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.

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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

$$T_L = T_L^0 + \sum_i f([\%X_i]), \quad [1]$$

where T_L^0 is the melting temperature of pure iron handled as a constant^[10,12] or, more specifically, separated into T_L^0 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 $f([\text{pct } X_i])$ describes the influence of the element X on the melting temperature of Fe depending on the concentration of

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X in mass percent. The individual functions $f([\text{pct } X_i])$ 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 $[\text{pct } X] \times [\text{pct } C]$ 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

$$T_L = T_L^0 + A_{\delta,\gamma} \left\{ [\%C] + \sum_i \left([\%X_i] \left(1 + a_{\delta,\gamma}^i + b_{\delta,\gamma}^i [\%X_i] \right) \right) \right\} + B_{\delta,\gamma} \left\{ [\%C] + \sum_i \left([\%X_i] \left(1 + a_{\delta,\gamma}^i + b_{\delta,\gamma}^i [\%X_i] \right) \right) \right\}^2 \quad [2]$$

where $A_\delta = -76.77$, $A_\gamma = -58.74$, $B_\delta = -6.89$ and $B_\gamma = -4.64$. The values for $a_{\delta,\gamma}^i$ and $b_{\delta,\gamma}^i$ 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
- often, 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 $\pm 4^\circ\text{C}$. 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

Table I. Selected Parameters of Presently Evaluated Empirical Liquidus Equations^[10–12,14] With Relevance for the Fe-C-Si-Mn-Al-P System

Phases	Kawawa ^[10]		Kagawa and Okamoto ^[11]		Howe ^[12]		Miettinen and Howe ^[14]	
	ferrite (δ)	austenite (γ)	ferrite (δ)	austenite (γ)	ferrite (δ)	austenite (γ)	ferrite (δ)	austenite (γ)
T_L^0 (°C)	1536	1534	1534	1491	1537	1528	1538	1528
$f([\text{Percent } X_i])$ [°C]	C	– 78 [pct C]	– 48.24 [pct C] – 63.04 [pct C] ²	+ 36.33 [pct C] – 61.90 [pct C] ²	[pct C] < 0.471: – 87 [pct C] [pct C] < 1: – 70 [pct C] – 8 1 < [pct C]: – 76 [pct C] – 2 [pct Si] < 1: – 9 [pct Si] 1 < [pct Si]: – [pct Si] ² – 9 [pct Si] + 1 – 5 [pct Mn]	– 76.24 [pct C] – 10.3542 [pct C] ²	– 76.24 [pct C] – 10.3542 [pct C] ²	– 60.09 [pct C] – 6.1399 [pct C] ²
	Si	– 7.6 [pct Si]	– 14.39 [pct Si]	– 17.10 [pct Si]	– [pct Si] ² – 9 [pct Si] + 1 – 5 [pct Mn]	– 11.66 [pct Si] – 4.3512 [pct C] [pct Si] – 5.62 [pct Mn] – 0.223 [pct C] [pct Mn]	– 11.66 [pct Si] – 4.3512 [pct C] [pct Si] – 5.62 [pct Mn] – 0.223 [pct C] [pct Mn]	– 11.49 [pct Si] – 5.6055 [pct C] [pct Si] – 4.26 [pct Mn] + 0.453 [pct C] [pct Mn]
	Mn	– 4.90 [pct Mn]	– 4.88 [pct Mn]	– 3.32 [pct Mn]	– 5 [pct Mn]	– 4.26 [pct Mn]	– 4.26 [pct Mn]	– 4.26 [pct Mn]
	Al	– 3.60 [pct Al]	–	–	0 [pct Al]	–	–	–
	P	– 34.40 [pct P]	– 31.83 [pct P]	– 27.07 [pct P]	– 34 [pct P]	– 24.78 [pct P] – 12.9409 [pct C] [pct P]	– 24.78 [pct P] – 12.9409 [pct C] [pct P]	– 30.92 [pct P] – 5.3494 [pct C] [pct P]

Table II. Parameters Derived by Schürmann and Stisovic^[13] for Fe-C-Si-Mn-Al-P Alloys (Note That P is Not Considered In This Equation)

	T_L^0 [°C]	Si	Mn	Al
Ferrite (δ)	1536	$a = -0.8384$ $b = 3.544E^{-3}$	$a = -0.9433$ $b = -2.6E^{-4}$	$a = -1.0011$ $b = -2.8154E^{-5}$
Austenite (γ)	1526	$a = -0.6931$ $b = -0.0459$	$a = -0.9323$ $b = -4.1584E^{-4}$	$a = -0.9169$ $b = -0.3084$

