concentration of magnesium in the initial alloy.

The activity coefficient of tin was calculated by numerical integration of the Gibbs-Duhem equation, using an auxiliary function $\alpha_{Mg} = \ln\gamma_{Mg} / x^2_{Sn}$, proposed by Darken [27]. After transformation [28] and substitution into the equation: $\ln\gamma_{Sn} = -\int_{\ln\gamma_{Mg\ at\ x_{Mg}=1}}^{\ln\gamma_{Mg\ at\ x_{Mg}}} \frac{x_{Mg}}{x_{Sn}} d\ln\gamma_{Mg}$, this function relates $\ln\gamma_{Mg}$ and $\ln\gamma_{Sn}$ in a form convenient for numerical integration:

$$\ln\gamma_{Sn} = -\frac{\ln\gamma_{Mg} \times x_{Mg} \times x_{Sn}}{x^2_{Sn}} + \int_{x_{Mg}=0}^{x_{Mg}} \frac{\ln\gamma_{Mg}}{(1 - {}_{Mg})} dx_{Mg}.$$

Determination of energy characteristics. The values of the partial evaporation functions were determined in accordance with the dependence: $\Delta\bar{G}^V_{Mg(Sn)} = -RT\ln\bar{p}_{Mg(Sn)}$, where $\Delta\bar{G}^V_{Mg(Sn}$ is the partial Gibbs energy of evaporation of magnesium or tin;

$\bar{p}_{Mg(Sn)}$ is the partial pressure of saturated magnesium or tin vapor in their alloys. Hence: $\left(\frac{\partial \Delta \bar{G}^V_{Mg(Sn}}{\partial T}\right)_P = -\Delta \bar{S}^V_{Mg(Sn}$, $\Delta \bar{H}^V_{Mg(Sn)} = \Delta \bar{G}^V_{Mg(Sn)} + T \times \Delta \bar{S}^V_{Mg(Sn)}$, where $\Delta \bar{S}^V_{Mg(Sn}$ and $\Delta \bar{H}^V_{Mg(Sn)}$ are the partial entropy and enthalpy of evaporation of magnesium or tin.

The integral values of the entropy and enthalpy of evaporation were calculated by summing the fractions of the partial functions in the initial alloy: $\Delta S^V_{Mg-Sn} = x_{Mg}\Delta \bar{S}^V_{Mg} + x_{Sn}\Delta \bar{S}^V_{Sn}$ and $\Delta H^V_{Mg-Sn} = x_{Mg}\Delta \bar{H}^V_{Mg} + x_{Sn}\Delta \bar{H}^V_{Sn}$.

The change in Gibbs integral free energy (ΔG^V_{Mg-Sn}) is determined by the formula: $\Delta G^V_{Mg-Sn} = \Delta H^V_{Mg-Sn} - T\Delta S^V_{Mg-Sn}$.

Results and Discussion

The total error in the determination the vapor pressure of dimagnesium stannide is calculated as the sum of the errors in independent measurements, %: temperature – 1; weighing – 0.1; pressure 0.5; approximation of experimental data – 7.74, equal to 9.34%.

The values of the decomposition pressure – dissociation of dimagnesium stannide (p^D) depending on temperature were approximated by the expression: $\ln p^D[atm] = -21{,}250 \times T^{-1} + 15.169$. The complete dissociation temperature at atmospheric pressure corresponds to 1401 K = 1128 °C.

The enthalpy of magnesium dissociative evaporation, calculated from the equation of magnesium vapor pressure dependence on temperature, is 176.7 ± 16.5 kJ/mol, entropy – 126.1 ± 11.8 J/(mol×K).

Mg_2Sn undergoes decomposition into constituent metals during dissociative evaporation. Decomposition process of the compound at a temperature of 850 °C and a pressure of 0.67 kPa was performed using an installation to confirm such decomposition.

