

## THERMODYNAMIC MODELING OF THE Sc-Zn SYSTEM COUPLED WITH FIRST-PRINCIPLES CALCULATION

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### *Abstract*

*The Sc-Zn system has been critically reviewed and assessed by means of CALPHAD (CALculation of PHase Diagram) approach. By means of first-principles calculation, the enthalpies of formation at 0 K for the ScZn, ScZn<sub>2</sub>, Sc<sub>17</sub>Zn<sub>58</sub>, Sc<sub>3</sub>Zn<sub>17</sub> and ScZn<sub>12</sub> have been computed with the desire to assist thermodynamic modeling. A set of self-consistent thermodynamic parameters for the Sc-Zn system is then obtained. The calculated phase diagram and thermodynamic properties agree well with the experimental data and first-principles calculations, respectively.*

*Keywords: Sc-Zn system; Thermodynamic calculation; First-principles calculation; CALPHAD*

### **1. Introduction**

Novel Al-Zn-Mg-Sc alloy, as a type of lightweight structure material, has attracted a great interest due to its high strength, high toughness, good corrosion resistance and ascendant welding performance [1, 2]. It is

reported that the addition of Sc in Al-Zn-Mg alloy is helpful for the grain refinement so as to decrease the density of the crack during solidification and to increase the strength of welding seam [3]. The amount of Sc utilized in alloys must be under control since even a little variation of its content will possibly have a

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great impact on material performance. Thus it is of great importance to know the interaction of Sc with other elements within the Al-Zn-Mg-Sc quaternary system. So far, no thermodynamic description on the Sc-Zn system has been carried out. The main purpose of the present work is to carry out thermodynamic investigation of Sc-Zn system by means of CALPHAD modeling and first-principles calculation.

## 2. Literature review

The experimental information about the Sc-Zn system was rather limited. The phase diagram data were reported by Palenzona and Manfrinetti [4] only. No experimental thermodynamic properties have been reported. The Sc-Zn phase equilibria between 0 to 60 at.% Sc were measured by Palenzona and [4] using metallography, differential thermal analysis (DTA) and X-ray diffraction (XRD) methods. Five intermetallic compounds ScZn [4, 5, 6, 7], ScZn<sub>2</sub> [4, 5], Sc<sub>17</sub>Zn<sub>58</sub> [4], Sc<sub>3</sub>Zn<sub>17</sub> [4, 8] and ScZn<sub>12</sub> [4, 8] exist in the Sc-Zn binary system, the crystallographic data of which were reviewed by Predel [9] and Okamoto [9]. No solubility of Sc in Zn has been detected as no significant changes in the lattice parameters of zinc have been observed [4]. No report for the solubility of  $\beta$ -Sc and  $\alpha$ -Sc has been published. The present optimization was based on the phase equilibria measured by Palenzona and Manfrinetti [4], which was reviewed by several groups of authors [10, 11, 12].

## 3. First-principles calculation

First-principles calculation has been

demonstrated to be one powerful method to assist CALPHAD modeling. In this work, first-principles method was employed to calculate the enthalpies of formation of the compounds ( $\Delta H_f$ ) at 0 K since no experimental thermodynamic properties were reported about the Sc-Zn system. The atomistic calculation results were considered reliable and used in the subsequent CALPHAD modeling.

The highly-efficient first-principles plane wave pseudopotential method as implemented in the Vienna ab initio simulation package (VASP) [13, 14] is utilized for the present first-principles calculation. The electron-ion interactions are described by the full potential frozen-core PAW method [15, 16], and the exchange-correlation is depicted by the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [17]. Convergence tests indicate that a cutoff of 400 eV is sufficient to insure the total energy differences are less than 1 meV/atom. The k-points meshes for Brillouin zone (BZ) sampling are constructed using Monkhorst-Pack scheme [18] and at least 1,0000 per reciprocal atom are used. Total energy calculations are performed by means of the tetrahedron method incorporation with Blöchl corrections [19]. The convergence criterion for electronic self-consistency and ionic relaxation loop are  $10^{-6}$  eV and  $10^{-3}$  eV/Å, respectively. It is worth mentioning that the unit cells of Sc-Zn compounds are fully relaxed with respect to the volume, the shape of the unit cell and the atomic positions.

