

THE MAGNESIUM-PALLADIUM-SILVER SYSTEM: THERMODYNAMIC PROPERTIES OF THE LIQUID PHASE

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Abstract

A drop calorimetry method was used to measure the partial and integral mixing enthalpies of Ag-Mg-Pd liquid solutions. The experiments were performed for six separate series of liquid alloys starting from the binary alloys with constant x_{Ag}/x_{Mg} ratios equal to 1/9, 1/3, 1/1, and 3/1 for $(Ag_{0.10}Mg_{0.90})_{1-x}Pd_x$ and $(Ag_{0.25}Mg_{0.75})_{1-x}Pd_x$ at 1116 K and $(Ag_{0.50}Mg_{0.50})_{1-x}Pd_x$ and $(Ag_{0.75}Mg_{0.25})_{1-x}Pd_x$ at 1279 K and x_{Mg}/x_{Pd} ratios of 9/1 and 4/1 for $(Mg_{0.90}Pd_{0.10})_{1-x}Ag_x$ and $(Mg_{0.80}Pd_{0.20})_{1-x}Ag_x$ at 1116 K. Then, using the thermodynamic properties of the binary systems in the form of the Redlich-Kister equations and the changes in mixing enthalpies provided by this study, the ternary interaction parameters were determined with the Muggianu model and our own software (TerGexHm). Based on the binary and ternary interaction parameters, the partial mixing enthalpies of Ag, Mg, and Pd were calculated for the same cross-sections where the measurements were conducted. These studies were the first step of an investigation of the Ag-Mg-Pd system before the calculation of the phase diagram for this ternary system.

Keywords: Magnesium-palladium-silver; Solution calorimetry; Thermodynamic properties; Thermodynamic modeling

1. Introduction

Magnesium-based alloys exhibit low densities, high strengths, and high corrosion resistances, and they are very attractive to many scientists and engineers engaged in designing new materials for various branches of industry and science [1]. The ability of these alloys to interact with hydrogen facilitates their potential use as hydrogen storage materials due to their many practical advantages. These abilities include their high gravimetric capacity for hydrogen storage (up to 7.6 mas % for MgH_2) and their relatively low costs. In addition, magnesium is nontoxic and readily available. However, because of the high temperatures needed and the slow kinetics for the hydrogen absorption/desorption reactions, the practical application of Mg for hydrogen storage is precluded. Therefore, MgH_2 needs to be destabilized, and the (de)hydrogenation reaction kinetics needs to be improved. One possible strategy for destabilizing Mg-H bonding is to alloy Mg with transition metals. Therefore, intensive research is currently being conducted worldwide to improve the kinetics for hydrogen absorption/desorption by magnesium alloys via modification with alloying additives [2-6]. To enhance the hydrogen sorption kinetics, transition

metals that catalyze hydrogen dissociation can also be added [6]. Silver and palladium are such metals, they have outstanding catalytic properties for the dissociation of molecular hydrogen, and they protect other metals from surface oxidation [7].

A literature review on thermodynamic studies of two binary (Ag-Mg and Mg-Pd) systems was previously presented in the papers [8-13]. In the case of thermodynamic studies on the Ag-Pd system, the liquidus line of the Ag-Pd system has been described by several authors with the use of various methods [14-16]. Oriani et al. [17] and Chan [18] determined the heats of formation for solid Ag-Pd alloys, and a torsion effusion method was used by Myles [19] to determine the vapor pressures of Ag over Ag-Pd solid solutions (activity measurements). Using the available literature data, the phase diagram was assessed by Karakaya and Thompson [20].

The Ag-Mg-Pd system was investigated by Karonik et al. [21], who performed X-ray diffraction and thermal analyses on Mg-rich alloys, as well as Sharma and Weiss [22], who investigated the quasibinary $Ag_{1-x}Pd_xMg$ ($0 \leq x \leq 0.5$) system with X-ray diffraction, thermal analysis, and microscopy studies. However, their studies were not consistent with each other. Because calorimetric measurements of the

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mixing enthalpies of ternary Ag-Mg-Pd solutions have not yet been carried out, measurements of the thermodynamic properties of the Ag-Mg-Pd system were initiated. In our research, high-temperature drop calorimetric studies were carried out to determine the partial and integral enthalpies for mixing liquid ternary alloys.

2. Materials and methods

The experimental procedure was very similar to the earlier studies of the Ag-Mg-Pb [23] and Mg-Pb-Pd [24] systems. For the study of the change in enthalpy of mixing liquid Ag-Mg-Pd solutions, metals and argon were used; the purity, manufacturer, and physical form of are listed in Table 1. Ceramic crucibles in which there was a metallic bath (Mg-Pd, Mg-Ag) were produced from magnesium oxide via Inn-Therm. The crucibles had the following dimensions: outer diameter = 12 mm, height = 60 mm, wall thickness = 2 mm, and flat bottom. The samples were cleaned mechanically by file to remove possible surface impurities before addition to the reaction crucible.

Table 1. Specifications of the materials used

Chemical name	Source	Purity [mas%]	The physical form
Magnesium	GoodFellow	99.9	Wire
			$\phi=3.2$ mm
Palladium	Safina a.s.	99.95	Wire
			$\phi=0.5$ mm
Silver	Innovator Sp. z o.o	99.9	Wire
			$\phi=3$ mm
Argon	Air Products	999.999	Gas

All measurements of the thermal effects of metal dissolution in the metal bath were made using the Setaram MHTC 96 Line Evo calorimeter with Calisto software. Before starting the tests, the calorimeter was evacuated several times with a turbomolecular vacuum pump and filled with high-purity argon to remove gases with which magnesium reacts easily, especially at the temperature of the tests. Then, the calorimeter was heated to the measurement temperature, and after stabilization of the baseline, the measurements began. First, the average value of the calibration constant was determined using silver or palladium. To determine this, 5 measurements of the thermal effects were made after adding Ag or Pd samples into the crucible in the calorimeter. Then, the change in enthalpy of mixing was measured for a binary solution (Ag-Mg, Mg-Pd) with a specific

x_{Ag}/x_{Mg} or x_{Mg}/x_{Pd} ratio by adding an appropriate amount of magnesium into the crucible containing Ag or Pd. This alloy was also the starting alloy for the study of the change in enthalpy of mixing Ag-Mg-Pd ternary solutions. In the last step, the measurements of the mixing enthalpy change of the ternary alloys were conducted by adding solid palladium or silver to the liquid binary (first portion of Ag or Pd) and next ternary liquid solutions. Each measurement series consisted of three stages.

