

ESTIMATION OF FORMATION ENTHALPIES USING AN EXTENDED MIEDEMA APPROACH

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ABSTRACT

Finding prospective high temperature materials for use in advanced coal-fired plants has proven to be an extreme materials challenge. We propose a new methodology to predict alloys with high melting temperatures by estimating their formation enthalpies. The Miedema's approach has been extended to ternary systems using an energy minimization scheme. The power of this approach is demonstrated by calculating the site preference of a number of ternary transition metals additions in β -NiAl to increase its thermal stability.

Keywords: Miedema's model, formation enthalpy, nickel aluminides.

INTRODUCTION

The enthalpy of formation is regarded as an indicator of alloy stability hence a number of methods, both computational and experimental, have been devised to estimate the formation enthalpies of alloys. In order to cast a wide search net for prospective alloys or alloy modifications, a rapid means of estimating the formation enthalpies would greatly speed discovery. Theoretical methods can be primarily classified into four types –

- a) First principles calculations, within the framework of density-functional theory¹,
- b) Statistical mechanics based approaches, using atomistic simulation techniques like molecular dynamics²,
- c) Solution thermodynamics, based on extrapolation of experimental data, as in case of the CALPHAD method^{3,4}, and
- d) Semi-empirical methods like Miedema's model⁵, or the BFS (Bozzolo-Ferrante-Smith) model⁶, which is in turn based on the equivalent crystal theory⁷.

Each of these methods has their own pros and cons. First-principles calculations can yield highly accurate values; however they also have a high computing cost and require prior information on the crystal structure. Atomistic simulations of energy can be carried out in a number of methods like harmonic methods, ab-initio calculations, molecular dynamics simulations and Monte Carlo methods. The harmonic methods can be used only for solid

phases since they are based on broken translational and rotational symmetries and localized atomic vibrations. Here, the Helmholtz energy is calculated as a sum of the static potential energy and the vibrational energy. The vibrational frequencies used in the sum can be obtained from the quasiharmonic lattice theory.

The CALPHAD method is based on expressing the thermodynamic variables as a polynomial function of temperature. These functions are stored in databases, e.g. Scientific Group Thermodata Europe (SGTE) database ⁴. In this method, random substitutional solution models are typically used for solid solutions, where components can take up any position available to the phase. While the original approach was used exclusively for binary alloys, a number of researchers have extended this approach for multicomponent alloys as well. While these approaches are fairly fast, they require a prior extensive database. In absence of such a database the CALPHAD approach can't be used.

Amongst the semi-empirical approaches, Miedema's approach is perhaps the most commonly used one. Miedema's method can be adapted for extremely fast calculation of enthalpies; these approaches, though, are not as accurate as ab-initio techniques. However, in situations where a large number of alloys have to be considered in absence of a prior thermodynamic database, an approach like Miedema's provides an excellent starting point. While the original Miedema's model was postulated for binary alloys, in this paper we extend it to ternary systems and apply it to estimating formation enthalpies of a large number of Ni based alloys.

THEORY

MIEDEMA'S MODEL

The Miedema model is built on the "macroscopic atom" picture ⁵. The basic assumption in this case is that the reference can be chosen as atoms embedded in a metal, instead of free atoms. The essence of the model lies in estimating quantitatively the effects of the change in the Wigner-Seitz cell boundary electron density. Dissimilar cells, in contact with each other, shift their electron densities to remove the cell boundary discontinuities in order to form the alloy. Elimination of such discontinuities is expected to require energy; hence the electron density difference Δn_{ws} accounts for a positive contribution to the interface energies. The enthalpy is given by:

$$\Delta H_{ch} = c_A c_B \{ f_B^A \Delta H_{ic}^{AB} + f_A^B \Delta H_{ic}^{BA} \} \quad (1)$$

f_B^A represents the degree to which species A is surrounded by B, and is given as:

$$f_B^A = c_B^s [1 + \gamma (c_A^s c_B^s)^2] \quad (2)$$

where c_A^s represents the concentration of A at the surface and ΔH_{ic}^{AB} represents the interfacial enthalpy for A surrounded by B. The factor γ takes the values 8, 5 and 0 for

intermetallics, metallic glasses and solid solutions respectively. The surface concentrations may be given as –

$$c_B^s = \frac{c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}} \quad (3)$$

