Optimization and Calculation of Pt-Sn Phase Diagram

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Abstract. Optimization and calculation of the phase diagram of Pt-Sn binary system were presented by Pandat software.The Gibbs free energy of the pure component (Au and Pt) was described by the expression of the SGTE (Science Group Thermodata Europe) database, Using the solid solution phase thermodynamic model to describe the liquid and solid solution phases. Using the PanOptimizer optimization platform and the latest experimental data，the parameters for each phase of the Pt-Sn binary system were optimized. Both calculated phase diagram and thermodynamic properties agree well with most of relative experimental data.

Introduction

Precious metal alloys widely used in aviation, spaceflight, navigation, missile, rocket, atomic energy, microelectronics, chemical, petrochemical, glass fiber, exhaust gas purification and in metallurgical industry, due to their unique physical and chemical properties, therefore it is called "the vitamin of modern industry" and "modern new metal"[1-3].

In the precious metal alloys, Pt-Sn binary system has a certain application in brazing[4-5], heterogeneous catalysis[6-7], dental and jewelry industry[8-10]. Pt-Sn binary alloy is one of the important materials of Pt base welding wire [11]. For Pt-Sn system has these special fields of application, so the calculation of phase diagram to describe the multiple systems containing Pt-Sn system and phase equilibrium relations become very valuable. Durussel etc.[12] first determined phase diagram of Pt-Sn binary system, and later Doerinckel[13] Podkopajew[14], Ferro[15] and Schaller[16] successively studied the phase diagram of Pt-Sn binary system. Boer et.al[17] has carried on the semi-quantitative calculation on solid phase and liquid phase of the binary system. Anres etc[11] restudied the determination of the system and the formation enthalpy of the system. Su etc [18] also did the thermodynamic calculation and optimization to phase diagram of Pt-Sn binary system, but by the limiting condition such as the development of experimental conditions and the thermodynamic model, therefore, it is necessary for further optimization and calculation of Pt-Sn binary phase diagram.

The present research situation of Pt-Sn binary system

Durussel etc[12] studied the intermetallic compounds of Pt-Sn binary system in temperature range of 500-1500 ℃ by electron microprobe analysis, differential thermal analysis and X-ray diffraction (XRD) analysis in 1994, and pointed out that the decomposition temperatures of Pt3Sn (1402 ° C) and PtSn (1276 ° C) and Pt2Sn3 (898 ° C), PtSn2 (748 ° C) and PtSn4 (540 ° C) intermetallic compound, and by analysis of metallograph and XRD quenching samples, points out that PtSn and PtSn3 with similar structure(P63/mmc), they also calculate the lattice parameters of all intermetallic compounds of Pt-Sn system. Anres etc[11] measured the liquid formation enthalpy of Pt-Sn system in temperature range 870K to 1660K and the formation enthalpy of PtSn and Pt3Sn

through the calorimetric experiment in 1998. The experiments showed that PtSn had two different structure in low temperature and high temperature, at low temperature the formation enthalpy of PtSn is -74 kJ mol^{-1}, the formation enthalpy of PtSn at high temperature is 63.5 kJ mol^{-1}, and the formation enthalpy of Pt3Sn is -55.3 kJ mol^{-1}. Su etc[18] calculated the phase diagram of Pt-Sn system and researched the thermodynamic parameters of Pt-Sn system in 2001. They used self consistent thermodynamic model parameters to describe the phase equilibrium on the system, and the mesophase of system used stoichiometric ratio model, the phase diagram and thermodynamic parameters optimized by the calculation agreed well with the experimental data. The main existing phase in the Pt-Sn binary system were liquid phase, intermediate phase and FCC phase, the equilibrium reaction temperature and component from different references of Pt-Sn system as shown in table 1.