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

chemical composition range, but suggests for high-alloyed Cr-Ni steels that the T_L^0 temperature should be relevant to the ternary Fe-Cr-Ni system and that Cr and Ni have to then be excluded from the summation. On the other hand, Miettinen and Howe^[14] derived two separated sets of equations (ferrite and austenite) for both low-alloyed and stainless steels by performing a large number of thermodynamic calculations using the IDS database.^[9] Schürmann and Stisovic^[13] evaluated their equation with the experimental data documented by Howe^[12] and additional thermal analysis measurements from different steel plants ([pct C] < 1, [pct Si] < 4, [pct Mn] < 10, and [pct Cr] < 1.6) but the exact chemical analysis of the commercial steel grades was not documented in the study. In this work,^[13] the parameter for phosphorus was not derived by the authors. Phosphorus strongly decreases the melting point of steel by ~ 25 to 35 °C per mass pct. (see Table I). If P is only considered as trace element in steel (P < 0.025 mass pct.), the equation will give accurate liquidus predictions but in rephosphorized grades with typical concentration of 0.10 [pct P],^[16–18] the resulting error of about 3 to 4 °C is significant in optimizing the superheat in the continuous casting process.

In total, liquidus temperatures of 180 alloys in the Fe-C-Si-Mn-Al-P system were determined using differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The alloys studied cover a wide composition range (see Table III) with great practical relevance for the continuous slab casting of flat products as various recently developed advanced steel grades are based on constituent thermodynamic systems:

- high-strength interstitial free (HSIF) with 0.30 pct Mn and P < 0.10 pct^[16]
- transformation-induced plasticity (TRIP) steels with classic alloying concepts of 0.175 to 0.25 pct C, 1.5 to 2 pct Mn, 2 pct (Al + Si), and P up to 0.1 pct,^[17]
- electrical steel sheets with 1 to 3.5 pct Si,^[18] P < 0.1 pct, 0.5 pct Mn, and 0.5 pct Al,
- low carbon (C < 0.10 pct) medium Mn steels with manganese content ranging from 3 to 10 mass percent,^[19] and
- dual-phase (DP) steels with a typical composition of 0.06 to 0.15 pct C, 1.5 to 3 pct Mn,^[20] and 0.5 to 1 pct Si.

A part of the DSC/DTA dataset has already been published in previous work of the authors^[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,

Table IV. Selected Experimental Data of Previous Work^[21–26] and the Present Work (Fe-C-Al and Fe-Si-Mn-Al) Along With Calculations Using Analytical Equations From Literature.^[10–14]

Sample	References	C [Mass Percent]	Si [Mass Percent]	Mn [Mass Percent]	Al [Mass Percent]	P [Mass Percent]	T_L (DSC/DTA)	$\Delta T_L^{[10]}$	$\Delta T_L^{[11]}$	$\Delta T_L^{[12]}$	$\Delta T_L^{[13]}$	$\Delta T_L^{[14]}$	ΔT_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	—	1521.7	-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	22	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		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	23	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	26	0.3070	2.060	2.050	—	—	1478.3	8.1	-4.7	0.0	-5.5	-3.1	-3.1
Fe-P_1		—	—	—	—	0.026	1535.1	0.0	-1.9	1.0	0.9	2.3	1.9
Fe-P_2		—	—	—	—	0.044	1534.9	-0.4	-2.3	0.6	1.1	2.0	1.5
Fe-P_3		—	—	—	—	0.102	1532.4	0.1	-1.6	1.1	3.6	3.1	1.8
Fe-P_4	—	—	—	—	—	0.147	1529.1	1.8	0.2	2.9	6.9	5.3	3.4
Fe-P_5		—	—	—	—	0.322	1525.3	-0.4	-1.5	0.8	10.7	4.7	0.8
Fe-P_6		—	—	—	—	0.419	1520.5	1.1	0.2	2.3	15.5	7.1	2.0
Fe-P_7		—	—	—	—	0.480	1520.9	-1.4	-2.2	-0.2	15.1	5.2	-0.7
Fe-P_8	—	—	—	—	—	0.660	1515.0	-1.7	-2.0	-0.4	21.0	6.6	-1.5
Fe-P_9		—	—	—	—	0.700	1512.8	-0.9	-1.1	0.4	23.2	7.9	-0.8
Fe-C-P_1		0.0040	—	—	—	0.107	1531.1	0.9	-0.7	1.9	4.6	3.9	2.6
Fe-C-P_2		0.0330	—	—	—	0.106	1529.3	0.5	-0.3	1.2	4.2	3.5	2.2
Fe-C-P_3	—	0.0590	—	—	—	0.108	1527.5	0.2	0.0	0.7	3.9	3.2	1.9
Fe-C-P_4		0.0990	—	—	—	0.110	1524.6	-0.1	0.5	0.0	3.7	2.9	1.5
Fe-C-P_5		0.0960	—	—	—	0.101	1525.1	-0.1	0.5	0.1	3.5	2.9	1.6
Fe-C-P_6		0.1360	—	—	—	0.105	1520.6	1.2	2.3	1.0	4.8	4.1	2.8
Fe-C-P_7	—	0.2030	—	—	—	0.106	1515.9	0.6	2.3	-0.2	4.2	3.3	2.0
Fe-C-P_8		0.2960	—	—	—	0.110	1507.6	1.5	3.1	-0.1	5.1	3.8	2.5
Fe-C-P_9		0.3780	—	—	—	0.106	1500.8	2.1	2.6	-0.3	5.2	3.8	2.5
Fe-C-P_10		0.6900	—	—	—	0.099	1478.3	0.5	5.6	-1.0	5.0	1.9	1.9
Fe-C-P_11	—	1.0000	—	—	—	0.099	1457.8	-3.2	5.0	-2.2	4.8	0.4	0.4