The equilibrium enthalpies of formation for the Sc-Zn intermetallics are evaluated by

the following equation:

$$\Delta E^{eq}(\text{Sc}_p\text{Zn}_q) = E(\text{Sc}_p\text{Zn}_q) - [x_{\text{Sc}}E^{eq}(\text{Sc}) + x_{\text{Zn}}E^{eq}(\text{Zn})] \quad (1)$$

where  $E(\text{Sc}_p\text{Zn}_q)$ ,  $E^{eq}(\text{Sc})$  and  $E^{eq}(\text{Zn})$  are static energies (per atom) at 0 K for compound and  $\text{Sc}_p\text{Zn}_q$  element Sc, Zn, respectively.  $x_{\text{Sc}} = p / (p + q)$  and  $x_{\text{Zn}} = q / (p + q)$  are the concentrations of Sc and Zn, respectively.

## 4. Thermodynamic modeling

### 4.1. Unary phases

The Gibbs energy function,  $G_i^{0,\phi}(T) = G_i^\phi(T) - H_i^{\text{SER}}$ , for the element  $i$  ( $i = \text{Sc}, \text{Zn}$ ) in  $\Phi$  phase ( $\Phi = \text{Zn}(\text{Hcp\_A3})$ ) is given as follows:

$$G_i^{0,\phi}(T) = a + b \cdot T + c \cdot T \ln T + d \cdot T^2 + e \cdot T^3 + f \cdot T^{-1} + g \cdot T^7 + h \cdot T^{-9} \quad (2)$$

where  $H_i^{\text{SER}}$  is the molar enthalpy of the element  $i$  at 298.15 K and 1 bar in its stable element reference (SER) state, and  $T$  is the absolute temperature. In the present modeling, the Gibbs energy as a function of temperature is taken from the SGTE compilation by Dinsdale [20].

### 4.2. Solution phases

The Gibbs energy for the solution phase  $\Phi$  ( $\Phi = \text{liquid}, (\alpha\text{Sc})$  and  $(\beta\text{Sc})$ ) is described by the Redlich–Kister polynomial [21]:

$$G_m^\phi - H^{\text{SER}} = (1-x) \cdot {}^0G_{\text{Zn}}^\phi + x \cdot {}^0G_{\text{Sc}}^\phi + R \cdot T \cdot [(1-x) \cdot \ln(1-x) + x \cdot \ln x] + x \cdot (1-x)[a_0 + b_0 \cdot T + (1-2x) \cdot (a_1 + b_1 \cdot T) + \dots] \quad (3)$$

in which  $H^{\text{SER}}$  denotes  $(1-x) \cdot H_{\text{Zn}}^{\text{SER}} + x \cdot H_{\text{Sc}}^{\text{SER}}$ ,  $R$  is

the gas constant, The interaction coefficients  $a_j$  and  $b_j$  ( $j = 0, 1, 2, \dots$ ) are to be evaluated in the optimization process.

### 4.3. Intermetallic phases

No considerable solubility ranges for the compounds,  $\text{ScZn}$ ,  $\text{ScZn}_2$ ,  $\text{Sc}_{17}\text{Zn}_{58}$ ,  $\text{Sc}_3\text{Zn}_{17}$  and  $\text{ScZn}_{12}$ , were reported [4]. Therefore all the intermetallic compounds were modeled as stoichiometric phases. The Gibbs energy of each phase per mole-atoms is described by the following formula:

$$G(\text{Sc}_x\text{Zn}_y) - x \cdot H_{\text{Sc}}^{\text{SER}} - y \cdot H_{\text{Zn}}^{\text{SER}} = x \cdot {}^0G_{\text{Sc}}^{\text{Hcp}} + y \cdot {}^0G_{\text{Zn}}^{\text{Hcp}} + A + B \cdot T \quad (4)$$

where  ${}^0G_{\text{Sc}}^{\text{Hcp}}$  and  ${}^0G_{\text{Zn}}^{\text{Hcp}}$  are the Gibbs energies of Hcp-Sc and Hcp-Zn, respectively. The parameters  $A$  and  $B$  are to be optimized in the present work.

