A Thermodynamic Assessment of Liquid Mn–Si Alloy

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The solution model of Mn–Fe–Si–C system is essential in the development of high Mn containing steels and alloys, and its effectiveness depends on the well established information of constituting lower order systems. The solution property of Mn–Si system, which is one of such constituting binary systems, is not well established yet because the experimental data are limited in number and scope. The present study determines the temperature independent partial enthalpy and excess entropy of Mn and Si from the relevant experimental data. The resulting excess Gibbs free energy function was found to adequately describe the solution properties of Mn–Si system.

KEY WORDS: Mn and Si; thermodynamics; activity; enthalpy; excess entropy.

1. Introduction

A recent development of high performance steels is motivated by the unusual combination of the strength with formability of high Mn containing steels, and it necessitates reliable information for solution properties of high Mn containing alloys as well as steels. Such requirement can be met by the solution model of Mn–Fe–Si–C system. The effectiveness of the multi-component model depends on the well established information of constituting lower order systems. Such establishment is done by defining the behavior of solution as the excess properties. A popular course of it is to express the excess properties as the activity coefficients, and, in turn, the activity coefficients are represented in polynomial functions. A success of such approach is guaranteed by confident sets of data. However, the Mn–Si system, which is one of the constituting binary systems, had not been well studied so far. Its experimental investigation is small in number and scope. Even its phase diagram is not complete yet.11 The limited information has not facilitated to establish the reliable and confident representation for solution properties of Mn–Si system. Recently, several investigators2–4) examined the Mn–Si system and made a contribution to the study of Mn–Si system. Still, the limited nature of information had not helped to develop a successful representation to reproduce the critical industrial processing parameters. A further improvement is desired.

This study critically examines the available experimental data of Mn–Si system and determines the temperature independent partial enthalpies (ΔHi) and partial excess entropies (ΔSxi) from the relevant experimental data. The resulting excess Gibbs free energy function (Gxs) is found to adequately describe the solution behavior of Mn–Si melt in a wide range of composition and temperature.

2. Review of Available Experimental Data of Mn–Si Melt

2.1. Activity Coefficient of Mn

Gee et al.,5) Tanaka,6) and Ahmad et al.7) measured the vapor pressure of Mn from Mn–Si melt by the transportation and torsion-effusion technique, respectively. The activity coefficients of Mn, taking the pure Mn melt as the reference state, were determined from their measurement of Mn vapor pressure and reproduced in Fig. 1. The activity coefficients of Mn by Tanaka are shown to deviate from those by Gee et al. and Ahmad et al. at high Si contents.

Gee et al. and Ahmad et al. had some experimental difficulties in measuring vapor pressure of Mn when Si content increased, and they needed to adjust evaporation rates of Mn. This adjustment was made by increasing experimental temperatures from about 1550 to 1850 K as Si content increased in Mn–Si alloy, indicating that their results may

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Fig. 1. Activity coefficients of Mn and Si in Mn–Si melt from experiments (pure Mn and Si melt as reference states).
not be interpreted as an isothermal investigation. The spread of data at a given Si content in Fig. 1 indicates the extent of variation of their experimental temperatures. The range of their experimental temperature was about 200 K. This temperature range permitted the determination of the partial enthalpy and excess entropy of Mn at various Si contents. However, Tanaka limited his investigation to two temperatures, 1623 and 1673 K, and his data were not included in the present assessment.

2.2. Activity Coefficient of Si

Unlike the solution properties of Mn, the available experimental data for the activity of Si are limited to the terminal composition of dilute solution of Si in Mn.

Fischer et al.8) and Kor9) determined the Si contents in Mn melt contained in a MnO crucible, and their results are reproduced in Table 1. Their experimental data permit the determination of activity coefficient of Si from the consideration of equilibrium as given by the Eq. (1).

\[
2 \text{MnO(s)} + \text{Si(l)} = 2 \text{Mn(l)} + \text{SiO}_2(s, \text{tridymite}) \cdots (1)
\]

The standard Gibbs free energy of the reaction (1) was taken from the recent compilation by Pankratz10) and Barin.11) The calculation for the activity coefficient of Si requires the values for the activity of SiO\(_2\) in MnO–SiO\(_2\) system at saturation with MnO, and the recent work by Eriksson et al.12) provided the necessary information. The results are also listed in Table 1. As the variation of Si content with temperature is small, the calculated activity coefficients of Si are amenable to determination of the partial enthalpy of Si, \(\Delta H_{\text{Si}}\), at the averaged Si content of \(x_{\text{Si}}=0.0263\).