Table 1 A comparison of calculated and experimental equilibria in the Pt–Sn system

Reaction	Temperature, K	Liquid composition (at.% Sn)	Reference
Liq.→Pt(fcc)+Pt$_3$Sn	1638	Uncertain	
	1643±2	0.196	
	1656.2	0.215	This study
Liq.→Pt$_3$Sn	1693	0.25	
	1675	0.25	
	1674.83	0.251	This study
Liq.→Pt$_3$Sn+ PtSn	1343	0.40	
	1340	0.394	
	1341.16	0.382	This study
Liq.→PtSn	1578	0.485-0.50	
	1549	0.5	
	1548.61	0.498	This study
Liq.+PtSn→Pt$_2$Sn$_3$	1121	0.75	
	1171	0.728	
	1171.01	0.726	This study
Liq.+Pt$_2$Sn$_3$→PtSn$_2$	1018	0.81	
	1021	0.812	
	1021.84	0.825	This study
Liq.+PtSn$_2$→PtSn$_4$	795	0.95	
	813	0.95	
	812.48	0.939	This study
Liq.→PtSn$_4$+β(Sn)	501	0.995	
	501	0.994	
	505.01	0.999	This study

The selection, optimization and calculation of the thermodynamic model

The thermodynamic model of each binary system.

Gibbs free energy of pure components

Gibbs free energy expression of pure components used $G_i^{0,\phi}(T) = G_i^{\phi}(T) - H_i^{SER}$, which element i (i = Pt, Sn) is componentof Φ phase (Φ = FCC (Pt, Sn), BCT Sn and liquid), the relationship between free energy and the temperature is:

$$G_i^{0,\phi}(T) = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \qquad (1)$$

Type H_i^{SER} is the molar enthalpy of pure element i at 298.15 K and under 1 atmospheric pressure, T is the absolute temperature, a, b, c, d, e, f... is the fitting undetermined coefficients, Gibbs free

energy expression of pure component (Pt and Sn) using SGTE (Science Group Thermodata Europe) expression in the database [19].

Thermodynamics model of liquid phase.

In actual solution, atoms binding energy often influenced by temperature, composition and other factors, the interaction are not always the constant, therefore, to modify the interaction parameters, making it the function related to the temperature and composition, in order to achieve the more accurate description of the liquid phase and the FCC phase in Pt-Sn system, choose the subregular solution model to describe the Gibbs free energy, the Gibbs free energy expression is:

$$G^L(T,\{y_i\}) = \sum_i y_i G_i^{0,L}(T) + RT\sum_i y_i \ln y_i + \sum_{i,j>i} y_i y_j \sum_v L_{i,j}^{L,v}(y_i - y_j)^v \qquad (2)$$

Type y_i is the mole fraction in the liquid phase of element i, i(j) on behalf of each phase, namely Pt, Sn and PtSn. $G_{Pt}^{0,L}(T)$ and $G_{Sn}^{0,L}(T)$ in formula (2) is the gibbs free energy of Pt, Sn liquid phase, adopts the SGTE database expression [20]. The gibbs free energy $G_{PtSn}^{0,L}(T)$ using the following formula:

$$G_{PtSn}^{0,L}(T) = G_{Pt}^{0,L}(T) + G_{Sn}^{0,L}(T) + a_{PtSn}^L + b_{PtSn}^L T \qquad (3)$$

Type a_{PtSn}^L and b_{PtSn}^L is formation enthalpy and entropy of PtSn respectively, the two parameters were optimized.

The thermodynamic model of solid phase (Pt)

The computation formula gibbs free energy of face-centered cubic phase Pt is as follows:

$$G^{(Pt)} = x_{Pt}G_{Pt}^{0,fcc} + x_{Sn}G_{Sn}^{0,fcc} + RT(x_{Pt}\ln x_{Pt} + x_{Sn}\ln x_{Sn}) + x_{Pt}x_{Sn}L_{Pt,Sn}^{0,(Pt)} \qquad (4)$$

