

AN APPROACH TO DETERMINE ENTHALPIES OF FORMATION FOR TERNARY COMPOUNDS

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Abstract

An integrated approach of experiment and theoretical computation to acquire enthalpies of formation for ternary compounds is described. The enthalpies of formation (ΔH_f) for $Al_{71}Fe_{19}Si_{10}$ and $Al_{31}Mn_6Ni_2$ are measured via a calorimeter. Miedema model, CALPHAD and first-principles method are employed to calculate ΔH_f for the above compounds and several Al-based ternary compounds. It is found that first-principles generated data yield good agreements with experimental values and thus can be used as key "experimental data", which are needed for CALPHAD approach.

Keywords: Aluminum alloys; Intermetallic compounds; First-principle calculations; CALPHAD; Calorimetry

1. Introduction

Knowledge of phase diagram and thermodynamic properties [1,2] 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. Knowledge of thermodynamics is a prerequisite for improving various physical, chemical and mechanical properties of these alloys, and even for exploring new materials [3]. Among the huge number of ternary

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compounds discovered so far, thermodynamic data are available only for a few percent of the reported compounds [4]. The enthalpy of formation, as the leading term of Gibbs energy, is the predominant quantity among various thermodynamic properties. Thermodynamic descriptions for ternary systems are the nucleus of a multi-component thermodynamic database. Consequently, thermodynamic data for ternary compounds are of the utmost importance for obtaining reliable thermodynamic descriptions of ternary systems.

Currently, several experimental methods, such as calorimetric method, electromotive force (emf) technique and Knudsen effusion method, are in use to measure enthalpies of formation for ternary compounds. Although the experimental method is regarded to be the reliable one, it is usually costly and time-consuming. For many investigated ternary compounds, there exist noticeable discrepancies for the measured enthalpies of formation from different sources [5]. Because of the high vaporization in some systems, such as Mg-based alloys, the composition of the sample is changed during the measurement process. In this case, employing experimental method to obtain reliable enthalpy of formation is nearly impossible.

To remedy this situation, various computational approaches have been developed. The widely used methods to calculate enthalpy of formation include, among others, Miedema model, CALPHAD (CALculation of PHase Diagram) approach and first-principles calculation. The Miedema model, which was developed by

Miedema et al. [6,7] combining concepts from the thermodynamics of solids with energy band theory in the mid 1970's, is straightforward. However, systematic deviations from experimental data are often observed in binary and ternary alloys due to intrinsic simplifications associated with this model [7]. Recently, several modified Miedema models have been proposed in order to obtain more reasonable results [8-10]. CALPHAD method predicts enthalpy of formation for any alloy from the Gibbs energy expressions of individual phases [11]. These expressions are optimized from various experimental phase equilibria and thermodynamic properties. The accuracy of this process relies on a reasonable thermodynamic model for each phase, accurate experimental information as well as the quality for thermodynamic descriptions of the lower-order systems. Recent calculations [14,15] show that first-principles method (e.g. density functional theory (DFT)) [16] provides an alternate way to obtain enthalpies of formation. Accurate crystal structure is a prerequisite for obtaining enthalpy of formation by means of first-principles method. For a phase with a few hundred atoms per unit cell, first-principles calculation is, however, extremely time-consuming.

Thus, any individual experimental or theoretical method mentioned above cannot give entirely satisfactory results. In the present work, we propose an effective approach to obtain enthalpies of formation for ternary compounds highly efficiently. Such an approach is the integration of Miedema model, CALPHAD approach, first-principles calculations, and high temperature

reaction calorimetry (HTRC). To verify this methodology, we focus on the Al-Fe-Si and Al-Mn-Ni ternary systems, which are two important sub-systems of multi-component Al alloys.

2. Theoretical models

In order to get insight into the approximate value of enthalpy of formation, the Miedema model is employed in the first step of the methodology. The calculations based on the original Miedema model (OMM) [6,7] usually show large deviations from experimental values, and the discrepancies are mainly due to the assumption in the OMM that the third element has no effect on the other two elements when calculating the interfacial energy between them [8,9]. Such an interfacial energy is one of the several parameters used in Miedema model. Recently, several improved models have been developed by taking the interactions between the third element and the other two into account [8-10]. Among them, the geometric model (GM) from Ouyang et al. [10] shows promise. The advantage of GM is that it simplifies the calculations with no need for integration computation when considering the effect of an added element on the interaction between the other two elements, and can be easily extended into multi-component systems. Consequently, GM is employed to estimate the approximate value for the enthalpy of formation in the present calculations.

