An Assessment of Analytical Liquidus Equations for Fe-C-Si-Mn-Al-P-Alloyed Steels Using DSC/DTA Techniques

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Analytical liquidus equations were evaluated using differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Results of 180 measurements in the Fe-C-Si-Mn-Al-P subsystems were considered, where the experimental methodology was demonstrated for four alloys in the Fe-Si-Mn-Al system. Excellent agreement between the DSC/DTA dataset and the most recently published equation was found (error 2.1 ± 1.6 °C). For this equation, suggested modifications of phosphorus parameters will help to improve calculations for P-alloyed steels.

https://doi.org/10.1007/s11663-021-02251-1
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I. INTRODUCTION

Precise knowledge of the liquidus temperature $T_{L}$ is essential to adjust the superheat in the continuous casting of steel and optimize the casting operations. In order to predict the solidification progress in the casting machine, it is required to extend the estimation of $T_{L}$ down to solidus temperature with respect to microsegregation modeling. The actual temperature of the interdendritic melt corresponds to the liquidus temperature of its changing chemical composition due to the enrichment of alloying elements in the liquid phase during solidification.[1,2] Microsegregation models can be used to calculate the non-equilibrium solidus temperature depending on the solidification kinetics or to characterize the hot tear sensitivity of a steel grade close to the final solidification stage.[3]

In general, two methods are available to estimate $T_{L}$ based on the chemical composition of a steel grade: Within (i) the CALculation of PHAse Diagram (CALPHAD) framework,[4,5] the phase equilibrium temperature is obtained by minimizing the Gibbs energy of the system. For this purpose, various commercial software packages with comprehensive thermodynamic databases are available, e.g., FactSage,[6] ThermoCalc,[7] Pandat,[8] and IDS.[9] The great advantage of self-consistent CALPHAD databases is their accurate extrapolation to high concentration and the possibility to perform phase equilibrium calculations over the whole composition range of multicomponent alloys. In practical steelmaking, a simplified way of calculating $T_{L}$ is (ii) the application of empirically derived equations that are more or less linear regressions fitted to experimental data. Based on regression analysis and phase diagram calculations, several equations have been proposed in the past.[10–14] Empirical equations enable fast calculations of $T_{L}$ within defined alloying limits, can be used without thermodynamic databases and numerical solvers and are, therefore, cost-saving alternatives for a successful casting process control in steelmaking plants. Nevertheless, the published equations are only valid in the investigated composition range and may lead to significant errors in the case of higher concentrations and stronger interaction of the alloying elements in the liquid phase.

Analytical liquidus equations are expressed in the form of

$$T_{L} = T_{0}^{L} + \sum_{i} f([\%X_i]),$$

where $T_{0}^{L}$ is the melting temperature of pure iron handled as a constant[10,12] or, more specifically, separated into $T_{0}^{L}$ of δ-iron (1534 °C[11] 1536 °C[13] and 1538 °C[14]) and γ-iron (1491 °C[11] 1526 °C[13] and 1528 °C[14]). Note that, if separated equations for δ-Fe and γ-Fe are proposed[11,13,14] (Table I and II) then the phase with the higher value of $T_{L}$ is the primary phase at the liquidus temperature. The parameter $f([\%X_i])$ describes the influence of the element $X$ on the melting temperature of Fe depending on the concentration of...
against thermal analysis results of carbon steels and
often, the change in the solidifying phase (austenite or
ferrite) — ferrite (\(T_L\)) — ferrite (\(T_L\)).

\(\begin{equation}
T_L = T_L^0 + A_{a,b} \left[ \% \text{C} + \sum_i \left( \% X_i \left[ 1 + d_{a,b} + b_{a,b} \left[ \% X_i \right] \right] \right) \right]
+ B_{a,b} \left[ \% \text{C} + \sum_i \left( \% X_i \left[ 1 + d_{a,b} + b_{a,b} \left[ \% X_i \right] \right] \right) \right]^2
\end{equation}\)

where \(A_a = -76.77, A_c = -58.74, B_a = -6.89\) and
\(B_c = -4.64\). The values for \(d_{a,b}\) and \(b_{a,b}\) are summarized in Table II.

Miettinen and Howe\(^{[14]}\) evaluated various liquidus equations\(^{[10–15]}\) based on extensive experimental data from literature and pointed out the following difficulties in comparing each of the equations and possible reasons for differences in the calculations:

- the equations relate closely to the alloys studied, and
- the corresponding composition of the alloys is only roughly reported (low-alloyed or stainless steels),
- the number of investigated alloys is too small or the alloys studied show only minor variation in their chemical composition,
- the focus was placed on the selection of specific alloys or some solutes are only found in a few alloys, and
- the change in the solidifying phase (austenite or ferrite) was not taken into account.

It was, therefore, not the aim of this work to introduce another empirical equation but to critically evaluate the available expressions from the literature\(^{[10–14]}\) and check the valid composition range of the calculations based on a comprehensive experimental dataset obtained from thermal analysis techniques.