When the starting alloy for the measurements of ternary solutions was one of the binary Ag-Mg alloys ($x_{Ag}/x_{Mg} = 1/9, 1/3, 1/1, 3/1$), the subsequent measurement steps were in the form of the following reactions:

1) Calibration process:

for a series at 1116 K: $xAg_{(s,TD)} \textcircled{R} xAg_{(s,TM)}$ and

for a series at 1279 K: $xAg_{(s,TD)} \textcircled{R} xAg_{(l,TM)}$;

2) Measurements of the mixing enthalpies of the binary alloys:

for a series at 1116 K: $xAg_{(s,TM)} + yMg_{(s,TD)} \textcircled{R} Ag_xMg_y_{(l,TM)}$ and

for a series at 1279 K: $xAg_{(l,TM)} + yMg_{(s,TD)} \textcircled{R} Ag_xMg_y_{(l,TM)}$;

3) Measurements of the mixing enthalpies of the ternary alloys for both above temperatures:

$Ag_xMg_y_{(l,TM)} + zPd_{(s,TD)} \textcircled{R} Ag_xMg_yPd_z_{(l,TM)}$;

When the binary starting alloy for the measurements of ternary solutions was Mg-Pd alloy (x_{Mg}/x_{Pd} ratios of 9/1 and 4/1), the subsequent stages were represented by the following reaction sequence:

1) Calibration process for a series at 1116 K:

$zPd_{(s,TD)} \textcircled{R} zPd_{(s,TM)}$;

2) Measurements of the mixing enthalpies of the binary alloys:

$zPd_{(s,TM)} + yMg_{(s,TD)} \textcircled{R} Mg_yPd_z_{(l,TM)}$;

3) Measurements of the mixing enthalpies of the ternary alloys:

$Mg_yPd_z_{(l,TM)} + xAg_{(s,TD)} \textcircled{R} Ag_xMg_yPd_z_{(l,TM)}$;

where T_D is the room temperature (298 K); T_M is the measurement temperature; "s" is the solid (crystalline); "l" denotes liquid states; x, y, z are the numbers of moles of Ag, Mg, or Pd; $Ag_xMg_y_{(l,TM)}$ or $Mg_yPd_z_{(l,TM)}$ represents the formation of a starting binary Ag-Mg or Mg-Pd liquid alloy and includes the increments in enthalpy for pure magnesium and the melting enthalpy at the measurement temperature; $Ag_xMg_yPd_z_{(l,TM)}^i$ represents the formation of the i^{th} ternary alloy ($i=1, 2, 3, \dots$) and includes the changes in enthalpy for the added metal (Pd or Ag) and the melting enthalpy for the added metal at the measurement temperature.

Due to the high vapor pressure of magnesium and to verify possible weight losses, the total mass of the samples and the crucible before and after the measurements were measured at both experimental temperatures. The observed maximal weight loss in



each series was no larger than ca. 16 mg (Series 3). Considering that only magnesium could evaporate at that temperature, this weight loss produced an error of less than 0.007 in the mole fraction of the alloy compositions shown in Table 2 and Table 3.

To determine the integral enthalpies of mixing ($\Delta_{\text{mix}}H$) of the Ag-Mg-Pd liquid alloys, the equations listed below were used:

$$\Delta_{\text{mix}}H = \frac{\Delta_{\text{mix}}H_{\text{Bin}} + \sum H_{\text{DISS-X}}}{n_{\text{Ag}} + n_{\text{Mg}} + n_{\text{Pd}}} \quad (1)$$

$$H_{\text{DISS-X}} = (\Delta H_{\text{Signal}} \Delta K) - (\Delta H_X^{T_D \rightarrow T_M} \Delta n_X) \quad (2)$$

$$K = \frac{\Delta H_X^{T_D \rightarrow T_M} \Delta n_X}{\Delta H_{\text{Calibration}}} \quad (3)$$

where $\Delta_{\text{mix}}H_{\text{Bin}}$ is the mixing enthalpy change of the binary alloy; $H_{\text{DISS-X}}$ is the enthalpy of dissolution for pure magnesium or palladium; n_X (n_{Ag} , n_{Mg} , n_{Pd}) is the number of moles of silver, magnesium, and palladium, respectively; ΔH_{Signal} is the voltage signal given in $\mu\text{V}\cdot\text{s}$, which is caused by the heat increment from each added metal (Ag or Pd); K is the calibration constant; $\Delta H_X^{T_D \rightarrow T_M}$ is the molar enthalpy difference for element X ($X = \text{silver, magnesium, and palladium}$) between room temperature ($T_D = 298 \text{ K}$) and the temperature of the measurement (T_M), which is calculated using [25]; and $\Delta H_{\text{Calibration}}$ is the voltage signal, in $\mu\text{V}\cdot\text{s}$, caused by the heat increment from the added Ag or Pd sample that is used for calibration.

3. Results and discussion

The calorimetric studies of the Ag-Mg-Pd system were conducted for six separate experimental series with constant $x_{\text{Ag}}/x_{\text{Mg}}$ ratios of 1/9, 1/3, 1/1, 3/1 for ($\text{Ag}_{0.10}\text{Mg}_{0.90}$) $_{1-x}\text{Pd}_x$ and ($\text{Ag}_{0.25}\text{Mg}_{0.75}$) $_{1-x}\text{Pd}_x$ at 1116 K and ($\text{Ag}_{0.50}\text{Mg}_{0.50}$) $_{1-x}\text{Pd}_x$ and ($\text{Ag}_{0.75}\text{Mg}_{0.25}$) $_{1-x}\text{Pd}_x$ at 1279 K and $x_{\text{Mg}}/x_{\text{Pd}}$ ratios of 9/1 and 4/1 for ($\text{Mg}_{0.90}\text{Pd}_{0.10}$) $_{1-x}\text{Ag}_x$ and ($\text{Mg}_{0.80}\text{Pd}_{0.20}$) $_{1-x}\text{Ag}_x$ at 1116 K for verification of the obtained results. The compositions of all alloys investigated in these studies are shown in Figure 1. The circles and stars indicate measurements in the liquid phase and measurements in the liquid–solid area, respectively.