This expression can be easily extended to multicomponent alloys as well. The interfacial enthalpy is given by –

$$\Delta H_{ic}^{AB} = \frac{V_A^{2/3}}{(n_{ws}^{-1/3})_{av}} \{-P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2\} \quad (4)$$

The values of P and Q are dependent on the type of metals forming the alloy / intermetallic compound. Usually, the value of P is taken as 14.2 for metals with valency greater than 2, and 10.7 for metals with valency of 1 or 2. The P/Q ratio is maintained at 9.4⁸. Equation 4 has to be modified with an additional enthalpy term, R^* , for transition metal/non-transition metal alloys due to filling of the Brillouin zones of a particular crystal structure. The modified relation reads –

$$\Delta H_{ic}^{AB} = \frac{V_A^{2/3}}{(n_{ws}^{-1/3})_{av}} \{-P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R^*\} \quad (5)$$

Analysis of the model indicates that the introduction of surface concentrations in equation (3) results in the deviation from the regular solution behavior. The quantity $(n_{ws}^{-1/3})_{av}$ in equation (5) is supposed to reflect the influence of the electronic screening length on the width of the dipole layer at the A-B interface⁹.

As Pettifor points out¹⁰, while the model provides very simple and useful rules for alloy formation, the physical concepts upon which it is based finds no justification in quantum mechanics. The attractive contribution in Miedema model is assumed to be ionic in nature¹¹. This clearly is not the case for metallic systems. Despite this, the Miedema's model is still capable of yielding fast and fairly accurate estimates of the formation enthalpy.

The usefulness of Miedema's theory has led to extensive studies on understanding the microscopic origins of the theory¹², as well as numerous applications like eliciting structural information¹³, diffusion of impurity elements¹⁴, glass formation and crystallization^{15,16}, estimation of bulk modulus¹⁷ and formation of point defects¹⁸.

EXTENDING MIEDEMA'S MODEL

A number of investigators have attempted to extend Miedema's approach to multicomponent systems^{16,19-24}. Gallego et. al.¹⁶ approximated the formation enthalpy as a sum of the formation enthalpies of the respective binary systems. Such an approach however neglects the role of ternary interaction parameters and the relative compositions of the individual binaries, since the partitioning coefficients need not be the same for all the binaries. Goncalves and Almeida¹⁹ devised an ingenious approach for estimation of enthalpies based on the relative positions of atoms. This approach was devised for

MgCu₂, MgZn₂, CaCu₅ structure types. In principle the approach can be extended to other structure types as well, once the crystallographic information is available. However, this approach can't be applied in absence of relevant crystallographic information.

Zhang and Jesser²⁰ attempted to extend the Miedema model using the same approach as Gallego et. al.¹⁶ while incorporating an additional strain energy component. The strain energy was calculated using Eshelby's model²⁵. However, Eshelby's model is a continuum approach, devised to treat the stresses arising from inclusions and hence, in the strictest sense, can not be applied to alloying at atomistic levels. Herbst²¹ used an extended version of Miedema model to predict the hydrogen content in ternary hydrides. However, he had to establish and incorporate polynomial fits based on the data for a large number of hydrides. Hence this approach is not a general approach and can't be applied directly to multi-metallic systems.

De Tandler et. al.²² adopted an approach similar to Gallego et. al.¹⁶ while adding an entropy component to estimate the Gibbs free energy. Ouyang et. al.²³ used a geometric approach similar to Toop's approach³. However, it is known that Toop's approach is largely applicable to ionic solids rather than metallic materials. Bera et. al.²⁴ estimated the formation enthalpies using a pseudo-binary approach. However, their approach was based on crystallography and hence can't be used in absence of crystallographic information.