All equations\(^{[10–14]}\) were derived for specific applications. Kawawa\(^{[10]}\) tested his proposed description of \(T_L\) against thermal analysis results of carbon steels and reported an average error of \(\pm 4 \degree\) C. Kagawa and Okamoto\(^{[11]}\) not only focused on the influence of small amounts of alloying elements (typically < 3 mass pct.) on the peritectic phase transformation but also gave a liquidus equation for the dilute solutions of Fe. Howe’s studies\(^{[12]}\) and later, those of Miettinen and Howe\(^{[14]}\) are general in nature and provide the possibility to estimate \(T_L\) for low-alloyed and stainless steels. In the calculation scheme, Howe\(^{[12]}\) therefore, lists various different parameters for C, Si, Ni, and V depending on the

\(X\) in mass percent. The individual functions \(f(\% X_i)\) of analytical equations from literature\(^{[10–12,14]}\) with relevance for Fe-C-Si-Mn-Al-P alloys are given in Table I. Typically, these are linear\(^{[10–12,14]}\) and parabolic functions\(^{[11,12]}\) representing the slope of the liquidus line in binary Fe-X systems. As carbon is in general the most dominating alloying element in steel, additional cross products \([\% \text{C}] \times [\% \text{C}]\) were introduced by Miettinen and Howe\(^{[14]}\) in order to describe the interaction of the alloying element \(X\) with C. A slightly different approach was proposed in the work of Schürmann and Stisovic\(^{[13]}\) assigning the decrease of \(T_L\) caused by an alloying element to an equivalent factor of carbon. The equation is given by

\(\begin{align*}
T_L &= T_L^0 \\
&\quad + A_{a,b} \left( \% \text{C} + \sum_i \left( \% X_i \left[ 1 + d_{a,b} + b_{a,b} \left( \% \text{C} \right) \left[ \% X_i \right] \right] \right) \right) \\
&\quad + B_{a,b} \left( \% \text{C} + \sum_i \left( \% X_i \left[ 1 + d_{a,b} + b_{a,b} \left( \% \text{C} \right) \left[ \% X_i \right] \right] \right) \right)^2
\end{align*}\)
Table II. Parameters Derived by Schürmann and Stisovic\cite{13} for Fe-C-Si-Mn-Al-P Alloys (Note That P is Not Considered In This Equation)

| Constituent Systems | T_L [°C] | Si [Mass Percent] | Mn [Mass Percent] | Al [Mass Percent] | P [Mass Percent] | No. of Alloys |
|---------------------|----------|-------------------|-------------------|------------------|----------------|--------------|
| Ferrite (δ)         | 1536     | a = −0.8384       | a = −0.9433       | a = −1.0011      |                |              |
|                     |          | b = 3.544E−3      | b = 2.6E−4        | b = 2.8154E−5    |                |              |
| Austenite (γ)       | 1526     | a = −0.6931       | a = −0.9323       | a = −0.9169      |                |              |
|                     |          | b = 0.0459        | b = −4.1584E−4    | b = −0.3084      |                |              |

Table III. Composition Range of the Samples Investigated Using DSC/DTA Techniques

| Constituent Systems | C [Mass Percent] | Si [Mass Percent] | Mn [Mass Percent] | Al [Mass Percent] | P [Mass Percent] | No. of Alloys |
|---------------------|-----------------|------------------|-------------------|------------------|----------------|--------------|
| Fe-C-Si             | 0.007 to 1.56   | 0.49 to 4.39     | —                 | —                | —              | 46           |
| Fe-C-Mn             | 0.054 to 0.30   | —                | 1.02 to 5.39      | —                | —              | 10           |
| Fe-C-Al             | 0.035 to 0.59   | —                | —                 | 0.37 to 1.97     | —              | 28           |
| Fe-P, Fe-C-P        | 0.004 to 1.38   | —                | —                 | —                | 0.026 to 0.76  | 26           |
| Fe-Si-P, Fe-Al-P    | < 0.006         | < 2.96           | —                 | < 1.66           | 0.092 to 0.096 | 8            |
| Fe-Si-Mn, Fe-C-Si-Mn, Fe-Si-Mn-Al | 0.005 to 0.32 | 0.54 to 4.12 | 0.03 to 6.05 | < 0.87 | — | 49 |
| Fe-C-Mn-P, Fe-C-Si-Mn-Al-P | 0.012 to 0.24 | < 0.44 | 1.58 to 2.01 | < 0.74 | 0.005 to 0.33 | 12 |
| All Data            | 0.007 to 1.56   | < 4.39           | < 6.05            | < 1.97           | < 0.76         | 179          |

A part of the DSC/DTA dataset has already been published in previous work of the authors\cite{21–26} and further liquidus data in the Fe-C-Al and Fe-Si-Mn-Al key-systems are provided in the present study, see Table IV. Additional background results of ternary (Fe-C-Si, Fe-C-Mn, Fe-Si-P, Fe-Al-P), quaternary (Fe-C-Si-Mn, Fe-C-Mn-P, and multicomponent (Fe-C-Si-Mn-Al-P) alloys within the composition range of Table III are considered in the discussion.

