

First-Principle Calculation Assisted Thermodynamic Assessment of the Pt-Pb System

Z.H. Long, X.M. Tao, H.S. Liu, and Z.P. Jin

(Submitted November 9, 2008)

Thermodynamic assessment of the Pt-Pb binary system has been performed by combining first-principle calculations with the CALPHAD method. The formation enthalpies of the Pt₃Pb and PtPb₄ were calculated by using the projector-augmented-wave (PAW) method within the generalized gradient approximation (GGA). The CALPHAD assessment of the Pt-Pb system was then performed. The solution phases (liquid and fcc) were treated as substitutional solutions, the excess Gibbs energies of which were modeled using the Redlich-Kister polynomial. The three intermetallic compounds, Pt₃Pb, PtPb, and PtPb₄, were described as stoichiometric phases. Thermodynamic parameters of all the phases were optimized, which reproduces the most experimental data.

Keywords CALPHAD, first principles, thermodynamic assessment

1. Introduction

Platinum was shown to be the only active and stable pure metal catalyst for dissociative chemisorption of ethanol in acidic media.^[1] However, Pt is prone to be poisoned by the intermediates such as carbon monoxide and thus becoming inactive for ethanol oxidation in the potential region of fuel cells of interest. Fortunately, many studies have shown that addition of other metals such as Sn,^[2,3] Mo,^[4] and Pb^[5] into Pt can mitigate poisoning and increase the catalytic activity of Pt. In order to better understand the role of Pb in Pt-Pb catalysts, study of the Pt-Pb phase diagram is necessary.

The phase diagram of the Pt-Pb binary system has been established by Hansen and Anderko^[6] based on the data reported by Doerinckel.^[7] The thermodynamic properties of this system have been investigated.^[8,9] Thermodynamic assessment of the Pt-Pb system has not been reported. This study calculates the formation enthalpies of the intermetallic compounds using the first principles based on the density functional theory (DFT) and then uses the data to evaluate the Pt-Pb binary phase diagram by means of the CALPHAD technique^[10] so as to obtain a consistent and reliable description of the phase relations.

2. Evaluation of Experimental Data

2.1 Phase Diagram Data

The phase diagram of the Pt-Pb system reported by Hansen and Anderko^[6] exhibits three intermediate compounds, Pt₃Pb, PtPb, and PtPb₄. These compounds decompose peritectically at 1188, 1068, and 633 K, respectively. Later, Amzil and Castanet^[8] reported some liquidus data based on calorimetry. Subsequently, Lbibb et al.^[9] calculated most of the liquidus values, and the results were in good agreement with the experimental phase diagram reported by Hansen and Anderko.^[6] All the phase relations mentioned above are adopted in the present assessment.

2.2 Thermodynamic Data

Enthalpies of mixing of the liquid Pt-Pb alloys at 923, 1023, 1123, 1239, and 1316 K were measured using direct reaction calorimetry by Amzil and Castanet.^[8] In light of these data, it was known that enthalpy of mixing of the liquid alloys is temperature dependent. This indicates the obvious tendency of formation of associates in the Pt-Pb liquid. So, the temperature dependence of mixing enthalpy was taken into account for the liquid.

Formation enthalpy of the PtPb compound was determined with reaction calorimetry at room temperature by Lbibb et al.^[9] No experimental thermodynamic data were reported for Pt₃Pb and PtPb₄. First-principle calculations were utilized to determine the formation enthalpies of the compounds Pt₃Pb and PtPb₄.