Thermodynamics model of intermediate phase

Pt-Sn system have five intermediate phase, namely PtSn, PtSn2, Pt2Sn3, Pt3Sn, PtSn4, among them PtSn crystal structure belongs to the hexagonal system, has the NiAs type structure, the space group is P63/mmc, crystal parameters are a=b=4.104 Å, c=5.436 Å, α=β=90 °, γ=120 °, cell contains four atoms; Crystal structure of PtSn2 belongs to the cubic system, the space group is Fm-3m, crystal parameters are a = b = c = 6.4331Å, α=β=γ=90 °, cell contains 12 atoms; Pt2Sn3 crystal structure belongs to the hexagonal system, the space group is P63/mmc, crystal cell parameters are a=b= 4.325Å, c = 12.934 Å, α=β= 90 °, γ= 120 °, the cell contains 10 atoms; Pt3Sn crystal structure belong to cubic system, with AuCu3 type structure, space group is Pm-3m, crystal cell parameters are a=b=c=4Å, α=β=γ= 90 °, the cell contains 4 atoms; PtSn4 crystal structure belongs to the orthogonal system, space group is ABA2, crystal cell parameters are a = 6.397Å, b = 6.426Å, c = 11.381Å, α=β=γ= 90 °, the cell contains 20 atoms [20-23]. The computation formula of gibbs free energy of five intermediate phase is:

$$G^{Pt_pSn_q}(T) = \frac{p}{p+q}G_{Pt}^{0,fcc}(T) + \frac{q}{p+q}G_{Sn}^{0,bct}(T) + A' + B'T \qquad (5)$$

Type A 'and B' is optimized parameters.

The optimized and calculated of thermodynamic parameters.

PanOptimizer is the parameters module in C/C++ software environment, which evaluated experiment thermodynamics, kinetics and thermal physical model, not only can be used as a thermodynamic model parameters optimization tools, as well as optimization of thermal physical properties and dynamic model parameters [24]. Using the recent related experimental data, and combined with PanOptimizer optimization platform, optimized each phase parameters. Raub.E, S.N.Tripathi, T.B.Massalski, J.Korb, Okamoto.H and S.R.Bharadwaj successively has carried on the experiment and thermodynamics calculation for Pt-Sn binary system. Among them the work of S.R.Bharadwaj and J.Korb is more comprehensive and reliable, so optimization mainly chose their experimental data and SGTE proposed data in 2010.

Optimization carried by PanOptimizer program. First, optimization the phase parameters one by one, and then overall optimization. The Optimized parameters as shown in table 2.

Table 2 Evaluated thermodynamic parameters for Pt-Sn system

Phase type	Phase	Thermodynamic parameters （Jmol^{-1}）
Solid solution phase	Liquid	$G_{PtSn}^{0,Liq} = -94663.3 + G_{Pt}^{0,Liq} + G_{Sn}^{0,Liq}$
		$L_{Pt,PtSn}^{0,Liq} = -71062.3 + 25.6461T$
		$L_{Pt,PtSn}^{1,Liq} = -10754.4$
		$L_{PtSn,Sn}^{0,Liq} = -33610.0 + 18.8021T$
	（Pt）	$L_{Pt,Sn}^{0,(Pt)} = -125000 - 2T$
Intermediate phase	Pt$_3$Sn	$G^{Pt_3Sn} = -35826.2 - 0.5T + (\frac{3}{4})G_{Pt}^{0,fcc} + (\frac{1}{4})G_{Sn}^{0,bct}$
	PtSn	$G^{PtSn} = -59500 + 4.3833T + (\frac{1}{2})G_{Pt}^{0,fcc} + (\frac{1}{2})G_{Sn}^{0,bct}$
	Pt$_2$Sn$_3$	$G^{Pt_2Sn_3} = -52240 + 4.83T + (\frac{2}{5})G_{Pt}^{0,fcc} + (\frac{3}{5})G_{Sn}^{0,bct}$
	PtSn$_2$	$G^{PtSn_2} = -45160 + 4.02T + (\frac{1}{3})G_{Pt}^{0,fcc} + (\frac{2}{3})G_{Sn}^{0,bct}$
	PtSn$_4$	$G^{PtSn_4} = -29000 + 2.4T + (\frac{1}{5})G_{Pt}^{0,fcc} + (\frac{4}{5})G_{Sn}^{0,bct}$

