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Al-Fe-P 三元系的热力学优化

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摘要: 采用 CALPHAD 方法对 Al-Fe-P 三元系进行了热力学评估, 并根据相关的实验数据对边际二元系 Al-P 进行了热力学再优化, Al-Fe 和 Fe-P 边际二元系的热力学参数取自之前的研究并做了局部调整. 根据相图数据和热力学数据优化了 Al-Fe-P 三元系的热力学模型参数, 获得了体系中所有相的 Gibbs 自由能表达式. 所得参数之间自洽且能很好地重现 Al-Fe-P 体系的大部分实验相图信息. 通过驱动力判据和本文优化所得的模型参数, 从热力学上解释了该体系非晶形成能力与组成之间的关系.

关键词: Al-Fe-P; 相图; 热力学; 评估; 非晶形成能力

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Thermodynamic Optimization of the Al-Fe-P Ternary System

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Abstract: A critical thermodynamic optimization of the Al-Fe-P ternary system was performed using the CALPHAD method. Among the sub-binary systems in the Al-Fe-P system, the Al-P system was reassessed according to its related experimental information. The thermodynamic descriptions of the Al-Fe and Fe-P binary systems were taken from previous studies with minor modifications. The parameters of the thermodynamic model of the Al-Fe-P ternary system were optimized based on available experimental phase diagram data and thermodynamic properties. One set of consistent parameters of the Gibbs energies of all phases, which can satisfactorily reproduce most of the experimental phase diagram data, was obtained. By employing the driving force criterion with the present thermodynamic description, the experimentally reported composition dependence of the glass-forming ability of the Al-Fe-P system could be explained thermodynamically.

Key Words: Al-Fe-P; Phase diagram; Thermodynamics; Optimization; Glass forming ability

1 Introduction

Phosphorus has known to be an essential metalloid element in forming an amorphous phase exhibiting useful engineering properties, such as, the Invar effect,¹ corrosion resistance,² and catalysis.³ The Al-Fe-P ternary system has drawn more and more

attention due to that amorphous phase formation has been found in the Al-Fe-P system by using a melt-spinning technique.⁴ The evaluation of the glass-forming ability (GFA) of alloys is of great importance by judging in advance whether amorphous phases could be formed at given conditions. The successful evaluation⁵⁻⁷ of

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GFA of some alloys indicates that the expressions of the Gibbs energies of the phases are very powerful in qualitatively analyzing the composition dependency of the GFA. The Al-Fe-P system is also a fundamental ternary system of the Fe-based and P-containing multi-component alloys, which are very important for the advanced metallurgy and materials. Knowledge of the thermodynamic properties of the Al-Fe-P system is significant for the development of Fe-based and P-containing multi-component alloys by providing information regarding the phases that are present at service temperature, their compositions and volume fractions and so on. Therefore, the interest in this system is increasing, as shown by a recent publication,⁸ in which, however, the researchers only gave a description of the Fe rich side and merely accounted for one isothermal section at 723 K during the calculation.

Thus, our study was aimed to give a thermodynamic optimization of the Al-Fe-P system over the whole composition range based on all available experimental information in the literature by using CALPHAD (CALculation of PHase Diagram) approach with Thermo-Calc software package.⁹ The optimized self-consistent thermodynamic parameters of the Al-Fe-P system are expected to be helpful for both the better understanding of the composition dependency of the GFA in the Al-Fe-P system and the development of the Fe-based and P-containing multi-component alloy thermodynamic database.

2 Information on the binary and the ternary systems

2.1 Al-P system

The Al-P system was extensively investigated by many researchers. White *et al.*¹⁰ released the existence of only one intermediate phase, AlP, which was further confirmed by Panish and Ilegems^{11,12} during the study of the Ga-rich corner of the Ga-Al-P ternary system. Tu *et al.*¹³ confirmed the existence of AlP again in the investigation of the 723 K isothermal section of the Al-P-Zn ternary system with the help of combined techniques of optical microscopy, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS), and X-ray diffraction (XRD). Kischio¹⁴ reported the melting point of AlP to be (2803 ± 50) K without experimental detail. Czochrallski¹⁵ established a possible upper limit to the solubility of P in γ -Al of 0.0007 at mole fraction of P.

Several researchers experimentally measured the heat of formation of AlP using different methods and large difference existed among the experimental results. Kischio¹⁴ obtained $\Delta_f H_{295\text{ K}}(\text{AlP}) = (-82630 \pm 1050) \text{ J} \cdot \text{mol}^{-1} \cdot \text{atom}^{-1}$ from the heat of dissolution of AlP in aqueous HCl and the known formation of the products. Wang and Zaheervuddin¹⁶ measured the heats of combustion of AlP and equal mol mixtures of Al and red P. Adjusting their results to white P as reference state, $\Delta_f H_{298\text{ K}}(\text{AlP}) = (-69500 \pm 4600) \text{ J} \cdot \text{mol}^{-1} \cdot \text{atom}^{-1}$ was obtained. Maria *et al.*¹⁷ measured the partial pressures of Al and P_2 vapor equilibrium with AlP, from 1270 to 1800 K using the Knudsen effusion