According to GM [10], the enthalpy of formation for a ternary alloy can be expressed as follows:

$$\begin{aligned} \Delta H_f^{298K} = & \frac{x_A x_B}{y_{AB}^A y_{AB}^B} \Delta H_{AB}(y_{AB}^A, y_{AB}^B) + \\ & + \frac{x_A x_C}{y_{AC}^A y_{AC}^C} \Delta H_{AC}(y_{AC}^A, y_{AC}^C) + \\ & + \frac{x_B x_C}{y_{BC}^B y_{BC}^C} \Delta H_{BC}(y_{BC}^B, y_{BC}^C) \end{aligned} \quad \text{.....(1)}$$

Where ΔH_{AB} , ΔH_{AC} and ΔH_{CB} are enthalpies of formation in the A-B, A-C, and B-C binary systems, respectively. ΔH_{AB} is calculated at the composition of y_{AB}^A and y_{BA}^A for A and B components, respectively. x_A , x_B and x_C are the mole fractions of A, B, and C in the A-B-C ternary system, respectively. y_{AB}^A and y_{AB}^B are given by the following expressions:

$$\begin{aligned} y_{AB}^A &= x_A + \frac{\lambda_A}{\lambda_A + \lambda_B} x_C; \\ y_{AB}^B &= x_B + \frac{\lambda_B}{\lambda_A + \lambda_B} x_C \end{aligned} \quad \text{.....(2)}$$

$$\begin{aligned} \lambda_A &= [\Delta H_{B \text{ in } A}^C - \Delta H_{C \text{ in } A}^C]^2; \\ \lambda_B &= [\Delta H_{A \text{ in } B}^C - \Delta H_{C \text{ in } B}^C]^2 \end{aligned} \quad \text{.....(3)}$$

in which $\Delta H_{i \text{ in } j}^c$ ($i=A$ or B ; $j=B$ or C) is the heat of solution of i in j regardless of the effect of the third element. Similar equations can be derived for y_{AC}^A , y_{AC}^C , y_{BC}^B and y_{BC}^C .

CALPHAD is another theoretical approach to obtain the enthalpy of formation. The essence of this approach is to evaluate the parameters of thermodynamic models for the Gibbs energies of the individual phases via a thermodynamic optimization applied to the measured thermodynamic and phase equilibrium data. With the optimized thermodynamic parameters, any phase equilibria and thermodynamic properties can

be computed. Using the GM model predicted enthalpies of formation as reliable estimates for Gibbs energies of ternary compounds, Du et al. [15] and Liu [16] performed thermodynamic optimizations for the Al–Fe–Si and Al–Mn–Ni systems, respectively. The obtained Gibbs energy expressions [15,16] for $\text{Al}_{71}\text{Fe}_{19}\text{Si}_{10}$, Al_3FeSi_2 , $\text{Al}_2\text{Fe}_3\text{Si}_4$, and $\text{Al}_{31}\text{Mn}_6\text{Ni}_2$ are employed to calculate $\Delta H_f^{298\text{K}}$ for the corresponding compounds in the present work.

While the CALPHAD approach is a macroscopic method to acquire enthalpy of formation, first-principles calculation is a microscopic technique. Up-to-date advances in first-principles calculation based on DFT have enabled one to compute thermodynamic and structural properties of phases using only atomic numbers and crystal structure information as input. The crystal data [17,18] shown in Table 1 provide the accessibility to predict enthalpies of

formation for the compounds. In the present work, DFT calculations within the generalized gradient approximation (GGA) [19], as implemented in the highly efficient Vienna ab-initio simulation package (VASP) [20], were utilized to calculate the enthalpies of formation at 0K. The Perdew-Burke-Ernzerhof GGA[21] for the exchange-correlation potential was used for all the calculations, and the valence electrons were explicitly treated by projector augmented plane-wave (PAW) potentials [22]. The atoms were relaxed toward equilibrium until the Hellmann–Feynman forces were less than 10^{-2} eV \AA^{-1} . A plane-wave cutoff energy of 400 eV and an energy convergence criterion of 10^{-5} eV for electronic structure self-consistency were used in the calculations. Brillouin zone integrations were performed using the Monkhorst–Pack k-point meshes scheme [23], and the total energy differences were converged to within 0.1 kJ (mol atoms) $^{-1}$. Both the unit cell sizes

Table 1. Crystal structure data of representative ternary compounds in the Al-Fe-Si and Al-Mn-Ni systems. ^a