Discussion and analysis

The calculated phase diagram is shown in figure 1. For comparison, the phase diagram calculation and optimization by Su etc is also shown in figure 2. By contrast figure 1 and figure 2, Pt-Sn binary phase diagram calculated by Su etc[18] with Pandat software[25] in the Sn-rich area more than 900 ℃ has miscibility phenomenon in liquid phase. But this area of miscibility is actually not exist, nor related experiment verified, so this study abandoned the liquid miscibility, and the liquid area was redefined, introduced liquid phase PtSn, the gibbs free energy of liquid Pt, Sn, calculated by SGTE database expression and gibbs free energy of PtSn liquid can adopt the above formula (3) to calculate. The functions used in the calculation are shown in table 3.
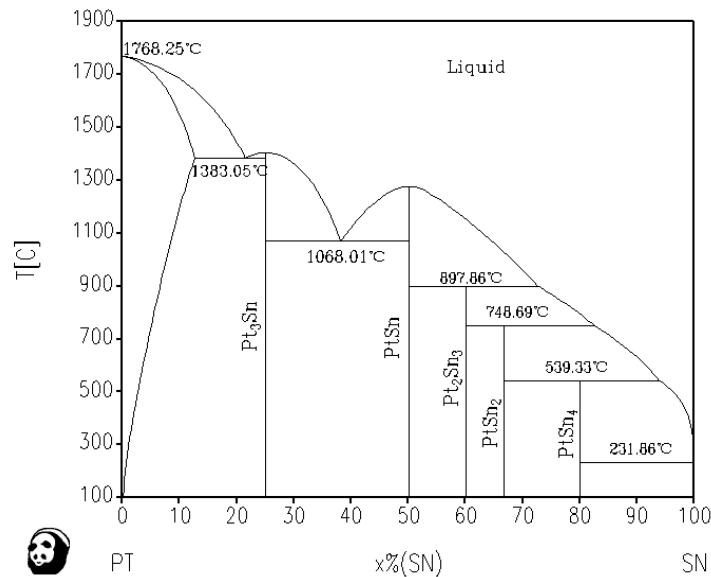

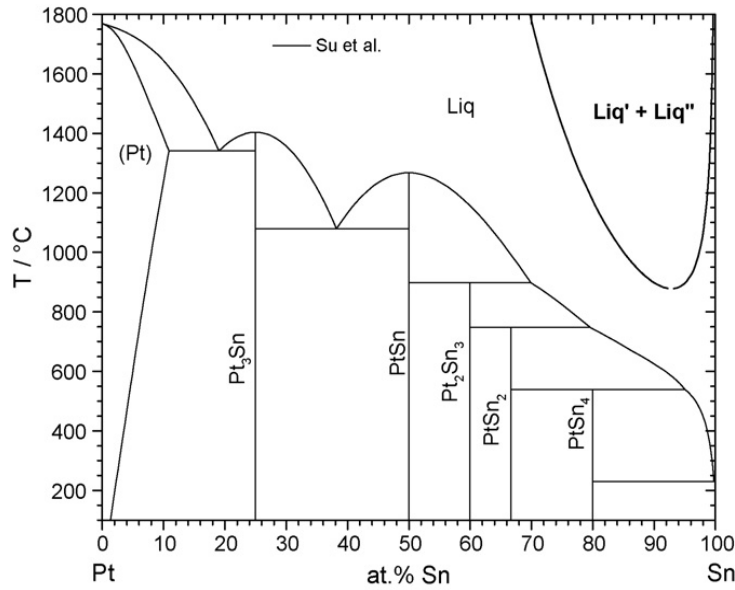Fig.1. Calculated the Pt-Sn phase by Pandat software