## 5. Results and discussion

### 5.1. First-principles calculations

Table 1 compares the first-principles calculated crystallographic data for the intermetallic compounds in the Sc-Zn system along with the experiment values. As shown in Table 1, the calculated crystallographic data for the intermetallic phases using first-principles calculations agree reasonably with those from experiments. The good agreement between the first-principles calculations and experiments indicates that the present first-principles calculations are reliable.

Figure 1 shows the  $\Delta H_f$  for the compounds according to the present calculations. As shown in Fig. 1, the absolute value for the enthalpies of formation decreases with the increase of the

Table 1. The crystallographic data for the intermetallic compounds in the Sc-Zn system obtained from present first-principles calculations along with the literature data.

Phase	Pearson	Space group	Lattice parameter(Å)		Ref.
	symbol		a	c	
$(\alpha\text{Sc})$	<i>hP2</i>	$P6_3/mmc$	3.318	5.154	<sup>a</sup> FP
			3.308	5.265	[22]
$(\beta\text{Sc})$	<i>cF4</i>	$Fm-3m$	4.618	-	<sup>a</sup> FP
			4.52	-	[23]
Zn	<i>hP2</i>	$P6_3/mmc$	2.634	5.142	<sup>a</sup> FP
			2.665	4.945	[24]
ScZn	<i>cP2</i>	$Pm-3m$	3.357	-	<sup>a</sup> FP
			3.35	-	[6]
ScZn <sub>2</sub>	<i>hP3</i>	$P6_3/mmc$	5.277	8.481	<sup>a</sup> FP
			5.251	8.477	[7]
ScZn <sub>12</sub>	<i>tI26</i>	$I4/mmm$	8.807	5.181	<sup>a</sup> FP
			8.806	5.158	[4]
Sc <sub>13</sub> Zn <sub>58</sub>	<i>hP142</i>	$P6_3/mmc$	13.897	13.698	<sup>a</sup> FP
			13.741	13.632	[4]
Sc <sub>3</sub> Zn <sub>17</sub>	<i>cI160</i>	$Im-3$	13.784	-	<sup>a</sup> FP
			13.79	-	[8]

<sup>a</sup>FP = First-principles calculations in the present work.

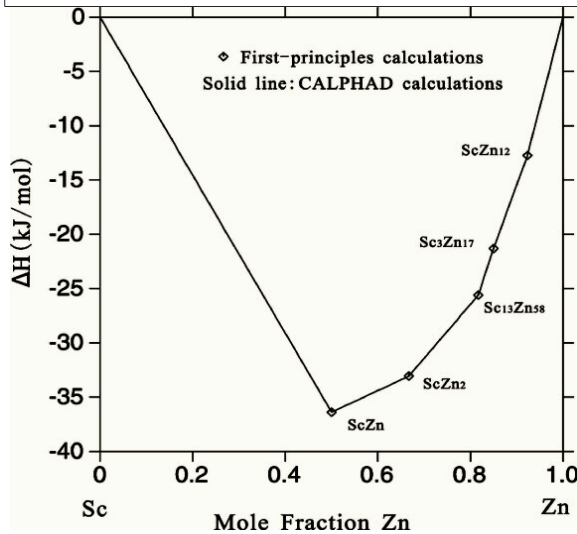


Fig. 1. Enthalpies of formation at 0 K according to the present calculations. The reference states are *Hcp\_A3*(Sc) and *Hcp\_Zn*(Zn).

content of Zn for the Sc-Zn compounds. ScZn has the most negative enthalpy of formation since it has the highest melting point among the reported compounds. The CALPHAD-type calculated enthalpies of formation for the compounds are in well consistent with the first-principles calculation results.

## 5.2. CALPHAD modeling

The optimization of the thermodynamic parameters were carried out by the computer-operated optimization program PARROT [25] of Thermo-Calc software, which works by minimizing the squared sum of the differences between experimental values and computed ones. The step by step optimization procedure carefully described by Du *et al.* [26] was utilized in the present work. Reliable experimental data [4] and enthalpies of formation calculated via the first-principles method were employed in the optimization.

