Thermodynamic evaluation of the Fe-Zn binary system with reference to the latest experimental phase diagram.

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Abstract

The phase diagram of the Fe-Zn binary system was evaluated based on the CALPHAD method with reference to the latest experimental data. The solubility ranges of the intermetallic compound (IMC) phases, Γ-Fe_4Zn_9, Γ_1-$Fe_{11}Zn_{40}$, δ_{1k}-$FeZn_7$, δ_{1p}-$Fe_{13}Zn_{126}$, and ζ-$FeZn_{13}$ were modeled considering their structures consisting of Zn_{12} icosahedra with Fe at the center (Fe_1Zn_{12} clusters) as well as glue-like Fe and Zn atoms, and the miscibility gap between the δ_{1k} and δ_{1p} phases was also taken into account in the present calculations. The solubility of Fe in the liquid and (ηZn) phases that was confirmed as dozens of times larger than the values reported in the earlier literature could be calculated by introducing Fe_1Zn_{12} associates to these solution phases. Consequently, all phase equilibria were adequately reproduced by the thermodynamic models and parameters revised in the present study.

1. Introduction

Because of their importance for the high anticorrosive coating formed by hot-dip galvanizing (GI) or galvannealing (GA) [1], phase equilibria in the Zn-Fe binary system have been studied repeatedly for several decades [2-15]. A great deal of effort has also been devoted to measuring the thermodynamic

properties of the equilibrium phases in the Fe-Zn system over the whole composition range from low

to high temperatures [16-22]. Thanks to these valuable experimental data, the phase diagram of the

Fe-Zn binary system was assessed by Burton and Perrot [23], which has been accepted as the most

reliable experimental phase diagram, and much progress has also been made in attempting phase

diagram calculations. Several authors have assessed the phase diagram thermodynamically in the early

days of CALPHAD [24-26], however, the intermetallic compound (IMC) phases were defined as line

compounds, and the magnetic contribution to the Gibbs energy was not taken into account explicitly

in those early studies. The experimental phase diagram assessed by Burton and Perrot [23] was first

adequately reproduced by thermodynamic calculations reported by Su *et al.* [27], and the revised

evaluation proposed by Nakano *et al.* [28, 29], in which the thermodynamic description of the IMC

phases was examined using sublattice models based on their crystallographic characteristics. The latter

appears to have been adopted in a commercial thermodynamic database of steel materials. After that,

some shortcomings in these evaluations were pointed out by Xiong *et al.* [30]. For instance, an inverse

miscibility gap appears in the liquid phase with a minimum-temperature critical point at 1529 °C,

which is caused by the negatively large temperature dependence of the composition dependent

interaction parameter ($^1L_{\text{Fe,Zn}}^{\text{Liq.}}$) shown in Table 1. Xiong *et al.* introduced a small negative temperature

dependence in $^1L_{\text{Fe,Zn}}^{\text{Liq.}}$ [30], and Tang *et al.* introduced an exponential temperature dependence in

$^0L_{\text{Fe,Zn}}^{\text{Liq.}}$ and $^1L_{\text{Fe,Zn}}^{\text{Liq.}}$ [31] as listed in Table 1, thereby resolving the problem of the inverse miscibility

gap.

In our previous study, we determined the phase equilibria involving the IMC phases in the Fe-Zn

binary system at temperatures from 400 °C to 1000 °C by the alloying method described in [32]. In

the latest phase diagram shown in Fig. 1 [32], five IMC phases, Γ, Γ_1, δ_{1k}, δ_{1p}, and ζ, exist stably as

equilibrium phases, in which the δ_{1k} and δ_{1p} phases were considered as a single phase of δ_1 in both

experimental [23] and calculated [27-31] phase diagrams. Since significant differences in the