X-ray phase analysis of the condensate sample revealed 91.6 % Mg, 1.52 % Mg_2Sn, and 6.95 % SiO_2 (figure 1). X-ray fluorescence analysis revealed 95.35 % magnesium, 0.25 % tin, and 4.84 % silicon (figure 2). The presence of Mg_2Sn can be explained by entrainment of the initial alloy by the magnesium vapor flow formed during compound dissociation. As a result of the experiment to determine the composition of the vapor condensate, a significant number of spherical granules was found, indicating the fusion of tin droplets after the evaporation of magnesium from the alloy. The presence of SiO_2 is apparently due to its entry into the condensate sample when it was removed from the condenser.

The total measurement error in determining the values of magnesium vapor pressure above tin alloys was found to be equal to the errors of independent measurements: temperature – 1 %, weighing – 0.1 %, pressure 0.5 %, approximation of experimental data – 5.47 %, equal to 7.07 %.

We approximated the values of partial pressure of saturated magnesium vapor ($\bar{p}_{Mg}$) over alloys with tin by the dependence (1):

$$\ln \bar{p}_{Mg}[atm] = (-259{,}546x^4_{Mg} + 642{,}802x^3_{Mg} - 554{,}808x^2_{Mg} + 202{,}550x_{Mg} - 47{,}344) \times T^{-1} + 210.75x^4_{Mg} - 524.42x^3_{Mg} + 452.67x^2_{Mg} - 160.55x_{Mg} + 33.453 + \ln x_{Mg} \quad (1)$$

where: x_{Mg} – atomic fraction of magnesium in the alloy; T – temperature, K.

The saturated vapor pressure above elemental magnesium corresponds to the equation (2):

$$\ln p^o_{Mg}[atm] = -16{,}346 \times T^{-1} + 11.903 \quad (2)$$

The partial pressure of saturated tin vapor in the Mg–Sn system, was calculated by us by numerical integration of the Gibbs–Duhem equation and corresponds to the dependence (3):

$$\ln \bar{p}_{Sn}[atm] = (-259{,}546x^4_{Sn} + 741{,}443x^3_{Sn} - 776{,}751x^2_{Sn} + 384{,}200x_{Sn} - 125{,}543 - 16{,}884\ln x_{Sn}) \times T^{-1} + 210.75x^4_{Sn} - 599.58x^3_{Sn} + 621.78x^2_{Sn} - 302.35x_{Sn} + 81.96 + 15.53\ln x_{Sn} \quad (3)$$

The dependence of the vapor pressure above metallic tin was taken from [26] and converted by us to the form (4):

$$\ln p^o_{Sn}[atm] = -36{,}197 \times T^{-1} + 12.56 \quad (4)$$

The decomposition pressure of dimagnesium stannide (1401 ± 131 K), determined by the boiling point method (isobaric variant) within the limits of the determination errors, coincides with the boiling point of the melt (1494 ± 105 K), determined by the same method (isothermal variant).

The partial and integral entropies of evaporation are shown in Figure 3, and the enthalpies of evaporation of alloys calculated by us using the above equations are summarized in Table 1.