3. First-Principle Calculations

The first-principle calculations were carried using the scalar relativistic all-electron Blöchl's projector-augmented-wave (PAW)^[11,12] method within the generalized gradient approximation (GGA), as implemented in the highly

Z.H. Long, X.M. Tao, H.S. Liu, and Z.P. Jin, School of Materials Science and Engineering, Central South University, Changsha, Hunan 410083, People's Republic of China. Contact e-mail: jin@mail.csu.edu.cn.

efficient Vienna ab initio simulation package (VASP).^[13,14] The Perdew-Wang parameterization (PW91)^[15,16] was employed in the GGA exchange-correlation function. For the two intermetallic compounds, i.e., Pt₃Pb and PtPb₄, the plane-wave energy cutoff was 400 eV. Brillouin zone integrations were performed using Monkhorst-Pack K-point meshes and reciprocal space (k-point) meshes are increased to achieve convergence to a precision of 0.3 kJ/mol of atom. The k-point meshes for Pt₃Pb and PtPb₄ were 15×15×15 and 11×11×11, respectively. The total energy was converged numerically to less than 1×10⁻⁶ eV/unit cell with respect to electronic, ionic, and unit cell degrees of freedom. The latter two relaxed using Hellmann-Feynman forces with a preconditioned conjugated gradient algorithm. After structural optimization, the total forces on each ion were less than 0.01 eV/Å. In order to avoid wrap-around errors, all the calculations are performed using the “high” setting within VASP.

The formation enthalpies for the intermetallic compounds were calculated by the following equation

$$\Delta H(\text{Pt}_x\text{Pb}_y) = E_{\text{total}}(\text{Pt}_x\text{Pb}_y) - xE_{\text{total}}(\text{Pt}) - yE_{\text{total}}(\text{Pb}) \quad (\text{Eq 1})$$

where $E_{\text{total}}(\text{Pt}_x\text{Pb}_y)$, $E_{\text{total}}(\text{Pt})$, and $E_{\text{total}}(\text{Pb})$ are the calculated total energies (per atom at $T = 0$ K) of the intermetallic compound, pure Pt, and pure Pb, respectively.

4. Thermodynamic Modeling

4.1 Solution Phases

A substitutional solution model based on random mixing of the constituent atoms is employed to describe liquid, fcc (Pt), and fcc (Pb). The molar Gibbs energy of a solution phase Φ ($\Phi = \text{liquid, fcc (Pt), fcc (Pb)}$) can be represented as a sum of the weighted Gibbs energy for the pure components, the ideal entropy term describing a random mixing of the components, and the excess Gibbs energy describing the degree of deviation from ideal mixing, i.e.,

$$G_{\text{m}}^{\Phi} = \sum_{i=\text{Pt,Pb}} x_i^0 G_i^{\Phi} + RT \sum_{i=\text{Pt,Pb}} x_i \ln x_i + {}^E G_{\text{m}}^{\Phi} \quad (\text{Eq 2})$$

where G_{m}^{Φ} is the molar Gibbs energy of a solution phase Φ , ${}^0 G_i^{\Phi}$ the Gibbs energy of pure element i ($i = \text{Pt, Pb}$) in the structural state of Φ , R the gas constant, and T the temperature. And the excess Gibbs energy, ${}^E G_{\text{m}}^{\Phi}$, can be expressed by the Redlich-Kister polynomial functions as follows:

$${}^E G_{\text{m}}^{\Phi} = x_{\text{Pt}} x_{\text{Pb}} \sum_{j=0}^n {}^{(j)} L^{\Phi} (x_{\text{Pt}} - x_{\text{Pb}})^j \quad (\text{Eq 3})$$

where x_{Pt} and x_{Pb} are the mole fractions of component Pb and Pt, respectively. ${}^{(j)} L^{\Phi}$ is the interaction parameter between Pt and Pb, which is formulated as

$${}^{(j)} L^{\Phi} = A_j + B_j T + C_j T \ln T \quad (\text{Eq 4})$$

where A_j , B_j , and C_j are model parameters to be optimized, and when $j = 0$, ${}^{(j)} L^{\Phi}$ means the nearest-neighbor interaction between atomic Pt and Pb. In order to model the temperature dependence of the mixing enthalpy of the liquid in this system, at least C_0 value should be of non-zero.