formation behavior [33] and mechanical properties [34] are recognized between the δ_{1k} and δ_{1p} phases, the phase equilibria, including the miscibility gap (*see footnote) associated with these two phases, need to be properly evaluated by thermodynamic calculations. Furthermore, the solubility ranges of IMC phases in the Zn-rich portion mostly shift toward the Fe-rich direction [32, 35] in comparison with the phase diagram in the literature as shown in Fig. 1. It is also noteworthy that the Fe solubility in the liquid Zn, for instance 0.5 at.% at 450 °C, was revised to be 17 times as large as the generally assessed value in the literature, 0.03 at.%. Therefore, there remains the potential for improving the thermodynamic evaluation of the Fe-Zn binary phase diagram. To improve the accuracy of the thermodynamic calculation based on the latest experimental data, the crystal structures as well as the solubility composition range of the five IMC phases need to be considered. Recently, Inui *et al*. suggested that all the IMC phases in the Fe-Zn system have a principle for constructing their crystal structures [36], which can be understood by considering the packing of coordinated polyhedra with the common structural unit being the Zn_{12} and/or $(Zn, Fe)_{12}$ icosahedron whose central site is exclusively occupied by an Fe atom. They also suggested that with increasing Fe content in the IMC phases the geometry linking the Fe-centered icosahedra changes from vertex-sharing to face-sharing, Zn atoms on the face-sharing sites are partially substituted by Fe atoms, and the fraction of isolated Zn atoms decreases. These crystallographic characteristics need to be considered for a thermodynamic model of the IMC phases. Furthermore, the strong tendency for the crystal structures of all IMC phases to consist of icosahedral Fe_1Zn_{12} clusters suggests that Fe_1Zn_{12} clusters may coexist with Fe and Zn solute atoms in the Zn-rich liquid phase and ηZn (hcp) phase. In view of the above situation, the associate solution model considering Fe_1Zn_{12} clusters was adopted for the Gibbs energy description of the Zn-rich liquid and ηZn (hcp) phases.

Therefore, we carried out a thermodynamic evaluation of the Fe-Zn binary system in this study to solve the above issues remaining from previous thermodynamic evaluations [27-31] by applying the associate solution model for the Gibbs energy description of the liquid and ηZn (hcp) phases.

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*footnote: A "miscibility gap" is a type of two-phase equilibrium between isostructural phases that share a single Gibbs energy curve with an upward convexity due to positive interaction, magnetic transition, order-disorder transition, *etc.*, and a second order phase transformation may occur between them at higher temperatures. In the present study, however, the Gibbs energies of the disordered δ_{1p} and the ordered δ_{1k} phases were evaluated separately.

2. Thermodynamic description

2.1. Gibbs energy of solution phases

The molar Gibbs energy of the αFe (bcc) and γFe (fcc) solution phases were described by sub-regular solution approximation,

$$G_m^\phi = G_{Fe}^\phi \cdot x_{Fe} + G_{Zn}^\phi \cdot x_{Zn} + RT\{x_{Fe}\ln(x_{Fe}) + x_{Zn}\ln(x_{Zn})\} + x_{Fe}x_{Zn} \cdot L_{Fe,Zn}^\phi \ , \tag{1}$$

where G_{Fe}^ϕ and G_{Zn}^ϕ represent the Gibbs energies of pure Fe and pure Zn, respectively, in the corresponding structure of ϕ. x_{Fe} and x_{Zn} are the mole fractions of Fe and Zn, respectively. $L_{Fe,Zn}^\phi$ represents the interaction parameter, which has a composition dependence in the form of the Redlich-Kister (RK) polynomial [37] described by the following equation:

$$L_{Fe,Zn}^\phi = \sum_n (x_{Fe} - x_{Zn})^n \cdot {}^n L_{Fe,Zn}^\phi. \tag{2}$$

In addition to the Gibbs energy described by eq. (1), the magnetic contribution to the Gibbs energy, G_{mag}^{ϕ}, which was originally proposed by Inden [38, 39] and simplified by Hillert and Jarl [40], is appended for the αFe bcc (A2) and γFe fcc (A1) phases.

On the other hand, the Gibbs energies of the liquid (L) and ηZn (hcp) phases were described by the associate solution model [41, 42],

$$
\begin{aligned}
G^{\Psi} = {} & y_{\mathrm{Fe}} G_{\mathrm{Fe}}^{\Psi} + y_{\mathrm{Zn}} G_{\mathrm{Zn}}^{\Psi} + y_{\mathrm{Fe_1 Zn_{12}}} G_{\mathrm{Fe_1 Zn_{12}}}^{\Psi} \\
& + RT \left\{ y_{\mathrm{Fe}} \ln(y_{\mathrm{Fe}}) + y_{\mathrm{Zn}} \ln(y_{\mathrm{Zn}}) + y_{\mathrm{Fe_1 Zn_{12}}} \ln(y_{\mathrm{Fe_1 Zn_{12}}}) \right\} \\
& + y_{\mathrm{Fe}} y_{\mathrm{Zn}} L_{\mathrm{Fe,Zn}}^{\Psi} + y_{\mathrm{Fe}} y_{\mathrm{Fe_1 Zn_{12}}} L_{\mathrm{Fe,Fe_1 Zn_{12}}}^{\Psi} + y_{\mathrm{Zn}} y_{\mathrm{Fe_1 Zn_{12}}} L_{\mathrm{Zn,Fe_1 Zn_{12}}}^{\Psi} ,
\end{aligned}
\tag{3}
$$

