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Activities of binary baths with 1% solute as standard states①

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[Abstract] The relationships of activities with 1% solute as standard state and mass fraction of solute, and hot-dip temperature, were given on the base of Miedema's model, Tanaka expression, some basic thermodynamic relationships; and discussion was carried out on Zn-Mn and Zn-Ti binary alloys by calculation, in which varied colors can be achieved on the hot-dip steel sheets. The results indicate that the activity of solute shows positive deviation relative to Henry's law for both Zn-Mn and Zn-Ti binary dilute solution. The degree of deviation increases with increasing solute and decreases with increasing bath temperature. As the solution is very dilute solution (w(Mn) ≤40% for Zn-Mn alloy, w(Ti) ≤8% for Zn-Ti alloy), the two binary baths can all be treated as ideal dilute solutions.

[Key words] activities; colored hot dip galvanization; solution
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1 INTRODUCTION

The compositions of alloys are almost presented as molar fractions in general thermodynamics handbook and in the thermodynamic formulae, and its corresponding activities are expressed as Raoultian activities whose standard states are pure substances[1]. However, mass fraction are presented more frequently as the concentration of solute in the calculation of metallurgical engineering, especially in fire metallurgy, therefore, it is convenient that activities are presented as standard states of 1% solute.

Different colors can be achieved directly on the hot-dip galvanized steel sheets after being treated in Zn baths with Mn or Ti as additives in properly controlling its additions and its operating technological conditions[2~4]. We have gained good results after carrying out a large number of experiments in recent years[5~7]. Whereas, there is not any reports on the thermodynamics properties of this kind of hot-dip bath yet. In order to optimize the technological conditions of colored hot-dip galvanization further and go deep into its theory, it is necessary to study its thermodynamics properties.

There are some difficulties in the measurement of thermodynamic activities due to the complexities of high temperature experiments, strong volatility of zinc, and the complex structures of transition metals and their intermetallic compounds. Consequently, there is inaccuracy in the experimental data and their reproducibility is poor. Therefore, it is significant way to obtain thermodynamics data of alloys through models.

The relationships of activities with 1% solute (Mn or Ti) as standard states and solute percentage, and hot-dip bath temperature as well, were represented in this paper for both Zn-Mn and Zn-Ti binary dilute alloys through Miedema's model for enthalpy of mixture, Tanaka relationship for excess entropy, and combined with some basic thermodynamics expressions. It provides the groundwork for further study theoretically.

2 CALCULATION METHOD

2.1 Calculation of enthalpy of mixture

After carrying out a lot of research work in detail on the regularities of enthalpys empirical values of mixture for liquid or solid alloys and solid compounds formed by transition metals, non-transition metals, and noble metals, Miedema et al[8] put forward a semi-empirical model for calculating enthalpy of mixture, which was applied by many researchers[9, 10]. The deviation of value between calculated and experimental does not exceed 8 kJ/mol in general[11]. The complete revised expression is

$$\Delta H_{\mathrm{mix}} = 4.18 f(x^s, V^a) \times \left[-(\Delta\Phi^*)^2 + \frac{Q}{P}(\Delta n_{\mathrm{WS}}^{1/3})^2 - \frac{R}{P} \right] \quad (1)$$

The detail statements of notations in the formula can be seen in Ref. [8].

2.2 Activities with pure substance as standard states

By Tanaka approximant excess mixture entropy can be expressed as[12]:

$$\Delta S_{\mathrm{mix}}^{\mathrm{E}} = 0.1 \Delta H_{\mathrm{mix}} \cdot \left(\frac{1}{T_{mA}} + \frac{1}{T_{mB}} \right) \quad (2)$$

There are following relationships of thermodynamics properties for i-j binary solution in constant

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temperature and pressure:

$$\Delta S^{E}_{mix} = \Delta H_{mix} - T\Delta S^{E}_{mix} \quad (3)$$

$$\Delta \overline{G}^{E}_{i} = \Delta G^{E}_{mix} + (1 - x_i)\frac{\partial(\Delta G^{E}_{mix})}{\partial x_i} \quad (4)$$

$$\Delta \overline{G}^{E}_{i} = RT \ln \gamma^{R}_{i} \quad (5)$$

$$\Delta G^{E}_{mix} = RT(x_i \ln \gamma^{R}_{i} + x_j \ln \gamma^{R}_{j}) \quad (6)$$

