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Statistically based assessment of formation enthalpy for intermetallic compounds

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ABSTRACT

A simplified composition-independent atomic size difference factor is proposed to account for the statistical deviation of original Miedema's model for formation enthalpies of binary intermetallic compounds from experimental data. We demonstrate that with the incorporation of this new factor, one can achieve a high level of correlation with respect to available experimental data. Using this statistically refined model, we propose a methodology for assessing where the next level of statistical refinement is needed, utilizing a data-mapping framework of 'critical descriptors'. This provides a way to identify the search space where needs further experimental work to be performed.

A decade ago, by comparing the experimental values published by Kleppa et al. and Meschel et al. [1–6] with the calculated ones from original Miedema's theory, it was found interestingly that over 90% of the calculated values are lower or more negative than the experimentally determined ones [7,8]. Such systematical deviation arose much interest and attention in materials community, and accordingly some modification schemes (see Ref. [8] and related references cited therein) have been proposed to improve its predictability. Among these studies, the atomic size difference (ASD) factor proposed by Zhang et al. [7] has been generally believed to play an important role in affecting the precision of the calculation, yet was not considered in the original Miedema's theory. The introduction of ASD factor is not trivial, but based on the fact that the predicted values with large deviation from experiments always appears in the binary transition-metal systems featuring with large atomic size difference [7]. In order to account for it, ASD factor is proposed to be the intrinsic origin and included into Miedema's model, and consequently its predictability is much improved indeed, demonstrating the success of discovering the underlining physics from intuitive data mining.

In the following years, several groups tried different version of modification of ASD factor to further improve the model predictability (e.g. [8]), unfortunately no significant progress has been obtained so far due to the restriction of the form modification in modeling, not to a discovery of new physics. In this letter, we develop a parameterization scheme for a compositional independent atomic size difference factor in Miedema's model. We use this new improved model to map a continuous phase space of enthalpy data, by using data interpolation methods. By then comparing our new statistical refinement with experimental data, we demonstrate that we have a robust model over a wide composition space and at the same time identify specific regions where refinements can still be made.

According to Miedema's theory, the standard formation enthalpy of the intermetallic compounds consisting of transition, lanthanides and actinide metals, can be evaluated by two critical parameters, i.e. the electronegativity difference and the electron-density discontinuity. The electronegativity difference (is expressed by modified work function) $\Delta\Phi^*$ between two constituent metals is responsible for a negative contribution to the formation energy/enthalpy. It provides a major driving force for the formation of an intermetallic compound by the charge transfer, which decreases the contact potential difference between two dissimilar metals. This parameter can be expressed by the quadratic difference of work function of two constituent metals. The discontinuity of the electron density at the boundaries of the dissimilar Wigner–Seitz (WS) cells is defined as $\Delta n_{WS}^{1/3}$, and the formation enthalpy of an intermetallic compound can be expressed by [9–12],

$$\Delta H_{\mathrm{Mied}}^{\mathrm{for}} = c_A^s \cdot c_B^s \cdot \{1 + 8(c_A^s \cdot c_B^s)^2\} \frac{c_A V_A^{2/3} + c_B V_B^{2/3}}{(n_{WS}^{-1/3})_{av}} \{-P(\Delta\Phi^*)^2 + Q(\Delta n_{WS}^{1/3})^2\} \quad (1)$$

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where, $c_A^s = c_A V_A^{2/3}/(c_A V_A^{2/3} + c_B V_B^{2/3})$, $c_B^s = c_B V_B^{2/3}/(c_A V_A^{2/3} + c_B V_B^{2/3})$, $(n_{ws}^{-1/3})_{av} = (n_{wsA}^{-1/3} + n_{wsB}^{-1/3})/2$. c_i and V_i ($i = A$ or B) are the atomic concentration and molar volume of component i respectively (where the molar volumes account for volume changes during alloying due to charge transfer [11,12].). $\Delta\Phi^*$ is the electronegativity difference parameter or chemical potential difference, and $\Delta n_{ws}^{1/3}$ is the electronic density discontinuity at the boundary of the Wigner–Seitz cell. P, Q are the empirical parameters and their ratio $Q/P = 9.4$ is a critical value which makes $(\Delta\Phi^*)^2$ versus $(\Delta n_{ws}^{1/3})^2$ plot separate the positive and negative alloy systems [9–12].