Phase	Pearson symbol, Space group, Prototype	Lattice parameter (Å)	
		Measured	Calculated (This work)
Al_3FeSi_2	tI24, I4/mcm, PdGa ₅	a = 6.0887(1)	a = 6.0637
		c = 9.5039(3)	c = 9.4672
$\text{Al}_2\text{Fe}_3\text{Si}_4$	oC36, Cmma, Al ₂ Fe ₃ Si ₄	a = 3.6690(2)	a = 3.6528
		b = 12.385(7)	b = 12.2157
		c = 10.147(5)	c = 10.0784
$\text{Al}_{71}\text{Fe}_{19}\text{Si}_{10}$	hp245, P6 ₃ /mmc, Fe ₂ Al _{7.4} Si	a = 12.404(1)	
		c = 2.6234(2)	
$\text{Al}_{31}\text{Mn}_6\text{Ni}_2$	oS156, Cmcmm, Al ₃₁ Mn ₆ Ni ₂	a = 23.8	a = 23.821
		b = 12.5	b = 12.398
		c = 7.55	c = 7.7618

^a The measured crystal data for the compounds in the Al-Fe-Si system are from Krendelsberger et al. [17], and that for $\text{Al}_{31}\text{Mn}_6\text{Ni}_2$ from Robson [18].

and the ionic coordinates were fully relaxed to find the stable state. The enthalpy of formation at 0K for Al_3FeSi_2 is given by an equation of the form:

$$\Delta H(Al_3FeSi_2) = E(Al_3FeSi_2) - [0.5E(Al) + 0.17E(Fe) + 0.33E(Si)] \quad ..(4)$$

where $E(Al_3FeSi_2)$, $E(Al)$, $E(Fe)$ and $E(Si)$ are the energies of the compound, Al, Fe and Si components, respectively. Each species is relaxed to its equilibrium geometry at zero pressure. The reference states are fcc_Al (nonmagnetic) for Al, bcc_A2 (ferromagnetic) for Fe, and diamond (nonmagnetic) for Si. Similar equations can be written for the other compounds.

3. Experimental procedure

In order to verify the reliability of the above calculations, Kleppa-type HTRC [24] is employed to measure ΔH_f^{298K} for $Al_{71}Fe_{19}Si_{10}$ and $Al_{31}Mn_6Ni_2$ compounds. Details of this high-temperature calorimeter have been published elsewhere [24,25]. The calorimeter is maintained continuously at 1173 and 873 K for the compounds in the Al-Fe-Si and Al-Mn-Ni systems, respectively. During the measurement, a protective argon atmosphere is used. The weight of each sample prepared is about 120 mg. The Fe (99.99 wt.%), Mn (99.95 wt.%) and Ni (99.996 wt.%) powders were reduced in hydrogen prior to preparation of the samples in order to remove oxygen and carbon. The purchased Al (99.97 wt.%) and Si (99.5 wt.%) powders were used directly.

The enthalpy of formation for each compound is measured via two steps. Firstly, elemental powders are mixed in a mortar and

then pressed into a small pellet. This pellet is dropped from room temperature into the calorimeter at the specified temperature to form the compound. Secondly, the above obtained pellet was subsequently removed and again dropped from room temperature into the calorimeter to obtain the heat content of the compound. Taking $Al_{71}Fe_{19}Si_{10}$ for example, the corresponding reactions associated with the above two steps are:

$$0.71Al(s, 298K) + 0.19Fe(s, 298K) + 0.1Si(s, 298K) = Al_{0.71}Fe_{0.19}Si_{0.1}(1173K) \Delta H_1 \quad ..(5)$$

$$Al_{0.71}Fe_{0.19}Si_{0.1}(s, 298K) = Al_{0.71}Fe_{0.19}Si_{0.1}(1173K) \Delta H_2 \quad \dots(6)$$

where s refers to the solid state, and ΔH_1 and ΔH_2 are the enthalpy changes for reactions 1 and 2, respectively. The difference between the two reactions yields the enthalpy of formation for $Al_{71}Fe_{19}Si_{10}$ at room temperature:

$$\Delta H_f^{298K}(Al_{0.71}Fe_{0.19}Si_{0.1}) = \Delta H_1 - \Delta H_2 \quad \dots(7)$$

The finally accepted is the average of 6 individual measurements. With the standard deviations from the two steps designated as δ_1 and δ_2 and from the calibration using pure Cu as δ_3 , the overall uncertainty δ in the ΔH_f^{298K} measurement was estimated to be $\delta = (\delta_1^2 + \delta_2^2 + \delta_3^2)^{1/2}$.

