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Formation enthalpies of Fe–Al–RE ternary alloys calculated with a geometric model and Miedema's theory

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Abstract

A method to estimate the thermodynamic properties of ternary alloys from those of constitutive binary alloys was proposed. The thermodynamic data of binaries were calculated by Miedema's theory. The asymmetry of constitutive binary alloys in the ternary system was considered in the present extrapolating procedure. The dependence of asymmetric constituent on the choice in Toop's model was overcome. The present method was used to calculate the formation enthalpies of Fe–Ni–V alloys. The agreement between the calculation and experiment is reasonable. So the formation enthalpies of Fe–Al–RE (RE = lanthanide metal) ternary alloys were calculated with the present method. The relative stability of $RE(Fe_{1-x}Al_x)_{13}$, $RE_2(Fe_{1-x}Al_x)_{17}$ and $RE_5(Fe_{1-x}Al_x)_{17}$ were also studied with the present method.

Keywords: Ternary alloy; Formation enthalpy; Geometric model; Miedema's theory

1. Introduction

The thermodynamic properties of ternary alloys are very important for the evaluation of ternary alloy phase and understanding of relative stability of alloys. Thermodynamic properties of alloys can be obtained via experiments. However, it is impossible now for all alloys to perform experimental measurement due to not only the technological difficulties but also the expenses and time consume. So, systematic prediction via theory is a significant and effective approach to obtain thermodynamic properties of alloys, especially for multi-component alloys.

The thermodynamic properties can be predicted from the first principles or ab initio calculations [1,2]. But there are a great amount of calculations to be performed for prediction of formation enthalpy of a ternary alloy using the first principles. However, the empirical method costs fewer calculations compared with the first principles, so the empirical methods are important approaches. At the present time, the extrapolating methods to estimate the properties of multi-component alloy from those of constitutive binary alloys are also very important to some extent.

The methods to estimate the thermodynamic properties of ternary system by means of extrapolation from constitutive binary systems include symmetric and asymmetric ones [3–10]. The prediction methods of formation enthalpy for multi-component system based on Miedema's theory were also proposed [11–13] since the formation enthalpies of most of binary systems can be calculated with Miedema's theory [14–17]. Goncalves et al. [11] proposed extend Miedema model (EMM) to calculate formation enthalpies of ternary compounds by applying a modified contact factor including information of crystallographic position of the atoms. Zhang's method [12] used mole fraction weighted average of properties of constitutive binary alloys to obtain those of ternary alloys. Takeuchi et al. [13] used the regular solution model. The effect of additive element on the binary was not included in the last two methods. The deviation of calculation from the experiment arose from the neglecting of the effect, especially for the three constituents with large different physical properties. Toop's model included

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the effect, but the choice of asymmetric constituent depends on experience. So, a simple geometric model was proposed in the present paper. The present geometric model is basically based on the model of Chou [10], but it is simpler in the calculation than that of Chou because the integration should be performed in the model of Chou.

Fe–Al–RE (RE = lanthanide metal) systems, as easy amorphous form alloys [18], were more and more important from both technical and scientific points of view. The formation enthalpies of these alloys are very important for understanding the amorphous formation ability and the thermal stability of amorphous phases. For the formation enthalpies of Fe–Al–RE ternary alloys, there is no systematic investigation.

The formation enthalpies of Fe–Ni–V, Fe–Al–RE solid solution were calculated with the proposed method. And formation enthalpies of Mg–Cu–Ni, Mg–Cu–Zn, Fe–Al–Zr ternary intermetallic compounds were also calculated. The relative stability of some intermetallic compounds of Fe–Al–RE systems was predicted with the present method.

2. A geometric model for extrapolation of thermodynamic properties

2.1. Geometric model for extrapolation

According to those of binary alloys, the formation enthalpies of ternary alloy can be written as following

$$\Delta H_{ijk} = \frac{x_i x_j}{y^i_{ij} y^j_{ij}} \Delta H_{ij}(y^i_{ij}, y^j_{ij}) + \frac{x_i x_k}{y^i_{ik} y^k_{ik}} \Delta H_{ik}(y^i_{ik}, y^k_{ik}) + \frac{x_j x_k}{y^j_{jk} y^k_{jk}} \Delta H_{jk}(y^j_{jk}, y^k_{jk}) \quad (1)$$

where ΔH_{ijk} is the formation enthalpy of ternary alloy. ΔH_{ij}, ΔH_{ik} and ΔH_{jk} are formation enthalpies of the three constitutive binary systems. x_i, x_j and x_k are mole fractions of three constituents in the ternary system, y^i_{ij} and y^j_{ij} are the mole fractions of constituents i and j extrapolated to binary system from ternary system. They were expressed as following for binary