The optimization started with the intermetallic phases. The first-principles calculated  $\Delta H_f$  of the intermetallic compounds was used to evaluate the value of coefficient *A* in Eq. (4). Next, the liquid phase was considered. In this work, it was found that three coefficients ( $a_0$ ,  $a_1$  and  $b_0$ ) should be introduced in order to describe the properties of the liquid phase satisfactorily. Coefficient *B* in Eq. (4) was optional and only used where it is indispensable to describe the correlative phase equilibria. Finally, the thermodynamic parameters for all the phases were adjusted simultaneously using all the measured phase equilibrium information. The finally obtained parameters in the present work are listed in Table 2.

Figure 2 presents the calculated Sc-Zn phase diagram along with the experimental data [4].

Table 2 Summary of the thermodynamic parameters in the Sc-Zn system.

Liquid : (Sc,Zn) <sub>1</sub>
${}^0L_{Sc,Zn}^{liq} = -83967 + 10.7848 \cdot T$
${}^1L_{Sc,Zn}^{liq} = +15273$
ScZn: (Sc) <sub>1/2</sub> (Zn) <sub>1/2</sub>
${}^0G_{Sc,Zn}^{ScZn} - 0.5 \cdot G_{Sc}^{hcp} - 0.5 \cdot G_{Zn}^{hcp} = -36379 + 5.1667 \cdot T$
ScZn <sub>2</sub> : (Sc) <sub>1/3</sub> (Zn) <sub>2/3</sub>
${}^0G_{Sc,Zn}^{ScZn_2} - (1/3) \cdot G_{Sc}^{hcp} - (2/3) \cdot G_{Zn}^{hcp} = -33063 + 5.1345 \cdot T$
Sc <sub>13</sub> Zn <sub>58</sub> (Sc) <sub>13/71</sub> (Zn) <sub>58/71</sub>
${}^0G_{Sc,Zn}^{Sc_{13}Zn_{58}} - (13/71) \cdot G_{Sc}^{hcp} - (58/71) \cdot G_{Zn}^{hcp} = -25600 + 6.0471 \cdot T$
Sc <sub>3</sub> Zn <sub>17</sub> : (Sc) <sub>3/20</sub> (Zn) <sub>17/20</sub>
${}^0G_{Sc,Zn}^{Sc_3Zn_{17}} - 0.15 \cdot G_{Sc}^{hcp} - 0.85 \cdot G_{Zn}^{hcp} = -21287 + 3.9010 \cdot T$
ScZn <sub>12</sub> : (Sc) <sub>1/13</sub> (Zn) <sub>12/13</sub>
${}^0G_{Sc,Zn}^{ScZn_{12}} - (1/13) \cdot G_{Sc}^{hcp} - (12/13) \cdot G_{Zn}^{hcp} = -12741 + 4.0350 \cdot T$
★ In J mole-atoms <sup>-1</sup> ; Temperature (T) in Kelvin.