method in combination with mass spectrometry, and $\Delta_f H_{298\text{ K}}(\text{AlP}) = (-59000 \pm 6700) \text{ J} \cdot \text{mol}^{-1} \cdot \text{atom}^{-1}$ was obtained. A second law fit to Maria's experimental results¹⁷ was carried out by McAlister¹⁸ and $\Delta_f H_{298\text{ K}}(\text{AlP}) = (-57600 \pm 17700) \text{ J} \cdot \text{mol}^{-1} \cdot \text{atom}^{-1}$ with statistical error was yielded. Martosudirdjo and Pratt¹⁹ reported $\Delta_f H(\text{AlP}) = (-74000 \pm 900) \text{ J} \cdot \text{mol}^{-1} \cdot \text{atom}^{-1}$ using precipitation calorimetry in liquid Sn at 582 K.

Tu *et al.*¹³ gave a description of the Al-P binary system during the thermodynamic analysis of the Al-P-Zn ternary system. Unfortunately, their description could not reflect the phase relation of AlP with other phases correctly when extrapolating the parameters into the Al-Fe-P ternary system. Therefore, the thermodynamic parameters of the Al-P system were re-optimized in this work.

2.2 Al-Fe and Fe-P binary systems

In the Al-Fe system the equilibrium phases are the liquid, the α -Fe solid solution based on body-centered cubic (bcc) Fe, the γ -Fe solid solution based on face-centered cubic (fcc) Fe, the AlFe formed through ordering of α -Fe, Al_3Fe_4 , Al_5Fe_2 , Al_2Fe , Al_3Fe_4 , and the γ -Al based on fcc Al. Many researchers, including Kaufman and Nesor,²⁰ Saunders and Rivlin²¹ and Seierstein²², optimized the Al-Fe binary system. The assessment by Seierstein²² is the first consistent description of the Al-Fe phase diagram and has been successfully extrapolated to the related ternary system by many researchers.^{23–25} Thus, the parameters optimized by Seierstein²² have been adopted in present assessment, except that the thermodynamic parameters of Al_2Fe phase have been slightly modified to ensure the Al_2Fe phase be stable in the Al-Fe-P ternary system. The optimized parameters are shown in Table 1, and the calculated Al-Fe phase diagram is shown in Fig.1(a).

The Fe-P system is composed of the liquid, the α -Fe solid solution based on bcc Fe, the γ -Fe solid solution based on fcc Fe, Fe_3P , Fe_2P , FeP , FeP_2 , FeP_4 , and P (red and white P). A critical assessment of the Fe-P system has been carried out by Okamoto,²⁶ Ohtani²⁷ and Tokunaga²⁸ *et al.* However, in all these evaluations the valuable thermodynamic properties in the Fe-P system measured by Zaitsev *et al.*²⁹ using differential scanning calorimetry and Knudsen effusion method with mass-spectrometric analysis of the gaseous phase were omitted. Most recently, a thermodynamic re-optimization of the Fe-P system has been carried out by Cao *et al.*,³⁰ and satisfactorily reproduced most experimental phase diagram and thermodynamic properties. Hence, the parameters assessed by Cao *et al.*³⁰ with minor modification were used in present work. The modified parameters and calculated phase diagram of Fe-P system are shown in Table 1 and Fig.1b, respectively.

2.3 Al-Fe-P ternary system

Because of the high volatilization of P, the Al-Fe-P ternary phase diagram has been studied only for the Fe rich corner of this system. Vogel and Klose³¹ studied the phase equilibria in the Fe-Fe₃P-AlP-Fe₅₀Al₅₀ region of the Al-Fe-P ternary system using differential thermal analysis (DTA) and metallography