4.2 Intermetallic Compounds

The intermetallic compounds, Pt₃Pb, PtPb, and PtPb₄ are all treated as stoichiometric compounds since there are no experimental data to indicate any appreciable homogeneity range. Because of lack of heat capacity data of these compounds, the Neumann-Kopp rule is adopted to cope with the formation enthalpy of these compounds. Thus, the Gibbs energy per mole of molecules Pt_mPb_n is calculated as

$$G^{\text{Pt}_m\text{Pb}_n} = m {}^0 G_{\text{Pt}}^{\text{fcc}} + n {}^0 G_{\text{Pb}}^{\text{fcc}} + A + BT \quad (\text{Eq 5})$$

where A and B are the parameters to be optimized.

5. Results and Discussion

Crystal structures, calculated lattice constants, and formation enthalpies of the intermetallic compounds are listed in Table 1. The lattice constants of pure elements were previously calculated with first principles proposed

Table 1 Crystal structures and formation enthalpies of the compounds in Pt-Pb by the first-principle calculation

Phase	Person symbol	Space group	Prototype	Lattice, Å		ΔH , kJ/g atom	Reference
				a	c		
Pt	cF4	$Fm\bar{3}m$	Cu	3.9854	This work
				3.985	[17]
				3.97	[18]
Pt ₃ Pb	cP4	$Pm\bar{3}m$	AuCu ₃	4.1371	...	-11.64176	This work
				4.058	[20]
PtPb ₄	tP10	$P4/nbm$	PtPb ₄	6.8148	6.0913	-14.05445	This work
Pb	cF4	$Fm\bar{3}m$	Cu	6.65	5.96	...	This work
				5.0248	[17]
				5.049	[19]
				4.9506	

Section I: Basic and Applied Research

by Wang et al.^[17] It is clear that the results obtained in the present calculation are in good agreement with Wang et al.^[17] The lattice constants of pure elements obtained from experiments^[18,19] are also listed in Table 1. The calculated values agree reasonably well with the experimental data. In addition, the calculated lattice parameters of the two intermetallic compounds are in good agreement with the experimental data from literature.^[20,21] In view of these, it is reasonable to accept the formation enthalpies of these compounds obtained by the first-principle calculations.

With the lattice stabilities for elements Pt and Pb adopted from Dinsdale,^[22] thermodynamic parameters for all the phases occurring in the Pt-Pb binary system have been optimized using the PARROT module of the Thermo-Calc program developed by Sundman et al.,^[23] and listed in Table 2.

Table 2 Thermodynamic parameters of the Pt-Pb system obtained in this study

Phase	Thermodynamic parameters
Liquid (Pt, Pb)	${}^0L^{\text{Liq}} = -84177.589 + 236.106T$ $- 26.024T \ln T$ ${}^1L^{\text{Liq}} = 4387 - 4.689T$
fcc (Pt, Pb)	${}^0L^{\text{fcc}} = 46000$
Pt ₃ Pb	$G^{\text{Pt}_3\text{Pb}} = 3{}^0G_{\text{Pt}}^{\text{fcc}} + {}^0G_{\text{Pb}}^{\text{fcc}}$ $- 50562.516 + 24.555T$
PtPb	$G^{\text{PtPb}} = {}^0G_{\text{Pt}}^{\text{fcc}} + {}^0G_{\text{Pb}}^{\text{fcc}} - 42348.892$ $+ 22.123T$
PtPb ₄	$G^{\text{PtPb}_4} = {}^0G_{\text{Pt}}^{\text{fcc}} + 4{}^0G_{\text{Pb}}^{\text{fcc}} - 66399.035$ $+ 52.157T$