In this paper, we adopt an approach similar to Gallego, with each of the binaries having a certain weight. These weights are determined by numerical minimization of enthalpy. In this approach, the formation enthalpy is given as:

$$\Delta H = \phi_1 \Delta H_{AB}(\alpha) + \phi_2 \Delta H_{BC}(\beta) + \phi_3 \Delta H_{CA}(\gamma) \quad (6)$$

where α , β and γ are atom fraction of species A, B and C in the AB, BC and CA binaries respectively and ϕ_1 , ϕ_2 and ϕ_3 are weights assigned to each of the binaries. These weights are found by minimizing ΔH under the following constraints:

$$\begin{aligned} \sum_{i=1}^3 \phi_i &= 1 \\ \phi_1 \alpha + \phi_3 (1 - \gamma) &= x_A \\ \phi_2 \beta + \phi_1 (1 - \alpha) &= x_B \\ \phi_3 \gamma + \phi_2 (1 - \beta) &= x_C \end{aligned} \quad (7)$$

Once the values of the weights and binary compositions have been determined, the formation enthalpy can be easily computed.

RESULTS AND DISCUSSIONS

A comparison of the calculated formation enthalpies for a number of Ni-Al-X vis-à-vis the experimental values have been given in figure 1a. The experimental values have been taken from a review on formation enthalpies of Ni-Al-X alloys by Hu and Nash²⁶. It can be seen that the calculated and experimental values are in fairly good agreement, considering the semi-empirical nature of the model. Figure 1b shows the comparison specifically for Ni-Al-Hf alloys. It can be seen that in this case the calculated values are in excellent agreement with the experimental values. Figure 1c shows the same comparison for Ni-Al-Ti alloys. We have a large amount of scatter for this alloy system. This is ascribed to the uncertainty in the correct values of the ϕ^* parameter for Ti. Recent work by Chen and Podloucky shows that this parameter can vary between 3.7 and 3.9²⁷. Hence the calculations done in this paper for Ti, using a constant value of ϕ^* is not accurate.