where considerable amount of $\mathrm{Fe_1 Zn_{12}}$ associates is assumed to co-exist with Fe and Zn atoms in these Zn-rich solution phases as mentioned in Introduction. G_i^{Ψ}, y_i, and $L_{i,j}^{\Psi}$ represent the Gibbs energy of each component i (i = Fe, Zn and $\mathrm{Fe_1 Zn_{12}}$ associate), the site fraction of i, and the interaction parameter between components i and j, respectively. $L_{i,j}^{\Psi}$ also has a composition dependence in the form of the Redlich-Kister (RK) polynomial [37] in the same way with eq. (2), however, values both $L_{\mathrm{Fe,Fe_1 Zn_{12}}}^{\Psi}$ and $L_{\mathrm{Zn,Fe_1 Zn_{12}}}^{\Psi}$ were assumed to be zero for simplification. G values for pure elements of Fe and Zn were taken from the SGTE database [43], whereas $G_{\mathrm{Fe_1 Zn_{12}}}^{\Psi}$ and L values were evaluated based on experimental data from the literature [4,16-22, 32] using the PARROT module of Thermo-Calc software [44].

2.2. Gibbs energy of intermetallic compound phases

As described in the Introduction, five kinds of IMC phases, ζ, δ_{1k}, δ_{1p}, Γ_1, and Γ appear stably in the phase diagram of the Fe-Zn system and all IMC phases are basically composed of $\mathrm{Fe_1 Zn_{12}}$ clusters with different linkage geometries and glue-like elements of Fe and Zn. To describe the Gibbs energy of these IMC phases, such complicated crystal structures ideally need to be incorporated into their

thermodynamic models. For the practical reasons, however, a three sublattice model, $(\text{Fe})_p^{\text{I}}(\text{Zn})_q^{\text{II}}(\text{Fe}, \text{Zn})_r^{\text{III}}$, for the five IMC phases was applied to describe their Gibbs energy,

$$G_m^{\theta} = G_{\text{Fe:Zn:Fe}}^{\theta} \cdot y_{\text{Fe}}^{\text{III}} + G_{\text{Fe:Zn:Zn}}^{\theta} \cdot y_{\text{Zn}}^{\text{III}} + rRT\{y_{\text{Fe}}^{\text{III}} \ln(y_{\text{Fe}}^{\text{III}}) + y_{\text{Zn}}^{\text{III}} \ln(y_{\text{Zn}}^{\text{III}})\} + y_{\text{Fe}}^{\text{III}} y_{\text{Zn}}^{\text{III}} \cdot L_{\text{Fe:Zn:Fe,Zn}}^{\theta} \quad (4)$$

Values of p, q, and r ($p + q + r = 1$), where the ratio p/q and the value of r are not exactly but roughly assumed as the Fe/Zn substitution in the $\text{Fe}_1\text{Zn}_{12}$ icosahedra cluster and the fraction of the glue-like site, respectively, were fixed to reproduce the solubility composition range of each IMC phase θ ($\theta = \zeta, \delta_{1k}, \delta_{1p}, \Gamma_1,$ or Γ) as listed in Table 2 which also includes the crystal structure information of the stable phases in the Fe-Zn system. $G_{\text{Fe:Zn:Fe}}^{\theta}$ and $G_{\text{Fe:Zn:Zn}}^{\theta}$ represent the Gibbs energy of the $\text{Fe}_p\text{Zn}_q\text{Fe}_r$ and $\text{Fe}_p\text{Zn}_q\text{Zn}_r$ compound phases, respectively. $y_{\text{Fe}}^{\text{III}}$ and $y_{\text{Zn}}^{\text{III}}$ represent the site fractions of Fe and Zn, respectively, and $L_{\text{Fe:Zn:Fe,Zn}}^{\theta}$ is the interaction parameter between Fe and Zn in the third sublattice (III). Temperature dependent functions of $G_{\text{Fe:Zn:Fe}}^{\theta}$, $G_{\text{Fe:Zn:Zn}}^{\theta}$, and $L_{\text{Fe:Zn:Fe,Zn}}^{\theta}$ with the eq.(2)-type composition dependence were evaluated to reproduce experimental data from the literature [4,16-22, 32]. It should be noted that the δ_{1k} and δ_{1p} phases were reported to have a order-disorder (O-DO) relationship with both first- and second-order transformations [9,10]. In the present study, however, the Gibbs energies of the δ_{1k} and δ_{1p} phases were defined with the same formula of $(\text{Fe})_{0.0714}^{\text{I}}(\text{Zn})_{0.7143}^{\text{II}}(\text{Fe}, \text{Zn})_{0.2143}^{\text{III}}$, but treated as different phases without considering the O-DO relationship for simplicity. Evaluated thermodynamic parameters were summarized in Table 3.

