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THERMAL ANALYSIS AND PREDICTION OF PHASE EQUILIBRIA IN TERNARY Pb-Zn-Ag SYSTEM

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Abstract

Ternary Pb-Zn-Ag system is typical for some physicochemical processes going on in refining phase in the extractive metallurgy of lead. Therefore, investigation of mentioned system is important from both theoretical and practical research of the phenomena occurring during the lead desilverizing process. The results of experimental investigation using differential thermal analysis (DTA) and thermodynamic calculation of phase equilibria in Pb-Zn-Ag system according to CALPHAD method, in the sections with Zn:Ag mass ratio equal to 90:10, 70:30 and 50:50, are presented in this paper.

Keywords Pb-Zn-Ag system, thermal analysis, phase equilibria, thermodynamics

1. Introduction

One of the most important phases in lead refining process is the phase of desilverizing. Although presents a technique with a long history, dating to ancient times [1], the beginning of modern desilverizing process in extractive metallurgy of lead is connected to 1842 when Karsten found out how to separate silver from lead by zinc addition [2]. Ten years later, Parkes used that fact and improved well known technology based on metal zinc addition to the lead melt, while silver foam stands on the surface due to the limited solubility of zinc in the lead (about 0.6% to 673K) and the selective reaction between zinc and silver. From the moment of invention, Parkes procedure for lead

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desilverizing underwent relatively few changes and, up to now, retained primacy in lead refining process just with certain modifications.

Lead desilverizing process binds to ternary system Pb-Zn-Ag, which was the reason for numerous investigations, both from thermodynamic point of view and in terms of testing and determining the phase diagram, bearing in mind the theoretical, and practical importance of knowledge processes the above system going.

Thermodynamics of Pb-Zn-Ag system was investigated by numerous scientists [3-7], but phase diagram of this system is not fully explored, although there are some references in this field [2, 8-11]. Therefore, a contribution to better understanding of Pb-Zn-Ag system important in lead metallurgy is presented in this paper including prediction of phase equilibria and thermal analysis.

2. Experimental

For the experimental research in this paper, samples were prepared from three vertical sections from lead corner with mass ratio of the two other components equal to Zn: Ag = 90:10 (section A); 70:30 (section C) and 50:50 (section E). Data on the composition of the investigated alloys are given in Table 1.

All samples were prepared from Pb, Zn and Ag of 99.99 % purity. The samples, having masses approximately 5 g, were prepared by induction melting under argon atmosphere. The alloys were melted and cooled repeatedly to improve homogeneity.

Table 1. Composition of the investigated alloys

Alloy	%wt Pb	%wt Zn	%wt Ag	xPb	xZn	xAg
A1	98	1.8	0.2	0.941	0.055	0.004
A2	85	13.5	1.5	0.651	0.327	0.022
A3	66	31	3	0.388	0.578	0.034
A4	42.5	52	5.5	0.195	0.756	0.048
A5	25	67.5	7.5	0.099	0.844	0.057
C1	98	1.4	0.6	0.946	0.043	0.011
C2	85.5	10	4.5	0.679	0.252	0.069
C3	69	22	9	0.442	0.447	0.111
C4	59	35	15	0.264	0.585	0.152
C5	27.5	51	21.5	0.034	0.769	0.197
E1	98	1	1	0.951	0.031	0.019
E2	90.5	5	4.5	0.787	0.138	0.075
E3	78.5	11	10.5	0.588	0.261	0.151
E4	62.5	19	18.5	0.395	0.38	0.225
E5	38.5	31	30.5	0.197	0.503	0.299

The DTA measurements were carried out with the Derivatograph (MOM Budapest) apparatus under following conditions: argon atmosphere, sample masses about 2 g, heating rate 10 K/min and alumina as the reference material. The phase transition temperatures were taken from the peak maximum. The accuracy of the given temperatures is ±2 K for DTA results.

3. Thermodynamic models

The pure solid elements in their stable form at 298.15 K and under the pressure of 1 bar were chosen as the reference state for the systems (SER). The Version 4.4 of the SGTE Unary Database (Scientific Group Thermodata Europe) of phase stabilities for stable and metastable states of pure elements [12] was used.