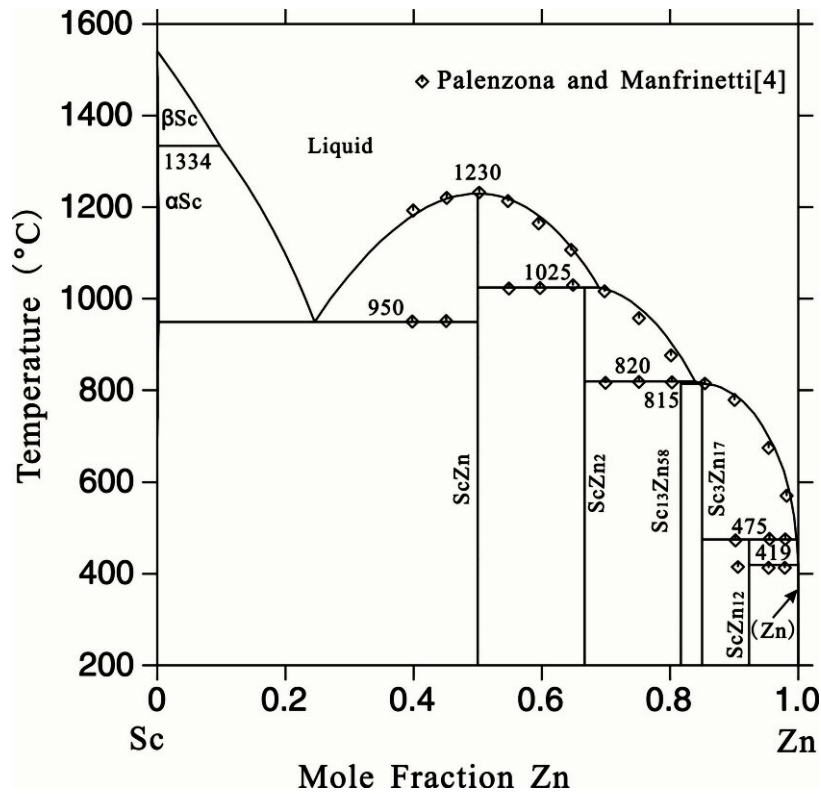


Fig. 2. Calculated Sc-Zn phase diagram in comparison with the experimental data [4]

Table 3 Calculated invariant reactions along with the experimental ones.

Reaction	Type	Composition(at.% Zn)	T/°C	Reference
$\beta\text{Sc} \leftrightarrow \text{Liquid} + \alpha\text{Sc}$	Eutectic	-	-	-
		0.16 9.77 0.14	1334	This work
Liquid $\leftrightarrow$ ScZn	Congruent	- -	1230	[4]
		50.00 50.00	1230	This work
Liquid+ScZn $\leftrightarrow$ ScZn <sub>2</sub>	Peritectic	- - -	1025	[4]
		68.93 50.00 66.67	1025	This work
Liquid $\leftrightarrow$ ScZn+Hcp_A3	Eutectic	- - -	950	[4]
		24.55 50.00 0.24	950	This work
Liquid+ScZn <sub>2</sub> $\leftrightarrow$ Sc <sub>13</sub> Zn <sub>58</sub>	Peritectic	- - -	820	[4]
		83.92 66.67 81.69	820	This work
Liquid $\leftrightarrow$ Sc <sub>13</sub> Zn <sub>58</sub> +Sc <sub>3</sub> Zn <sub>17</sub>	Eutectic	- - -	815	[4]
		85.17 81.69 85.00	815	This work
Liquid+Sc <sub>3</sub> Zn <sub>17</sub> $\leftrightarrow$ ScZn <sub>12</sub>	Peritectic	- - -	475	[4]
		99.73 85.00 92.30	475	This work
Liquid $\leftrightarrow$ (Zn)+ScZn <sub>12</sub>	Eutectic	- - -	415	[4]
		99.97 100.00 92.30	419	This work

The calculated invariant reaction temperatures along with the experimental ones [4] are shown in Table 3. It can be seen that the present calculation can well describe the experimental data [4]. The deviation between the assessed and measured invariant reaction temperature is within 4°C. According to the present calculation, the computed eutectic reaction: liquid = ScZn+ $\alpha$ Sc is located at 950 °C and 77.45 at.% Sc.

Knowledge of phase diagram and thermodynamic properties [27, 28] is of fundamental importance in many applications. High-throughput discovery of new materials strongly depends on the establishment of an accurate thermodynamic database in a multi-component system. The present work is a continuing effort of our previous attempts [29-33] to establish a thermodynamic database for multicomponent Al alloys.

## 6. Conclusions

By first-principles calculation, the enthalpies of formation for the ScZn, ScZn<sub>2</sub>, Sc<sub>17</sub>Zn<sub>58</sub>, Sc<sub>3</sub>Zn<sub>17</sub> and ScZn<sub>12</sub> have been calculated. The first-principles calculated values for these compounds are used as input in the thermodynamic optimization.

The Sc-Zn system has been thermodynamically optimized based on the experimental data and first-principles calculation. A set of self-consistent thermodynamic parameters has been obtained. The present thermodynamic calculation can reproduce the phase diagram boundaries and thermodynamic data satisfactory. Furthermore, due to the employment of first-principles calculation, the present thermodynamic modeling for the Sc-Zn system is

physically reasonable.

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