3. Results

3.1. Thermodynamic properties

The calculated activities of Zn over the entire composition range at 700, 750 and 800 °C, and in the αFe (bcc) phase at 900 °C, where the liquid Zn was chosen as a reference state, are shown in Fig. 2 together with the experimental results reported by Wriedt [18,19] and Tomita et al. [22]. Overall, there

is satisfactory agreement between the present calculations and the experimental results. Other examples of comparisons between calculated thermodynamic properties and corresponding experimental data are shown in Fig. 3. Figure 3(a) shows good agreement between the calculated activity of Zn in liquid alloys at 1585 °C and its experimental data reported by Stell [16]. The Gibbs energies of formation of the solid phases at 344 °C reported by Cigan [17] were used rather than those of Gellings et al. [21] due to the large measurement error of ± 2 kJ mol^{-1} of Gellings et al. as shown in Fig. 3(b).

3.2. Phase diagrams

The calculated phase diagram of the Fe-Zn system over the entire composition range is shown in Fig. 4(a), compared with the latest experimental data reported by Han et al. [32] and the calculated phase diagram using the TCFE12 thermodynamic database [45]. On the solubility of Zn in the αFe(bcc) phase, both of calculated phase boundaries and experimental data are in close agreement, whereas the calculated liquidus curves in the Fe-rich composition side exhibit considerable discrepancy, which cannot be resolved due to lack of experimental data. The focus is on the γ-loop, *i.e.* the phase equilibrium between the γFe (fcc) and αFe (bcc) phases in Fig. 4(b). The agreement between the present calculations and the experimental data [4] appears to be better at temperatures in the lower half of the γ-loop than with TCFE12 and worse in the upper half. The phase diagram associated with the five IMC phases of ζ, δ_{1k}, δ_{1p}, Γ_1, and Γ on the Zn-rich composition side at lower temperatures is shown in Fig. 4(c). As discussed in the Introduction, there were considerable discrepancies between the latest experimental data and the calculations of the phase boundaries using TCFE12, which has been dramatically improved by the present calculations, as shown in Fig. 4(c). Furthermore, the δ_{1k} and δ_{1p} phases, which in previous calculations were regarded as a single phase of δ_1, were reasonably distinguished in the present assessment. An enlarged phase diagram of the vicinity of the liquid → (ηZn) + ζ-FeZn$_{13}$ eutectic reaction is shown in Fig. 4(d), where considerable discrepancy is observed

between the Fe solubility in the liquid and ηZn (hcp) phases from the latest experimental data and the phase boundaries from previous experiments and calculations. In the present evaluation, the introduction of Fe_1Zn_{12} associates in the Gibbs energy model of the liquid and (ηZn) solution phases adequately reproduced the Fe solubility of about 0.3 at.% in the (ηZn) phase and more than 0.4 at.% in the liquid Zn phase, which are almost twenty times as large as the values reported in the literature, as shown in Fig. 4(d).