To reduce the loss of magnesium from the alloy, calorimetric measurements were performed at two temperatures (1279 K and 1116 K) depending on the concentration of Mg in the liquid alloy. For the two measurement series (Series 5 and 6), where the concentrations of Mg in starting binary alloys were 50 and 25 atomic %, measurements were made at the temperature of 1279 K. In these two measurement series, the magnesium content in the alloy was the lowest and its vapor pressure was significantly limited because the free energy of Mg in the solution was much lower in comparison to that for pure Mg. For these experimental series, the measurements

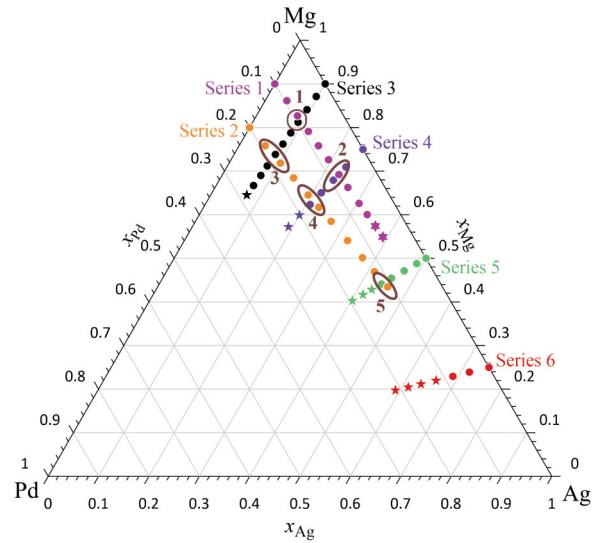


Figure 1. Compositions of the Ag-Mg-Pd alloys studied together with marked points near the intersections. The filled circles and stars show measurements in the liquid phase and measurements in the liquid–solid area, respectively

were carried out at a temperature exceeding the melting point of silver by approximately 50 K. In the case of other measurement series, where the magnesium content was higher and there was a greater risk of magnesium evaporation from the alloy, tests were performed at a temperature of 1116 K, slightly above the melting point of the AgMg phase ($\sim 1093 \text{ K}$).

Calorimetric studies were performed for six separate series of Ag-Mg-Pd alloys starting from the binary alloys with constant ratios of $x_{\text{Ag}}/x_{\text{Mg}}$ and $x_{\text{Mg}}/x_{\text{Pd}}$, as mentioned above. The experimental values of the heat effects, the integral molar mixing enthalpies of the liquid Ag-Mg-Pd alloys, the mole fractions of the pure elements, the drop enthalpies, and other information measured in these studies are listed in Table 2 and Table 3.

Table 4 summarizes the integral molar enthalpies of the mixing data for respective sections in the vicinity of the cross points (the points from 1 to 5 are marked in Fig. 1). Based on the obtained standard uncertainties (less than 2 kJ/mol) listed in Tables 2 and 3 and the differences in the chemical compositions, our studies showed good agreement.

As presented in Tables 2 and 3, the obtained data for the mixing enthalpy changes of liquid Ag-Mg-Pd solutions were used to establish the thermodynamic properties ($\Delta_{\text{mix}}H$) of the Ag-Mg-Pd liquid alloys via the Muggianu model [26], with an additional mathematical expression describing the ternary interactions. In this case, the model can be represented as follows:

Table 2. Integral mixing enthalpies for $(Mg_{0.90}Pd_{0.10})_{1-x}Ag_x$ and $(Mg_{0.80}Pd_{0.20})_{1-x}Ag_x$. Standard states: pure liquid metals

Number of added moles of Ag [mol]	Heat effect $\Delta H_{Signal} \cdot K$ [kJ]	Drop enthalpy H_{DISS-x} [kJ]	Mole fraction x_{Ag}	Integral molar enthalpy ¹ $\Delta_{mix}H$ [kJ/mol]	Mole fraction ² x_{Ag}	Partial molar enthalpy $\Delta \bar{H}_{Ag}$ [kJ/mol]	Standard uncertainties $u(\Delta_{mix}H)$ [kJ/mol]
Series 1. $(Mg_{0.90}Pd_{0.10})_{1-x}Ag_x$; starting amount: $n_{Mg} = 0.023575$ mol; $n_{Pd} = 0.002619$ mol; $K = 0.000003517$ kJ/ μ Vs; $T_D = 298$ K; $T_M = 1116$ K; kJ/mol; $\Delta H_{Ag}^{T_D \rightarrow T_M} = 33.7485$ kJ/mol; $\Delta H_{Mg}^{T_D \rightarrow T_M} = 32.8525$ kJ/mol; $\Delta H_{Pd(s)}^{T_D \rightarrow T_M} = 22.4773$ kJ/mol; $\Delta H_{Pd(l)}^{T_D \rightarrow T_M} = 35.1342$ kJ/mol; $\Delta_{mix}H_{Mg_{0.90}Ag_{0.10}} = -17.1$ kJ/mol. Standard uncertainties: $u(n_{Ag}) = 0.0000009$ mol; $u(n_{Mg}) = 0.000004$ mol; $u(n_{Pd}) = 0.0000009$; $u(T_D) = 1$ K; $u(T_M) = 1$ K; $u(p) = 10$ kPa; $u(K) = 0.00000022$ kJ/ μ Vs; $u(\Delta_{mix}H_{Mg_{0.90}Ag_{0.10}}) = 0.23$ kJ/mol.							
0.0011801	-0.005065	-0.045	0.0431	-18.0	0.0216	-38.0	0.24
0.0011430	-0.003545	-0.042	0.0815	-18.7	0.0623	-36.9	0.24
0.0012840	-0.004207	-0.048	0.1210	-19.5	0.1013	-37.0	0.24
0.0012988	-0.001864	-0.046	0.1577	-20.2	0.1394	-35.2	0.24
0.0013785	0.000728	-0.046	0.1935	-20.7	0.1756	-33.2	0.24
0.0015843	0.005666	-0.048	0.2310	-21.2	0.2123	-30.2	0.24
0.0015074	0.008220	-0.043	0.2636	-21.5	0.2473	-28.3	0.24
0.0020933	0.016268	-0.054	0.3045	-21.7	0.2841	-26.0	0.24
0.0016205	-0.007306	-0.062	0.3332	-22.4	0.3189	-38.3	0.24
0.0018096	-0.073255	-0.134	0.3626	-24.7	0.3479	-74.2*	0.26
0.0018522	-0.084416	-0.147	0.3901	-27.0	0.3764	-79.3*	0.27
Series 2. $(Mg_{0.80}Pd_{0.20})_{1-x}Ag_x$; starting amount: $n_{Mg} = 0.018498$ mol; $n_{Pd} = 0.004624$ mol; $K = 0.000004065$ kJ/ μ Vs; $T_D = 298$ K; $T_M = 1116$ K; kJ/mol; $\Delta H_{Ag}^{T_D \rightarrow T_M} = 33.7485$ kJ/mol; $\Delta H_{Mg}^{T_D \rightarrow T_M} = 32.8525$ kJ/mol; $\Delta H_{Pd(s)}^{T_D \rightarrow T_M} = 22.4773$ kJ/mol; $\Delta H_{Pd(l)}^{T_D \rightarrow T_M} = 35.1342$ kJ/mol; $\Delta_{mix}H_{Mg_{0.80}Ag_{0.20}} = -33.8$ kJ/mol. Standard uncertainties: $u(n_{Ag}) = 0.0000009$ mol; $u(n_{Mg}) = 0.000004$ mol; $u(n_{Pd}) = 0.0000009$; $u(T_D) = 1$ K; $u(T_M) = 1$ K; $u(p) = 10$ kPa; $u(K) = 0.00000046$ kJ/ μ Vs; $u(\Delta_{mix}H_{Mg_{0.80}Ag_{0.20}}) = 0.35$ kJ/mol.							
0.0012673	0.005235	-0.038	0.0520	-33.6	0.0260	-29.6	0.35
0.0013609	0.009764	-0.036	0.1021	-33.2	0.0771	-26.6	0.36
0.0012914	0.015312	-0.028	0.1449	-32.7	0.1235	-21.9	0.36
0.0016288	0.026177	-0.029	0.1935	-31.8	0.1692	-17.7	0.37
0.0013090	0.023950	-0.020	0.2287	-31.1	0.2111	-15.5	0.38
0.0016501	0.029246	-0.026	0.2690	-30.3	0.2489	-16.0	0.39
0.0025883	0.049379	-0.038	0.3243	-29.1	0.2967	-14.7	0.41
0.0026912	0.049834	-0.041	0.3735	-28.1	0.3489	-15.2	0.42
0.0024845	0.083430	0.000	0.4130	-26.4	0.3933	-0.2	0.45
0.0031436	0.089645	-0.016	0.4564	-24.8	0.4347	-5.2	0.47