Fig.2. The phase diagram of Pt-Sn system calculated by Su[18]

Table 3 Functions used in the calculation procedure

G_Pt_FCC $-7595.63+124.388T-24.5526T\ln(T)-0.00248297\ T^2-2.0138\ E^{-8}*\ T^3+7974\ T^{-1}$	$(298.15 < T < 1300)$

$-9253.17+161.53T-30.2527T\ln(T)+0.00232167\ T^2-6.56946\ E^{-7}*\ T^3-272106\ T^{-1}$ $\quad(1300 < T < 2041.5)$
$-222048+1019.36T-136.193T\ln(T)+0.0204549\ T^2 2-7.59259\ E^{-7}*\ T^3\ 3+7.1539\ E^7\ *T^{-1}$ $\quad(2041.5< T < 4000)$
G_Pt_LIQUID $\quad 12518.4+115.113T-24.5526T\ln(T)-0.00248297\ T^2-2.0138E^{-8}\ *T^3+7974\ T^{-1}$ $\quad(298.15 < T < 400)$
$19023.5+32.9418T-12.3404T\ln(T)-0.0115515\ T^2+9.31516\ E^{-7}*\ T^3\ -601426\ T^{-1}$ $\quad(600 < T < 2041.5)$
$\qquad 1404.47+205.859T-36.5T\ln(T)$ $\quad(2041.5< T < 4000)$
G_Sn $\quad -7958.52+122.765T-25.858T\ln(T)\ +0.00051185T^2-3.19277E^{-6}T^3+18440T^{-1}$ $\quad(0 < T < 250)$
$-5855.14+65.4433T-15.961T\ln(T)\ -0.0188702T^2+3.12117E^{-6}T^3-61960T^{-1}$ $\quad(250 < T < 505.08)$
$2524.72+4.00527T-8.25905T\ln(T)-0.0168144T^2+2.62313E^{-6}T^3-1.08124E^6T^{-1}-1.2307E^{25}T^{-9}$ $(505.08 < T < 800)$
$-8256.96+138.997T-28.4512T\ln(T)-1.2307E+025T^{-9}$ $\quad(800 < T < 3000)$
G_Sn_FCC $\quad -345.135+56.9833T-15.961T\ln(T)-0.0188702T^2+3.12117E^{-6}T^3-61960T^{-1}$ $\quad(298.15 < T < 505.08)$
$8034.72-4.45473T-8.25905T\ln(T)-0.0168144T^2+2.62313E^{-6}T^3-1.08124E^6T^{-1}-1.2307E^{25}T^{-9}$ $\quad(505.08 < T < 800)$
$-2746.96+130.537T-28.4512T\ln(T)-1.2307E^{25}T^{-9}$ $\quad(800 < T < 3000)$
G_Sn_LIQUID $\quad -855.425+108.678T-25.858T\ln(T)+0.00051185T^2-3.19277E^{-6}T^3+18440T^{-1}+1.47031E^{-18}T^7$
$(0 < T < 250)$
$1247.96+51.3555T-15.961T\ln(T)-0.0188702T^2+3.12117E^{-6}T^3-61960T^{-1}+1.47031E^{-18}T^7$ $\quad(250 < T < 505.08)$
$9496.31-9.80911T-8.25905T\ln(T)-0.0168144T^2+2.62313E^{-6}T^3-1.08124E^6T^{-1}$ $\quad(505.08 < T < 800)$
$-1285.37+125.182T-28.4512T\ln(T)$ $\quad(800 < T < 3000)$

Conclusion

Using the latest experimental data and the thermodynamic model optimized the parameters of Pt-Sn system, In Pt-Sn system, there is no liquid immiscible area, introduced PtSn into liquid when optimize the system. According to the optimization parameters calculated the Pt-Sn binary phase diagram, the calculated phase diagram are good agreement with the most recent phase diagram in terms of zero variable reaction temperature and ingredients, at the same time, the thermodynamic properties was also coincident.

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