Kor9) and Tuset et al.13) determined the Si content in Mn–Si alloy in equilibrium with SiO\(_2\) saturated MnO–SiO\(_2\) slag, and their results are listed in Table 2. The activity of Si in Mn–Si alloy may be determined by invoking the Eq. (1) only when the prior knowledge of the associated activity of Mn is available. Because of the lack of such information, no attempt was made to develop the information of the activity coefficient of Si from these data. As they are relevant to the processing condition of SiMn alloy, however, the experimental data by Kor and Tuset et al. were used to optimize the parameters for the excess entropies of Si and Mn as discussed later.

3. Previous Attempts for \(\ln \gamma_{\text{Mn}}\) and \(\ln \gamma_{\text{Si}}\) in Analytical Representation

As shown in Fig. 1, the experimental values for the activity coefficient of Mn are available for a wide range of Si content, but, the information for the activity coefficient of Si is too small in number and scope to draw a meaningful interpretation for its behavior. A reasonable strategy to assess their solution properties is to develop an analytical representation for the activity coefficient of Mn and, then, to determine the activity coefficient of Si with the use of Gibbs-Duhem relationship. The present author made several attempts to develop analytical representations in Redlich-Kister formalism but failed to produce a consistent set of analytical expression which would reasonably represent the activity coefficients of Mn and Si. The unsuccessful attempts may have been caused by the inhomogeneous nature of data in composition as well as in temperature.

Alternatively, the available but relevant experimental data are analyzed to determine the partial enthalpy and excess entropy of Mn and Si, which are temperature independent, and the solution properties are represented by virtue of the excess free energy function.

4. Excess Properties of Fe–Si Melt

Fe–Si and Mn–Si systems are considered to be energetically similar, and the thermodynamic properties of Fe–Si system may serve as useful references in the present assessment of solution properties of Mn–Si melt. Chart14) critically assessed the thermodynamic properties of Fe–Si system and organized them in terms of \(\Delta H_{\text{Fe}}, \Delta S_{\text{Fe}}, \Delta S_{\text{Si}}, \) and \(\Delta S_{\text{Si}}\). Figure 2 reproduces his assessed partial enthalpies and excess entropies in Fe–Si melt. The resulting excess Gibbs free energy defined by the Eq. (3) was found to reproduce well the experimentally determined activity coefficients of Si and Fe in Fe–Si melt.

\[
G^\text{ex} = RT \ln \gamma_i = \Delta H_i - T \Delta S^\text{ex}_i \cdots ... (3)
\]

5. Assessment of Partial Enthalpies of Solution in Mn–Si Melt

5.1. Partial Enthalpies of Mn, \(\Delta H_{\text{Mn}}\)

The partial enthalpy of Mn, \(\Delta H_{\text{Mn}}\), in Mn–Si melt may be

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<th>Table 1. Mn–Si melt in equilibrium with MnO (s) saturated MnO–SiO(_2) slag.</th>
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Note: reference states for Mn and Si are pure liquid Mn and Si and for MnO and SiO\(_2\) pure solid MnO (s) and SiO\(_2\) (s, tridymite).

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<th>Table 2. Mn–Si melt in equilibrium with SiO(_2) (s) saturated MnO–SiO(_2) slag.</th>
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Note: reference states for Mn and Si are pure liquid Mn and Si and for MnO and SiO\(_2\) pure solid MnO (s) and SiO\(_2\) (s, tridymite).
determined from the temperature dependency of ln$\gamma_{\text{Mn}}$ by invoking the Eq. (4).

$$\Delta H_{\text{Mn}} = [\delta(R \ln \gamma_{\text{Mn}}) / \delta(1/T)]_P \quad \cdots \quad (4)$$

As mentioned above, Gee et al. and Ahmad et al. measured the vapor pressure of Mn in the temperature range of about 200 K, and this is sufficient enough to determine a reliable temperature dependency of activity coefficient of Mn. Figure 3 presents the partial enthalpy of Mn, $\Delta H_{\text{Mn}}$, at various Si contents as determined from their data. It shows a slowly decreasing tendency with increasing Si content. However, they show some degree of scattering and do not lend a confidence in deriving a reliable expression for $\Delta H_{\text{Mn}}$.

Useful clues may be developed from the energetic similarity between Fe–Si and Mn–Si systems. In Fig. 3, the relationship of $\Delta H_{\text{Fe}}$ with Si content in Fe–Si melt is compared with the experimentally determined $\Delta H_{\text{Mn}}$ in Mn–Si melt. It shows that the experimentally determined $\Delta H_{\text{Mn}}$ in Mn–Si melt are scattered around the superimposed curve for $\Delta H_{\text{Fe}}$ in Fe–Si melt but their behavior appears to be represented reasonably well by that of $\Delta H_{\text{Fe}}$. This observation is taken as a justification for the assumption to take $\Delta H_{\text{Fe}}$ in Fe–Si melt as $\Delta H_{\text{Mn}}$ in Mn–Si melt. In the following analysis, $\Delta H_{\text{Fe}}$ in Fe–Si system is taken as $\Delta H_{\text{Mn}}$ in Mn–Si.