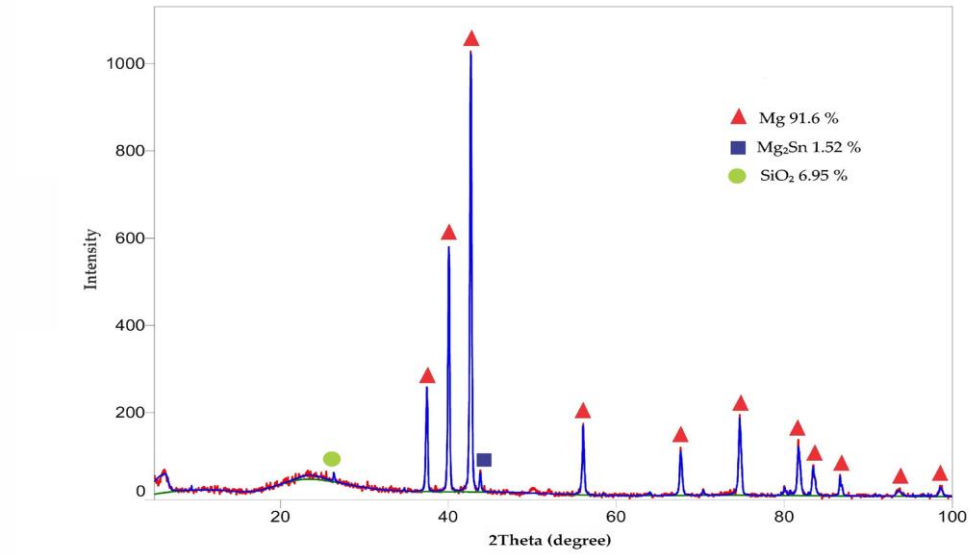

Figure 1 - X-ray diffraction pattern of the obtained magnesium condensate

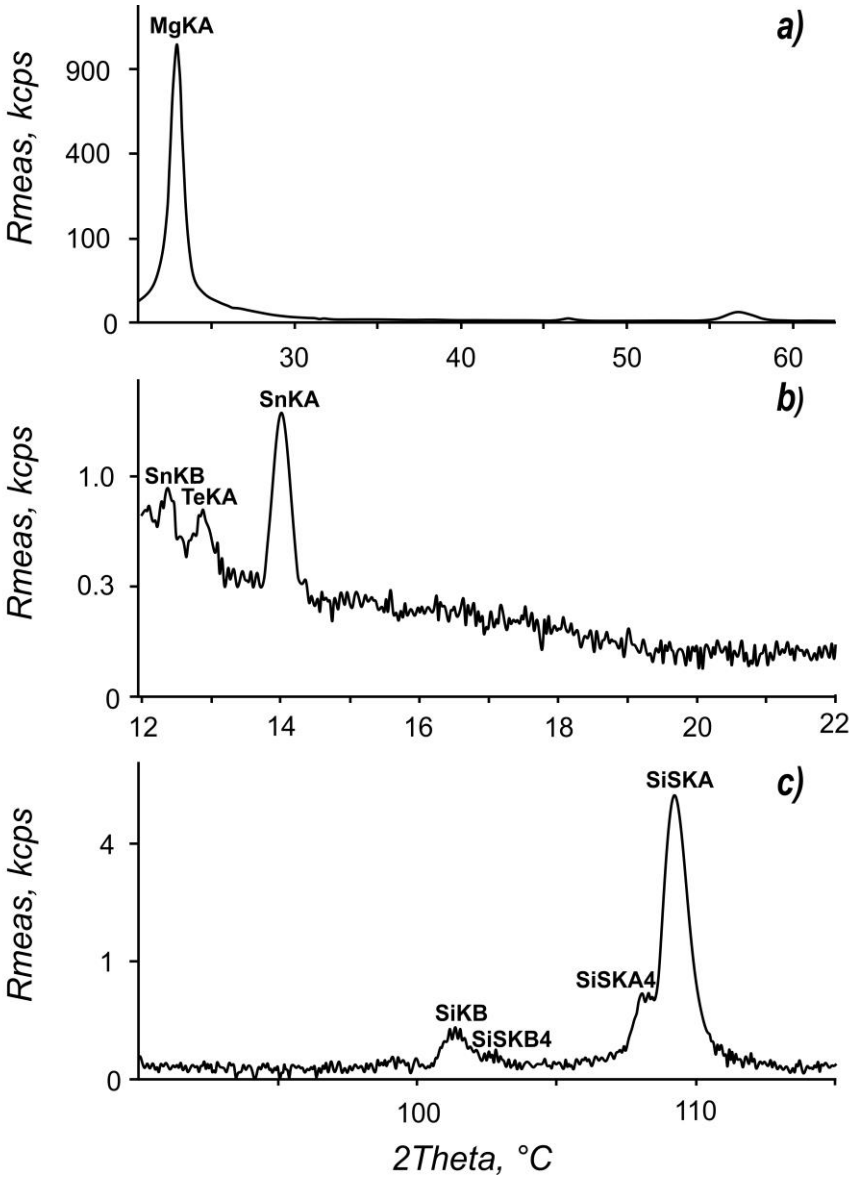

Figure 2 - Sections of the spectrogram of magnesium condensate obtained on different crystals (a - PX1; b - LiF200; c - PE) using the X-ray fluorescence wave-dispersive analysis method