¹ Per mole of mixture² Average value before and after the drop

$$\Delta_{mix}H = \sum_i \sum_{j>i} \left(x_i \cdot x_j \cdot \sum_k L_{i,j}^{Liquid} (x_i - x_j)^k \right) + x_i x_j x_k \cdot \left({}^0L_{123}^{Liquid} + {}^1L_{123}^{Liquid} \cdot x_i + {}^2L_{123}^{Liquid} \cdot x_j + {}^3L_{123}^{Liquid} \cdot x_k \right) \quad (4)$$

where $\Delta_{mix}H$ is the mixing enthalpy change for the liquid silver-magnesium-palladium alloys, x_i, x_j, x_k are mole fractions of metals (Ag, Mg, and Pd) of the Ag-Mg-Pd alloys, respectively; $L_{i,j}^k$ are the binary interaction parameters in the Redlich-Kister polynomial [27] for the Ag-Mg, Ag-Pd, and Mg-Pd binary systems; and L_{123}^k ($k=1, 2, 3$) are the ternary

interaction parameters. A more detailed description can be found in [28].

The calorimetric data for the mixing enthalpies of the Ag-Mg-Pd liquid alloys were placed into our own optimization program (TerGexHm software), and the L_{123}^k parameters were calculated. The optimization program used the least squares method. The standard deviation obtained from the program was 871 J/mol, and the values for all parameters in Eq. 4 are shown in Table 5.

Based on calorimetric studies, the values of the



Table 3. Integral mixing enthalpies of $(Ag_{0.10}Mg_{0.90})_{1-x}Pd_x$ and $(Ag_{0.25}Mg_{0.75})_{1-x}Pd_x$, $(Ag_{0.50}Mg_{0.50})_{1-x}Pd_x$ and $(Ag_{0.75}Mg_{0.25})_{1-x}Pd_x$. Standard states: pure liquid metals