From Eqns. (2) ~ (6), the activity coefficient in Raoultian standard state can be given as a function of its molar fraction and temperature of solution:

$$\ln \gamma^{R}_{i} = \alpha_T \left| \Delta H_{mix} + (1 - x_i)\frac{\partial H_{mix}}{\partial x_i} \right| \quad (7)$$

where

$$\alpha_T = \frac{1}{RT} - \frac{1}{10R}\left| \frac{1}{T_{mA}} + \frac{1}{T_{mB}} \right| \quad (8)$$

in addition

$$\Delta G^{E}_{mix} = RT(x_i \ln \gamma^{R}_{i} + x_j \ln \gamma^{R}_{j}) \quad (9)$$

The relationship between the two activity coefficients of binary alloy can be given by

$$\ln \gamma^{R}_{j} = \frac{1}{x_j}[\alpha_T \Delta H_{mix} - (1 - x_j)\ln \gamma^{R}_{i}] \quad (10)$$

2.3 Activities with 1% solute as standard state

The relationship between vapor pressure and the activities while pure substance, imaginary pure substance, or 1% solute as standard state, i. e. Raoultian activity a^{R}_{i}, and Henry's activity a^{H}_{i} for imaginary pure substance and $a^{1\%}_{i}$ for 1% solute respectively, is given by

$$a^{R}_{i} = p_i / p^{0}_{i} \quad (11)$$

$$a^{H}_{i} = p_i / k_i \quad (12)$$

$$a^{1\%}_{i} = p_i / k'_i \quad (13)$$

The ratios among Eqns. (11) ~ (13) are

$$\frac{a^{R}_{i}}{a^{H}_{i}} = \frac{\gamma_i x_i}{\gamma'_i x_i} = \frac{\gamma_i}{\gamma'_i} = \frac{k_i}{p^{0}_{i}}\gamma^{0}_{i} \quad (14)$$

$$\frac{a^{R}_{i}}{a^{1\%}_{i}} = \frac{k'_i}{p^{0}_{i}} = \gamma^{0}_{i} \cdot \frac{k'_i}{k_i} \quad (15)$$

Vapor pressure can be expressed as following by Henry's law:

$$p_i = k_i x_i = k'_i w_i \quad (16)$$

then

$$a^{1\%}_{i} = \frac{\gamma^{R}_{i}}{\gamma^{0}_{i}} w_i = f_i w_i \quad (17)$$

$$\ln f_i = \ln \gamma^{R}_{i} - \ln \gamma^{0}_{i} \quad (18)$$

$\gamma'_i = 1$ when solution is diluted infinitely, then $\gamma^{0}_{i} = \gamma_i$ from Eqn. (14), which indicates that γ^{0}_{i} is equal to activity coefficient of solute while pure substance as standard state, i. e.

$$\gamma^{0}_{i} = \lim_{x_i \to 0} \gamma^{R}_{i} \quad (19)$$

The activity coefficient of solute i in i-j binary solution, and then its activity further, while 1% solute as standard state, can be calculated by combining Eqns. (1), (7), (17) and (19).

3 CALCULATION OF SOLUTE ACTIVITIES OF Zn-Ti AND Zn-Mn DILUTE SOLUTIONS

Applying the above method to both Zn-Mn and Zn-Ti binary alloy, the relationships between their enthalpies of mixture and molar fractions of minor element (Mn or Ti) are obtained respectively:

$$\Delta H^{Zn\text{-}Mn}_{mix} = -2194.5\frac{x_{Mn}(1 - x_{Mn})}{22 - 3x_{Mn}} \quad (20)$$

$$\Delta H^{Zn\text{-}Ti}_{mix} = -3817.5\frac{x_{Ti}(1 - x_{Ti})}{11 + x_{Ti}} \quad (21)$$