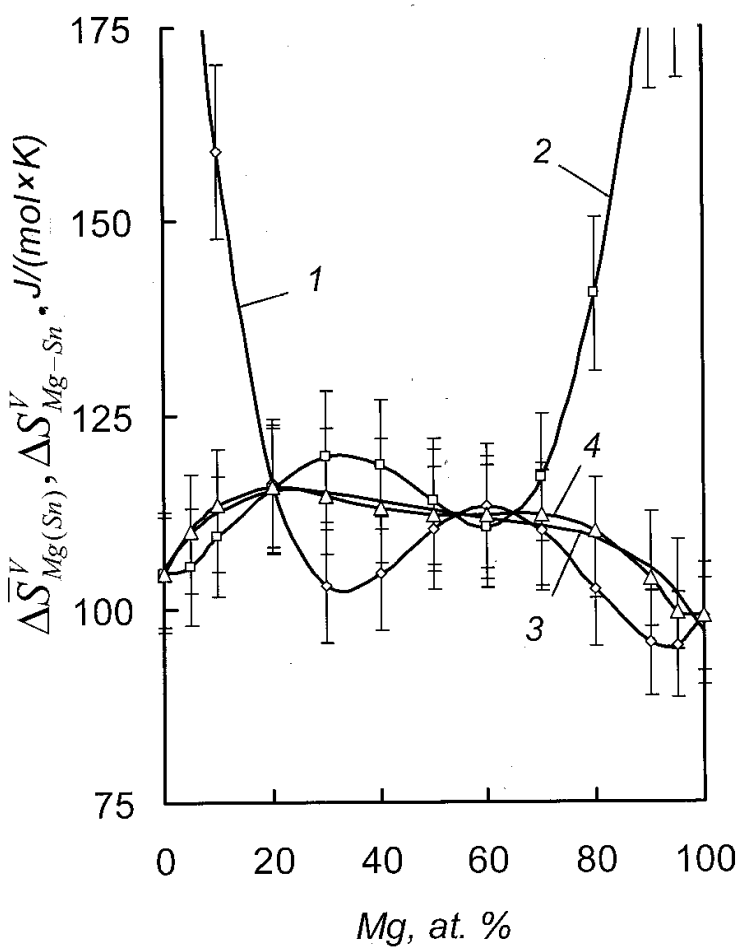

Figure 3 - Change in the entropies of evaporation of magnesium-tin alloys: 1 – change in the partial entropy of evaporation of magnesium; 2 – the same for tin; 3 – change in the integral entropy; 4 – calculated change in the integral entropy

The data shown in Figure 3 predictably indicate an increase in the partial entropies of evaporation of magnesium and tin when their content in the alloy (each) decreases to less than 20 at. %. Extremes are noted: a maximum for magnesium and a minimum for tin at a concentration corresponding to the stoichiometric composition of dimagnesium stannide (60 at. % Mg). The latter indicates the presence of a dissociating compound in the liquid phase that affects evaporation.

Based on the data we obtained, the change in the integral entropy of evaporation within the limits of measurement errors is approximated by the expression (5). In turn, the change in the integral enthalpy of evaporation can be determined by the formula (6), which was obtained by processing our experimental data.

$$\Delta S_{Mg-Sn}[J/(mol \times K)] = -255.29x^4_{Mg} + 522.5x^3_{Mg} - -383.48x^2_{Mg} + 108.08\ _{Mg} + 105.14 \quad (5)$$

$$\Delta H_{Mg-Sn}[kJ/mol] = -134.3x^2_{Mg} - 30.96x_{Mg} + 302.18 \quad (6)$$

The values of the change in Gibbs integral free energy (ΔG^V_{Mg-Sn}) in the liquid phase region up to the boiling point of magnesium at atmospheric pressure (1100 °C) are determined by us by the formula $\Delta G^V_{Mg-Sn} = \Delta H^V_{Mg-Sn} - T\Delta S^V_{Mg-Sn}$ and summarized in Table 2.