### 5.2. Partial Enthalpies of Si, $\Delta H_{\text{Si}}$

Unfortunately, the information for the partial enthalpy of Si, $\Delta H_{\text{Si}}$, in Mn–Si melt is limited to the terminal composition region of dilute solution of Si.

Chart reported the partial enthalpies of Si, $\Delta H_{\text{Si}}$, in infinite dilute solution of Si in Mn to be $\sim 115.060$ J/mol. This value is shown in Fig. 3.

As discussed above, Fischer et al. and Kor determined the Si contents in Mn which is in equilibrium with MnO(s) saturated MnO–SiO$_2$ slag. They vary from $x_{\text{Si}}=0.014$ to $0.037$ in the temperature range of 1,683 to 1,968 K. If the small variation in Si contents is neglected, $\Delta H_{\text{Si}}$ may be derived from the temperature dependency of activity coefficients of Si for the averaged composition, $x_{\text{Si}}=0.0263$. Figure 4 shows the activity coefficient of Si by Fischer et al. and Kor with an inverse of temperature. This yields $\Delta H_{\text{Si}}= -124,323$ J/mol at $x_{\text{Si}}=0.0263$ (avg.) in Mn–Si melt and is plotted also in Fig. 3.

These two values for $\Delta H_{\text{Si}}$ are used as boundary conditions in determination of the composition dependency of the partial enthalpy of Si, $\Delta H_{\text{Si}}$, in the present assessment.

### 5.3. Redlich-Kister Formalism for Analytical Representation of Solution Properties

The solution properties of Mn–Si melt is organized in terms of excess Gibbs free energy which is further resolved into partial as well as integral enthalpy and excess entropy as defined by the Eq. (3). Their respective analytical representations are approximated with polynomial forms using mole fraction as variable across the entire composition range. The Redlich-Kister formalism is adopted for the analytical representation in the present study. The enthalpy and excess entropy, integral and partial, of Mn–Si system may be described adequately with their respective polynomial functions of four parameters as expressed by the following Eqs. (5) and (6).

$$\Delta H = x_{\text{Si}}(1-x_{\text{Si}})[A_0 + A_1(2x_{\text{Si}}-1) + A_2(2x_{\text{Si}}-1)^2 + A_3(2x_{\text{Si}}-1)^3] \quad \cdots \quad (5a)$$

$$\Delta H_{\text{Mn}} = x_{\text{Si}}^2[A_0 + A_1(4x_{\text{Si}}-3) + A_2(6x_{\text{Si}}-5)(2x_{\text{Si}}-1) + A_3(8x_{\text{Si}}-7)(2x_{\text{Si}}-1)^2]\cdots \quad (5b)$$

$$\Delta H_{\text{Si}} = (1-x_{\text{Si}})[A_0 + A_1(4x_{\text{Si}}-1) + A_2(6x_{\text{Si}}-1)(2x_{\text{Si}}-1) + A_3(8x_{\text{Si}}-1)(2x_{\text{Si}}-1)^2] \cdots \quad (5c)$$

$$\Delta S_{\text{sic}} = x_{\text{Si}}(1-x_{\text{Si}})[a_0 + a_1(2x_{\text{Si}}-1) + a_2(2x_{\text{Si}}-1)^2 + a_3(2x_{\text{Si}}-1)^3] \cdots \quad (6a)$$
\[ \Delta S_{\text{Mn}}^{\text{ex}} = x_{\text{Si}}^2 [a_0 + a_1 (4x_{\text{Si}} - 3) + a_2 (6x_{\text{Si}} - 5) (2x_{\text{Si}} - 1) + a_3 (8x_{\text{Si}} - 7)(2x_{\text{Si}} - 1)^2] \]

\[ \Delta S_{\text{Si}}^{\text{ex}} = (1-x_{\text{Si}})^2 [a_0 + a_1 (4x_{\text{Si}} - 1) + a_2 (6x_{\text{Si}} - 1) (2x_{\text{Si}} - 1) + a_3 (8x_{\text{Si}} - 1)(2x_{\text{Si}} - 1)^2] \]

These polynomial expressions are consistent thermodynamically and convenient because the same set of coefficients, \( a_i \) or \( a_i \), are used for both representations of integral and partial properties. The task in the present assessment is to determine the sets of parameters, \( a_i \) and \( a_i \).

