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THERMODYNAMIC ANALYSIS OF DISTILLATION PROCESS OF MULTICOMPONENT CADMIUM ALLOYS

ANALIZA TERMODYNAMICZNA PROCESU DESTYLACJI WIELOSKŁADNIKOWYCH STOPÓW KADMU

Thermodynamic analysis was carried out for evaporation process of components in multicomponent cadmium alloys. Thermodynamic description was performed by binary formalism, basing on the available literature data, and for missing system Cd-Tl, optimisation procedure by CALPHAD method was applied. Partial pressures of components were then calculated, confirming the efficient rate of cadmium evaporation from the alloy.

Przeprowadzono analizę termodynamiczną procesu odparowania komponentów z wieloskładnikowych stopów kadmu. Opracowano opis termodynamiczny badanych stopów na podstawie dostępnych danych literaturowych przy pomocy tzw. formalizmu dwójkowego, a brakujące dane dla stopów Cd-Tl uzyskano, stosując metodę CALPHAD. Na podstawie tych informacji obliczono parcjalne prężności par składników rozpatrywanych stopów, co było podstawą prognozowania efektywnego odparowania z nich kadmu.

1. Introduction

Utilisation of the cadmium-bearing industrial waste is one of the main problems of the polish zinc-metallurgy industry. Methods employed so far, both hydro- and pyrometalurgical are energy consuming and environmental not friendly because cadmium is classified as a toxic metal. Moreover cadmium itself, in the form of the sponge is contaminated by other hazardous heavy metals like: lead, thallium and zinc. On the other hand cadmium is an important component in brazing and low melting alloys, used in bearings, solders, and nuclear reactor control rods. Consumption of cadmium is in batteries, as corrosion-resistant coating and plating, pigments, plastics stabilizers and synthetic products, and alloys. High purity cadmium is a strategic electronic material used for preparation of compound semiconductors such as CdTe, HgCdTe, CdZnTe, CdS, CdSe etc. The Cd based semiconductor devices are primarily used as solar cells, IR detectors, imaging devices, electro-optic modulators, fluorescence, and thermoelectric coolers in the areas of defense, military and aerospace [1]. Other areas of applications include telecommunications, electric vehicle and remote area storage systems. Therefore idea appeared to extract metallic cadmium from the waste on the way of distillation, to produce the metal of high purity for other applications [2, 3]. To do this, the knowledge on the phase equilibria involving gas phase in multicomponent quaternary system Cd-Pb-Tl-Zn is necessary. Thermodynamic analysis of the heterogeneous system, mentioned above is given below on the basis of the all available literature data, using binary formalism and relevant thermodynamic properties of components are derived in the form of vapour pressure relations. Since thermodynamic data on the alloy vapours are scarce, gas phase is assumed to be ideal.

2. Theoretical background

The method of calculation come from two fundamental conclusions formulated by Hertz [4]:

1. every substance has maximum rate of evaporation dependent only on the surface temperature and the properties of such substance
2. the maximum rate of evaporation cannot exceed the number of molecules from the vapor phase that are

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incident on the surface of condensate when equilibrium conditions are established.

From later conclusion arises that partial vapor pressure P in the Hertz-Knudsen equation for the molar flux J from a unit area of open surface in vacuum

$$J = \frac{P}{\sqrt{2\pi MRT}} \tag{1}$$

cannot exceed the equilibrium vapor pressure P_e. Here M is the molar mass, R is the gas constant and T is absolute temperature in K.

When a substance evaporates in the presence of a foreign gas, the molar vapor flux from a plane is governed by the Langmuir relation

$$J = \frac{PD}{zRT} \tag{2}$$

where D is the coefficient of vapor diffusion in the foreign gas, and z is the distance from the evaporation surface to the sink (at which partial pressure drops to zero). It is easy to conclude from relations (1) and (2) that in both cases of evaporation the molar vapor flux is proportional to the partial vapor pressure.

The vapor pressure relations dependent on the thermodynamic properties of components are derived by Calphad type thermodynamic analysis of the heterogeneous system, using binary formalism.