In order to account for the statistical deviation of the calculated values by original Miedema's model from the experimental ones, a third parameter, i.e. the atomic size difference (ASD) factor [7], was introduced into the modeling because it would frequently lower the contact area between the two dissimilar WS cells and decrease the binding energy between the two dissimilar atoms. In addition, the atomic size difference factor was previously proposed by Hume-Rothery et al. [13] as one of the critical parameters in determining the formation of intermetallic compounds, which however, was not explicitly considered in the original Miedema's model. Accordingly, the modified version can be expressed in a general form,

$$\Delta H_m^{\text{for}} = \text{Sc} \cdot \Delta \text{H}_{\text{Mied}}^{\text{for}} \tag{2}$$

where, Sc is the ASD factor which was originally introduced by Zhang et al. [7] to account for the systematical deviation of calculated values from experiments. It was originally proposed to be dependent on two fundamental parameters such as the atomic sizes of constituent metals and the composition of solute components, indicating its composition-dependent feature. Notice that one must distinguish the solute and solvent atoms when applying the previously proposed ASD by Zhang et al. [7]. Since the composition-dependence cannot be considered as an intrinsic origin of the systematical deviation, we may remove it and consequently the reformulated model is expressed as,

$$\Delta H_m^{\text{for}} = \frac{\alpha \cdot V_A^{2/3} \cdot V_B^{2/3}}{(V_A^{2/3} + V_B^{2/3})^2} \cdot \Delta H_{\text{Mied}}^{\text{for}} \quad \text{i.e. Sc} = \frac{\alpha \cdot V_A^{2/3} \cdot V_B^{2/3}}{(V_A^{2/3} + V_B^{2/3})^2} \tag{3}$$

or in its full form as

$$\Delta H_m^{\text{for}} = \frac{\alpha \cdot V_A^{2/3} \cdot V_B^{2/3}}{(V_A^{2/3} + V_B^{2/3})^2} \cdot c_A^s \cdot c_B^s \cdot \{1 + 8(c_A^s \cdot c_B^s)^2\} \frac{c_A V_B^{2/3} + c_B V_B^{2/3}}{(n_{ws}^{-1/3})_{av}} \times \{-P(\Delta\Phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2\} \tag{4}$$

where, α is an empirical parameter which is determined by a statistical data-driven regression. Because of one single undetermined parameter, linear regression is used to model the relationship between a dependent variable and one or more explanatory variables. The case of one explanatory variable is called simple linear regression. Consequently, the empirical parameter α is determined as $\alpha = 3.2598$ ($P = 14.2$) or $\alpha = 3.2829$ ($P = 14.1$) for the intermetallic compounds consisting of transition, lanthanides and actinides metals. $\text{Sc} = \alpha \cdot V_A^{2/3} \cdot V_B^{2/3}/(V_A^{2/3} + V_B^{2/3})^2$ can be expressed in a more physically understandable way as $\text{Sc} = \alpha^* \cdot (1 - (V_A^{2/3} - V_B^{2/3})^2/(V_A^{2/3} + V_B^{2/3})^2) = \alpha \cdot V_A^{2/3} \cdot V_B^{2/3}/(V_A^{2/3} + V_B^{2/3})^2$ It can be seen that the ASD factor, i.e. Sc, reflects in fact the magnitude of contact surface mismatch during alloying, and is an intrinsic properties of a binary alloy system when dissimilar atoms combines together since it does not depend on the composition of solute anymore. More expressive is its simplified form in a similar manner to electronic density misfit $\Delta n_{ws}^{1/3}$ and electronegativity difference $\Delta\Phi^*$. In addition, we have tried different nonlinear form of ASD besides of the linear regression. For example, assuming that $\chi = (V_A^{2/3} \cdot V_B^{2/3})/(V_A^{2/3} + V_B^{2/3})^2$ and $\text{Sc} = \alpha\chi + \beta\chi^2$, we can get a similar good statistical agreement with experiments (as will be shown below) too, however, a negative regressed value of β without any constraints will result in an unphysical trend of ASD