5.4. Assessment of \( \Delta H_{\text{Mn}} \) and \( \Delta H_{\text{Si}} \)

The values for \( \Delta H_{\text{Mn}} \) were developed at the increment of \( \Delta x_{\text{Si}}=0.05 \) for the entire composition range of Si content. These values and those for \( \Delta H_{\text{Si}} \) at infinite dilute solution of Si and at \( x_{\text{Si}}=0.0263 \) were taken as a set of data, and a multiple regression analysis was performed to determine the coefficients of polynomial terms in Redlich-Kister formalism. The final representations for \( \Delta H_{\text{Mn}} \) and \( \Delta H_{\text{Si}} \) were determined from the best correlation, and the results are given as the following Eqs. (6) and (7), respectively.

\[ \Delta H_{\text{Mn}} = x_{\text{Si}} (1-x_{\text{Si}}) [A_0 + A_1 (2x_{\text{Si}} - 1) + A_2 (2x_{\text{Si}} - 1)^2 + A_3 (2x_{\text{Si}} - 1)^3] \]

\[ \Delta H_{\text{Si}} = (1-x_{\text{Si}})^2 [A_0 + A_1 (4x_{\text{Si}} - 1) + A_2 (6x_{\text{Si}} - 1) (2x_{\text{Si}} - 1) + A_3 (8x_{\text{Si}} - 1)(2x_{\text{Si}} - 1)^2] \]

These polynomial expressions are calculated values for \( \Delta S_{\text{Mn}}^{\text{ex}} \) were developed at the increase of \( \Delta x_{\text{Si}}=0.05 \) for the entire composition range of Si content. These values and those for \( \Delta S_{\text{Si}}^{\text{ex}} \) at infinite dilute solution of Si and at \( x_{\text{Si}}=0.0263 \) were taken as a set of data, and a multiple regression analysis was performed to determine the coefficients of polynomial terms in Redlich-Kister formalism. The final representations for \( \Delta H_{\text{Mn}} \) and \( \Delta H_{\text{Si}} \) were determined from the best correlation, and the results are given as the following Eqs. (6) and (7), respectively.

\[ \Delta S_{\text{Mn}}^{\text{ex}} = x_{\text{Si}}^2 [a_0 + a_1 (4x_{\text{Si}} - 3) + a_2 (6x_{\text{Si}} - 5) (2x_{\text{Si}} - 1) + a_3 (8x_{\text{Si}} - 7)(2x_{\text{Si}} - 1)^2] \]

\[ \Delta S_{\text{Si}}^{\text{ex}} = (1-x_{\text{Si}})^2 [a_0 + a_1 (4x_{\text{Si}} - 1) + a_2 (6x_{\text{Si}} - 1) (2x_{\text{Si}} - 1) + a_3 (8x_{\text{Si}} - 1)(2x_{\text{Si}} - 1)^2] \]

6. Partial Excess Entropies of Solution, \( \Delta S_{\text{Mn}}^{\text{ex}} \) and \( \Delta S_{\text{Si}}^{\text{ex}} \)

Partial excess entropy is determined with the use of Eq. (8).

\[ \Delta S_{\text{ex}}^{\text{Si}} = \Delta H_{\text{Si}} / T - R \ln \gamma_{\text{Si}} \] ..........................(8)

The required partial enthalpies are calculated by the Eqs. (6) and (7), and the activity coefficients are taken from the experimental data mentioned in the Chapter 2.

6.1. Partial Excess Entropy of Mn, \( \Delta S_{\text{Mn}}^{\text{ex}} \)

The partial excess entropy of Mn, \( \Delta S_{\text{Mn}}^{\text{ex}} \), was calculated from the experimentally determined activity coefficients of Mn by Gee et al.\(^5\) and Ahmad et al.\(^7\). However, the calculated values for \( \Delta S_{\text{Mn}}^{\text{ex}} \) are shown to vary with temperature. In order to treat them as temperature independent property, they were averaged over the investigated temperature range. The resulted \( \Delta S_{\text{Mn}}^{\text{ex}} \) are plotted with Si content in Fig. 5. The partial excess entropy of Mn determined with experimental data by Gee et al. is in good agreement with that by Ahmad et al. in their behavior with Si content. In general, it decreases non-linearly with increasing Si content.

6.2. Partial Excess Entropy of Si, \( \Delta S_{\text{Si}}^{\text{ex}} \)

Partial excess entropies of Si, \( \Delta S_{\text{Si}}^{\text{ex}} \), was calculated for the Si contents examined by Fischer et al.\(^5\) and Kor,\(^6\) and Fig. 5 shows their results.