It can be seen, when analyzing the change in the values of partial and integral enthalpies and Gibbs free energy of vaporization, that the functions increase monotonically from Mg to Sn in accordance with the second-degree dependencies on the concentration of components in the alloy and linearly (Gibbs energy) with temperature. The very small change in the integral value of the free energy of evaporation of magnesium (0.03 ± 0.002 kJ/mol) at 1373 K (1100 °C) indicates a practical coincidence with the boiling point of magnesium.

Table 1 - Change in the partial and integral enthalpy of evaporation of magnesium-tin alloys

Composition of alloys, at. %		$\Delta\bar{H}^V_{Mg}$, kJ/mol	$\Delta\bar{H}^V_{Sn}$, kJ/mol	$\Delta\bar{H}^V_{Mg-Sn}$, kJ/mol
Mg	**Sn**			
100	0	135.91 ± 9.61	-	135.91 ± 9.61
95	5	132.32 ± 9.36	478.94 ± 33.86	149.65 ± 10.58
90	10	134.10 ± 9.48	459.77 ± 32.51	166.59 ± 11.78
80	20	146.14 ± 10.33	391.46 ± 27.68	195.20 ± 13.00
70	30	160.06 ± 11.32	348.75 ± 24.66	216.67 ± 15.32
60	40	169.09 ± 11.95	331.45 ± 23.43	234.03 ± 16.54
50	50	171.63 ± 12.13	328.17 ± 23.20	249.90 ± 17.67
40	60	171.26 ± 12.11	328.55 ± 23.23	265.63 ± 18.78
30	70	176.75 ± 12.50	325.87 ± 23.04	281.14 ± 19.88
20	80	202.03 ± 14.28	317.87 ± 22.47	294.70 ± 20.83
10	90	266.23 ± 18.82	307.09 ± 21.71	303.00 ± 21.42
5	95	320.31 ± 2264	302.80 ± 21.41	303.68 ± 21.47
0	100	-	301.03 ± 21.28	301.03 ± 21.28

Table 2 - Values of the change in Gibbs free energy of evaporation

Composition of alloys, at. %		ΔG^V_{Mg-Sn} (kJ/mol) at temperature, K:							
Mg	**Sn**	673	773	873	973	1073	1173	1273	1373
100	0	-	-	49.51 ± 3.50	39.62 ± 2.80	29.72 ± 2.10	19.83 ± 1.40	9.93 ± 0.70	0.03 ± 0.002
90	10	-	-	75.87 ± 5.36	65.48 ± 4.63	55.09 ± 3.89	44.70 ± 3.16	34.31 ± 2.43	23.92 ± 1.69
80	20	-	-	-	88.12 ± 6.23	77.12 ± 5.45	66.11 ± 4.67	55.11 ± 3.90	44.10 ± 3.12
70	30	-	-	-	-	96.33 ± 6.81	85.11 ± 6.02	73.90 ± 5.22	62.68 ± 4.43
60	40	-	-	-	-	113.73 ± 8.04	102.52 ± 7.23	91.30 ± 6.45	80.09 ± 5.66
50	50	-	-	-	-	129.62 ± 9.16	118.42 ± 8.37	107.21 ± 7.58	96.00 ± 6.79
40	60	-	-	-	155.71 ± 10.99	144.42 ± 10.21	133.12 ± 9.41	121.82 ± 8.61	110.53 ± 7.81
30	70	-	-	181.06 ± 12.80	169.60 ± 11.99	158.14 ± 11.18	146.67 ± 1.37	135.21 ± 9.6	123.75 ± 8.75
20	80	-	205.31 ± 14.52	193.74 ± 13.70	182.18 ± 12.88	170.61 ± 12.06	159.05 ± 11.24	147.48 ± 10.43	135.92 ± 9.61
10	90	226.68 ± 16.03	215.34 ± 15.22	204.00 ± 14.42	192.66 ± 13.62	181.31 ± 12.82	169.97 ± 12.02	158.63 ± 11.22	147.29 ± 10.41
0	100	230.75 ± 16.31	220.30 ± 15.58	209.86 ± 14.84	199.42 ± 14.10	188.97 ± 13.36	178.53 ± 12.62	168.09 ± 11.88	157.65 ± 11.15