Number of added moles of Pd [mol]	Heat effect $\Delta H_{Signal} \cdot K$ [kJ]	Drop enthalpy $H_{Diss-Pd}$ [kJ]	Mole fraction xPd	Integral molar enthalpy ¹ $\Delta_{mix}H$ [kJ/mol]	Mole fraction ² xPd	Partial molar enthalpy Δ Pd [kJ/mol]	Standard uncertainties $u(\Delta_{mix}H)$ [kJ/mol]
Series 3. $(Ag_{0.10}Mg_{0.90})_{1-x}Pd_x$: starting amount: $n_{Ag} = 0.002397$ mol; $n_{Mg} = 0.021568$ mol; $K = 0.000003493$ kJ/ μ Vs; $T_D = 298$ K; $T_M = 1116$ K; $\Delta H_{Ag(s)}^{T_D \rightarrow T_M} = 22.7234$ kJ/mol; $\Delta H_{Ag(l)}^{T_D \rightarrow T_M} = 33.7485$ kJ/mol; $\Delta H_{Mg}^{T_D \rightarrow T_M} = 32.8525$ kJ/mol; $\Delta H_{Pd}^{T_D \rightarrow T_M} = 35.1342$ kJ/mol; $\Delta_{mix}H_{Ag_{0.10}Mg_{0.90}} = -4.5$ kJ/mol. Standard uncertainties: $u(n_{Ag}) = 0.0000009$ mol; $u(n_{Mg}) = 0.000004$ mol; $u(n_{Pd}) = 0.0000009$; $u(T_D) = 1$ K; $u(T_M) = 1$ K; $u(p) = 10$ kPa; $u(K) = 0.00000012$ kJ/ μ Vs; $u(\Delta_{mix}H_{Ag_{0.10}Mg_{0.90}}) = 0.14$ kJ/mol.							
0.0007950	-0.105612	-0.134	0.0321	-9.8	0.0161	-168.0	0.15
0.0008955	-0.112978	-0.144	0.0659	-15.1	0.0490	-161.3	0.17
0.0009105	-0.115290	-0.147	0.0979	-20.1	0.0819	-161.8	0.18
0.0008166	-0.103348	-0.132	0.1248	-24.3	0.1114	-161.7	0.20
0.0009134	-0.103481	-0.136	0.1531	-28.3	0.1390	-148.4	0.21
0.0009115	-0.097613	-0.130	0.1795	-31.9	0.1663	-142.2	0.22
0.0010891	-0.115328	-0.154	0.2090	-35.8	0.1943	-141.0	0.23
0.0009425	-0.053298	-0.086	0.2329	-37.5	0.2210	-91.7	0.24
0.0011088	-0.056058	-0.095	0.2591	-39.1	0.2460	-85.7	0.24
0.0010806	0.015811	-0.022	0.2831	-38.5*	0.2711	-20.5*	0.25
Series 4. $(Ag_{0.25}Mg_{0.75})_{1-x}Pd_x$: starting amount: $n_{Ag} = 0.004947$ mol; $n_{Mg} = 0.014836$ mol; $K = 0.000003584$ kJ/ μ Vs; $T_D = 298$ K; $T_M = 1116$ K; $\Delta H_{Ag(s)}^{T_D \rightarrow T_M} = 22.7234$ kJ/mol; $\Delta H_{Ag(l)}^{T_D \rightarrow T_M} = 33.7485$ kJ/mol; $\Delta H_{Mg}^{T_D \rightarrow T_M} = 32.8525$ kJ/mol; $\Delta H_{Pd}^{T_D \rightarrow T_M} = 35.1342$ kJ/mol; $\Delta_{mix}H_{Ag_{0.25}Mg_{0.75}} = -9.7$ kJ/mol. Standard uncertainties: $u(n_{Ag}) = 0.0000009$ mol; $u(n_{Mg}) = 0.000004$ mol; $u(n_{Pd}) = 0.0000009$; $u(T_D) = 1$ K; $u(T_M) = 1$ K; $u(p) = 10$ kPa; $u(K) = 0.00000155$ kJ/ μ Vs; $u(\Delta_{mix}H_{Ag_{0.25}Mg_{0.75}}) = 0.99$ kJ/mol.							
0.0011295	-0.144834	-0.185	0.0540	-18.0	0.0270	-163.4	1.29
0.0009340	-0.118003	-0.151	0.0945	-24.1	0.0743	-161.5	1.52
0.0009613	-0.110391	-0.144	0.1326	-29.4	0.1136	-150.0	1.73
0.0009820	-0.047264	-0.082	0.1684	-31.6	0.1505	-83.3	1.81
0.0009914	0.016519	-0.018	0.2017	-31.1	0.1851	-18.5*	1.84
0.0011445	0.016637	-0.024	0.2369	-30.7	0.2193	-20.6*	1.87
Series 5. $(Ag_{0.50}Mg_{0.50})_{1-x}Pd_x$: starting amount: $n_{Ag} = 0.01735$ mol; $n_{Mg} = 0.01735$ mol; $K = 0.000003532$ kJ/ μ Vs; $T_D = 298$ K; $T_M = 1279$ K; $\Delta H_{Ag(s)}^{T_D \rightarrow T_M} = 27.8720$ kJ/mol; $\Delta H_{Ag(l)}^{T_D \rightarrow T_M} = 38.8970$ kJ/mol; $\Delta H_{Mg}^{T_D \rightarrow T_M} = 38.4448$ kJ/mol; $\Delta H_{Pd}^{T_D \rightarrow T_M} = 41.0125$ kJ/mol; $\Delta_{mix}H_{Ag_{0.50}Mg_{0.50}} = -12.9$ kJ/mol. Standard uncertainties: $u(n_{Ag}) = 0.0000009$ mol; $u(n_{Mg}) = 0.000004$ mol; $u(n_{Pd}) = 0.0000009$; $u(T_D) = 1$ K; $u(T_M) = 1$ K; $u(p) = 10$ kPa; $u(K) = 0.000000281$ kJ/ μ Vs; $u(\Delta_{mix}H_{Ag_{0.50}Mg_{0.50}}) = 0.50$ kJ/mol.							
0.0008692	-0.069701	-0.105	0.0244	-15.6	0.0122	-121.2	0.66
0.0012535	-0.099937	-0.151	0.0576	-19.2	0.0410	-120.7	0.87
0.0013390	-0.054401	-0.109	0.0907	-21.4	0.0742	-81.6	0.99
0.0011614	-0.024193	-0.072	0.1175	-22.6	0.1041	-61.8	1.04
0.0011887	0.017758	-0.031	0.1434	-22.7	0.1305	-26.1*	1.07
0.0011417	0.022060	-0.025	0.1669	-22.6	0.1552	-21.7*	1.11
0.0014245	0.027117	-0.031	0.1944	-22.6	0.1807	-22.0*	1.16
Series 6. $(Ag_{0.75}Mg_{0.25})_{1-x}Pd_x$: starting amount: $n_{Ag} = 0.016822$ mol; $n_{Mg} = 0.00561$ mol; $K = 0.000003344$ kJ/ μ Vs; $T_D = 298$ K; $T_M = 1279$ K; $\Delta H_{Ag(s)}^{T_D \rightarrow T_M} = 27.8720$ kJ/mol; $\Delta H_{Ag(l)}^{T_D \rightarrow T_M} = 38.8970$ kJ/mol; $\Delta H_{Mg}^{T_D \rightarrow T_M} = 38.4448$ kJ/mol; $\Delta H_{Pd}^{T_D \rightarrow T_M} = 41.0125$ kJ/mol; $\Delta_{mix}H_{Ag_{0.75}Mg_{0.25}} = -10.5$ kJ/mol. Standard uncertainties: $u(n_{Ag}) = 0.0000009$ mol; $u(n_{Mg}) = 0.000004$ mol; $u(n_{Pd}) = 0.0000009$; $u(T_D) = 1$ K; $u(T_M) = 1$ K; $u(p) = 10$ kPa; $u(K) = 0.000000281$ kJ/ μ Vs; $u(\Delta_{mix}H_{Ag_{0.75}Mg_{0.25}}) = 0.02$ kJ/mol.							
$u(n_{Ag}) = 0.0000009$ mol; $u(n_{Mg}) = 0.000004$ mol; $u(n_{Pd}) = 0.0000009$; $u(T_D) = 1$ K;							
$u(T_M) = 1$ K; $u(p) = 10$ kPa; $u(K) = 0.000000281$ kJ/ μ Vs; $u(\Delta_{mix}H_{Ag_{0.75}Mg_{0.25}}) = 0.02$ kJ/mol.							
0.0010449	-0.050824	-0.094	0.0445	-14.0	0.0223	-89.7	0.07
0.0009556	-0.037724	-0.077	0.0819	-16.6	0.0632	-80.5	0.11
0.0010637	0.005333	-0.038	0.1202	-17.4	0.1011	-36.0*	0.11
0.0010299	0.020932	-0.021	0.1544	-17.6	0.1373	-20.7*	0.13
0.0009171	0.021734	-0.016	0.1826	-17.6	0.1685	-17.3*	0.15
0.0010242	0.021811	-0.020	0.2120	-17.6	0.1973	-19.7*	0.17

*Liquid-solid

¹ Per mole of mixture

² Average value before and after the drop



Table 4. Values of the integral molar enthalpy of mixing near the points of sections for the experimental series