6.3. Assessment of \( \Delta S_{\text{Mn}}^{\text{ex}} \) and \( \Delta S_{\text{Si}}^{\text{ex}} \)

A multiple regression analysis in the Redlich-Kister formalism was carried out with the above determined values of \( \Delta S_{\text{Mn}}^{\text{ex}} \) and \( \Delta S_{\text{Si}}^{\text{ex}} \). As mentioned above, the experimental results by Kor\(^9\) and Tuset et al.\(^13\) are relevant to the smelting condition of SiMn alloy, and the desired analytical representation for \( \Delta S_{\text{Mn}}^{\text{ex}} \) and \( \Delta S_{\text{Si}}^{\text{ex}} \) was obtained by optimizing the parameters of Redlich-Kister formalism to reproduce their experimentally determined compositions of Mn–Si melt in equilibrium with SiO2 saturated MnO–SiO2 slag. It was found that three parameters in Redlich-Kister formalism are adequate to describe the excess entropy in Mn–Si system and listed in Table 3. The resulting analytical representation is given by the following Eqs. (9) and (10), respectively.

\[ \Delta S_{\text{Mn}}^{\text{ex}} = x_{\text{Si}}^2 [132.125 - 4.414 (4x_{\text{Si}} - 3) + 16.74 (6x_{\text{Si}} - 5) (2x_{\text{Si}} - 1)] \]

\[ \Delta S_{\text{Si}}^{\text{ex}} = (1-x_{\text{Si}})^2 [32.125 - 4.414 (4x_{\text{Si}} - 1) + 16.74 (6x_{\text{Si}} - 1) (2x_{\text{Si}} - 1)] \]

As shown in Fig. 5, the reproduction by the assessed \( \Delta S_{\text{Mn}}^{\text{ex}} \) and \( \Delta S_{\text{Si}}^{\text{ex}} \) in Mn–Si system is reasonable.

7. Reproductions of Solution Properties of Mn–Si Melt

The partial excess Gibbs free energies for Mn and Si, \( G_{\text{Mn}}^{\text{ex}} = RT \ln \gamma_{\text{Mn}} \) and \( G_{\text{Si}}^{\text{ex}} = RT \ln \gamma_{\text{Si}} \), were defined in terms of the assessed representations for \( \Delta H_{\text{Mn}} \), \( \Delta H_{\text{Si}} \), \( \Delta S_{\text{Mn}}^{\text{ex}} \), and \( \Delta S_{\text{Si}}^{\text{ex}} \).
ΔS_{Si}, and the activity coefficients of Mn and Si, in reference to their respective pure liquids, were calculated at various composition and temperature in Mn–Si melt. As shown in Tables 1 and 2, the present excess Gibbs free energy function reproduces well the experimentally determined Si contents in Mn, which is in equilibrium with MnO(s) or SiO$_2$(s) saturated MnO–SiO$_2$ slags, as reported by Fischer et al., Kor, and Tuset et al. This information is relevant to the industrial practice of processing FeMn and SiMn alloys. The observed good agreement with experimental data lends credence to the present assessment.

The assessed partial Gibbs free energies for Mn and Si were used to determine the variation of the activity coefficient of Mn and Si with Si content at 1673, 1773, and 1873 K. In Fig. 6, the results are compared with experimentally observed solution properties of Mn and Si. It shows that the present assessment reproduces reasonably well the experimentally determined activity coefficients of Mn and Si.

The activity coefficient of Si at infinite dilute solution of Si in Mn, lnγ$^o_{Si}$, was determined from the present assessment, and it is given by the following Eq. (11).

$$\ln{\gamma}^o_{Si} = 1.3196 - 13942/T \hspace{1cm} (11)$$

8. Conclusion

The experimental data in Mn–Si system are not sufficient enough to develop a reliable representation for activity coefficients of Mn and Si. However, the experimental data by Gee et al. and Ahmad et al. are amenable to determination of temperature independent partial enthalpies of Mn and Si. With an assumption of identity of ΔH$_{Fe}$ in Fe–Si with ΔH$_{Mn}$ in Mn–Si system, the information allowed to develop the partial excess entropies of solution in Mn–Si melt. The resulted excess Gibbs free energy of solution describes reasonably well the solution properties of Mn–Si melt in a wide range of temperature and composition. Also, it reproduces the experimentally determined composition of Mn–Si alloy in equilibrium with SiO$_2$ saturated MnO–SiO$_2$ slag. The good agreement with experimental data provides a confidence to the present assessment.

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