4. Results and discussion

Enthalpies of formation for representative ternary compounds in the Al-Fe-Si and Al-Mn-Ni systems resulting

from modified Miedema model, CALPHAD method, first-principles calculations, and calorimetric experiment are summarized in Table 2. To the best of our knowledge, this is the first systematic investigation on the enthalpy of formation using a hybrid approach of semi-empirical correlation (Miedema model), macroscopic method (CALPHAD), microscopic one (first-principles calculations), and experiment.

In order to check the general validity of the presently proposed approach, this effective approach is also applied to representative ternary compounds in the Al–Ni–Si [26] and Al–Fe–Ni [27] systems. The enthalpies of formation from various sources are presented in Table 2 and Figure 1, where the calculations are compared with the experimental data from the present work and the literature values [26–28]. The

enthalpies of formation resulting from measurement, CALPHAD and Miedema model are given at 298 K, while those due to first-principles calculations are at 0 K. It has been demonstrated that there is only a minor difference between the enthalpy of formation at 0 K and that at room temperature computed from first-principles method [27]. No first - principles calculation was performed for $\text{Al}_{71}\text{Fe}_{19}\text{Si}_{10}$ since there are 245 atoms per unit cell for this compound. As mentioned before, first-principles calculation is extremely time-consuming for a phase with a few hundred atoms per unit cell.

As shown in Table 2, the measured enthalpies of formation agree reasonably with those from first-principles calculations within the generally accepted accuracy of $\pm 5 \text{ kJ (mol atoms)}^{-1}$. Such accuracy is the

Table 2. Comparisons of enthalpies of formation for ternary compounds in several Al-based systems according to the present work and the literature.

Phase	$\Delta H_f, \text{ kJ (mol atoms)}^{-1}$			
	Calorimetry	First-principles method	CALPHAD	Miedema model
Al_3FeSi_2	-20.48 ± 1.2 [28]	-24.71^a	-15.50^a	-4.2^a
$\text{Al}_2\text{Fe}_3\text{Si}_4$	-35.85 ± 1.8 [28]	-41.36^a	-24.12^a	-9.0^a
$\text{Al}_{71}\text{Fe}_{19}\text{Si}_{10}^b$	-24.6 ± 1.32^a		-20.26^a	-9.4^a
$\text{Al}_{31}\text{Mn}_6\text{Ni}_2$	-23.14 ± 1.34^a	-21.64^a	-22.00^a	-21.9^a
Al_9FeNi	-25.80 ± 1.4 [27]	-27.70 [27]	-22.80^a	-17.0^a
$\text{Al}_{10}\text{Fe}_3\text{Ni}$	-36.20 ± 1.9 [27]	-37.10 [27]	-33.30^a	-23.6^a
AlNi_2Si	-56.43 ± 2.0 [26]	-56.36 [26]	-55.00^a	-38.1^a

^a This work .

^b No first-principles calculation was performed for $\text{Al}_{71}\text{Fe}_{19}\text{Si}_{10}$ since there are 245 atoms per unit cell for this compound. First-principles calculation is extremely time-consuming for a phase with a few hundred atoms per unit cell.