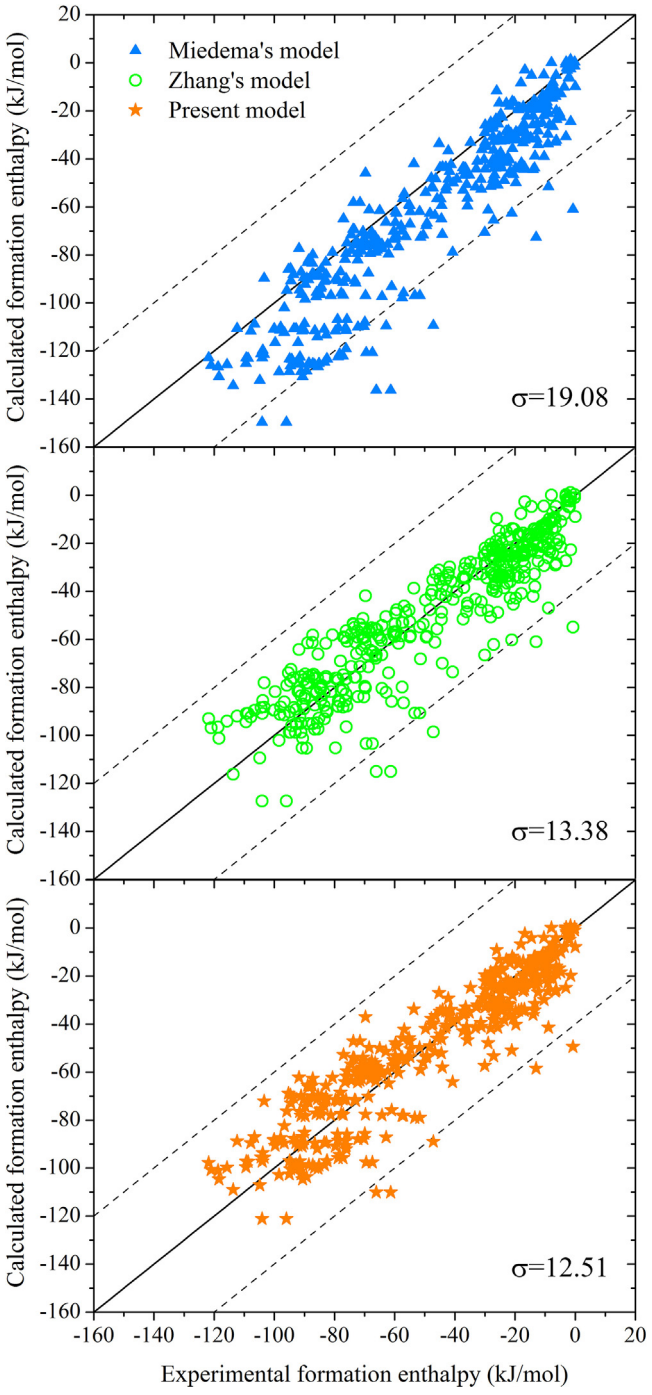

Figure 1. The relationship between experimental data and the calculated standard formation enthalpies of 435 intermetallic compounds by (a) original Miedema's model [9–12], (b) Zhang's previously modified version [7] and (c) the present statistical model. Triangle symbols indicate the values from original Miedema's model, circle symbols stands for Zhang's previously modified model, and star symbols for the present statistical model. Standard deviation between experimental and predicted values is defined as $\sigma = \sqrt{(1/N) \cdot \sum_{i=1}^{N} (y_i^p - y_i^e)^2}$, where y_i^p and y_i^e are the predicted and experimental values respectively. Two dashed lines are set to define a data zone with an error bar of ±30 kJ/mol. Units in kJ/mol.