According to the above enthalpies of mixture calculated, the natural logarithms of Raoultian activity coefficients for the two systems can be expressed as

$$\ln \gamma^{R}_{Mn} = \left| 29232 - \frac{1390}{T} \times 10^3 \right| \left| \frac{x_{Mn} - 1}{22 - x_{Mn}} \right|^2 \quad (22)$$

$$\ln \gamma^{R}_{Ti} = \left| 236.85 - \frac{1209}{T} \times 10^3 \right| \left| \frac{x_{Ti} - 1}{11 + x_{Ti}} \right|^2 \quad (23)$$

$$\ln \gamma^{0}_{Mn} = \ln\left[\lim_{x_{Mn} \to 0} \gamma^{R}_{Mn}\right] = \lim_{x_{Mn} \to 0}(\ln \gamma^{R}_{Mn}) = \left| 0.603 - \frac{2872}{T} \right| \quad (24)$$

$$\ln \gamma^{0}_{Ti} = \left| 1.96 - \frac{9992}{T} \right| \quad (25)$$

The relationship between molar fraction and mass fraction(%) of solutes is

$$x_i = \frac{M_j w_i}{100M_i + (M_j - M_i)w_i} \approx \frac{M_j}{100M_i} w_i \quad (26)$$

then

$$x_{Mn} \approx \frac{1}{84} w(Mn), \quad x_{Ti} \approx \frac{1}{73} w(Ti) \quad (27)$$

$$\ln f_{Mn} = \left| \frac{2872}{T} - 0.603 \right| \cdot w(Mn)\frac{70224 - 475w(Mn)}{(1848 - 3w(Mn))^2} \quad (28)$$

$$\ln f_{Ti} = \left| \frac{9992}{T} - 1.96 \right| \cdot w(Ti)\frac{19272 - 120w(Ti)}{(803 + w(Ti))^2} \quad (29)$$

4 RESULTS AND DISCUSSION

The hot-dip temperature range is 703~ 883 K in the experiments of colored hot-dip galvanization technology. Samples show different colors in the different temperature regions within this range as other technological conditions are the same; coloration regions are different within this temperature range as other conditions are altered[5, 6], 883 K and 703 K are the upper and lower limit of temperature for the two binary dilute solutions. Therefore, we calculated the activity coefficients and activities under such limit temperatures.

They are curves of activity coefficients (f_i) and activities ($a_i^{1\%}$) of solutes in 1% solute as standard state vs mass fraction (%) of solutes (w_i) for Zn-Mn and Zn-Ti dilute solutions respectively in Figs. 1 and 2.