Conclusions

Thus, as a result of the research, the values of partial pressure of magnesium and tin were determined, which served as the basis for determining the energy functions: changes in entropy, enthalpy and free energy of evaporation. As the content of each component in the alloy decreases to less than 20 at.%, the partial entropies of evaporation of magnesium and tin increase.

Extrema were established: a maximum for magnesium and a minimum for tin, which correspond to the dimagnesium stannide compound containing stoichiometrically 60 at. % Mg. It was found that the values of the partial and integral enthalpies, as well as the Gibbs free energy of evaporation, increase monotonically from magnesium to tin, with their concentration dependences described by second-degree polynomials, and the temperature dependence of the Gibbs free energy being linear. It was shown that the change in the integral value of the free energy of evaporation of elemental magnesium corresponds to 0.03±0.002 kJ/mol at 1373 K and indicates almost complete coincidence with the boiling point of magnesium. Thermodynamic functions of evaporation of magnesium-tin melts, determined on the basis of the values of vapor pressure of the system components, supplement the base of physical and chemical data and can be used for heat engineering calculations in the design of distillation processes and equipment.

Conflicts of interest. The corresponding author declare that there is no conflict of interest.

CRediT author statement: **V. Volodin**: Data Curation, Writing – original draft preparation, Conceptualization, Visualization, Investigation, Project administration; **S. Trebukhov, A. Nitsenko, A. Mukangaliyeva, X. Linnik, N. Burabayeva**: Data curation, Methodology, Writing – original draft preparation, Writing – Review & Editing. All authors have read and agreed to the published version of the manuscript.

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Володин В.Н., Требухов С.А., Мұқанғалиева А.Ө., Линник К.А., Ниценко А.В, Бурабаева Н.М.

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ТҮЙІНДЕМЕ

Магнийдің қайнау температурасы әдісімен (сәйкесінше изобарлық және изотермиялық нұсқалар) анықталатын димагний станниді мен қалайы балқымасына және қалайыға парциалды қысымының мәндерін негізге ала отырып, термодинамикалық функциялар, энтропияның, энтальпияның және буланудың бос энергиясының өзгеруі белгілі өрнектерге сәйкес сандық интегралдау арқылы есептелген Гиббс-Дюгем теңдеуі арқылы анықталды. Қайнау температурасы әдісінің изобарлық және изотермиялық нұсқаларының бу қысымын анықтау және термодинамикалық шамаларды есептеу әдістері сипатталған. Магний мен қалайының парциалды бу қысымының мәндерінің тәуелділіктері анықталып, олардың негізінде энергетикалық функциялар анықталды. Өлшеудегі қателік 7,07 % болды. Булану энтропиясының өзгеруі туралы мәліметтер графикалық түрде берілген. Қорытпадағы магний мен қалайының үлесі (әрқайсысының) 20 ат. %-дан азайған кезде олардың булану энтропияларының артуы байқалды Экстремумдар белгіленді:: магний үшін максимум және қалайы үшін минимум димагний станнидінің (60 ат.% Mg) стехиометриялық құрамына сәйкес келетін концентрацияда Соңғысы сұйық фазада булануға әсер ететін диссоциацияланатын қосылыстың болуын көрсетеді. Энтальпияның өзгеру мәндері және Гиббс бос булану энергиясы кестеде келтірілген. Парциалды және интегралды энтальпиялардың және Гиббстің булануының еркін энергиясының мәндері Mg-ден Sn-ге қарай қорытпадағы компоненттер концентрациясынан екінші дәрежелі тәуелділікке сәйкес монотонды түрде артады және температураға байланысты сызықтық түрде (Гиббс энергиясы) артады. Магнийдің еркін булану энергиясының интегралдық мәндерінің өте аз мөлшердегі өзгерістері (1373 К (1100 °С) температурада 0,03±0,002 кДж/моль) магнийдің қайнау температурасымен іс жүзінде сәйкес келетінін көрсетеді. Магний-қалайы жүйесінің балқымаларының булануының энергетикалық функциялары термодинамикалық мәліметтер қорын толықтырады және дистилляция процестері мен аппараттарын жобалау кезінде жылу техникасының есептеулері үшін пайдаланылуы мүмкін.