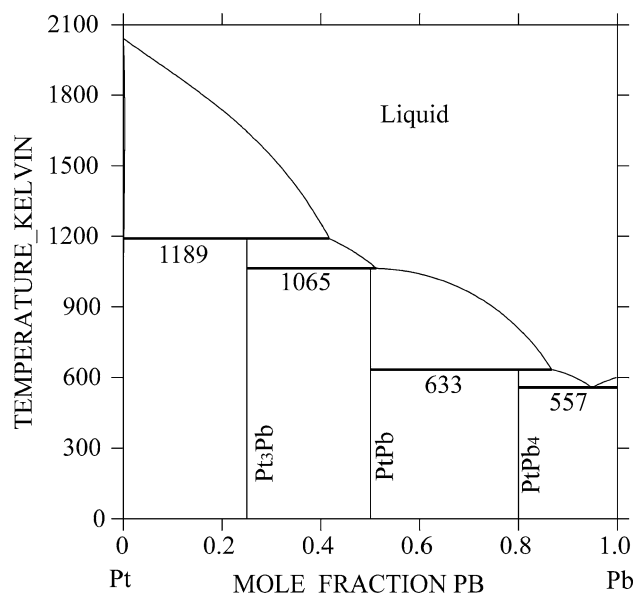


Fig. 1 The assessment phase diagram of the Pt-Pb system in this study

The phase diagram calculated in this study is shown in Fig. 1 and its comparison with experimental data is illustrated in Fig. 2, while Table 3 lists all the invariant reactions in Pt-Pb system. An agreement within 6 K between the calculated and the experimentally determined temperatures for these invariant reactions has been obtained.

Enthalpies of mixing of liquid Pt-Pb alloys at different temperatures are calculated in comparison with reported experimental data as shown in Fig. 3. We can see that not only most of the measured data but also the temperature dependence of mixing enthalpy of liquid alloys were reasonably reproduced.

A further check on the reliability of the thermodynamic modeling is provided by Fig. 4, where the calculated enthalpies of formation of intermetallic phases at 298 K are compared with the experimental data and values by the first principles. It is demonstrated that the experimental and calculated data are well reproduced by the parameters obtained in this study.

Table 3 Invariant reactions of the Pt-Pb system; L: liquid

Invariant reaction	Reaction type	T, K	x_{Pb}^{L}	Reference
L + fcc (Pt) \rightleftharpoons Pt ₃ Pb	Peritectic	1188	0.42	[6]
L + Pt ₃ Pb \rightleftharpoons PtPb	Peritectic	1189	0.417	This work
L + PtPb \rightleftharpoons PtPb ₄	Peritectic	1068	0.525	[6]
L + PtPb ₄ \rightleftharpoons PtPb	Peritectic	1065	0.512	This work
L + PtPb \rightleftharpoons PtPb ₄	Peritectic	633	0.867	[6]
L + PtPb ₄ \rightleftharpoons PtPb	Peritectic	633	0.867	This work
L \rightleftharpoons PtPb ₄ + fcc (Pb)	Eutectic	563	0.947	[6]
L \rightleftharpoons PtPb ₄ + fcc (Pb)	Eutectic	557	0.948	This work

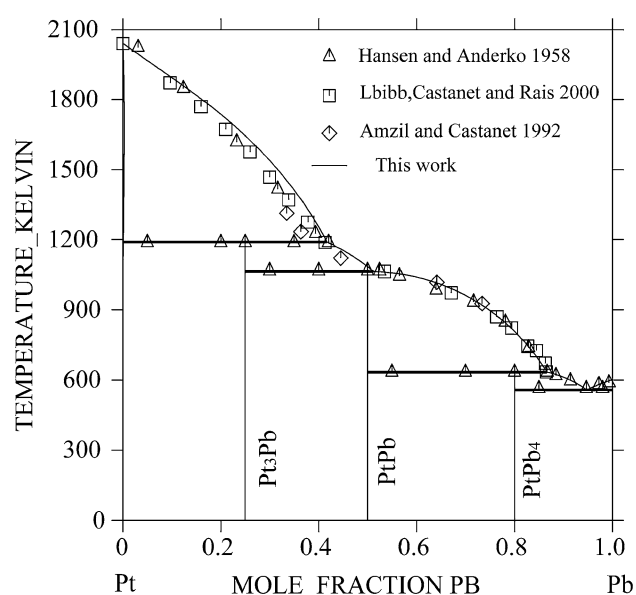


Fig. 2 Comparison of the calculated phase boundaries with reported experimental data