The typical experimental methodology is demonstrated by examining four alloys in the Fe-Si-Mn-Al quaternary system using DSC. The specimens for the DSC measurements were prepared in a 25 kg induction furnace by taking lollipop steel samples without any deoxidizing agents (Al or Zr). The bath level was protected by argon flushing in order to minimize the contact between the atmosphere and the liquid steel. The chemical analysis was determined using an optical emission spectrometer (OES), type Spectromax Version F (SPECTRO Analytical Instruments & Co.KG,
| Sample | References | C [Mass Percent] | Si [Mass Percent] | Mn [Mass Percent] | Al [Mass Percent] | P [Mass Percent] | $T_L$ (DSC/DTA) | $\Delta T_L^{[10]}$ | $\Delta T_L^{[11]}$ | $\Delta T_L^{[12]}$ | $\Delta T_L^{[13]}$ | $\Delta T_L$ (PW) |
|--------|------------|------------------|------------------|------------------|------------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Fe-C-Si_1 | 21 | 0.0461 | 1.026 | — | — | — | 1521.6 | 3.0 | -4.7 | 2.1 | -2.5 | 0.7 | 0.7 |
| Fe-C-Si_2 | 0.0839 | 0.993 | — | — | — | 1519.3 | 2.6 | -4.1 | 1.5 | -2.8 | 0.3 | 0.3 |
| Fe-C-Si_3 | 0.1423 | 0.980 | — | — | — | 1512.3 | 5.2 | -0.5 | 3.5 | -0.3 | 2.6 | 2.6 |
| Fe-C-Al_1 | 0.2244 | — | — | 1.996 | — | 1512.7 | 10.4 | -1.7 | 4.2 | 50.3 | -1.3 | -1.3 |
| Fe-Si-Mn_1 | 25 | 0.0071 | 2.900 | 0.033 | — | — | 1501.7 | 11.5 | -9.9 | 1.0 | -6.4 | 1.7 | 1.7 |
| Fe-Si-Mn_2 | 0.0073 | 3.070 | 1.050 | — | — | 1495.7 | 11.3 | -11.4 | 0.6 | -5.8 | -0.1 | -0.1 |
| Fe-Si-Mn_3 | 0.0140 | 3.090 | 3.060 | — | — | 1486.7 | 9.7 | -12.8 | 2.6 | -5.9 | -3.2 | -3.2 |
| Fe-Si-Mn_4 | 0.0155 | 2.925 | 5.996 | — | — | 1477.3 | 5.9 | -15.4 | 5.5 | -8.7 | -8.5 | -8.5 |
| Fe-Si-Mn_5 | 0.016 | 2.950 | 6.050 | — | — | 1475.8 | 6.9 | -14.6 | 4.7 | -7.5 | -7.6 | -7.6 |
| Fe-C-Al_2 | 0.2244 | — | — | 0.394 | — | 1520.6 | -3.5 | -0.6 | 3.1 | -2.1 | 0.2 | -0.2 |
| Fe-C-Al_3 | 0.2286 | — | — | 1.475 | — | 1520.0 | -7.1 | -0.3 | 2.9 | 24.3 | 0.0 | 0.0 |
| Fe-C-Si-Mn_1 | 23 | 0.1140 | 1.001 | 1.996 | — | — | 1508.4 | 1.3 | -4.9 | 0.3 | -3.5 | 2.7 | 2.7 |
| Fe-C-Si-Mn_2 | 0.1430 | 1.031 | 2.053 | — | — | 1504.2 | 2.8 | -3.2 | 0.8 | -2.4 | 1.6 | 1.6 |
| Fe-C-Si-Mn_3 | 0.1850 | 1.031 | 2.051 | — | — | 1501.7 | 2.0 | -3.6 | 0.4 | -3.4 | 2.6 | 2.6 |
| Fe-C-Si-Mn_4 | 0.2640 | 1.034 | 2.027 | — | — | 1495.0 | 2.6 | -2.9 | 0.5 | -3.2 | 2.6 | 2.6 |
| Fe-C-Si-Mn_5 | 0.2995 | 1.034 | 2.027 | — | — | 1492.2 | 2.6 | -3.1 | 0.8 | -3.4 | 2.9 | 2.9 |
| Fe-C-Si-Mn_6 | 24 | 0.0270 | 2.040 | 2.080 | — | — | 1502.2 | 6.0 | -9.1 | 0.5 | -5.3 | 2.0 | 2.0 |
| Fe-C-Si-Mn_7 | 0.1270 | 2.050 | 2.060 | — | — | 1492.8 | 7.6 | -5.5 | 1.2 | -4.4 | 1.3 | 1.3 |
| Fe-C-Si-Mn_8 | 0.1660 | 2.040 | 2.070 | — | — | 1490.8 | 6.6 | -6.0 | 0.1 | -5.6 | 2.7 | 2.7 |
| Fe-C-Si-Mn_9 | 0.2250 | 2.040 | 2.060 | — | — | 1485.1 | 7.8 | 4.6 | 0.5 | -4.9 | 2.2 | 2.2 |
| Fe-C-Si-Mn_10 | 0.3070 | 2.060 | 2.050 | — | — | 1478.3 | 8.1 | 4.7 | 0.0 | -5.5 | 3.1 | 3.1 |
| Fe-P_1 | 26 | — | — | — | — | — | 1535.1 | 0.0 | -1.9 | 1.0 | 0.9 | 2.3 | 1.9 |
| Fe-P_2 | — | — | — | — | — | — | 1534.9 | -0.4 | -2.3 | 0.6 | 1.1 | 2.0 | 1.5 |
| Fe-P_3 | — | — | — | — | — | — | 1524.2 | 0.1 | 1.6 | 1.1 | 3.6 | 3.1 | 1.8 |
| Fe-P_4 | — | — | — | — | — | — | 1529.1 | 1.8 | 0.2 | 29 | 6.9 | 5.3 | 3.4 |
| Fe-P_5 | — | — | — | — | — | — | 1525.3 | -0.4 | -1.5 | 0.8 | 10.7 | 4.7 | 0.8 |
| Fe-P_6 | — | — | — | — | — | — | 1520.5 | 1.1 | 0.2 | 2.3 | 15.5 | 7.1 | 2.0 |
| Fe-P_7 | — | — | — | — | — | — | 1520.9 | 1.4 | -2.2 | 0.2 | 15.1 | 5.2 | -0.7 |
| Fe-P_8 | — | — | — | — | — | — | 1515.0 | 1.7 | -2.0 | 0.4 | 21.0 | 6.6 | -1.5 |
| Fe-P_9 | — | — | — | — | — | — | 1512.8 | -0.9 | 1.1 | 0.4 | 23.2 | 7.9 | -0.8 |
| Fe-C-P_1 | 0.0040 | — | — | — | — | — | 1531.1 | 0.9 | 0.7 | 1.9 | 4.6 | 3.9 | 2.6 |
| Fe-C-P_2 | 0.0330 | — | — | — | — | — | 1529.3 | 0.5 | 0.3 | 1.2 | 4.2 | 3.5 | 2.2 |
| Fe-C-P_3 | 0.0590 | — | — | — | — | — | 1527.5 | 0.2 | 0.0 | 0.7 | 3.9 | 3.2 | 1.9 |
| Fe-C-P_4 | 0.0990 | — | — | — | — | — | 1524.6 | -0.1 | 0.5 | 0.0 | 3.7 | 2.9 | 1.5 |
| Fe-C-P_5 | 0.0960 | — | — | — | — | — | 1525.1 | -0.1 | 0.5 | 0.1 | 3.5 | 2.9 | 1.6 |
| Fe-C-P_6 | 0.1360 | — | — | — | — | — | 1520.6 | 1.2 | 2.3 | 1.0 | 4.8 | 4.1 | 2.8 |
| Fe-C-P_7 | 0.2030 | — | — | — | — | — | 1515.9 | 0.6 | 2.3 | -0.2 | 4.2 | 3.3 | 2.0 |
| Fe-C-P_8 | 0.2960 | — | — | — | — | — | 1507.6 | 1.5 | 3.1 | -0.1 | 5.1 | 3.8 | 2.5 |
| Fe-C-P_9 | 0.3780 | — | — | — | — | — | 1500.8 | 2.1 | 2.6 | 0.3 | 5.2 | 3.8 | 2.5 |
| Fe-C-P_10 | 0.6900 | — | — | — | — | — | 1478.3 | 0.5 | 5.6 | -1.0 | 5.0 | 1.9 | 1.9 |
| Fe-C-P_11 | 1.0000 | — | — | — | — | — | 1457.8 | -3.2 | 5.0 | -2.2 | 4.8 | 0.4 | 0.4 |
Table IV. Continued