Table 1 Optimized thermodynamic parameters for the binary and ternary systems

System	Phase	Model	Thermodynamic parameters/(J·mol ⁻¹ ·atom ⁻¹)	Ref.
Al-Fe	liq	(Al,Fe) ₁	${}^0L_{\text{Al,Fe}}^{\text{liq}} = -91976.5 + 22.1314T$, ${}^1L_{\text{Al,Fe}}^{\text{liq}} = -5672.58 + 4.8728T$, ${}^2L_{\text{Al,Fe}}^{\text{liq}} = 121.9$	22
	α	(Al,Fe) ₁	${}^0L_{\text{Al,Fe}}^{\alpha} = -122960 + 31.9888T$, ${}^1L_{\text{Al,Fe}}^{\alpha} = 3089.2$	22
	γ	(Al,Fe) ₁	${}^0L_{\text{Al,Fe}}^{\gamma} = -76066.1 + 18.6758T$, ${}^1L_{\text{Al,Fe}}^{\gamma} = 21167.4 + 1.3398T$	22
	AlFe	(Al,Fe) _{0.5} (Al,Fe) _{0.5}	$G_{\text{AlFe}}^{\text{AlFe}} = G_{\text{FeFe}}^{\text{AlFe}} = 0$, $G_{\text{AlFe}}^{\text{AlFe}} = G_{\text{FeAl}}^{\text{AlFe}} = -14300.9572$	22
	Al ₅ Fe ₂	(Al) _{0.7143} (Fe) _{0.2857}	$G_{\text{AlFe}}^{\text{Al}_5\text{Fe}_2} = 0.7143G_{\text{Al}}^{\text{fcc}} + 0.2857G_{\text{Fe}}^{\text{bcc}} - 32653.7 + 6.99929T$	22
	Al ₂ Fe	(Al) _{0.6667} (Fe) _{0.3333}	$G_{\text{AlFe}}^{\text{Al}_2\text{Fe}} = 0.6667G_{\text{Al}}^{\text{fcc}} + 0.3333G_{\text{Fe}}^{\text{bcc}} - 33000 + 6.36667T$	this work
	Al ₁₃ Fe ₄	(Al) _{0.6275} (Fe) _{0.235} (Al:Va) _{0.1375}	$G_{\text{AlFeAl}}^{\text{Al}_{13}\text{Fe}_4} = 0.765G_{\text{Al}}^{\text{fcc}} + 0.235G_{\text{Fe}}^{\text{bcc}} - 30714.4 + 7.447T$	22
			$G_{\text{AlFeVa}}^{\text{Al}_{13}\text{Fe}_4} = 0.6275G_{\text{Al}}^{\text{fcc}} + 0.235G_{\text{Fe}}^{\text{bcc}} - 27781.3 + 7.2566T$	22
	Al ₃ Fe ₄	(Al,Fe) ₁	$G_{\text{Al}}^{\text{Al}_3\text{Fe}_4} = G_{\text{Al}}^{\text{fcc}} + 12178.9 - 4.813T$, $G_{\text{Fe}}^{\text{Al}_3\text{Fe}_4} = G_{\text{Fe}}^{\text{bcc}} + 5009.03$	22
			${}^0L_{\text{Al,Fe}}^{\text{Al}_3\text{Fe}_4} = -131649 + 29.4833T$, ${}^1L_{\text{Al,Fe}}^{\text{Al}_3\text{Fe}_4} = -18619.5$	22
Fe-P	liq	(Fe,P) ₁	${}^0L_{\text{Fe,P}}^{\text{liq}} = -248000 + 50T$, ${}^2L_{\text{Fe,P}}^{\text{liq}} = 110000 - 57T$	this work
	α	(Fe,P) ₁	${}^0L_{\text{Fe,P}}^{\alpha} = -172000 + 4.7T$	30
	γ	(Fe,P) ₁	${}^0L_{\text{Fe,P}}^{\gamma} = -156000 + 6T$	30
	Fe ₃ P	(Fe) _{0.75} (P) _{0.25}	$G_{\text{Fe,P}}^{\text{Fe}_3\text{P}} = -49167.25125 + 157.35T - 27.725T \ln T - 0.0014625T^2 + 134875T^{-1}$	30
	Fe ₂ P	(Fe) _{0.667} (P) _{0.333}	$G_{\text{Fe,P}}^{\text{Fe}_2\text{P}} = -58880.7 + 121.48T - 22.2233T \ln T - 0.00478333T^2$	this work
	FeP	(Fe) _{0.5} (P) _{0.5}	$G_{\text{Fe,P}}^{\text{FeP}} = -74259.25 + 117.43T - 21.125T \ln T - 0.005225T^2$	this work
	FeP ₂	(Fe) _{0.3333} (P) _{0.6667}	$G_{\text{Fe,P}}^{\text{FeP}_2} = 0.3333G_{\text{Fe}}^{\text{bcc}} + 0.6667G_{\text{P}}^{\text{white}} - 76666 + 16.33T$	30
	FeP ₄	(Fe) _{0.3} (P) _{0.8}	$G_{\text{Fe,P}}^{\text{FeP}_4} = 0.2G_{\text{Fe}}^{\text{bcc}} + 0.8G_{\text{P}}^{\text{white}} - 62000 + 14.6T$	30
Al-P	liq	(Al,P) ₁	${}^0L_{\text{Al,P}}^{\text{liq}} = 86161 - 65.14T$	this work
	Al	(Al) _{0.5} (P) _{0.5}	$G_{\text{Al,P}}^{\text{AlP}} = 0.5G_{\text{Al}}^{\text{fcc}} + 0.5G_{\text{P}}^{\text{white}} - 74000 + 7.14T$	this work
Al-Fe-P	liq	(Al,Fe,P) ₁	${}^0L_{\text{Al,Fe,P}}^{\text{liq}} = 127280.1 - 120T$, ${}^1L_{\text{Al,Fe,P}}^{\text{liq}} = 60000 - 120T$, ${}^2L_{\text{Al,Fe,P}}^{\text{liq}} = 200000 - 170T$	this work
	α	(Al,Fe,P) ₁	${}^0L_{\text{Al,Fe,P}}^{\alpha} = {}^1L_{\text{Al,Fe,P}}^{\alpha} = {}^2L_{\text{Al,Fe,P}}^{\alpha} = 0$	this work
	AlFe	(Al,Fe,P) _{0.5} (Al,Fe,P) _{0.5}	${}^0L_{\text{Al,Fe,P}}^{\text{AlFe}} = {}^1L_{\text{Al,Fe,P}}^{\text{AlFe}} = {}^2L_{\text{Al,Fe,P}}^{\text{AlFe}} = 0$	this work
	γ	(Al,Fe,P) ₁	${}^0L_{\text{Al,Fe,P}}^{\gamma} = {}^1L_{\text{Al,Fe,P}}^{\gamma} = {}^2L_{\text{Al,Fe,P}}^{\gamma} = 0$	this work