Түйін сөздер: магний, қалайы, димагний станниді, термодинамика, энтропия, энтальпия, Гиббс энергиясы.

Володин Валерий Николаевич	***Авторлар туралы ақпарат:*** *Техника ғылымдарының докторы, профессор, Вакуумдық процестер зертханасының бас ғылыми қызметкері, Металлургия және кен байыту институты АҚ, Сәтбаев университеті, 050010, Шевченко көш., 29/133, Алматы, Қазақстан. Email: volodinv_n@mail.ru; ORCID ID: https://orcid.org/0000-0003-0116-1423*
Требухов Сергей Анатольевич	*Техника ғылымдарының докторы, профессор, Вакуумдық процестер зертханасының бас ғылыми қызметкері, Металлургия және кен байыту институты АҚ, Сәтбаев университеті, 050010, Шевченко көш., 29/133, Алматы, Қазақстан. Email: s.trebukhov@satbayev.university; ORCID ID: https://orcid.org/0000-0001-9708-0307*
Мұқанғалиева Арайлым Өмірзаққызы	*Техника ғылымдарының магистрі, Титан және сирек отқа төзімді металдар зертханасының инженері, Металлургия және кен байыту институты АҚ, Сәтбаев университеті, 050010, Шевченко көш., 29/133, Алматы, Қазақстан. Email: a.mukangaliyeva@satbayev.university; ORCID ID: https://orcid.org/0000-0001-7032-1764*
Линник Ксения Александровна	*Техника ғылымдарының магистрі, Вакуумдық процестер зертханасының кіші ғылыми қызметкері, Металлургия және кен байыту институты АҚ, Сәтбаев университеті, 050010, Шевченко көш., 29/133, Алматы, Қазақстан. Email: x.linnik@satbayev.university, xenija_linnik@mail.ru; ORCID ID: https://orcid.org/0000-0002-0683-1409*
Ниценко Алина Владимировна	*Техника ғылымдарының кандидаты, Вакуумдық процестер зертханасының меңгерушісі, Металлургия және кен байыту институты АҚ, Сәтбаев университеті, 050010, Шевченко көш., 29/133, Алматы, Қазақстан. Email: alina.nitsenko@gmail.com; ORCID ID: https://orcid.org/0000-0001-6753-0936*
Бурабаева Нурила Муратовна	*Техника ғылымдарының кандидаты, Вакуумдық процестер зертханасының аға ғылыми қызметкері, Металлургия және кен байыту институты АҚ, Сәтбаев университеті, 050010, Шевченко көш., 29/133, Алматы, Қазақстан. Email: nuri_eng@mail.ru; ORCID ID: https://orcid.org/0000-0003-2183-2239*

Термодинамика испарения жидких сплавов магния с оловом

Володин В.Н., Требухов С.А., Мукангалиева А.О., Линник К.А., Ниценко А.В. Бурабаева Н.М.