| Sample            | C [Mass Percent] | Si [Mass Percent] | Mn [Mass Percent] | Al [Mass Percent] | P [Mass Percent] | T \(\text{L} \) (DSC/DTA) | \(\Delta T \) \(\text{L} \) (DSC/DTA) |
|-------------------|------------------|-------------------|-------------------|-------------------|------------------|--------------------------|---------------------------------|
| Fe-C              | 1.3800           | —                 | —                 | —                 | 0.101            | 1520.6                   | 2.6                             |
| Fe-C-P             | 1.3800           | —                 | —                 | —                 | 0.057            | 1517.5                   | 0.5                             |
| Fe-C-P               | 1.3800           | —                 | —                 | —                 | 0.158            | 1514.6                   | 0.1                             |
| Fe-C-P               | 1.3800           | —                 | —                 | —                 | 0.430            | 1507.0                   | 0.9                             |
| Fe-C-Al             | 0.2130           | —                 | —                 | 0.390             | —                | 1520.6                   | 2.1                             |
| Fe-C-Al             | 0.3130           | —                 | —                 | 0.370             | —                | 1512.5                   | 2.2                             |
| Fe-C-Al             | 0.0350           | —                 | —                 | 1.671             | —                | 1535.9                   | 8.6                             |
| Fe-C-Al             | 0.1370           | —                 | —                 | 1.694             | —                | 1527.6                   | 8.2                             |
| Fe-Si-Mn-Al         | 0.0048           | —                 | —                 | —                 | —                | 1553.9                   | 3.7                             |
| Fe-Si-Mn-Al         | 0.0053           | —                 | —                 | —                 | —                | 1530.1                   | 2.4                             |
| Fe-Si-Mn-Al         | 0.0048           | —                 | —                 | —                 | —                | 1521.9                   | 0.3                             |
| Fe-Si-Mn-Al         | 0.0053           | —                 | —                 | —                 | —                | 1509.3                   | 3.6                             |
| Fe-Si-Mn-Al         | 2.4400           | 0.2130           | 0.698             | 0.688             | —                | 1580.0                   | 12.8                            |