Integral molar enthalpies of mixing [kJ/mol] near the points of intersection.					
Points of intersection	Series 1	Series 2	Series 3	Series 4	Series 5
1	-18.7		-20.1		
2	-21.2			-18.0 -24.1	
3		-33.6 -33.2	-31.9		
4		-31.8 -31.1		-31.6	
5		-24.8			-22.6

Table 5. Binary and ternary interaction parameters in Eq. 4 for the Ag-Mg-Pd liquid alloys

System	Interaction parameters [J/mol]	References
Ag-Mg	${}^0L_{Ag,Mg}^{Liquid} = -53346.5$	[8]
	${}^1L_{Ag,Mg}^{Liquid} = -3694$	
	${}^2L_{Ag,Mg}^{Liquid} = -905.8$	
Ag-Pd	${}^0L_{Ag,Pd}^{Liquid} = 18982.236$	[29]
	${}^1L_{Ag,Pd}^{Liquid} = -38662.468$	
Mg-Pd	${}^0L_{Mg,Pd}^{Liquid} = -294017$	[10]
	${}^1L_{Mg,Pd}^{Liquid} = 113972$	
Ag-Mg-Pd	${}^1L_{Ag,Mg,Pd}^{Liquid} = -274732.37$	This study
	${}^2L_{Ag,Mg,Pd}^{Liquid} = 1638.8683$	
	${}^3L_{Ag,Mg,Pd}^{Liquid} = 189657.87$	

mixing enthalpies of the silver-magnesium-palladium liquid alloys and those calculated with the use of Eq. 4 using the parameters shown in Table 5 are shown in Figures 2 and 3. The solid lines present the integral mixing enthalpy data calculated with Equation 4, and the symbols show the experimental results obtained in this study.

In the obtained results, a clear abrupt change in the partial molar enthalpy of Pd or Ag was observed, corresponding to the transition of the system from the homogeneous liquid area to the liquid–solid area. Similar behavior was found in [30]. For this reason, the compositions of the tested alloys were measured after this step change for their partial molar enthalpies and are marked with asterisks in the figures.

The partial and integral mixing enthalpies of the Ag-Mg-Pd liquid alloys were calculated (using Eq. 4) and are listed in Table 6.

From Table 6, the partial enthalpy of palladium for

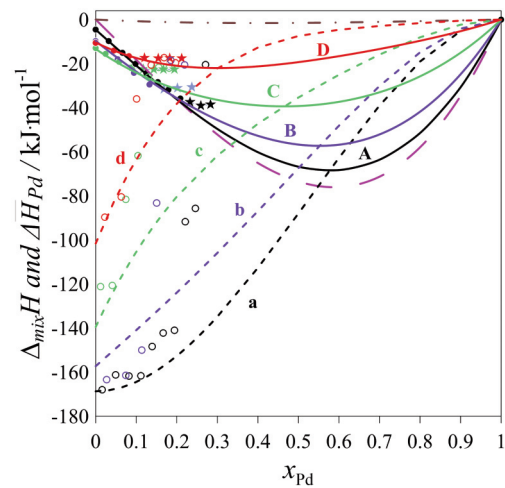


Figure 2. Comparison of the integral (solid lines and capital letters) and partial molar mixing enthalpy (dashed line and small letters) calculated with the use of Eq. 4 and the experimental data (integral molar mixing enthalpy - full symbols, and partial molar mixing enthalpy - empty symbols) for the following sections: (A/a) - $(Ag_{0.10}Mg_{0.90})_{1-x}Pd_x$ at 1116 K, (B/b) - $(Ag_{0.25}Mg_{0.75})_{1-x}Pd_x$ at 1116 K, (C/c) - $(Ag_{0.50}Mg_{0.50})_{1-x}Pd_x$ at 1279 K, and (D/d) - $(Ag_{0.75}Mg_{0.25})_{1-x}Pd_x$ at 1279 K. Purple dashed line - integral molar mixing enthalpies of the Mg-Pd [10] liquid alloys and brown dashed-dotted line - integral molar mixing enthalpies of the Ag-Pd [29] liquid alloys

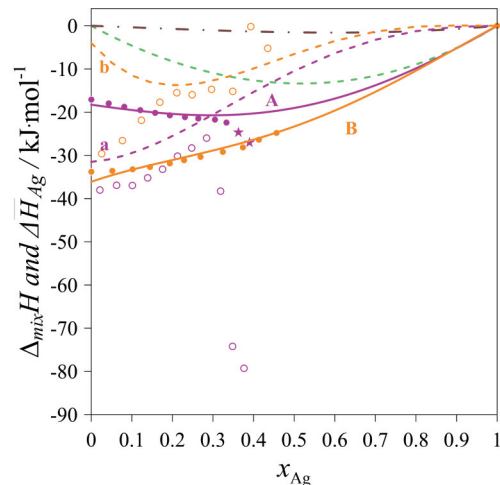


Figure 3. Comparison of the integral (solid lines and capital letters) and partial molar mixing enthalpy (dashed line and small letters) calculated with the use of Eq. 4 and the experimental data (integral molar mixing enthalpy - full symbols, and partial molar mixing enthalpy - empty symbols) for the following sections: (A/a) - $(Mg_{0.90}Pd_{0.10})_{1-x}Ag_x$ at 1116 K, (B/b) - $(Mg_{0.80}Pd_{0.20})_{1-x}Ag_x$ at 1116 K. Dashed green line - integral molar mixing enthalpies of the Ag-Mg liquid alloys [8]; brown dash-dot line - integral molar mixing enthalpies of the Ag-Pd liquid alloys [29]

Table 6. Calculated molar fractions and partial and integral functions of the Ag-Mg-Pd liquid solutions