4. Discussion

4.1. Effect of associates on the Gibbs energy of solution phases

As discussed above, the crystal structures of all the IMC phases appearing in the phase diagram of the Fe-Zn system are composed of Fe_1Zn_{12} clusters with different linkage geometries and glue-like elements of Fe and Zn, which indicates that a significant amount of Fe_1Zn_{12} clusters coexists with Fe and Zn solute atoms in the Zn-rich liquid and (ηZn) phases, affecting the thermodynamic stability of these Zn-rich phases. In the present calculation, it was quite difficult to reproduce the large Fe solubility in the Zn-rich liquid and (ηZn) phases without introducing the Fe_1Zn_{12} associate into the Gibb energy models of those solution phases. In order to confirm the effect of the Fe_1Zn_{12} associate on the Gibbs energy of the liquid phase, the site fraction of Fe_1Zn_{12} associates ($y_{Fe_1Zn_{12}}$) in the liquid phase under the equilibrium condition was calculated at temperatures from 450 °C to 800 °C over the entire composition range. Calculated results are shown in Fig. 5. All the $y_{Fe_1Zn_{12}}$–x_{Zn} curves exhibit a maximum peak and a shoulder, the latter of which corresponds to the chemical composition of the Fe_1Zn_{12} associate at $x_{Zn} = 0.923$. The $y_{Fe_1Zn_{12}}$ value of the maximum peak decreases with increasing temperature mainly due to the temperature dependence of the Gibbs energy parameter, $G^L_{Fe_1Zn_{12}}$, shown in Table 3. The x_{Zn} value at the maximum peak also decreases with increasing temperature, which may be due to the effect of increasing entropy at high temperatures. Figure 6 compares the

Gibbs energies of Fe-Zn liquid alloys calculated using the associate solution model at temperatures from 450°C to 800°C with those calculated excluding the Fe_1Zn_{12} associate. The reference states of Fe and Zn are bcc ($A2$) and liquid, respectively. The Gibbs energy at low temperatures, for instance at 450°C shown in Fig. 6(d), decreases significantly over the entire composition range, with a sharp decrease near the stoichiometric composition of Fe_1Zn_{12} (x_{Zn} = 0.923), which apparently makes it possible to reproduce the large solubility of Fe in the liquid Zn phase as well as in the hcp ηZn phase reported in the latest experimental phase diagram [32] as shown in Fig. 7 (c). On the other hand, the difference between the Gibbs energies including and excluding the Fe_1Zn_{12} associate decreases with increasing temperature, which just corresponds to the change with temperature in the site-fraction of the Fe_1Zn_{12} associates shown in Fig. 5.

4.2. Effect of associates on phase diagram

Figure 7 compares phase diagram of the Fe-Zn system calculated using the associate solution model with that calculated excluding the Fe_1Zn_{12} associate. As shown in Fig. 7(a), differences with and without Fe_1Zn_{12} associates are not recognized at temperatures above 800°C or in the Fe-rich composition range because the Fe_1Zn_{12} associate only affects the Gibbs energy of the liquid and (ηZn) phases, and disappears above 800°C. At temperatures below 800°C, the stability of the liquid phase is decreased by excluding Fe_1Zn_{12} associates, resulting in the decrease of Fe solubility in the liquid phase and in the slight increase of the peritectic temperatures as shown in Fig. 7(b). The effects of the Fe_1Zn_{12} associate are observed prominently at the phase boundaries of the Fe solubility in the liquid and (ηZn) phases as shown in Fig. 7(c), which were evaluated using the associate solution model to reproduce the latest experimental data reported by Han et al. [32]. The exclusion of Fe_1Zn_{12} associates from their Gibb energy descriptions reduces the stability of liquid and (ηZn) phases, resulting in a significant decrease in the Fe solubility in these two phases. Interestingly, the associate solution model has made it possible to reproduce the latest experimental data on the solubilities of Fe in the liquid and (ηZn)

hcp phases, both of which are about twenty times larger than those reported in the literature. As shown in Table 1, the interaction parameters of the liquid phase ($^{n}L_{\text{Fe,Zn}}^{\text{Liq.}}$) were revised in the present study without using strong or specific temperature dependences, which indicates that the introduction of Fe_1Zn_{12} associates into the liquid and (ηZn) hcp phases appears to be the essence of the atomic state of these phases in the Zn-rich composition range.

Using the consistent set of thermodynamic parameters evaluated in the present study, one can calculate not only the state-of-the-art phase diagram of the Fe-Zn binary system with high accuracy, but also the Gibbs energies of all stable phases in the appropriate solubility range, which can be applicable, for instance, to predict the early stage of the interfacial reaction between an iron sheet and molten Zn [33]. For the practical application to the hot-dip galvanizing (GI) or galvannealing (GA) processes, it is also expected that the present evaluation could play a fundamental role for constructing a multi-component thermodynamic database consisting of the elements in steels and molten galvanizing baths.