analysis. The vertical sections of $w(\text{P})=6\%$, 9% (mass fraction) and $w(\text{Al})=10\%$, 25% were determined. The isothermal section at room temperature and the liquidus surface in the Fe-Fe₂P-AlP-Fe₅₀Al₅₀ region were also investigated experimentally. There was found that the AlP-Fe₂P and AlP-Fe₅₀Al₅₀ sections are the quasi-binaries of the simple eutectic type. Kaneko *et al.*³² investigated the phase relationships between phosphide-phase and iron-phase in the Al-Fe-P system by chemical and X-ray examinations and the obtained results agree with those reported by Vogel and Klose.³¹ Limited thermodynamic properties relevant to the Al-Fe-P system are reported. Yamada and Kato^{33,34} determined the activity interaction coefficients of phosphorus in the Fe-P-*i* system at 1873 K using a Knudsen cell-mass spectrometer combination with the computation from the ratio of the intensities of P⁺ and Fe⁺ peaks, and $\varepsilon_{\text{P}}^{\text{Al}} = 4.6 \pm 0.7$ was obtained. Based on the Miedema model and Toop equation Ding *et al.*³⁵ thermodynamically predicted the activity interaction coefficients between alloying elements and P in liquid Fe at 1873 K and the value of predicted $\varepsilon_{\text{P}}^{\text{Al}}$ is 8.78, which is much larger than the measured mentioned above. On the basis of the above mentioned information, the phase equilibria in the Al-Fe-P ternary system were reviewed in references.³⁶⁻³⁸

Most recently, Wu *et al.*⁸ investigated the phase equilibrium in the Al-Fe-P system when the P content was below 20% (mass fraction) with SEM-EDS and XRD and released an isothermal section at 723 K of the Al-Fe-P system at low phosphorus contents. And up to now, no ternary phase has been found in this ternary system.

3 Thermodynamic models

The thermodynamic models adopted here for the phases of the Al-Fe-P system are summarized in Table 1 and briefly introduced below.

3.1 Pure elements

The Gibbs energy function $G_i^{\circ}(T) = {}^0G_i^{\circ}(T) - {}^0H_i^{\text{SER}}(298.15 \text{ K})$ for the element *i* (*i*=Al, Fe, P) in the phase φ , which is also called lattice stability, is described by an equation of the following form:

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

where ${}^0H_i^{\text{SER}}(298.15 \text{ K})$ is the molar enthalpy of the element *i* in its standard element reference (SER) state, bcc for Fe, fcc for Al, and white form for P; *T* is the absolute temperature in K. Different sets of coefficients *a* to *h* used in different temperature ranges in Eq.(1) are cited from the SGTE database compiled by Dinsdale.³⁹ The lattice stability parameters for Al, Fe, and P used in this work are summarized in Table 2.

3.2 Solution phases

The solution phases are modeled by the substitutional solution model and their Gibbs energies are described by the following expression:

$$G^{\circ}(T) = {}^{\text{ref}}G^{\circ} + {}^{\text{id}}G^{\circ} + {}^{\text{ex}}G^{\circ} \quad (2)$$

where the three terms assume different forms according to the nature of the phase. Substitutional solutions are represented by only one sublattice where all the atoms mix randomly. In the binary case (A,B)₁, the three contributions to the Gibbs energy are:

$$\begin{aligned}
{}^{\text{ref}}G^\varphi &= x_A G_A^\varphi + x_B G_B^\varphi \\
{}^{\text{id}}G^\varphi &= RT(x_A \ln x_A + x_B \ln x_B) \\
{}^{\text{ex-bin}}G^\varphi &= x_A x_B \sum_i L_{A,B}^\varphi(T)(x_A - x_B)^i
\end{aligned} \quad (3)$$

where G_A^φ and G_B^φ are the Gibbs energies of the pure elements

Fig.1 Calculated binary phase diagrams

(a) Al-Fe system,²² (b) Fe-P system,³⁰ (c) Al-P system in this work

in the φ structure and the $L_{A,B}^\varphi$ functions have the form:

$$L_{A,B}^\varphi = a_{A,B}^\varphi + b_{A,B}^\varphi T + c_{A,B}^\varphi T \ln T \quad (4)$$

where $a_{A,B}^\varphi$, $b_{A,B}^\varphi$, and $c_{A,B}^\varphi$ are model parameters to be optimized. In most cases, only the first two terms are used according to the temperature dependence on the experimental data.