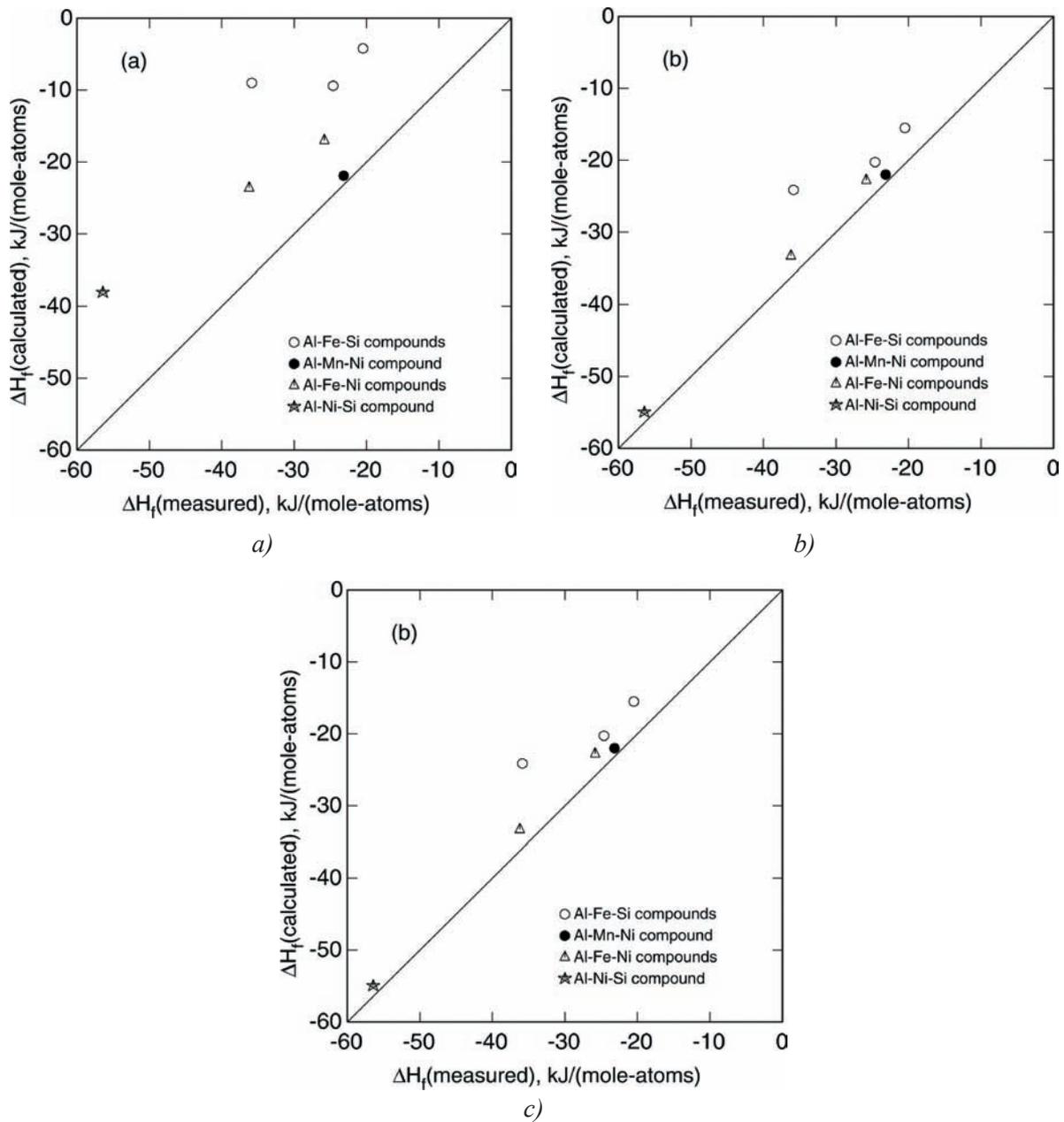


Fig. 1. Comparison of the measured and calculated enthalpies of formation for representative ternary compounds in several Al-based systems. The experimental values due to HTRC measurement are taken from the present work and the literature [26-28]. Along the diagonal line, the calculated value is equal to the experimental one. (a) Miedema model versus measurement; (b) CALPHAD approach versus measurement; and (c) First-principles method versus measurement.

average experimental error among the extensive enthalpy measurements reported in the literature [29]. Both Table 2 and Figure 1

indicate that an improved agreement to experiment is observed for first-principles calculations, in comparison with CALPHAD

approach. This means that the enthalpies of formation computed via first-principles method can be used as “experimental data”, which are needed in CALPHAD method for a thermodynamic modeling of the whole ternary system, when relevant experimental information is not available.

In the case of Miedema model, significant deviations from the experimental values are found for the Al-Fe-Si system. For the Al-Mn-Ni, Al-Fe-Ni, and Al-Ni-Si systems, a maximum deviation of 12 kJ (mol atoms)⁻¹ from the experimental value is indicated. Thus it could be mentioned that the enthalpy of formation estimated with Miedema model is usually far from a precise value although its predictive ability could be improved by including the size effect and effect of the third element [7-10]. In spite of this feature, the Miedema model can provide an approximate value for enthalpy of formation, which is then used as starting value for CALPHAD-type assessment.

5. Conclusion

In summary, we developed an integrated approach of experiment and theoretical computation to acquire reliable enthalpies of formation for ternary compounds in the Al-Fe-Si and Al-Mn-Ni systems. This proposed approach is also successfully applied to several ternary compounds in the Al-Ni-Si and Al-Fe-Ni systems. The calculations demonstrate that first-principles generated enthalpy of formation can be used as key “experimental data”, which are needed for CALPHAD approach, when such experimental data are not available. It is expected that this approach can be adopted

as an effective methodology to obtain enthalpies of formation for largely unexplored ternary compounds.

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