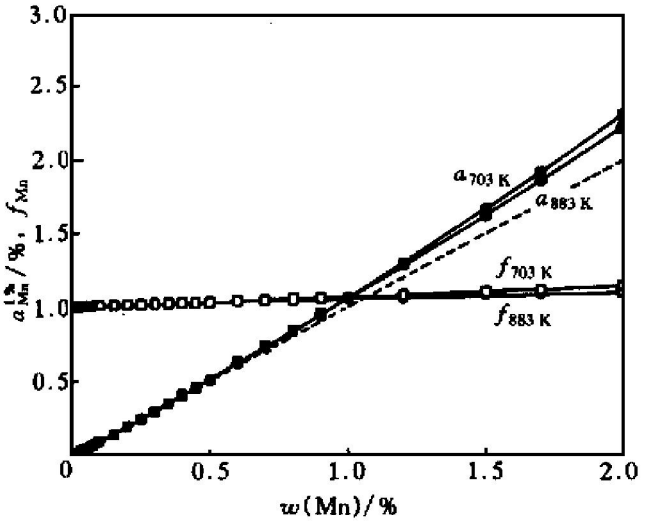

Fig. 1 $a_{Ti}^{1\%}$ vs w(Mn) for Zn-Mn binary alloy at 703 K and 883 K

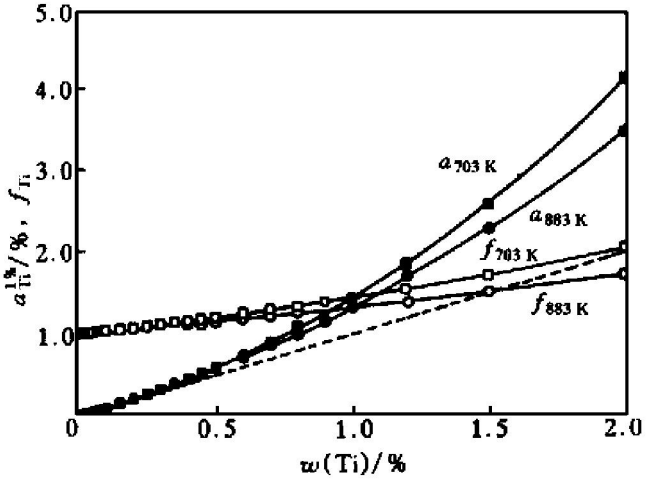

Fig. 2 $a_{Mn}^{1\%}$ vs w(Ti) for Zn-Ti binary alloy at 703 K and 883 K

From Figs. 1 and 2, the activities of solutes in 1% solute as standard state increase with the mass fraction of solute increasing for the two dilute solutions; increasing hot-dip temperature (703 K → 883 K), for the binary dilute solutions with the same compositions, their activities of solutes decrease, which is different from Raoultian activities in pure substance as standard state. It is maybe related with the decreasing reactivity of solute resulted from probability of formation into compound increasing at elevated temperature.

The calculating results also indicate that there are positive deviations relative to Henry's law for the two dilute solutions. The highest temperature, the less degree of deviation; and the deviation increases with increasing solute mass fraction. For Zn-Ti system, the degree of positive deviation and the degree influenced by hot-dip temperature and solute percentage are more significant than that for Zn-Mn system.

As solute is in lower mass fraction, i. e. solution is dilute (w(Mn) ≤40% for Zn-Mn and w(Ti) ≤ 8% for Zn-Ti), the activity coefficient of solute is approximately equal to 1, and activity in 1% solute as standard state is close to mass fraction(%) of solute, whose error does not exceed 2.9%. This kind of solution can be treated as ideal dilute solution. It also can be seen from the figures that when the mass fraction of solute does not exceed certain level (about 2% for Zn-Mn and about 1% for Zn-Ti), activity coefficient and activity change a little as hot-dip temperature is elevated from 703 K to 883 K, which indicates that hot-dip temperature takes fairly small effect on activity coefficient and activity in those dilute solutions.

5 CONCLUSIONS

In this paper, the relationships of activities with 1% solute as standard state and mass fraction of solute, and bath temperature as well, were given on base of Miedema model, Tanaka expression, and some basic thermodynamic relationships, discussion was also carried out on Zn-Mn and Zn-Ti binary dilute alloys by calculation, in which varied colors can be obtained on the hot-dip steel sheets. The obtained relationship of natural logarithms of activity coefficients and mass percentage and hot-dip temperature is as

$$\ln f_{Mn} = \left(\frac{2\,872}{T} - 0.603\right) \cdot w(Mn)\frac{70\,224 - 475w(Mn)}{(1\,848 - 3w(Mn))^2}$$

$$\ln f_{Ti} = \left(\frac{9\,992}{T} - 1.96\right) \cdot w(Ti)\frac{19\,272 - 120w(Ti)}{(803 + w(Ti))^2}$$

After calculating the solute activities of dilute binary Zn-Mn and Zn-Ti solutions (solute fraction are within 2%), the following results are obtained:

1) Activities in 1% solute as standard state increase with mass percentage of solute.

2) For the binary dilute solutions with the same compositions, activities of solutes decrease with increasing hot-dip temperature from 703 K to 883 K, which are different from Raoultian activities in pure substance as standard state. It maybe owe to the decreasing of reactivity of solute resulted from probability of formation into compound increasing at elevated temperature.

3) Activities of solute show positive deviation relative to Henry's law for both Zn-Mn and Zn-Ti bi-

nary dilute solution. The degree of deviation increases with increasing solute mass fraction and decreases with increasing bath temperature. As the solution is very dilute solution (w(Mn) ≤40% for Zn-Mn alloy, w(Ti) ≤8% for Zn-Ti alloy), the two binary baths can be treated as ideal dilute solutions.

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