Gibbs energies of the pure components of the system of interest of the component i (i = Cd, Pb, Tl, Zn) in the phase φ (φ = solid or liquid) are given by the well-known relation:

$$G^{0,\phi}_{i}(T) = a + b \cdot T + c \cdot T \cdot \ln T + d \cdot T^2 + e \cdot T^3 + \\ + f \cdot T^{-1} + g \cdot T^7 + k \cdot T^{-9} \tag{3}$$

where: a through h are material property coefficients related to its heat capacity; they are taken from SGTE database [5]. Gibbs energy values are referenced to Standard Element Reference (SER), i.e. to Gibbs energy of the elements having crystal structure stable at 298.15 K and 1 bar.

Thermodynamic properties of the phases in the binary subsystems are treated as substitutional solutions, and were described by the following, general relation with Redlich-Kister excess term [6]:

$$G = (1 - x_B) \cdot G^{0,\phi} + x_B \cdot G_b^{0,\phi} + R \cdot T \cdot [x_B \cdot \ln x_B + \\ + (1 - x_B) \cdot \ln(1 - x_B)] + x_B \cdot (1 - x_B) \cdot [L^{0,\pi}_{A,B} + \\ + (1 - 2x_B) \cdot L^{1,} \\ phi_{A,B} ...] \tag{4}$$

where: $G^{0,\phi}_{A}$, $G^{0,\phi}_{B}$ are respectively the Gibbs energy of the element A or B given by (3), x_B is mole fraction of B and $L^{k,\phi}_{A,B}$ – binary interaction coefficient of order k of the phase ϕ.

3. Data reliability check

Most of the numerical values of the $L^{k,\phi}_{A,B}$ interaction parameters were taken from the most recent literature data (listed in Table 1), and those missing for Cd-Tl system were derived in this work by means of the optimization procedure using Thermo-Calc package.

TABLE 1

Numerical values of binary interaction coefficients in the system Cd-Pb-Tl-Zn. System Cd-Tl was presented separately

System	Interaction coefficients
Cd-Pb [7]	$L^{0,liquid}_{Cd,Pb} = 10806.4 - 3.1803 \cdot T$ $L^{1,liquid}_{Cd,Pb} = 1698.8 - 0.8060 \cdot T$ $L^{2,liquid}_{Cd,Pb} = 1148.4 - 0.4889 \cdot T$ $L^{3,liquid}_{Cd,Pb} = 2233.6 - 2.9207 \cdot T$ $L^{4,liquid}_{Cd,Pb} = 509.7 - 0.6144 \cdot T$ $L^{0,hcp*}_{Cd,Pb}$ * $= 100 \cdot T$ $L^{0,fcc}_{Cd,Pb} = 14232.3 - 1.4130 \cdot T$
Cd-Zn [8]	$L^{0,liquid}_{Cd,Zn} = 8376.5 - 0.479 \cdot T$ $L^{1,liquid}_{Cd,Zn} = -58.2 - 0.412 \cdot T$ $L^{2,liquid}_{Cd,Zn} = 567.5$ $L^{0,hcp}_{Cd,Zn} = 17845.8 - 0.639 \cdot T$ $L^{1,hcp}_{Cd,Zn} = -7167.4 + 7.955 \cdot T$ $L^{0,fcc}_{Cd,Zn}$ * $= 100 \cdot T$
Pb-T1 [9]	$L^{0,liquid}_{Pb,Tl} = -6453.4 + 27.2331 \cdot T - 3.3949 \cdot T \cdot \ln(T)$ $L^{1,liquid}_{Pb,Tl} = 313 + 0.5929 \cdot T$ $L^{2,liquid}_{Pb,TL} = 538.29 + 0.8799 \cdot T$
Pb-Zn [10]	$L^{0,liquid}_{Pb,Zn} = 32263.4 - 13.1018 \cdot T$ $L^{1,liquid}_{Pb,Zn} = -14909.2 + 10.9296 \cdot T$ $L^{2,liquid}_{Pb,Zn} = 2829.4$ $L^{0,fcc}_{Pb,Zn} = 31590.7 - 7.0202 \cdot T$ $L^{0,hcp*}_{Pb,Zn} = 500 \cdot T$
Tl-Zn [11]	$L^{0,liquid}_{Tl,Zn} = 28072.8 - 12.1 \cdot T$ $L^{1,liquid}_{Tl,Zn} = 14718.6 - 7.1 \cdot T$ $L^{0,hcp}_{Tl,Zn} = 26000+29 \cdot T$

* Arbitrary chosen parameters to ensure lack of solubility

TABLE 2

The comparison of experimental and calculated invariant reactions in Cd-Tl system