Table IV. Continued

Sample	References	C [Mass Percent]	Si [Mass Percent]	Mn [Mass Percent]	Al [Mass Percent]	P [Mass Percent]	T_L (DSC/DTA)	$\Delta T_L^{[10]}$	$\Delta T_L^{[11]}$	$\Delta T_L^{[12]}$	$\Delta T_L^{[13]}$	$\Delta T_L^{[14]}$	ΔT_L (PW)
Fe-C-P_12	1.3800	—	—	—	0.101	1427.7	−2.8	−7.2	−1.0	8.4	1.8	1.8	
Fe-C-P_13	0.2060	—	—	—	0.057	1517.5	0.5	2.1	−0.4	2.4	2.8	2.1	
Fe-C-P_14	0.1990	—	—	—	0.103	1516.3	0.6	2.3	−0.1	4.1	3.3	2.1	
Fe-C-P_15	0.2030	—	—	—	0.158	1514.6	0.1	2.0	−0.6	5.5	3.2	1.3	
Fe-C-P_16	0.1700	—	—	—	0.430	1507.0	0.9	3.3	0.6	15.7	6.1	1.0	
Fe-C-P_17	0.3400	—	—	—	0.760	1481.7	1.6	4.4	−0.1	27.4	7.0	0.3	
Fe-C-Al_4	present work	0.2130	—	—	0.390	—	1520.6	−2.6	0.3	−2.1	−1.2	0.7	0.7
Fe-C-Al_5	—	0.3130	—	—	0.370	—	1512.5	−2.2	0.2	−2.7	−1.2	0.6	0.6
Fe-C-Al_6	—	0.0350	—	—	1.671	—	1535.9	−8.6	−3.7	−1.9	28.3	−0.6	−0.6
Fe-C-Al_7	—	0.1370	—	—	1.654	—	1527.6	−8.2	−1.4	−2.5	30.3	−0.2	−0.2
Fe-Si-Mn-Al_1	—	0.0048	0.539	0.698	0.125	—	1530.1	−2.4	−7.5	−1.9	−4.4	−2.7	−2.7
Fe-Si-Mn-Al_2	—	0.0056	1.150	0.688	0.342	—	1521.9	0.3	−8.1	0.5	−4.3	−1.6	−1.6
Fe-Si-Mn-Al_3	—	0.0053	2.270	0.683	0.579	—	1509.3	3.6	−11.6	−0.8	−7.5	−2.1	−2.1
Fe-Si-Mn-Al_4	—	0.0048	2.440	0.718	0.868	—	1508.0	2.4	−12.8	−1.9	−4.3	−2.9	−2.9

Note, that the present work (PW) differs from Miettinen and Howe's formula^[14] only in the modified P coefficient of ferrite. T_L in references^[21,25] were measured by DTA (NETZSCH STA409PG Luxx); in references^[22–24,26] and in the present work a NETZSCH DSC404F1 Pegasus was used. $\Delta T_L = T_L$ (calculated) – T_L (DSC/DTA).

Germany). The final compositions of alloys FeSiMnAl-I to FeSiMnAl-IV are listed in Table IV; the trace element levels are given as C ≤ 55 ppm, P ≤ 46 ppm, S ≤ 22 ppm, and N ≤ 44 ppm.