Thermodynamic data for binary systems

Pb-Zn, Zn-Ag and Ag-Pb, originally given in Refs. [13-15] were taken from the COST 531 Thermodynamic Database for Lead Free Solders [16]. The phases from these constitutive binaries considered for thermodynamic binary-based prediction, their crystal structures and thermodynamic descriptions are listed in Table 2, while optimized thermodynamic parameters used for calculation are shown in Table 3.

4. Theoretical Fundamentals

For calculation of the Pb-Zn-Ag system phase diagram presented in this paper, CALPHAD method [17-19] was applied, using the optimized thermodynamic parameters of constituent binary systems. Basic mathematical method used for calculation of phase equilibrium is limited by Gibbs energy minimization for a given temperature, pressure and overall composition. This approach is common to all currently available software packages for modeling thermodynamic properties and phase diagram of multi-component systems.

Molar Gibbs energy of the phase can be viewed as the sum of different contributions as follows:

$$G_m^{\phi} = G_{ref}^{\phi} + G_{id}^{\phi} + G_E^{\phi} + G_{mag}^{\phi} + G_P^{\phi}. \quad \text{... (1)}$$

where the sum of known molar Gibbs energies of i constituents of the system (elements, types, compounds, etc.) of the phase ϕ , is relative to the chosen reference state (usually state a stable element reference)

$$G_{ref}^{\phi} = \sum_{i=1}^{n} x_i^0 G_i^{\phi} \quad \text{... (2)}$$

and where temperature dependance is given as:

$$G(T) = a + bT + cT\ln(T) + \sum_i d_i T^n \quad \text{... (3)}$$

Also, the contribution of the Gibbs energy of random mixing of „n“ crystal lattive constituents, G_{id}^{ϕ} , should be taken into consideration:

$$G_{id}^{\phi} = RT\sum_{i=1}^{n} x_i \ln(x_i), i = 1,...,n \quad \text{... (4)}$$

The G_E^{ϕ} presents Gibbs excess energy, which describes the influence of mixing on thermodynamic characteristics of the solution under non-ideal conditions [18]:

$$G_E^{\phi} = \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} x_i x_j L_{ij} + \sum_{i=1}^{n-2}\sum_{j=i+1}^{n-1}\sum_{k=j+1}^{n} x_i x_j x_k L_{ijk} \quad \text{... (5)}$$

where the first term in Eq.(5) is usually presented using Redlich-Kister-Muggianu

Table 2. Phases, Crystal Structures and Model Descriptions

Binary system	Phase	Prototype	Pearson symbol	COST 531 TD Base title
Pb-Zn,Pb-Ag, Ag-Zn	Liquid			LIQUID
Ag-Pb, Pb-Zn	(Ag), (Pb)	Cu	cF4	FCC_A1
Ag-Zn Pb-Zn	(Zn)	Mg	hP2	HCP_ZN
Ag-Zn	ε	Mg	hP2	HCP_A3
Ag-Zn	β	W	cI2	BCC_A2
Ag-Zn	ζ	AgZn(LT)	hP9	AGZN_ZETA
Ag-Zn	γ	Cu5Zn8	Cl52	AGZN_BRASS

Table 3. Optimized thermodynamic parameters [16] for constitutive binaries used in this study