In the case of ternary solutions, the expressions of ${}^{\text{ref}}G^\varphi$ and ${}^{\text{id}}G^\varphi$ are easily derived from the binary ones. As for the excess Gibbs energy, it is obtained by combining the binary excess Gibbs energies according to the Muggianu extrapolation formula⁴⁰ and adding a ternary excess term:

$${}^{\text{ex-ter}}G^\varphi = x_A x_B x_C (x_A^0 L_{A,B,C}^\varphi(T) + x_B^1 L_{A,B,C}^\varphi(T) + x_C^2 L_{A,B,C}^\varphi(T)) \quad (5)$$

and the L functions have the form shown in Eq.(4).

This model has been adopted for the following phases: liq-uid, α , γ , and Al_3Fe_4 (see Table 1).

3.3 Ordered/disordered phases

The ordered AlFe phase with bcc_B2 structure is modeled as $(\text{Al,Fe})_{0.5}(\text{Al,Fe})_{0.5}$ in the Al-Fe system.²² In order to represent the Gibbs energy of the ordered/disordered transitions using a single function, the disordered α -Fe phase with bcc_A2 structure is described by $(\text{Al,Fe})_1$. Ansara *et al.*^{41,42} have derived an equation which allows the thermodynamic properties of the disordered phase to be evaluated independently. This is done by resolving the Gibbs energy into three terms as following:

$$G_m = G_m^{\alpha\text{-Fe}}(x_i) + G_m^{\text{AlFe}}(y_i', y_i'') - G_m^{\text{AlFe}}(x_i) \quad (6)$$

in which y_i' is the site fraction of i ($i=\text{Al}$ and Fe) in the first sublattice, and y_i'' in the second one. $G_m^{\alpha\text{-Fe}}(x_i)$ is the Gibbs energy of the disordered α -Fe phase. The second term $G_m^{\text{AlFe}}(y_i', y_i'')$ is described by the sublattice model and implicitly contains a contribution from the disordered state. The last term $G_m^{\text{AlFe}}(x_i)$ represents the contribution from the disordered state to the ordered one. When the site fractions are equal, i.e. $y_i' = y_i''$, the last two terms cancel each other. The ordered AlFe phase with bcc_B2 structure and the disordered α -Fe phase with bcc_A2 structure are modeled as $(\text{Al,Fe,P})_{0.5}(\text{Al,Fe,P})_{0.5}$ and $(\text{Al,Fe,P})_1$ in the Al-Fe-P ternary system, respectively. Due to lack of the experimental information on the ordered/disordered transition in the Al-Fe-P ternary system the ternary interaction parameters are assumed to be zero.

3.4 Intermetallic compounds

Stoichiometric compounds are represented with as many sublattices as the number of component elements, with only one atom type in each sublattice. In the binary case the model is $(\text{A})_u(\text{B})_{1-u}$ and the Gibbs energies are given by

$$G^\varphi = u G_A^{\text{SER}} + (1-u) G_B^{\text{SER}} + \Delta G_f^{\text{A}_u\text{B}_{1-u}} \quad (7)$$

where $\Delta G_f^{\text{A}_u\text{B}_{1-u}}$ is the Gibbs energy of formation of the phase referred to the component element in the SER state and also has the form shown in Eq.(4).

The Eq.(7) was adopted to describe the Gibbs energies of the stoichiometric compounds that were lack of heat capacity data: Al_3Fe_2 , Al_3Fe , FeP_2 , FeP_4 , and AlP (see Table 1).

For Fe_3P , Fe_2P , and FeP phases, the heat capacity data are available in a wide temperature range²⁹ and their Gibbs energies are given by