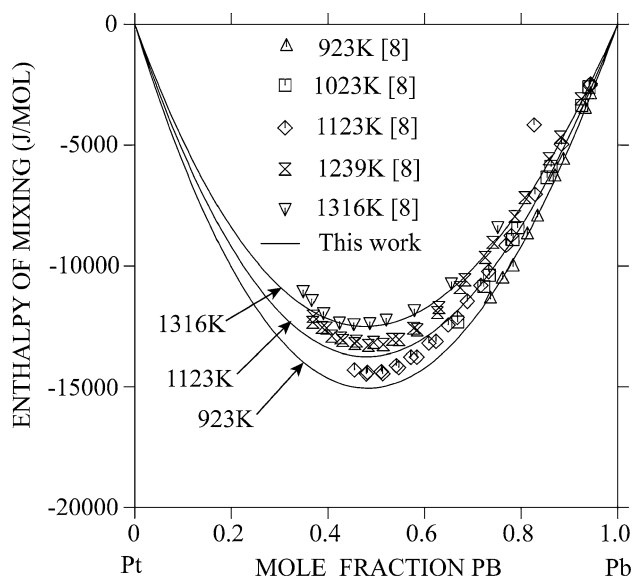


Fig. 3 Enthalpies of mixing of liquid Pt-Pb alloys: comparison between the assessed and experimental data. Reference states: liquid Pt and Pb

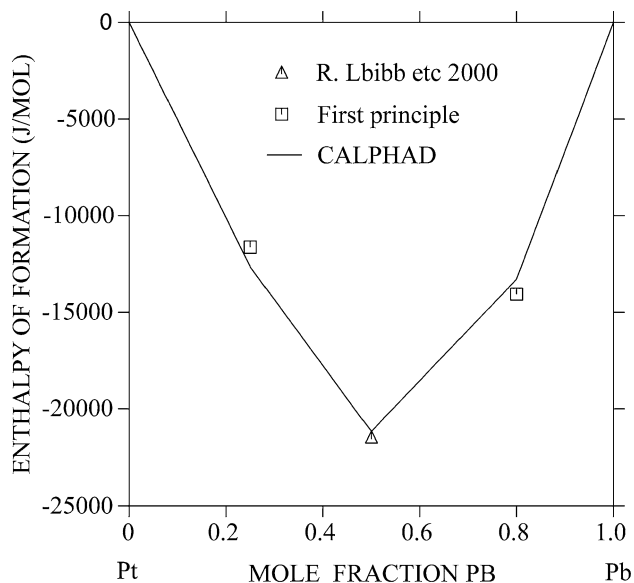


Fig. 4 Calculated enthalpies of formation of the compounds compared with experimental data in Ref 9 and values by the first principles. Reference states: fcc_A1 Pt and Pb

6. Conclusions

The phase diagram of the Pt-Pb binary system has been thermodynamically optimized based on experimental data and first-principle calculations of the phase equilibrium and thermodynamic properties. A set of self-consistent thermodynamic parameters have been obtained, which can

reasonably reproduce the experimental and thermodynamic data.

Acknowledgments

This study was financially supported by the National Science Foundation of China (No. 50671122) and Hunan Provincial Innovation Foundation for Postgraduate (No. 1343-74236000007).