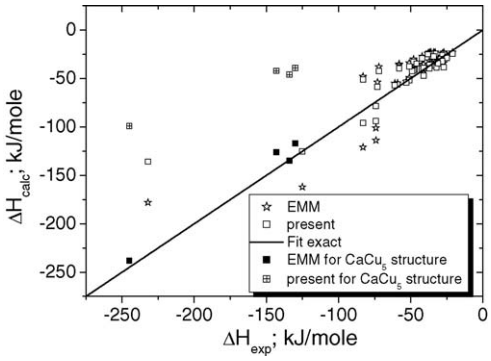

Fig. 1. Comparison between calculated formation enthalpies and experimental data for intermetallic compounds (EMM [11], exp. [21–25]).

systems

$$y^i_{ij} = x_i + \delta^i_{ij} x_k; \qquad y^j_{ij} = x_j + \delta^j_{ij} x_k \quad (2)$$

$$y^i_{ik} = x_i + \delta^i_{ik} x_j; \qquad y^k_{ik} = x_k + \delta^k_{ik} x_j \quad (3)$$

$$y^j_{jk} = x_j + \delta^j_{jk} x_i; \qquad y^k_{jk} = x_k + \delta^k_{jk} x_i \quad (4)$$

with

$$\delta^i_{ij} = \frac{\lambda_i}{\lambda_i + \lambda_j}; \qquad \delta^j_{ij} = \frac{\lambda_j}{\lambda_i + \lambda_j} \quad (5)$$

$$\delta^i_{ik} = \frac{\lambda_i}{\lambda_i + \lambda_k}; \qquad \delta^k_{ik} = \frac{\lambda_k}{\lambda_i + \lambda_k} \quad (6)$$

$$\delta^j_{jk} = \frac{\lambda_j}{\lambda_j + \lambda_k}; \qquad \delta^k_{jk} = \frac{\lambda_k}{\lambda_j + \lambda_k} \quad (7)$$

and

$$\lambda_i = [\Delta H^{\mathrm{C}}_{j\,\mathrm{in}\,i} - \Delta H^{\mathrm{C}}_{k\,\mathrm{in}\,i}]^2 \quad (8)$$

$$\lambda_j = [\Delta H^{\mathrm{C}}_{i\,\mathrm{in}\,j} - \Delta H^{\mathrm{C}}_{k\,\mathrm{in}\,j}]^2 \quad (9)$$

$$\lambda_k = [\Delta H^{\mathrm{C}}_{j\,\mathrm{in}\,k} - \Delta H^{\mathrm{C}}_{i\,\mathrm{in}\,k}]^2 \quad (10)$$

where $\Delta H^{\mathrm{C}}_{j\,\mathrm{in}\,i}$ is the dilute solution enthalpy of constituent j solved into i. Then the formation enthalpies of ternary system can be extrapolated if solution enthalpies of binary systems

Table 1
Calculated and experimental data of formation enthalpy for ternary solid solution Fe–Ni–V system, in kJ/mol

Mole fraction			Present	Zhang [12]	Takeuchi [13]	Toop model			Exp. [20]
Fe	Ni	V				V[a]	Ni[b]	Fe[c]	
0.50	0.00	0.50	−5.70	−5.59	−7.00	−5.70	−5.70	−5.70	−8.015
0.40	0.08	0.52	−7.64	−5.86	−9.06	−7.35	−7.79	−7.79	−7.546
0.35	0.12	0.53	−8.58	−6.23	−10.11	−8.20	−8.79	−8.75	−8.043
0.30	0.16	0.54	−9.49	−6.75	−11.14	−9.05	−9.75	−9.67	−8.984
0.25	0.20	0.55	−10.38	−7.45	−12.17	−9.91	−10.66	−10.55	−9.028
0.20	0.23	0.57	−11.11	−8.27	−13.00	−10.66	−11.39	−11.26	−9.617
0.30	0.60	0.10	−4.72	−2.41	−6.60	−4.40	−4.86	−4.57	−3.725
0.20	0.60	0.20	−7.93	−5.15	−10.72	−7.49	−8.16	−7.80	−4.234

[a] The asymmetric constituent is V.
[b] The asymmetric constituent is Ni.
[c] The asymmetric constituent is Fe.