Note: The present work (PW) differs from Miettinen and Howe’s formula \([14]\) only in the modified P coefficient of ferrite. \(T_s\) in references \([21,22,25]\) were measured by DTA (NETZSCH STA409PG Luxx); in references \([22–26]\) and in the present work a NETZSCH DSC404F1 Pegasus was used.

The DSC analysis was carried out in a DSC 404F1 Pegasus (NETZSCH Gerätebau GmbH, Germany) with an Rh furnace and a Pt DSC sensor instrumented with type S thermocouples. \(\text{Al}_2\text{O}_3\) crucibles with a volume of 85 \(\mu\)l and lids were used for all experiments; in each trial, the reference was an empty crucible. The protective tube of the Rh furnace was purged permanently with Ar 5.0 (purity 99.999 pct), and a thermally active Zr getter was placed below the DSC sensor to avoid oxidation of the sample at temperatures above 350 °C. The experimental setup was calibrated by measuring the melting points and melting enthalpies of NETZSCH’s standards of pure metals In, Bi, Al, Ag, Au, Ni, and Co. In all DSC experiments, a heating rate (HR) of 10 °C/min was applied and samples of 50 mg were used. In the following section an “onset” in the DSC signal represents the first deviation from the baseline and corresponds to the solidus temperature \(T_s\). A “peak” indicates the end of the phase transformation and is defined as \(T_L\). Detailed information on the analysis of DSC and DTA signals can be found in the NIST-recommended practice guide. \([27]\)

Melting of Fe-based alloys takes place under a large change in heat \((\Delta H > 200 \text{ J/g})\). Within the DSC analysis of strongly endothermic phase transformations, special care has to be taken in order to accurately determine the equilibrium peak temperature. While the onset \((T_o)\) in the DSC signal is less affected by the heating rate, the peak \((T_p)\) is shifted to higher temperatures with increasing HR. \([27]\) The generally accepted approach \([28]\) requires measuring the liquidus peak with several heating rates \((e.g. 5 \text{ to } 20 \text{ °C/min})\) using new samples in each trial, and the extrapolation of the HR-dependent peak to zero \(\text{°C/min}\) gives the equilibrium liquidus temperature. In daily DSC practice, the variation of heating rates represents a work-intensive procedure. A more effective way to exclude the experimental setup influences on the DSC signal is provided by NETZSCH’s Tau-R software. \([29,30]\) The Tau-R method enables the determination of the equilibrium data from only a single DSC experiment. At this point, the authors refer to their previous work \([26]\) regarding more detailed information on the Tau-R method and its successful application to characterize melting equilibria in steel using DSC.

The DSC signals of samples FeSiMnAl-I to FeSiMnAl-IV obtained from heating with 10 °C/min and the corresponding Tau-R calculations are shown in Figures (a) and (b), respectively. All signals were corrected to the base line of 0.0 mW/mg and the given solidus and liquidus temperatures are the average values of at least two independent DSC runs. The typical experimental error in measuring solid–liquid phase transformations with the present setup is suggested to be \(\pm 2 \text{ °C}\). \([26]\) As expected, the onset temperature \((T_o)\) is not dependent on the heating rate: \(T_s\) measured with 10 °C/min and the equilibrium data calculated using the Tau-R software are identical. In measuring the peak temperature \((T_p)\), the scanning
mode leads to significant superheating above the actual liquidus temperature; the deviation of 7 to 10 °C clearly demonstrates the necessary correction of the DSC signal to get the real value of $T_L$. With respect to the primary phase ($\delta, \gamma$) stable at $T_L$, the DSC signals indicate a single melting peak of the $\delta$-ferrite phase which is in reasonable agreement with the phase diagram calculated in Figure 1(c).[6] The thermodynamic calculations of the vertical phase diagram section were performed with a defined composition of
Fe-0.70 pct Mn and a constant [pct Al]/[pct Si] ratio of 0.25. Due to induction melting practice, the [pct Al]/[pct Si] ratio in the samples varies in the range of 0.23 to 0.36 (see Table IV). Hence, minor differences of ~ 5°C between the calculated and measured temperatures have to be considered in Figure 1(c).