Type of reaction	Temperature °C	Phase compositions At. % of Tl			Reference
(α-Tl) = (β-Tl)	234	–	–	100	[19]
	230	–	–	100	[15]
	234	–	–	100	this work
Eutectic L = (Cd) + (β-Tl)	203.5	71	0	94.4	[19]
	203.5	73	0	95.5	[15]
	203.4	71.7	0.24	95.0	this work
Eutectoid (β-Tl) = (Cd) + (α-Tl)	158	95.8	0	98.0	[19]
	165	97	0	97.8	[15]
	165	96.2	0.15	97.2	this work

4. Thermodynamic description of Cd-Tl system

The Cd-Tl phase diagram was proposed by Śliwa and Wojtaszek [12] on the basis of DTA analysis of 25 alloys. The liquidus boundaries are in good agreement with those determined by Kurnakow et al. [13]. Also recent data reviewed by Vol and Kagan [14] are in good agreement with [12]. So in the most recent review [15] the phase diagram of [12] (Table 2), quoted in Elliott [16], was redrawn.

The thermodynamic data of enthalpy of mixing of liquid alloys from direct reaction calorimetry [17, 18] agree well (±210 J/mol at.) and were tabulated by Hultgren [19] at 750 K.

The thallium activity data in Cd-Tl melt obtained from e.m.f studies by Sugino et at. [20] and Terpiłowski and Stróżecka [21] also agree well within ±3%.

All cited above experimental data of Cd-Tl system were utilized in the optimization procedure, using Parrot module of ThermoCalc software version Q (ThermoCalc AB, Sweden). In that procedure one liquid and three solid phases were described by substitutional solution model (4). The optimized binary interaction coefficients are shown in Table 3.

To check the reliability of the parameters for Cd-Tl system, phase diagram calcultions were carried out, and the results of calculations are presented graphically in Fig. 1. Additionally, the comparison of experimental and calculated enthalpies of mixing of liquid Cd-Tl solutions is presented in the Fig. 2.

5. Quaternary system description

Switching to quaternary system, the composition dependence of the Gibbs energy of the phases can be approximated from the Gibbs energies of binary subsystems using the Fitzner-Muggianu extrapolation formula [22, 23]:

$$G = \sum_i x_i^0 G_i + RT \sum_i x_i \ln(x_i + \sum_i \sum_{i \neq j} x_i x_j L_{i,j} + \\ + \sum_i \sum_{i \neq j} \sum_{k \neq j} X_i x_j x_k L_{i,j,k}) \tag{5}$$

where ${}^0G_i$ are the Gibbs energy of the pure components and $L_{i,j,k}$ are the ternary interaction parameters. In first approximation the $L_{i,j,k}$ parameters of equation (5) were not taken into account.

The gas phase in the system under interest was assumed, as mentioned before, to be ideal mixture of the species Cd, Pb, Pb_2, Tl and Zn, and its molar Gibbs energy is described as below:

$$G^{gas} - H^{SER} = \sum y_i \cdot [G_i^{gas} - H_i^{SER} + RT \cdot \\ \cdot \ln(y_i)] + RT \cdot \ln\left(\frac{P}{P_0}\right) \tag{6}$$

TABLE 3

Numerical values of binary interaction coefficients in the system Cd-Tl

Cd-Tl [this work]	$L_{Cd.Tl}^{0.liquid} = 9241.4 - 4.2753 \cdot T$
	$L_{Cd.Tl}^{1.liquid} = 2261.9 - 1.5864 \cdot T$
	$L_{Cd.Tl}^{2.liquid} = 290.5$
	$L_{Cd.Tl}^{0.hcp} = 13611.8 + 15.8530 \cdot T$
	$L_{Cd.Tl}^{1.hcp} = 7674.7$
	$L_{Cd.Tl}^{0.bcc} = 22534.1 - 8.3946 \cdot T$
	$L_{Cd.Tl}^{1.bcc} = 11674.0 - 9.0439 \cdot T$