LIQUID **CONSTITUENTS: PB,ZN,AG**
L(LIQUID,PB,ZN;0) = +35772.386-17.5434914*T
L(LIQUID,PB,ZN;1) = -15106.26+10.7424716*T
L(LIQUID,PB,ZN;2) = +2518.964
L(LIQUID,ZN,AG;0) =-27600+6.07*T
L(LIQUID,ZN,AG;1) = -5500
L(LIQUID,AG,PB;0) =+14665.80-7.92409*T
L(LIQUID,AG,PB;1) = -1350.24-0.11456*T
L(LIQUID,AG,PB;2) = -2670.89+0.69284*T
FCC_A1 **2 SUBLATTICES, SITES 1:1** **CONSTITUENTS: PB,ZN,AG: VA**
L(FCC_A1,PB,ZN:VA;0) = +30000
L(FCC_A1,AG,ZN:VA;0) = -24620+0.91*T
L(FCC_A1,AG,PB:VA;0) = +38965.00-20.57122*T
L(FCC_A1,AG,PB:VA;1) = -11846.97+15.77593*T
BCC_A2 **2 SUBLATTICES, SITES 1:1** **CONSTITUENTS: PB,ZN,AG: VA**
L(BCC_A2,PB,ZN;0) = +30000
L(BCC_A2,AG,ZN;0) = -30740+2.37*T
L(BCC_A2,AG,ZN;1) = -1880
L(BCC_A2,AG,PB;0) = +38965.00-20.57122*T
L(BCC_A2,AG,PB;1) = -11846.97+15.77593*T
HCP_A3 **2 SUBLATTICES, SITES 1:1** **CONSTITUENTS: PB,ZN,AG: VA**
L(HCP_A3,PB,ZN;0) = +30000
L(HCP_A3,AG,ZN;0) = -21360-2.5*T
L(HCP_A3,AG,ZN;1) = +37766.12-26.6016*T
L(HCP_A3,AG,PB;0) = +38965.00-20.57122*T
L(HCP_A3,AG,PB;1) = -11846.97+15.77593*T
HCP_ZN **2 SUBLATTICES, SITES 1:1** **CONSTITUENTS: PB,ZN,AG: VA**
L(HCP_ZN,PB,ZN:VA;0) = +30000
L(HCP_ZN,AG,ZN:VA;0) = 18700+1.237*T
L(HCP_ZN,AG,PB:VA;0) = +38965.00-20.57122*T
L(HCP_ZN,AG,PB:VA;1) = -11846.97+15.77593*T
AGZN_ZETA
2 SUBLATTICES, SITES 1:1
CONSTITUENTS: ZN,AG
L(ZETA_AGZN,ZN:AG;0) = 2*GBCCAG+GBCCZN-27200
L(ZETA_AGZN,ZN:AG,ZN;0) = -32070

Table continue on the next page

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AGZN_BRASS **2 SUBLATTICES, SITES 1:1** **CONSTITUENTS: ZN,AG**
L(GAMMA_AGZN,AG:AG:AG:ZN;0) = 7*GHSERAG+6*GHSERZN-49154.8
-10.0864*T*LN(T)
L(GAMMA_AGZN,AG:AG:AG:ZN;0) = 5*GHSERAG+8*GHSERZN-82103.6
-8.0032*T*LN(T)
L(GAMMA_AGZN,AG:AG:AG:ZN;0) = 5*GHSERAG+8*GHSERZN-12557.37
-18.7649*T*LN(T)
L(GAMMA_AGZN,ZN:ZN:AG:ZN;0) = 3*GHSERAG+10*GHSERZN-60084.83
-3.8147*T*LN(T)
L(GAMMA_AGZN,AG,ZN:AG:AG:ZN;0) = 0
L(GAMMA_AGZN,AG,ZN:ZN:AG:ZN;0) = 0
L(GAMMA_AGZN,AG:AG,ZN:AG:ZN;0) = 0
L(GAMMA_AGZN,ZN:AG,ZN:AG:ZN;0) = 0

formalism [20, 21], while interaction parameters, showing mutual interactions between constituents *i,j* and *k*, are denoted by *L*. The terms G_E^{ϕ} and G_{mag}^{ϕ} in Eq.(1) refers to the contribution of magnetic energy and pressure, respectivelly.

For the construction of phase diagrams, thermodynamic software package PANDAT [22] was used.

5. Results and Discussion

Three vertical sections from lead corner in the Pb-Zn-Ag ternary system were experimentally investigated by differential thermal analysis. The analysis of DTA measurements was performed on curves obtained during the heating of samples. The results are shown in Table 4.

The experimental transformation temperatures were compared with CALPHAD-type calculations results based on binary thermodynamic parameter values from COST531 database [16]. Mutual comparison between experimental DTA results and calculated vertical sections is presented in Fig. 1.