The final equilibrium liquidus temperatures \( T_L \) (Tau-R) in the system Fe-Si-Mn-Al are summarized in Table IV. In a first comparison with the analytical equations,\(^{[10–14]}\) the best agreement was found for the studies of Kawawa\(^{[10]}\) (error 2.2 ± 1.2 °C), Howe\(^{[12]}\) (error 1.3 ± 0.6 °C) and Miettinen and Howe\(^{[14]}\) (2.3 ± 0.5 °C). The deviations are close to or below the typical experimental error. However, for C-free Fe-Si-Mn-Al alloys, only the liquidus slopes of the binary system are of relevance, as the interaction parameters with carbon\(^{[14]}\) cannot be evaluated.

The comparison between the DSC/DTA dataset (Table III) and the calculations using the analytical liquidus equations\(^{[10–14]}\) is summarized graphically in Figures 2(a) through (e) and discussed in the following subsystems:

- **Fe-C-Si**: The binary coefficients of the Fe-Si system significantly differ in the equations. The liquidus slope of − 7.6 °C/[pct Si] as proposed by Kawawa\(^{[10]}\) systematically predicts too high values of \( T_L \) compared to the analytical calculations.
to the measurements, while Kagawa and Okamato’s equation \( \text{[11]} \) (14.39 °C/pct Si) results in slightly lower calculated liquidus temperatures. The equation of Schürmann and Stisovic\(^{[13]}\) gives good correlation up to 3 mass pct. Si; the error is typically smaller than 8 °C, which is in agreement with the evaluation of high-Si commercial steels in their work\(^{[13]}\) (error ± 10 °C). Deviations of more than 40 °C were found in the case of high amounts of Si (≈ 4 pct) and C (1–1.5 pct). Excellent results were obtained using Miettinen and Howe’s equations\(^{[14]}\) The small averaged error of 1.7 ± 1.2 °C indicates that the most suitable Fe-Si factor for ferrite and austenite corresponds to about –12 °C/pct Si. Even for the high-alloyed samples, the consideration of the Si-C interaction\(^{[14]}\) provides an accurate description of \( T_L \).

- **Fe-C-Mn:** As the liquidus slopes of each equation are consistent, all liquidus formulas give very similar results (error < ±2.5 °C). However, at [pct Mn] > 5, the calculations of \( T_L \) with equations\(^{[10–12,14]}\) lead to higher deviations from the DSC results (\( \Delta T = 4 \) to 6 °C). In this system, the equation of Schürmann and Stisovic\(^{[13]}\) provides reliable predictions of \( T_L \) up to the maximum alloying content of 5.3 mass pct. Mn (error 1 ± 1.1 °C).

- **Fe-C-Al:** Most recently published experimental data of Stein and Palm\(^{[31]}\) showed that the addition of aluminum increases the melting point of Fe in the binary Fe-Al system by + 1 °C/pct Al. A local maximum was reported at 1540 °C and ~5 mass pct. Al\(^{[31]}\) before \( T_L \) continuously decreases with increasing Al content, see Figure 3(a)\(^{[6, 31]}\). It is therefore evident that at high Al content, CALPHAD based thermodynamic optimizations are essential to accurately model the liquidus phase boundary. In this case, analytical equations for \( T_L \) have to include numerous fitting parameters to reproduce the curvature of the liquidus line for alloys with [pct Al] > 2.5. Hence, the authors decided to consider only alloys with Al content below the composition of the Fe-Al inflection point covering the typical composition range typical AHSS (2% Al)\(^{[17, 18]}\). However, the effect of Al on \( T_L \) is hardly measurable in ternary Fe-C-Al vertical sections with 0.40[pct Al], 1.60[pct Al] and 2[pct Al], see Figure 3(b). In this alloying range the minor change of \( T_L \) is within the experimental error of ± 2 °C\(^{[26]}\) and a clear influence of Al on the melting point in the Fe-C diagram\(^{[6]}\) cannot be observed. In analytical equations for \( T_L \) the effect of Al is considered in the expressions of Kawawa\(^{[10]}\) (−3.6 °C/pct Al) and Howe\(^{[12]}\) (0 °C/pct Al). It can be seen in Figure 2(c) and Table IV that the negative coefficient in Kawawa’s equation\(^{[10]}\) results in low values of \( T_L \). In agreement with Howe’s study\(^{[12]}\), setting the Fe-Al coefficient specifically to 0 °C/pct Al, Miettinen and Howe’s equation\(^{[14]}\) results in the lowest deviation from the DSC data (\( \Delta T_L = ± 1 \) °C). In the case of the Schürmann and Stisovic\(^{[13]}\) equation, the measurements are most presumably outside of the valid composition range for Al. This results in an unreliable stabilization effect of austenite and a very high liquidus temperature.

- **Fe-Si-Mn and Fe-C-Si-Mn:** In general, all liquidus equations evaluated provide sufficiently accurate predictions of \( T_L \), including calculations for alloys containing Si and Mn up to 4 pct. Again the work of Howe\(^{[12]}\) (error 1.0 ± 1.1 °C) and Miettinen and Howe\(^{[14]}\) (error 2.2 ± 1.5 °C) result in lowest deviation from the DSC/DTA data.