5. Conclusions

A thermodynamic evaluation of the Fe-Zn binary system was performed using the CALPHAD method over the entire composition range with reference to the latest experimental data. Compared with previous thermodynamic evaluations, the thermodynamic parameters were revised to reproduce the latest and previous experimental data with the following improvements.

(1) The associate solution model considering Fe_1Zn_{12} icosahedron clusters was applied to the Gibbs energy description of the liquid and (ηZn) hcp phases. Consequently, the solubility of Fe in these phases in the latest phase diagram was adequately calculated, and the artificial inverse miscibility gap in the liquid phase at high temperatures was avoided without using strong or specific temperature dependences in the interaction parameters of the liquid phase.

(2) The three sublattice model of $(\text{Fe})_p^{\text{I}}(\text{Zn})_q^{\text{II}}(\text{Fe}, \text{Zn})_r^{\text{III}}$, considering the crystal structures consisting of Zn_{12} icosahedra with Fe at the center ($\text{Fe}_1\text{Zn}_{12}$ clusters) as well as glue-like Fe and Zn atoms, was applied for the Gibbs energy description of the Γ-Fe_4Zn_9, Γ_1-$\text{Fe}_{11}\text{Zn}_{40}$, δ_{1k}-FeZn_7, δ_{1p}-$\text{Fe}_{13}\text{Zn}_{126}$, and ζ-FeZn_{13} IMC phases. Consequently, the composition ranges of these IMC phases in the latest phase diagram were reproduced well, and the $\delta_{1k} + \delta_{1p}$ miscibility gap was approximately reproduced.

(3) The phase diagrams and thermodynamic properties calculated using the present thermodynamic parameters are in good agreement with the latest phase equilibria and experimental data in the literature, respectively.

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Table and Figure captions

Table 1   Comparison between thermodynamic parameters of the liquid phase [28-31].

Table 2   Nominal symbols, stoichiometric ratios, crystal structures, and formula of Gibbs energy models in Zn-Fe binary system.

Table 3   Thermodynamic and magnetic parameters of the Fe-Zn system evaluated in this study. Gibbs energy parameters of pure elements are taken from reference [43] and the magnetic properties of disordered solution phases, γFe ($A1$) and αFe ($A2$), are from reference [28].

Figure 1   Phase diagrams of the Fe-Zn binary system experimentally determined by Han *et al*. [32]

Figure 2   Activity of Zn in equilibrated Fe-Zn alloys calculated at temperatures from 700 °C to 900 °C compared with experimental data [19, 22].

Figure 3   (a) Comparison of the activity of Zn in Fe-rich liquid alloys calculated at 1585°C with experimental data [16, 20]. (b) Comparison of the formation Gibbs energy of Fe-Zn alloys calculated at 344°C with experimental data [17, 21].

Figure 4 Comparison of the phase diagrams of the Fe-Zn binary system calculated in this study with the phase diagrams calculated using the TCFE12 thermodynamic database and experimental data [4, 32]. Calculated miscibility gap between δ_{1k} and δ_{1p} phases is colored yellow in (c). The legend shown in (b) is common to (a) through (d).

Figure 5 Site fraction of Fe_1Zn_{12} associates in liquid Fe-Zn alloys calculated at temperatures from 450 °C to 800 °C.

Figure 6 Gibbs energies of liquid Fe-Zn alloys calculated using the associate solution model at temperatures from 450 °C to 800 °C compared with those calculated excluding Fe_1Zn_{12} associates. Reference states of Fe and Zn are bcc ($A2$) and liquid, respectively.

Figure 7 Comparison of the phase diagrams of the Fe-Zn binary system calculated in this study with the phase diagrams calculated excluding Fe_1Zn_{12} associates (denoted by "excld. associate" in (a)) from the Gibbs energy parameters, $i.e.$, $G^{L}_{Fe_1Zn_{12}} = 0$ and $G^{A3}_{Fe_1Zn_{12}} = 0$, in Table 3, with the phase diagrams calculated using TCFE12 thermodynamic database, and with experimental data (solid and open circles) [32]. The legend shown in (a) is common to (a) through (c).