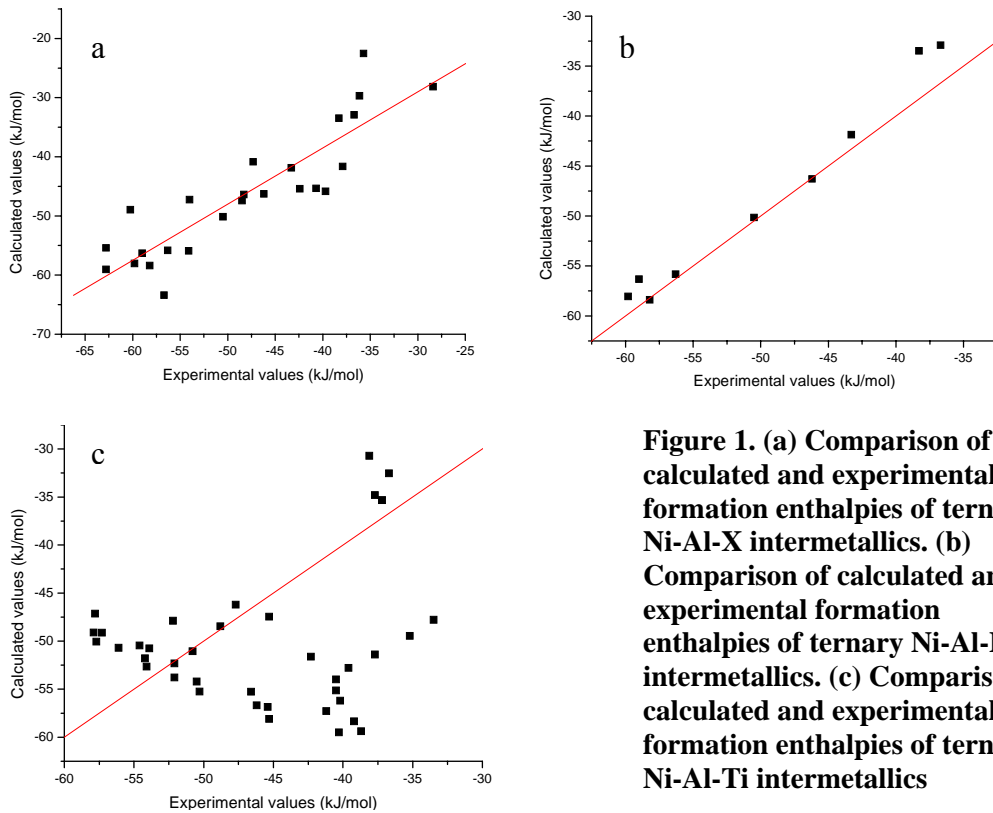


Figure 1. (a) Comparison of calculated and experimental formation enthalpies of ternary Ni-Al-X intermetallics. (b) Comparison of calculated and experimental formation enthalpies of ternary Ni-Al-Hf intermetallics. (c) Comparison of calculated and experimental formation enthalpies of ternary Ni-Al-Ti intermetallics

Figures 2a and 2c show the calculated iso-enthalpy contours for Ni-Al-Fe and Ni-Al-Cr. Figures 2b and 2d show the corresponding liquidus projections. It can be seen that there is a near one-to-one correspondence with the higher liquidus temperatures being present in areas of relatively more negative formation enthalpies, thereby indicating a link between enthalpy of formation and melting temperatures of the alloys.