Table 2 Lattice stability parameters used in the present optimization³⁹

Element	Phase	Lattice stability parameters/(J·mol ⁻¹)	T/K
Al	liq	${}^0G_{\text{Al}}^{\text{liq}} - {}^0H_{\text{Al}}^{\text{fcc}} = 3028.879 + 125.251171T - 24.3671976T \ln T - 0.001884662 \times 10^{-7}T^2 - 8.77664 \times 10^{-7}T^3 + 74092T^{-1} + 7.9337 \times 10^{-20}T^7$	298.15–700
		$= -271.21 + 211.206579T - 38.5844296T \ln T + 0.018531982T^2 - 5.764227 \times 10^{-6}T^3 + 74092T^{-1} + 7.9337 \times 10^{-20}T^7$	700–933.4
		$= -795.996 + 177.430178T - 31.748192T \ln T$	933.4–2900
	fcc	${}^0G_{\text{Al}}^{\text{fcc}} - {}^0H_{\text{Al}}^{\text{fcc}} = -7976.15 + 137.093038T - 24.3671976T \ln T - 0.001884662T^2 - 8.77664 \times 10^{-7}T^3 + 74092T^{-1}$	298.15–700
		$= -11276.24 + 223.048446T - 38.5844296T \ln T + 0.018531982T^2 - 5.764227 \times 10^{-6}T^3 + 74092T^{-1}$	700–933.4
		$= -11278.378 + 188.684153T - 31.748192T \ln T - 1.230524 \times 10^{-28}T^{-9}$	933.4–2900
	bcc	${}^0G_{\text{Al}}^{\text{bcc}} - {}^0H_{\text{Al}}^{\text{bcc}} = 2106.85 + 132.280038T - 24.3671976T \ln T - 0.001884662T^2 - 8.77664 \times 10^{-7}T^3 + 74092T^{-1}$	298.15–700
		$= -1193.24 + 218.235446T - 38.5844296T \ln T + 0.018531982T^2 - 5.764227 \times 10^{-6}T^3 + 74092T^{-1}$	700–933.4
		$= -1195.378 + 183.871153T - 31.748192T \ln T - 1.230524 \times 10^{-28}T^{-9}$	933.4–2900
	Fe	${}^0G_{\text{Fe}}^{\text{liq}} - {}^0H_{\text{Fe}}^{\text{bcc}} = 13265.87 + 117.57557T - 23.5143T \ln T - 0.00439752T^2 - 5.8927 \times 10^{-8}T^3 + 77359T^{-1} - 3.67516 \times 10^{-21}T^7$	298.15–1811
		$= -10839.7 + 291.302T - 46T \ln T$	1811–6000
		${}^0G_{\text{Fe}}^{\text{bcc}} - {}^0H_{\text{Fe}}^{\text{bcc}} = 1225.7 + 124.134T - 23.5143T \ln T - 0.00439752T^2 - 5.8927 \times 10^{-8}T^3 + 77359T^{-1}$	298.1–1811
P	liq	$= -25383.581 + 299.31255T - 46T \ln T + 2.29603 \times 10^{13}T^{-9}$ ($T_{\text{c Fe}}^{\text{a}} = 1043 \text{ K}$, $\beta_{\text{Fe}}^{\text{a}} = 2.22 \text{ J} \cdot \text{K}^{-1}$)	1811–6000
		$= -236.7 + 132.416T - 24.6643T \ln T - 0.00375752T^2 - 5.8927 \times 10^{-8}T^3 + 77359T^{-1}$	298.15–1811
		$= -27098.266 + 300.25256T - 46T \ln T + 2.78854 \times 10^{13}T^{-9}$ ($T_{\text{c Fe}}^{\text{f}} = -201 \text{ K}$, $\beta_{\text{Fe}}^{\text{f}} = -2.1 \text{ J} \cdot \text{K}^{-1}$)	1811–6000
	bcc	${}^0G_{\text{P}}^{\text{liq}} - {}^0H_{\text{P}}^{\text{white}} = -26316.111 + 434.943931T - 70.7440584T \ln T - 0.002898936T^2 + 3.9049341 \times 10^{-5}T^3 + 1141.47T^{-1}$	298.15–6000
		$= -7232.449 + 133.304873T - 26.326T \ln T$	298.15–6000
		$= -26316.111 + 434.943931T - 70.7440584T \ln T - 0.002898936T^2 + 3.9049341 \times 10^{-5}T^3 + 1141.47T^{-1}$	298.15–6000
	fcc	${}^0G_{\text{P}}^{\text{bcc}} - {}^0G_{\text{P}}^{\text{red}} = 44769 - 13.26T$	298.15–6000
		${}^0G_{\text{P}}^{\text{fcc}} - {}^0G_{\text{P}}^{\text{red}} = 36819 - 13.138T$	298.15–6000
		${}^0G_{\text{P}}^{\text{red}} - {}^0H_{\text{P}}^{\text{white}} = -25976.559 + 148.685002T - 25.55T \ln T + 0.0034121T^2 - 2.418867 \times 10^{-6}T^3 + 160095T^{-1}$	275–500
	red	$= -21723.721 + 77.684737T - 14.368T \ln T - 0.00957685T^2 + 3.93917 \times 10^{-7}T^3 - 141375T^{-1}$	500–852.35
		$= -119408.413 + 1026.04262T - 149.449556T \ln T + 0.067272364T^2 - 6.651929 \times 10^{-6}T^3 + 1249543T^{-1}$	852.35–1500
		$= -24524.119 + 153.852181T - 26.326T \ln T$	1500–3000
	white	${}^0G_{\text{P}}^{\text{white}} - {}^0H_{\text{P}}^{\text{white}} = -43821.799 + 1026.70689T - 178.426T \ln T + 0.290708T^2 - 1.04022667 \times 10^{-4}T^3 + 1632695T^{-1}$	250–317.3
		$= -9587.448 + 152.354487T - 28.7335301T \ln T + 0.001715669T^2 - 2.2829 \times 10^{-7}T^3 + 172966T^{-1}$	317.3–900
		$= -8093.075 + 135.889831T - 26.326T \ln T$	900–3000

T_c: Curie temperature, β: magnetic moment

$$G^{\theta} = \Delta_f H_{298 \text{ K}} + \int_{298 \text{ K}}^T C_p dT - T[S_{298 \text{ K}} + \int_{298 \text{ K}}^T (C_p/T) dT] \quad (8)$$

where $\Delta_f H_{298 \text{ K}}$ and $S_{298 \text{ K}}$ are the enthalpy of formation and the entropy at 298 K, and C_p is the heat capacities at constant pressure.