- **P-alloyed systems:** Excellent predictions of \( T_L \) in highly P-alloyed systems could be performed using the equation of Howe\(^{[12]}\) showing a deviation from the experimental results of only 1.4 ± 1.5 °C. Miettinen and Howe’s\(^{[14]}\) coefficients underestimate the decrease of \( T_L \) induced by alloying P, resulting in systematically higher values of \( T_L \) in the Fe-P and Fe-C-P systems. As all other ternary subsystems (Fe-C-Si, Fe-C-Al and Fe-C-Mn) are well described by their work, the deviation may result from a factor too large for phosphorus. Compared to other work\(^{[10–12]}\) the parameter of P is considered to be generally lower than –30 °C/pct P, whereas Miettinen and Howe\(^{[14]}\) suggest a value of –24.78 °C/pct P for ferrite and –30.92 °C/pct P for austenite. It has to be noted, that the P content of most alloys investigated by DSC/DTA exceeds the defined valid composition range of their derived equations (0.03 mass pct.\(^{[14]}\)). The increased error of the Schürmann and Stisovic\(^{[13]}\) equation is a consequence of the missing factor of P. For that reason, the results will not be discussed at this point.

By evaluating all 180 DSC/DTA measurements in Figures 4(a) and (b), highly accurate liquidus temperatures for steel were predicted using the equations of Howe\(^{[12]}\) (error 2.0 ± 2.7 °C) and Miettinen and Howe\(^{[14]}\) (error 2.1 ± 1.6 °C). Although both equations yield very similar calculation results, the work of Miettinen and Howe\(^{[14]}\) offers the significant advantage of providing two separated equations for ferrite and austenite. It is, therefore, possible (i) to identify the most stable phase at the liquidus temperature based on the initial chemical composition and (ii) to estimate the start of the peritectic reaction during solidification in conjunction with microsegregation models. For this equation, the authors suggest specifically setting the parameter of aluminum to 0 °C/pct Al for the best correlation in Al-alloyed systems up to 2 pct. Based on the present experimental DSC/DTA data, the results show clearly that Miettinen and Howe’s\(^{[14]}\) liquidus formula may be used without hesitation for liquidus calculations of steels even at elevated alloying content of C (< 1.56 pct), Si (< 4.5 pct), Mn (< 5 pct), and Al (< 2 pct) outside the originally documented valid composition limits\(^{[14]}\) in Table V.

However, for the strongly segregating element phosphorus, there is still some room to improve the liquidus slope in the expressions of Miettinen and Howe.\(^{[14]}\) By fitting the binary coefficient and the cross product parameter in their equations to the recently published data\(^{[26]}\) of Fe-P and Fe-C-P alloys in Table IV, values of -35.23 °C/pct P and -11.2 °C/(pct P x pct C) for δ-Fe were obtained. The binary Fe-P coefficient for ferrite is in reasonable agreement with the literature.
values\textsuperscript{10–12} (see Table I) and the interaction parameter with carbon is not changed significantly. As only a few liquidus data for austenite were available and the correlation between the calculations and the measurements is very accurate (1.4 ± 0.7 °C), the γ-Fe parameter set\textsuperscript{14} (Table I) was kept unchanged. By using the optimized factors for phosphorus, the error in the P-alloyed systems could be reduced from 3.0 ± 1.6 °C to 2.0 ± 1.2 °C, and the overall error is then decreased below the value of 2.0 °C (1.9 ± 1.4 °C). Further, by introducing the modified phosphorus coefficient, the concentration limit of Miettinen and Howe’s equation could be extended up to 0.10 mass pct. P (Table V). The improved calculations for highly P-alloyed samples are graphically represented in Figure 4(c).

In summary, various analytical liquidus equations\textsuperscript{10–14} for steel were evaluated based on a comprehensive DTA/DSC dataset of 180 alloys in the Fe-C-Si-Mn-Al-P thermodynamic subsystems. Excellent agreement was obtained with the most recently published expressions by Miettinen and Howe.\textsuperscript{13} The average error of 2.1 ± 1.6 °C is close to the typical experimental error of ± 2 °C in determining solid–liquid phase equilibria with the present DSC/DTA setups.\textsuperscript{16}

For this equation, the slight adjustments for the Fe-P and Fe-C-P liquidus slope suggested here may help to improve calculations for steel with higher P content.

The present work demonstrates a systematic methodology to evaluate liquidus equations using DSC and DTA. Future research will focus on measurements of the high-carbon austenite melting equilibria for systems already examined in the past (Fe-C-Al, Fe-C-P, Fe-C-Mn, Fe-C-Si-Mn, etc.) and further thermodynamic systems (e.g., Fe-C-Si-Mn-P, Fe-C-Si-Mn-Al, etc.) will be investigated.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support under the scope of the COMET support within the K2 Center “Integrated Computational Material, Process and Product Engineering (IC-MPPE)” (Project No 859480). This program is supported by the Austrian Federal Ministries for Climate Action, Environment, Energy, Mobility, Innovation, and Technology (BMK) and for Digital and Economic Affairs (BMDW), represented by the Austrian research funding association (FFG), and the federal states of Styria. Upper Austria and Tyrol.

FUNDING

Open access funding provided by Montanuniversität Leoben.