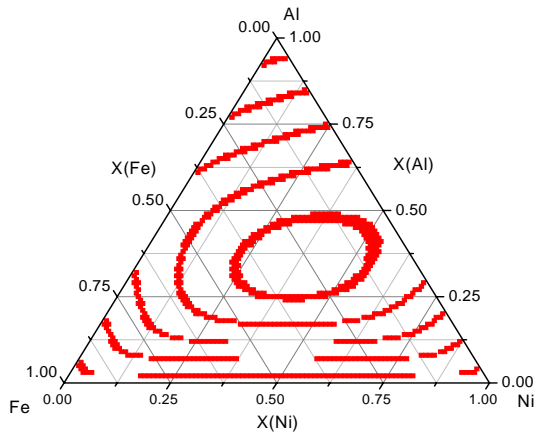


Figure 2a

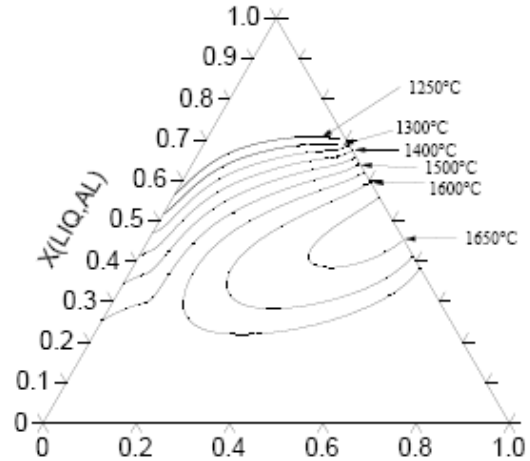


Figure 2b

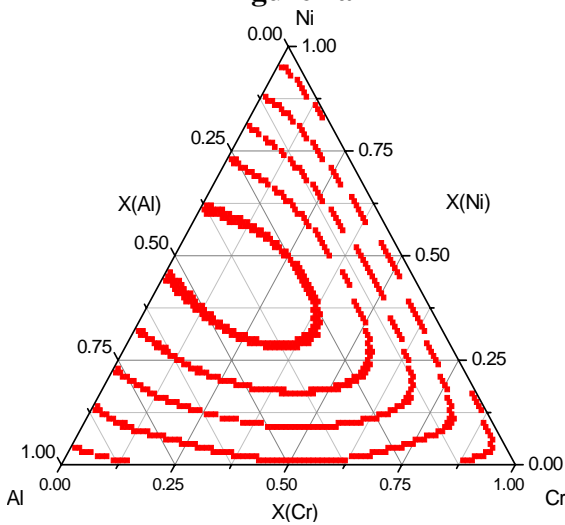


Figure 2c

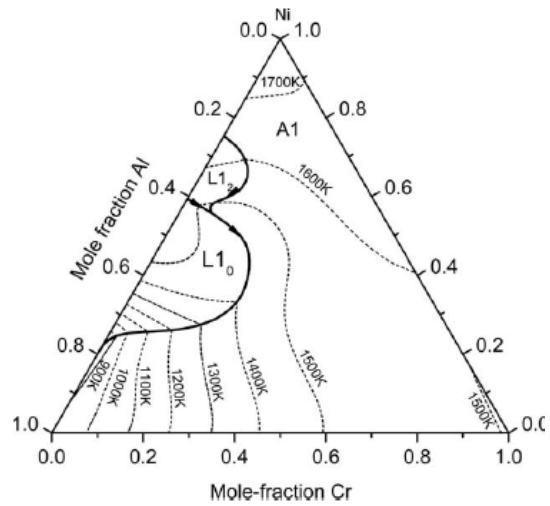


Figure 2d

Figure 2. (a) Iso-enthalpy contour for Fe-Ni-Al based on the extended Miedema model; (b) Liquidus projection for Fe-Ni-Al ²⁸; (c) Iso-enthalpy contour for Al-Cr-Ni based on the extended Miedema model; (d) Liquidus projections for Al-Cr-Ni ²⁸.

We also calculated the formation enthalpies of a number of $\text{Ni}_{50}\text{Al}_{50-x}\text{T}_x$ and $\text{Ni}_{50-y}\text{Al}_{50}\text{T}_y$ alloys, where T is a transition metal. The β -NiAl can be modeled as a combination of two sublattices. As a first approximation, it can be assumed that the transition metal goes into the Al sublattice for $\text{Ni}_{50}\text{Al}_{50-x}\text{T}_x$ alloys and Ni sublattice in case of the $\text{Ni}_{50-y}\text{Al}_{50}\text{T}_y$ alloys. A comparison of the formation enthalpies in the two cases for the same transition metal element addition can give an idea about whether the transition metal addition would be more stable if it goes to the Al sites, or the Ni sites. Table 1 summarizes our results and compares them with the results from experimental and first-principles literature. It can be seen that a fairly good agreement is observed with the literature results.

Table 1: Site preference in NiAl alloys

* Enthalpy values are so close that nothing definitive should be predicted

Element	Preferred site (present model)	Preferred site (Literature)	Reference
Pt	Ni	Ni	29
Ti	Al (lower Ti) / Ni (higher Ti)	Al	29
Zr	Al (lower Zr) / Ni (higher Zr)*	Al	29
Nb	Al	Al	29
Hf	Al (lower Hf) / Ni (higher Hf)	Al	29
Nb	Al	Al	30
Hf	Al (lower Hf) / Ni (higher Hf)	Al	30
Ta	Al (lower Ta) / Ni (very high Ta)	Al	30
Zr	Al (lower Zr) / Ni (higher Zr)*	Al	30
Ti	Al (lower Ti) / Ni (higher Ti)	Al	30

CONCLUSIONS

We have extended Miedema's semi-empirical model by using a simple energy minimization scheme. The extended model predicts the formation enthalpies of ternary intermetallics with fairly good accuracy, with the notable exception of nickel aluminides containing some amount of titanium. The model was also used to predict the site preference of a number of transition metals in β -NiAl. It should be noted that the approach outlined in this paper is an approximate approach. The approach can be improved upon by considering the shifts in atomic volume during alloy formation. This approach can also be extended to solid solutions once the strain energy term is added.

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