In Seierstein's study,²² non-stoichiometric compound, $\text{Al}_{13}\text{Fe}_4$, was modeled with three sublattices: $(\text{Al})_{0.6275}(\text{Fe})_{0.235}(\text{Al}, \text{Va})_{0.1375}$ in order to account for its binary solubility range. The Gibbs energy is given by

$$G^{\text{Al}_{13}\text{Fe}_4} = y_{\text{Al}}^{\text{m}} G_{\text{Al:Fe:Al}}^{\text{Al}_{13}\text{Fe}_4} + y_{\text{Va}}^{\text{m}} G_{\text{Al:Fe:Va}}^{\text{Al}_{13}\text{Fe}_4} + 0.1375RT(y_{\text{Al}}^{\text{m}} \ln y_{\text{Al}}^{\text{m}} + y_{\text{Va}}^{\text{m}} \ln y_{\text{Va}}^{\text{m}}) \quad (9)$$

where the superscript "m" denotes the third sublattice of the presented model, y_i^{m} is the site fraction of i in the third sublattice, Va is the vacancy in the third sublattice. $G_{\text{Al:Fe:Al}}^{\text{Al}_{13}\text{Fe}_4}$ and $G_{\text{Al:Fe:Va}}^{\text{Al}_{13}\text{Fe}_4}$ are the Gibbs energy of the two end members $(\text{Al})_{0.6275}(\text{Fe})_{0.235}(\text{Al})_{0.1375}$ and $(\text{Al})_{0.6275}(\text{Fe})_{0.235}(\text{Va})_{0.1375}$.

No ternary intermetallic compounds have been reported in previous study and all binary intermetallic phases were treated to have zero ternary solubility in the Al-Fe-P system in present work.

4 Optimization results and discussion

The binary and ternary interaction parameters have been optimized using the PARROT module included in the ThermoCalc software package.⁹ The phase diagram data and experimental thermodynamic information were used as the input to the program. Each datum value was given a certain weight by our personal evaluation of the datum source and considering the consistency between the phase diagram and the thermodynamic properties. The interaction parameters have been evaluated by trial and error method during the course of the optimization until most of the selected experimental information is reproduced within the expected uncertainty limits. As a result, a complete list of the thermodynamic parameters describing the Al-Fe-P system is summarized in Table 1. Computed phase equilibria are compared to the selected experimental information reviewed in Sections 2.1 and 2.3. And a brief discussion is given as below.

4.1 Al-P binary system

The calculated phase diagram of Al-P system is shown in Fig.1(c). The evaluated melting point of AlP is 2803 K, which agrees well with the experimental value (2803±50) K.¹⁴ As mentioned in Section 2.1, there are large differences among the experimental values of enthalpy formation of AlP determined by

different researchers. The calculated $\Delta_f H_{298\text{ K}}(\text{AlP}) = -74.0 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{atom}^{-1}$, is close to the value measured by Wang and Zaeheervuddin.¹⁶

4.2 Al-Fe-P ternary system

By using the present optimized parameters of the Al-P system along with the reported parameters of the Al-Fe²² and Fe-P³⁰ systems, and based on the vertical section and isothermal section diagram information, the Al-Fe-P ternary system is fur-

ther optimized. The parameters of the Al-Fe and Fe-P system were slightly modified in order to fit the experimental data better.

The experimental and calculated isothermal section diagrams at room temperature are shown in Fig.2. It is easy to see that most of the phase relations have been well reproduced. The representative calculated vertical section diagrams with experimental data are illustrated in Fig.3. Although there is, in

Fig.2 (a) Isothermal section diagram of the Al-Fe-P system at room temperature determined by Vogel and Klose³¹ and redrawn by Schmid-Fetzer and Tomashik³⁸ and (b) calculated isothermal section diagram at room temperature in this work

Fig.3 Calculated vertical section diagrams compared with the experimental data³¹

(a) $w(\text{P})=6\%$, (b) $w(\text{P})=9\%$, (c) $w(\text{Al})=10\%$, (d) $w(\text{Al})=25\%$

general, a satisfactory agreement between the experimental data reported by Vogel and Klose³¹ for the phase diagram, some differences still exist, e.g. a relative discrepancy on the liquidus line between the calculated and the experimental data was observed. Actually, great care has been taken to reduce these discrepancies in our assessment, but it was found that it is difficult to fit these experimental data very well. It is still necessary to get more new experimental data to solve this problem. Additionally, some of the equilibria with respect to the bcc phase are inconsistent with the measured vertical sections by Vogel and Klose,³¹ e.g. in our assessment, bcc phase is respectively in equilibrium with Fe₂P and liq+Fe₂P in the dashed regions, as shown in Fig.3(d), rather than AIP and liq+AIP reported by Vogel and Klose.³¹

It was worthy to point out that we calculated the isothermal section diagram of the Al-Fe-P system at 723 K and compared with the latest experimental data,⁸ which was published after the present assessment had been finished, and a good agree-

Fig.4 Calculated isothermal section diagram of the Al-Fe-P system at 723 K compared with the experimental data⁸