References

1. C. Lamy, E.M. Belgsir, and J.M. Leger, Electro-catalytic Oxidation of Aliphatic Alcohols: Application to the Direct Alcohol Fuel Cell (DAFC), *J. Appl. Electrochem.*, 2001, **31**, p 799-809
2. A.O. Neto, E.G. Franco, E. Arico, M. Linardi, and E.R. Gonzalez, Electro-oxidation of Methanol and Ethanol on Pt-Ru/C and Pt-Ru-Mo/C Electrocatalysts Prepared by Bönne-mann's Method, *J. Eur. Ceram. Soc.*, 2003, **23**, p 2987-2992
3. W.J. Zhou, Z.H. Zhou, S.Q. Song, W.Z. Li, G.Q. Sun, Q.P. Tsiakaras, and S. Xin, Pt Based Anode Catalysts for Direct Ethanol Fuel Cells, *Appl. Catal. B*, 2003, **46**, p 273-285
4. N. Fujiwara, K.A. Friedrich, and U. Stimming, Ethanol Oxidation on PtRu Electrodes Studied by Differential Electrochemical Mass Spectrometry, *J. Electroanal. Chem.*, 1999, **472**, p 120-125
5. G. Li and P.G. Pickup, The Promoting Effect of Pb on Carbon Supported Pt and Pt/Ru Catalysts for Electro-oxidation of Ethanol, *Electrochim. Acta*, 2006, **52**, p 1033-1037
6. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958
7. F. Doerinckel, Metallographische Mitteilungen aus dem Institut für anorganische Chemie der Universität Göttingen über einige Platinlegierungen, *Z. Anorg. Chem.*, 1907, **54**, p 358-365, in German
8. A. Amzil and R. Castanet, Thermodynamic Investigation of the Pt-Pb Binary Alloys, *Ber. Bunsengesel. Phys. Chem.*, 1992, **96**, p 1872-1876
9. R. Lbibb, R. Castanet, and A. Rais, Thermodynamic Investigation of Pt-Pb Binary Alloys, *J. Alloys Compd.*, 2000, **302**, p 155-158
10. L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams*, Academic Press, New York, 1970
11. P.E. Blöchl, Projector Augmented-wave Method, *Phys. Rev. B*, 1994, **50**, p 17953-17979
12. G. Kresse and J. Joubert, From Ultrasoft Pseudopotentials to the Projector Augmented-wave Method, *Phys. Rev. B*, 1999, **59**, p 1758-1775
13. G. Kresse and J. Furthmüller, Efficient Iterative Schemes for Ab Initio Total-energy Calculations Using a Plane-wave Basis Set, *Phys. Rev. B*, 1996, **54**, p 11169-11186
14. G. Kresse and J. Furthmüller, Efficiency of Ab initio Total Energy Calculations for Metals and Semiconductors Using a Plane-wave Basis Set, *Comput. Mater. Sci.*, 1996, **6**, p 15-50
15. J.P. Perdew and Y. Wang, Accurate and Simple Analytic Representation of the Electron-gas Correlation Energy, *Phys. Rev. B*, 1992, **45**, p 13244-13249
16. J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, and D.J. Singh et al., Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation, *Phys. Rev. B*, 1992, **46**, p 6671-6687

Section I: Basic and Applied Research

17. Y. Wang, S. Curtarolo, C. Jiang, R. Arroyave, T. Wang, G. Ceder, L.Q. Chen, and Z.K. Liu, Ab Initio Lattice Stability in Comparison with CALPHAD Lattice Stability, *CALPHAD*, 2004, **28**, p 79-90
18. J. Häglund, A.F. Guillermet, G. Grimvall, and M. Körling, Theory of Bonding in Transition-metal Carbides and Nitrides, *Phys. Rev. B*, 1993, **48**, p 11685-11691
19. H.K. Mao, Y. Wu, J.F. Shu, J.Z. Hu, R.J. Hemley, and D.E. Cox, High-pressure Phase Transition and Equation of State of Lead to 238 GPa, *Solid State Commun.*, 1990, **74**, p 1027-1029
20. M. Ellner, Relationship Between Structural and Thermodynamic Properties in Phase of the Copper Family in T**1**0-B**4 Systems, *J. Less-Common Metals*, 1981, **78**, p 21-32, in German
21. U. Rösler and K. Schubert, Kristallstruktur von PtPb₄, *Naturwissenschaften*, 1951, **38**, p 331, in German
22. A.T. Dinsdale, SGTE Data for Pure Elements, *CALPHAD*, 1991, **15**, p 317-425
23. B. Sundmann, B. Jansson, and J.O. Anderson, The ThermoCalc Databank System, *CALPHAD*, 1985, **9**, p 153-190