Table 4. DTA results for the investigated alloys of the Pb-Zn-Ag ternary system

Sample composition, xPb	Transformation temperatures [K]
Section A	
0.941	592, 697, 770
0.651	591, 699, 769
0.388	591, 698, 768
0.195	591, 699, 768
0.099	591, 699, 768
Section C	
0.946	591, 815, 845
0.679	590, 812, 845
0.442	591, 810, 845
0.264	591, 810, 845
0.034	591, 810, 845
Section E	
0.951	591, 890
0.787	591, 889
0.588	591, 891
0.395	592, 890
0.197	591, 890

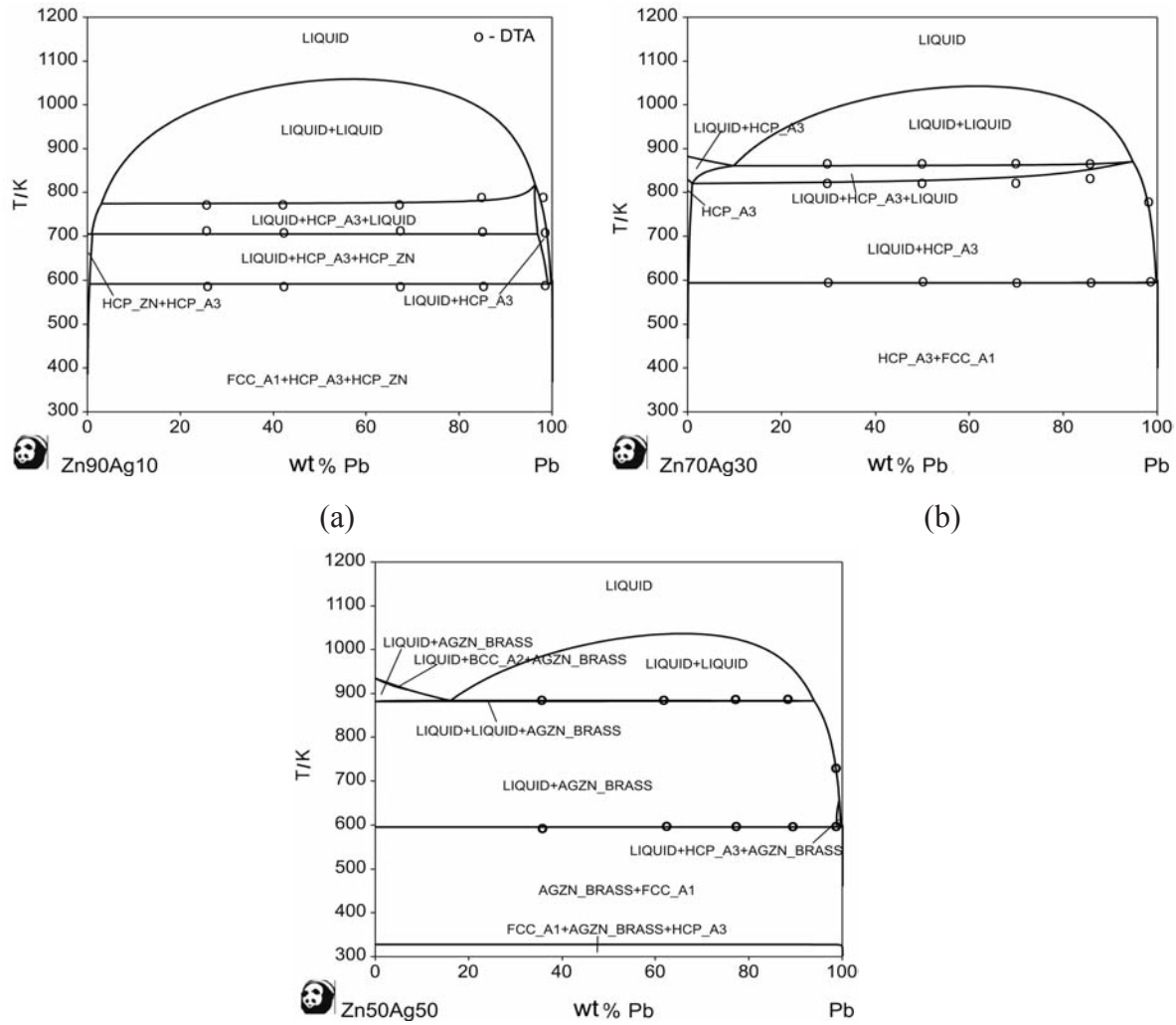


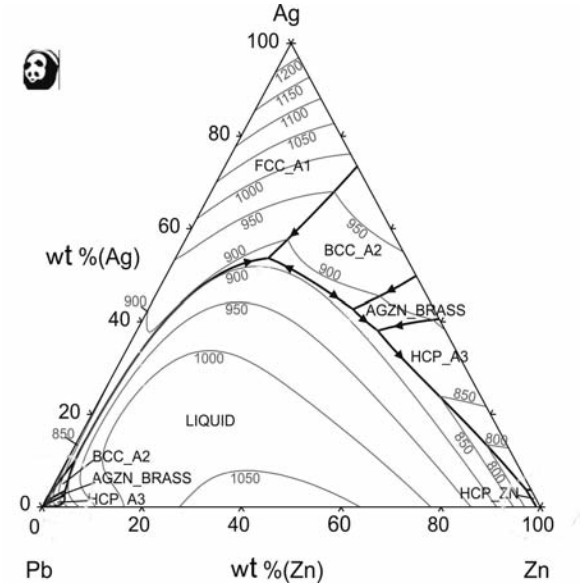
Fig. 1. Calculated vertical sections of the Pb-Zn-Ag ternary system compared with DTA results from the present study (ratio given in wt%): a) Section A - Zn:Ag=90:10, b) Section C - Zn:Ag=70:30, c) Section E - Zn:Ag=50:50

All calculated vertical sections show liquid miscibility gap existence, indicating to demixing tendencies between Zn-Ag rich phases (HCP_A3, AGZN_BRASS, BCC_A2) and Pb-based phases (FCC_A1, HCP_ZN). Good agreement between DTA results from this work and phase diagrams calculated using PANDAT thermodynamic software can be also noticed in Fig.1.

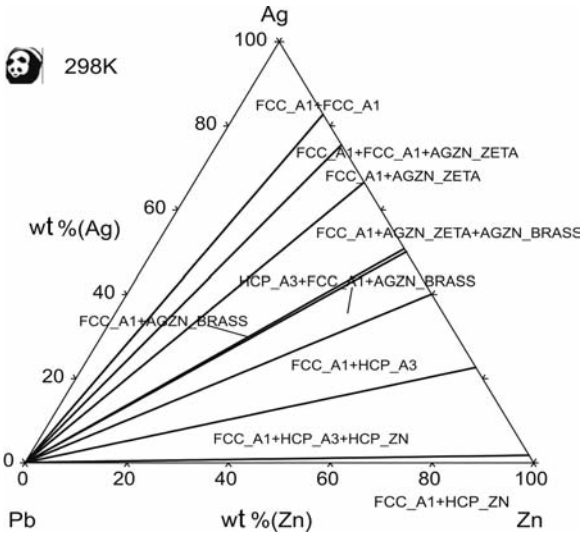
The calculation of Pb-Zn-Ag system liquidus projection and its phase diagram at 298K was also done and presented in Fig.2.

6. Conclusions

Phase transition temperatures in the ternary system Pb-Zn-Ag were investigated experimentally by DTA. Three characteristic



(a)



(b)

Fig. 2. Calculated liquidus projection (a) and phase diagram of the Pb-Zn-Ag ternary system at 298K (b)

vertical sections with mass ratios Zn:Ag = 90:10, 70:30 and 50:50 were calculated using optimized thermodynamic parameters for the constitutive binary systems from the literature and compared with thermal analysis results. Thermodynamic calculation results indicate the existence of the miscibility gap in the liquid phase, which is in the agreement with available literature [8-11]. Also, joint combination of CALPHAD method and PANDAT software in such investigations was confirmed as in [23, 24].

The results presented in this paper could be useful in further thermodynamic description of mentioned ternary system, which also has important technological role in lead desilverizing process.

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