x_{Ag}	x_{Mg}	x_{Pd}	$\Delta \bar{H}_{Ag}$	$\Delta \bar{H}_{Mg}$	$\Delta \bar{H}_{Pd}$	$\Delta_{mix} H$
			J/mol			
(Ag _{0.1} Mg _{0.9}) _{1-x} Pd _x alloys. Temperature = 1116 K						
0.1	0.9	0	-41650	-469	-168701	-4588
0.0968	0.8711	0.0321	-38375	-844	-168250	-9851
0.0934	0.8407	0.0659	-33810	-1436	-166829	-15360
0.0902	0.8119	0.0979	-28531	-2244	-164631	-20513
0.0875	0.7877	0.1248	-23447	-3152	-162181	-24775
0.0847	0.7623	0.1531	-17532	-4373	-159048	-29169
0.0821	0.7385	0.1795	-11544	-5799	-155626	-33164
0.0791	0.7119	0.2090	-4395	-7759	-151284	-37490
0.0767	0.6904	0.2329	1700	-9663	-147394	-40871
0.0741	0.6668	0.2591	8644	-12121	-142749	-44426
0.0717	0.6452	0.2831	15187	-14726	-138210	-47540
0.07	0.63	0.3	19880	-16786	-134846	-49637
0.06	0.54	0.4	48145	-33335	-112686	-60187
0.05	0.45	0.5	74827	-58928	-88000	-66776
0.04	0.36	0.6	96442	-95866	-62743	-68300
0.03	0.27	0.7	109365	-146591	-39010	-63606
0.02	0.18	0.8	109831	-213683	-19037	-51496
0.01	0.09	0.9	93939	-299863	-5195	-30724
0	0	1	57645	-407988	0	0
(Ag _{0.25} Mg _{0.75}) _{1-x} Pd _x alloys. Temperature = 1116 K						
0.25	0.75	0	-29880	-2972	-157285	-9699
0.2365	0.7095	0.054	-26220	-4519	-148521	-17428
0.2264	0.6792	0.0945	-22158	-6586	-141876	-22899
0.2168	0.6505	0.1326	-17387	-9268	-135494	-27762
0.2079	0.6237	0.1684	-12158	-12451	-129408	-32086
0.1996	0.5987	0.2017	-6706	-16021	-123624	-35866
0.1908	0.5723	0.2369	-404	-20459	-117394	-39596
0.175	0.525	0.3	12019	-30236	-105913	-45544
0.15	0.45	0.4	33509	-51106	-86958	-52755
0.125	0.375	0.5	55107	-79715	-67460	-56735
0.1	0.3	0.6	74101	-117692	-48163	-56795
0.075	0.225	0.7	87431	-167011	-30158	-52131
0.05	0.15	0.8	91692	-229997	-14882	-41821
0.025	0.075	0.9	83129	-309318	-4119	-24828
0	0	1	57645	-407988	0	0
(Ag _{0.5} Mg _{0.5}) _{1-x} Pd _x alloys. Temperature = 1279 K						
0.5	0.5	0	-14265	-12408	-139499	-13337
0.4877	0.4879	0.0244	-13090	-13811	-130161	-16298
0.4711	0.4713	0.0576	-11412	-16476	-118556	-19969
0.4546	0.4548	0.0907	-9609	-19943	-108135	-23245
0.4412	0.4413	0.1175	-8026	-23311	-100442	-25629
0.4282	0.4284	0.1434	-6376	-27011	-93599	-27723
0.4165	0.4166	0.1669	-4764	-30734	-87845	-29451
0.4027	0.4029	0.1944	-2731	-35516	-81603	-31271
0.3999	0.4001	0.2	-2297	-36542	-80397	-31618
0.3499	0.3501	0.3	6662	-57848	-61750	-36444
0.2999	0.3001	0.4	17818	-84546	-47272	-38934
0.2500	0.2501	0.5	30597	-116797	-35374	-39244
0.2000	0.2000	0.6	43837	-155345	-25052	-37341
0.1500	0.1500	0.7	55791	-201525	-15889	-32990
0.1000	0.1000	0.8	64123	-257256	-8056	-25765
0.0500	0.0500	0.9	65911	-325046	-2312	-15041
0	0	1	57645	-407988	0	0

*Table continues on the next page



*Table continued from the previous page

$(\text{Ag}_{0.75}\text{Mg}_{0.25})_{1-x}\text{Pd}_x$ alloys. Temperature = 1279 K						
0.75	0.25	0	-3895	-29880	-101627	-10391
0.7166	0.2389	0.0445	-1785	-37886	-82837	-14015
0.6886	0.2295	0.0819	-497	-45371	-69340	-16435
0.6599	0.2200	0.1202	495	-53669	-57456	-18384
0.6342	0.2114	0.1544	1198	-61564	-48344	-19721
0.6130	0.2044	0.1826	1702	-68387	-41782	-20560
0.5910	0.1970	0.2120	2203	-75781	-35781	-21211
0.525	0.175	0.3	3924	-99458	-22162	-21994
0.45	0.15	0.4	7080	-128975	-12715	-21246
0.375	0.125	0.5	12239	-161389	-7463	-19316
0.3	0.1	0.6	19635	-197340	-4613	-16612
0.225	0.075	0.7	28971	-238002	-2903	-13364
0.15	0.05	0.8	39416	-285081	-1605	-9626
0.075	0.025	0.9	49606	-340819	-524	-5272
0	0	1	57645	-407988	0	0
$(\text{Mg}_{0.90}\text{Pd}_{0.10})_{1-x}\text{Ag}_x$ alloys. Temperature $T=1116$ K						
0	0.9	0.1	-31506	23	-182763	-18256
0.0431	0.8612	0.0957	-30935	-973	-173943	-18818
0.0815	0.8267	0.0919	-30026	-1832	-166830	-19295
0.1210	0.7911	0.0879	-28771	-2731	-160169	-19720
0.1577	0.7580	0.0842	-27364	-3610	-154549	-20064
0.1935	0.7259	0.0807	-25806	-4536	-149542	-20355
0.2310	0.6921	0.0769	-24040	-5601	-144737	-20559
0.2636	0.6628	0.0736	-22417	-6621	-140886	-20666
0.3045	0.6259	0.0695	-20307	-8051	-136406	-20701
0.3332	0.6001	0.0667	-18799	-9163	-133453	-20664
0.3626	0.5737	0.0637	-17262	-10394	-130576	-20540
0.3901	0.5489	0.061	-15829	-11646	-127955	-20374
0.4	0.54	0.06	-15319	-12120	-127024	-20294
0.5	0.45	0.05	-10443	-17594	-117735	-19026
0.6	0.36	0.04	-6331	-24318	-107464	-16852
0.7	0.27	0.03	-3236	-32131	-94496	-13775
0.8	0.18	0.02	-1237	-40702	-76942	-9855
0.9	0.09	0.01	-245	-49531	-52746	-5205
1	0	0	0	-57947	-19681	0
$(\text{Mg}_{0.80}\text{Pd}_{0.20})_{1-x}\text{Ag}_x$ alloy. Temperature = 1116 K						
0	0.8	0.2	-3995	-1731	-173582	-36101
0.0520	0.7584	0.1896	-8670	-4614	-161465	-34566
0.1021	0.7184	0.1796	-11576	-6979	-150823	-33282
0.1449	0.6841	0.1710	-13023	-8803	-142524	-32281
0.1935	0.6452	0.1613	-13721	-10767	-133986	-31212
0.2287	0.6170	0.1543	-13711	-12180	-128353	-30449
0.2690	0.5848	0.1462	-13279	-13837	-122453	-29569
0.3243	0.5406	0.1352	-12127	-16264	-115207	-28295
0.3735	0.5012	0.1253	-10732	-18634	-109483	-27063
0.4130	0.4696	0.1174	-9464	-20706	-105308	-25993
0.4564	0.4349	0.1087	-8005	-23173	-101061	-24717
0.5	0.4	0.1	-6541	-25856	-97043	-23317
0.6	0.32	0.08	-3516	-32715	-88092	-19626