Fig.5 Calculated liquidus projection of the Al-Fe-P system

Table 3 Present calculated values for the invariant reactions in the Al-Fe-P system with the experimental data³¹

Reaction	T/K	Type	$x(\text{liq,Al})$	$x(\text{liq,Fe})$	Ref.
$\text{liq} \rightarrow \text{AIP} + \text{FeP}_2 + \text{FeP}_4$	1759	E1	0.009	0.267	this work
$\text{liq} \rightarrow \text{FeP} + \text{AIP} + \text{FeP}_2$	1663	E2	0.021	0.428	this work
$\text{liq} + \text{Al}_3\text{Fe}_4 + \text{Al}_3\text{Fe}_2 \rightarrow \text{Al}_2\text{Fe}$	1426	P3	0.675	0.321	this work
$\text{liq} + \text{Al}_3\text{Fe}_2 \rightarrow \text{AIP} + \text{Al}_{13}\text{Fe}_4$	1422	U1	0.751	0.245	this work
$\text{liq} + \text{Al}_3\text{Fe}_2 \rightarrow \text{Al}_2\text{Fe} + \text{AIP}$	1417	U2	0.651	0.331	this work
$\text{liq} \rightarrow \text{AIP} + \text{Al}_3\text{Fe}_4 + \text{Al}_2\text{Fe}$	1414	E3	0.628	0.349	this work
$\text{liq} \rightarrow \text{AlFe} + \text{Al}_3\text{Fe}_4 + \text{AIP}$	1403	E4	0.532	0.413	this work
$\text{liq} + \text{FeP} \rightarrow \text{Fe}_2\text{P} + \text{AIP}$	1383	U3	0.076	0.574	this work
$\text{liq} \rightarrow \alpha + \text{Fe}_2\text{P} + \text{Fe}_3\text{P}$	1303	E5	0.099	0.710	this work
	1298		0.140	0.680	31
$\text{liq} \rightarrow \text{AlFe} + \text{Fe}_2\text{P} + \text{AIP}$	1268	E6	0.206	0.575	this work
	1268		0.275	0.556	31
$\text{liq} \rightarrow \gamma + \text{Al}_{13}\text{Fe}_4 + \text{AIP}$	927	E7	0.991	0.009	this work
$\text{liq} \rightarrow \text{FeP}_4 + \text{P} + \text{AIP}$	852	E8	~0	~0	this work

ment between them was obtained, as shown in Fig.4. It proved that the thermodynamic parameters gained in our optimization are reliable.

Taking into account the available information on the binary and ternary systems, the complete liquidus projection for the whole Al-Fe-P system are illustrated in Fig.5. The calculated and experimental invariant temperatures and the corresponding compositions for the various invariant reactions are summarized in Table 3. Although the temperatures are generally in good agreement with the experimental values, there are still some differences in the compositions. Invariant reactions E7 and E8 are very near to the binary subsystems, so these two invariant reactions cannot be visible in Fig.5. Necessary experiments are also needed to validate the liquidus projection in the Al-Fe-P system.

5 Explanation on the glass-forming ability

The driving force (DF) criterion^{5,6} is based on the assumption that the phase having the highest driving force is most like-

Fig.6 Calculated driving force (DF) surface projection at 973 K superimposed with iso-DF lines and the experimental glass compositions denoted by Inoue⁴

The values of the DF shown in the color bar have been divided by RT, and thus are dimensionless.

ly to form first. Considering that the formation of an amorphous phase would be favored when the nucleation and growth of crystalline phases are retarded, then the composition with the highest glass-forming ability can be the one with the lowest driving force of formation of crystalline phases. In order to analyze the composition dependency of the glass-forming ability, the initial crystallization driving force, which can be regarded as a representation of the nucleation ability of the crystalline phases, was employed in this work. The initial driving forces of all crystalline phases under every specified liquid composition at 973 K were first calculated and then the maximal values under each composition were chosen to construct the DF surface projection, as shown in Fig.6. Iso-DF lines and the experimental glass compositions are superimposed on it. All the experimental data are in the region where the driving forces are lower than 0.9. This is in accordance with the driving force criterion: alloys having lower driving forces possess higher glass-forming abilities. This proves that the driving force criterion can be used as an index to predict the composition field most likely having the best glass-forming ability before any experiments.

6 Conclusions

Based on the available experimental information on the Al-P and the Al-Fe-P systems as well as the published assessment of the Al-Fe and the Fe-P binary systems, a critical assessment of the Al-P binary and the Al-Fe-P ternary system was carried out and a consistent thermodynamic description for describing all the phases in the Al-Fe-P system was obtained. The phase diagrams of the Al-Fe-P system over the entire composition range, including the vertical sections for $w(\text{P})=6\%$, 9% , and $w(\text{Al})=10\%$, 25% , the isothermal section at room temperature as well as the liquidus projection was constructed from present thermodynamic calculation. Most reported compositions of amorphous phase lie in the regions with low initial driving forces for the crystalline phases, which soundly proves the reasonability and reliability of the present thermodynamic description.

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