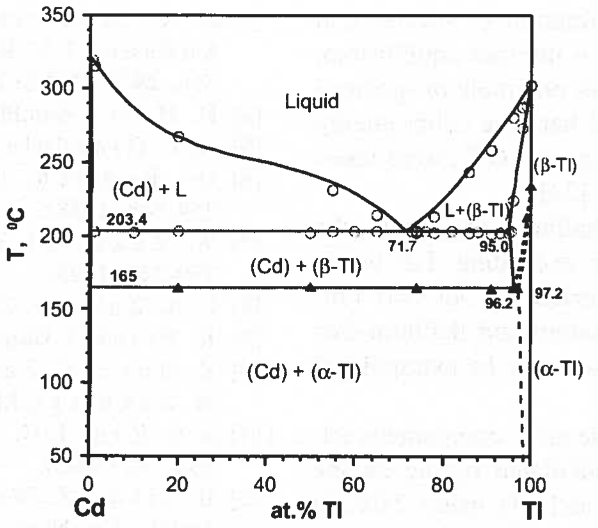

Fig. 1. Optimised phase diagram of Cd-Tl system. (Cd) and (α-Tl) are hcp solid solution of cadmium and thalium respectively. (β-Tl) denotes bcc solid solution of Tl. The experimental data from [12,14] were superimposed. The dashed line was used to point out the lack of data of α-Tl solubility limit

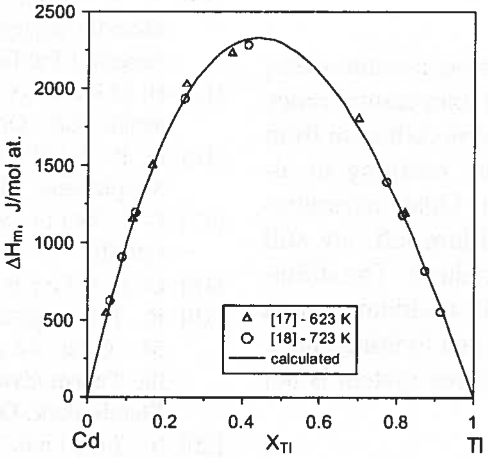

Fig. 2. The enthalpy of mixing of liquid Cd-Tl alloys calculated from assessed parameters. The experimental data are superimposed

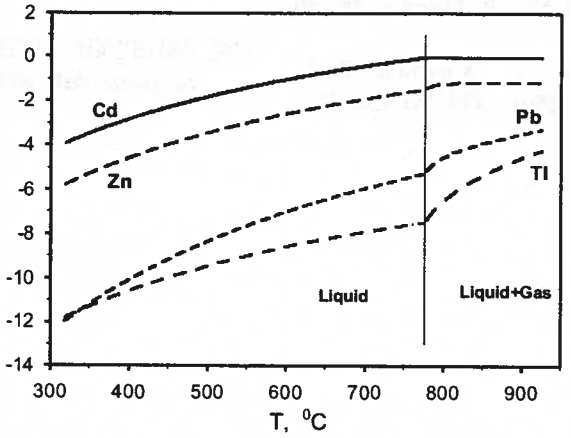

Fig. 3. Partial pressures of components of quaternary Cd-Pb-Tl-Zn alloy of 60 wt.% Cd, 20 wt.% Zn and 2 wt.% Tl

where: $y_i = (n_i/n)$ is the mole fraction of species i, n is the number of moles in gas in internal equilibrium, $G_i^{gas} - H_i^{SER}$ is the Gibbs energy of one mole of species i and P_0 is a standard pressure of 1 bar. The Gibbs energy functions, of the individual gas species $G_{\mathrm{i}}^{\mathrm{gas}}$, were taken from SGTE Substance Database [24].

Taking into account the thallium content in the cadmium-bearing materials not exceeding 1.2 wt.%, thermodynamic analysis was carried out for two limiting cases: 2 wt.% Tl in the system and thallium-free system. All the intermediate cases may be extrapolated from those defined above.

Vapour pressure values of the alloy components under considerations were then calculated basing on the above mentioned relations (6) and (7) using TCC Q software (ThermoCalc AB), and results are presented in Figure 3.

6. Conclusions

Looking at the graph presented above, it seems clear, that distillation process, carried out at temperature range 750-800 °C, is the optimal way to remove cadmium from the cadmium-bearing industrial waste, resulting in almost pure metallic cadmium product. Other hazardous waste components, like lead and thallium left, are still the challenge of other utilisation procedures. The difference in component partial pressures for thallium content in the cadmium-bearing materials for two limiting cases: 2 wt.% Tl in the system and thallium-free system is not distinguishable.

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