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. Al₂O₃ crucibles with a volume of 85 μ 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.^[26] 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 ($\Delta H > 200$ 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_S) in the DSC signal is less affected by the heating rate, the peak (T_L) 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 to 20 °C/min) using new samples in each trial, and the extrapolation of the HR-dependent peak to zero °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 1(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 ± 2 °C.^[26] As expected, the onset temperature (T_S) 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_L), the scanning

Fig. 1—DSC signals of the Fe-Si-Mn-Al alloys corrected to the baseline of 0.0 mW/mg using a heating rate of 10 °C/min (a) and Tau-R calculations of the original DSC signals (b). All experimental temperatures given are the average values of at least two independent measurements. Calculated phase diagram for the Fe-Si-Mn-Al alloys using FactSage 8.0 and FStel2019 database^[6] along with the experimental results (c).

Fig. 2—Comparison between calculated liquidus temperatures^[10–14] and experimentally determined values in the Fe-C-Si system (a), Fe-C-Mn system (b), Fe-C-Al system (c), Fe-Si-Mn/Fe-Si-Mn-Al/Fe-C-Si-Mn systems (d), and highly P-alloyed systems (e).

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 (δ , γ) stable at T_L , the DSC signals

indicate a single melting peak of the δ -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

Fig. 3—Binary Fe-Al system^[6] along with experimental data of Stein and Palm^[31] (a) and calculated Fe-C diagram^[6] compared with liquidus temperatures published in previous work^[21, 22] and ternary Fe-C-0.40 pct Al and Fe-C-1.60 pct Al alloys (b) (see also Table IV).

Fig. 4—Comparison between calculated liquidus temperature^[10–14] and experimentally determined values in all thermodynamic systems (a) and the corresponding enlarged section between 1450 °C and 1540 °C (b). Improved calculations in the P-alloyed system by modifying the P coefficients of δ -Fe in Miettinen and Howe's equation^[14] (c).

Table V. Originally Documented Limits of Howe and Miettinen's^[14] Equation Based on the Defined Composition Range in Their Thermodynamic Calculations Using IDS^[9] and Validated Composition Range of Their Work by Experimental DSC/DTA Data in the Present Work (PW)

Reference	C [Mass Percent]	Si [Mass Percent]	Mn [Mass Percent]	Al [Mass Percent]	P [Mass Percent]
[14]	0 to 1.20	0 to 2	0 to 2	—	0 to 0.03
PW	0 to 1.56	0 to 4.5	0 to 5	0 to 2	0 to 0.10

For calculations up to 0.10 [pct P] the proposed modifications of the P coefficients for δ -Fe are suggested.

Fe-0.70 pct Mn and a constant [pctAl]/[pctSi] 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 measurements, while Kagawa and Okamoto's equation^[11] ($-14.39\text{ °C/[pct Si]}$) 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 $\pm 10\text{ °C}$). Deviations of more than 40 °C were found in the case of high amounts of Si ($\sim 4\text{ pct}$) and C ($> 1\text{ pct}$). Excellent results were obtained using Miettinen and Howe's equations.^[14] The small averaged error of $1.7 \pm 1.2\text{ °C}$ 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 $< \pm 2.5\text{ °C}$). However, at $[\text{pct Mn}] > 5$, the calculations of T_L with equations^[10–12,14] lead to higher deviations from the DSC results ($\Delta T = 4\text{ to }6\text{ °C}$). 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 $1 \pm 1.1\text{ °C}$).
- **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 $+1\text{ °C/[pct Al]}$. A local maximum was reported at 1540 °C and $\sim 5\text{ mass pct. Al}$ ^[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 $[\text{pct Al}] > 2.5$. 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 ($[\text{pct Al}] < 2$).^[17, 18] However, the effect of Al on T_L is hardly measureable 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 $\pm 2\text{ °C}$ ^[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 too 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 ($\Delta T_L \sim \pm 1\text{ °C}$). 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 $1.0 \pm 1.1\text{ °C}$) and Miettinen and Howe^[14] (error $2.2 \pm 1.5\text{ °C}$) 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 $1.4 \pm 1.5\text{ °C}$. 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 $2.0 \pm 2.7\text{ °C}$) and Miettinen and Howe^[14] (error $2.1 \pm 1.6\text{ °C}$). 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 ($< 1.56\text{ pct}$), Si ($< 4.5\text{ pct}$), Mn ($< 5\text{ pct}$), and Al ($< 2\text{ pct}$) 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 $-11.2\text{ °C/([pct P] \times [\text{pct C}])}$ for δ -Fe were obtained. The binary Fe-P coefficient for ferrite is in reasonable agreement with the literature

values^[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^[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 ± 1.8 °C to 2.0 ± 1.2 °C, and the overall error is then decreased below the value of 2 °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^[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.^[14] 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.^[26] 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.

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