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REFERENCES

1. Y. Ueshima, S. Mizoguchi, T. Matsumiya, and H. Kajikawa: Metall. Trans. B, 1986, vol. 17, pp. 845–59.
2. A. Howe: Appl. Sci. Res., 1987, vol. 44, pp. 51–59.
3. R. Pierer, C. Bernhard, and C. Chimiani: Rev. Met. (Paris), 2007, vol. 104, pp. 72–83.
4. P. Spencer: Calphad, 2008, vol. 31, pp. 1–8.
5. H. Lukas, S. Fries, and B. Sundman: Computational Thermodynamics: The Calphad Method, Cambridge University Press, New York, 2007.
6. C. Bale, E. Bélisle, P. Chartrand, S. Decterov, G. Eriksson, A. Gheribi, K. Hack, I.-H. Jung, Y.-B. Kang, J. Melançon, A. Petlon, S. Petersen, C. Robelin, J. Sangster, P. Spencer, and M.-A. van Ende: Calphad, 2016, vol. 54, pp. 35–53.
7. J. Andersson, T. Helderan, L. Höglund, P. Shi, and B. Sundman: Calphad, 2002, vol. 26, pp. 73–312.
8. W. Cao, S.-L. Chen, F. Zhang, K. Wu, Y. Yang, Y. Chang, R. Schmid-Fetzer and W. Oates: Calphad, 2009, vol. 33, pp. 328–342.
9. J. Miettinen, S. Louhenkilpi, H. Kyönn, and J. Laine: Math. Comput. Simul., 2010, vol. 80, pp. 1536–50.
10. T. Kawawa: Report of 6th Meeting on Solidification of Steel, No. 6-III-9, Japan, 1973.
11. A. Kagawa and T. Okamoto: Mater. Sci. Technol., 1986, vol. 2, pp. 997–1008.
12. A. Howe: Ironmaking Steelmaking, 1988, vol. 15, pp. 134–42.
13. E. Schürmann and T. Stissovic: Stahl Eisen, 1989, vol. 118, pp. 97–102.
14. J. Miettinen and A. Howe: Ironmaking Steelmaking, 2000, vol. 27, pp. 212–27.
15. M. Wolf: Proceedings of Concast Metallurgical Seminar, Zurich, Switzerland, 1982.
16. X.-M. Chen, S.-H. Song, L.-Q. Weng, S.-J. Liu, and K. Wang: Mater. Sci. Eng. A, 2011, vol. 528, pp. 8299–04.
17. C. Bernhard, B. Linzer, P. Presoly, I. Watzinger and J. Watzinger: IOP Conf. Ser.: Mater. Sci. Eng., 2019, vol. 529, art. no. 012071.
18. P. Ghosh, R. Chromik, A. Knight, and S. Wakade: J. Magn. Magn. Mater., 2014, vol. 356, pp. 42–51.
19. Y.-K. Lee and J. Han: Mater. Sci. Technol., 2015, vol. 31 (7), pp. 843–56.
20. C. Tasan, M. Diehl, D. Yan, M. Bechtold, F. Roters, L. Schemmann, C. Zheng, N. Peranio, D. Ponge, M. Koayama, K. Tszuki, and D. Raabe: Annu. Rev. Mater. Res., 2015, vol. 45, pp. 391–31.
21. P. Presoly, R. Pierer, and C. Bernhard: Metall. Mater. Trans. A, 2013, vol. 44, pp. 5377–88.
22. P. Presoly, R. Pierer and C. Bernhard: IOP Conf. Ser.: Mater. Sci. Eng., 2012, vol. 33, art. no. 012064.
23. P. Presoly, C. Bernhard, N. Fuchs, J. Miettinen, S. Louhenkilpi and J. Laine: Proceedings of 9th ECCCE European Continuous Casting Conference, Vienna, Austria, 2017.
24. P. Presoly, C. Bernhard and J. Six: IOP Conf. Ser.: Mater. Sci. Eng., 2015, vol. 119, art. no. 012013.
25. P. Presoly, M. Bernhard, and C. Bernhard: Calphad XLVII Conference Proceedings, Queretaro, Mexico, 2018.
26. M. Bernhard, P. Presoly, N. Fuchs, C. Bernhard, and Y.-B. Kang: Metall. Mater. Trans. A, 2020, vol. 51, pp. 5351–64.
27. W. J. Boettinger, U. R. Kattner, K.-W. Moon and J. H. Perepezko, *DTA and Heat-flux DSC measurements of Alloy Melting and Freezing. NIST Recommended Practice Guide*, Special Publication 960-15, 2006.

28. L. Chapman: *J. Mater. Sci.*, 2004, vol. 39, pp. 7229–36.

29. Software: NETZSCH Tau-R Calibration 8.0.1 from Netzsch Gerätebau GmbH, Selb, Germany, 2019.

30. E. Moukhina and E. Kaisersberger: *Thermochim. Acta*, 2009, vol. 492, pp. 101–109.

31. F. Stein and M. Palm: *Int. J. Mat. Res.*, 2007, vol. 98 (7), pp. 580–88.

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