АО Институт металлургии и обогащения, Satbayev University, Алматы, Казахстан

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АННОТАЦИЯ

На основании величин парциальных давлений магния над станнидом димагния и расплавами с оловом, определенные методом точек кипения (изобарический и изотермический вариант соответственно) и олова, рассчитанного численным интегрированием уравнения Гиббса-Дюгема в соответствии с известными выражениями определены термодинамические функции: изменения энтропии, энтальпии и свободной энергии испарения. Описаны методики определения давления пара изобарического и изотермического вариантов метода точек кипения и расчета термодинамических величин. Определены зависимости величин парциального давления пара магния и олова, на основании которых определены энергетические функции. Погрешность измерения составила 7,07 %. Данные об изменении энтропий испарения представлены графически. Отмечено увеличение парциальных энтропий испарения магния и олова при уменьшении их содержания в сплаве (каждого) менее 20 ат. %. Отмечены экстремумы: максимум для магния и минимум для олова при концентрации, соответствующей стехиометрическому составу станнида димагния (60 ат. % Mg). Последнее свидетельствует о наличии диссоциирующего соединения в жидкой фазе, влияющего на испарение. Величины изменения энтальпий и свободной энергии испарения Гиббса табулированы. Величины парциальных и интегральных энтальпий и свободной энергии испарения Гиббса монотонно увеличиваются от Mg к Sn в соответствии с зависимостями второй степени от концентрации компонентов в сплаве и линейно (энергия Гиббса) с температурой. Весьма малая величина изменения интегральной величины свободной энергии испарения магния (0,03±0,002 кДж/моль) при 1373 К (1100 ° С) свидетельствует о практическом совпадении с температурой кипения магния. Энергетические функции испарения расплавов системы магний – олово пополнят базу термодинамических данных, и могут быть использованы для теплотехнических расчетов при проектировании дистилляционных процессов и аппаратов.

Ключевые слова: магний, олово, станнид димагния, термодинамика, энтропия, энтальпия, энергия Гиббса.

Володин Валерий Николаевич	***Информация об авторах:*** *Доктор технических наук, профессор, главный научный сотрудник лаборатории вакуумных процессов, АО Институт металлургии и обогащения, Satbayev University, 050010, ул. Шевченко, 29/133, Алматы, Казахстан. Email: volodinv_n@mail.ru; ORCID ID: https://orcid.org/0000-0003-0116-1423*
Требухов Сергей Анатольевич	*Доктор технических наук, профессор, главный научный сотрудник лаборатории вакуумных процессов, АО Институт металлургии и обогащения, Satbayev University, 050010, ул. Шевченко, 29/133, Алматы, Казахстан. Email: s.trebukhov@satbayev.university; ORCID ID: https://orcid.org/0000-0001-9708-0307*

Мукангалиева Арайлым Омирзаковна	*Магистр технических наук, инженер лаборатории титана и редких тугоплавких металлов, АО Институт металлургии и обогащения, Satbayev University, 050010, ул. Шевченко, 29/133, Алматы, Казахстан. Email: a.mukangaliyeva@satbayev.university; ORCID ID: https://orcid.org/0000-0001-7032-1764*
Линник Ксения Александровна	*Магистр технических наук, младший научный сотрудник лаборатории вакуумных процессов, АО Институт металлургии и обогащения, Satbayev University, 050010, ул. Шевченко, 29/133, Алматы, Казахстан. Email: x.linnik@satbayev.university, xenija_linnik@mail.ru; ORCID ID: https://orcid.org/0000-0002-0683-1409*
Ниценко Алина Владимировна	*Кандидат технических наук, заведующая лабораторией вакуумных процессов, АО Институт металлургии и обогащения, Satbayev University, 050010, ул. Шевченко, 29/133, Алматы, Казахстан. Email: alina.nitsenko@gmail.com; ORCID ID: https://orcid.org/0000-0001-6753-0936*
Бурабаева Нурила Муратовна	*Кандидат технических наук, старший научный сотрудник лаборатории вакуумных процессов, АО Институт металлургии и обогащения, Satbayev University, 050010, ул. Шевченко, 29/133, Алматы, Казахстан. Email: nuri_eng@mail.ru; ORCID ID: https://orcid.org/0000-0003-2183-2239*

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