the measured cross-section increased with increasing content in the alloy. The same behavior was observed for the mixing partial enthalpy of silver in alloys with a constant ratio $x_{Mg}/x_{Pd} = 9/1$. In the case of the mixing partial enthalpy for silver in alloys with a constant ratio $x_{Mg}/x_{Pd} = 4/1$, the values reached a minimum of -13721 J/mol for the mole fraction of silver $x_{Ag} = 0.1935$.

Figure 4 shows a comparison of the data calculated via the Muggianu model by using only the thermodynamic properties of the binary alloys with the thermodynamic properties modified by the ternary interaction parameters listed in Table 5. For three sections ($x_{Ag}/x_{Mg}=1/9$, $x_{Ag}/x_{Mg}=1/3$, and $x_{Mg}/x_{Pd}=9/1$), the differences between the two variants were less than 1.6 kJ/mol. In the case of the next two sections ($x_{Ag}/x_{Mg}=1/1$ and $x_{Mg}/x_{Pd}=4/1$), the differences were less than 2.4 kJ/mol. For the $x_{Ag}/x_{Mg}=3/1$ sections, the maximum difference was approximately 3 kJ/mol. The differences between the experimental data and those calculated via the Muggianu model for the Ag-Mg-Pd liquid solutions were less than approximately 3 kJ/mol.

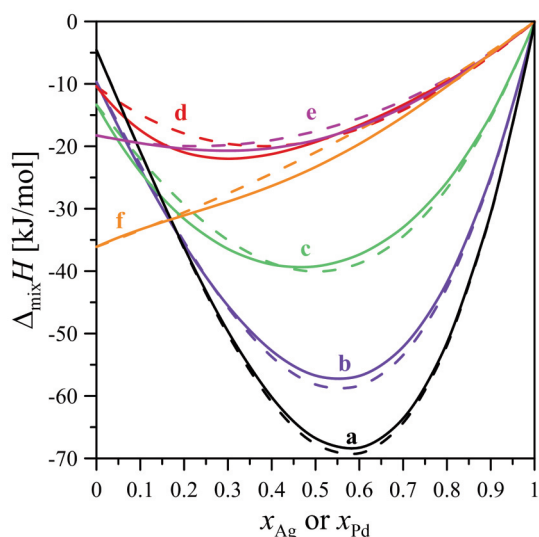


Figure 4. Comparison of the mixing enthalpies calculated with the Muggianu model (only binary systems; dashed lines) and using the same model with the ternary interaction parameter L_{ijk} shown in Table 5 (Eq. 4; continuous lines): a) $x_{Ag}/x_{Mg}=1/9$, b) $x_{Ag}/x_{Mg}=1/3$, c) $x_{Ag}/x_{Mg}=1/1$, d) $x_{Ag}/x_{Mg}=3/1$, e) $x_{Mg}/x_{Pd}=9/1$, f) $x_{Mg}/x_{Pd}=4/1$

4. Conclusion

This study provided the calorimetric results of the partial and integral molar mixing enthalpies of magnesium-palladium-silver liquid solutions. The results showed a negative deviation from Raoult's law for the entire tested concentration range.

Based on the calorimetric data for binary systems (our earlier data) and the data obtained in this study for the Ag-Mg-Pd liquid solutions, a thermodynamic description of the above ternary system was proposed in the form of the Muggianu model with the ternary interaction parameters, which were determined by using the least squares method. The calculated standard deviation was 871 J/mol. The partial mixing enthalpies for magnesium and palladium were negative for all intersections where the studies were performed, and in the case of silver, the partial mixing enthalpy had both positive and negative values. The presented modeled data for the integral enthalpies of mixing effectively described the experimental data.

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Author Contributions

A. Dębski: Conceptualization, Funding acquisition, Investigation, Methodology, Validation, Visualization, Writing – original draft. W. Gąsior: Methodology, Software, Writing – original draft, Validation. W. Gierlotka: Validation, Writing – original draft. A. Baran: Validation. M. Polański: Validation, Writing – original draft.

Data availability

No data were used for the research described in the article.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SISTEM MAGNEZIJUM-PALADIJUM-SREBRO: TERMODINAMIČKE OSOBINE TEČNE FAZE

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Apstrakt

U ovom radu je korišćena metoda drop-kalorimetrije kako bi se izmerile parcijalne i integralne entalpije mešanja Ag-Mg-Pd tečnih rastvora. Eksperimenti su izvedeni za šest odvojenih serija tečnih legura, počevši od binarnih legura sa konstantnim odnosima x_{Ag}/x_{Mg} jednakim 1/9, 1/3, 1/1 i 3/1 za $(Ag_{0.10}Mg_{0.90})_{1-x}Pd_x$ i $(Ag_{0.25}Mg_{0.75})_{1-x}Pd_x$ na 1116 K i $(Ag_{0.50}Mg_{0.50})_{1-x}Pd_x$ i $(Ag_{0.75}Mg_{0.25})_{1-x}Pd_x$ na 1279 K kao i odnosima x_{Mg}/x_{Pd} jednakim 9/1 i 8/1 za $(Mg_{0.90}Pd_{0.10})_{1-x}Ag_x$ i $(Mg_{0.80}Pd_{0.20})_{1-x}Ag_x$ na 1116 K. Zatim, koristeći termodinamičke osobine binarnih sistema u obliku Redlich-Kisterovih jednačina i promene entalpije mešanja dobijene ovim istraživanjem, određeni su ternarni parametri interakcije pomoću Muggianu modela i našeg sopstvenog softvera (TerGexHm). Na osnovu binarnih i ternarnih parametara interakcije, izračunate su parcijalne entalpije mešanja Ag, Mg i Pd za iste preseke gde su izvršena merenja. Ova istraživanja predstavljaju prvi korak u istraživanju sistema Ag-Mg-Pd pre nego što se izračuna fazni dijagram za ovaj ternarni sistem.

Ključne reči: Magnezijum-paladijum-srebro; Kalorimetrija rastvora; Termodinamičke osobine; Termodinamičko modelovanje

