Thermodynamic optimization of individual steel database by means of systematic DSC measurements according the CALPHAD approach

P Presoly¹, J Six² and C Bernhard¹
¹Chair of Ferrous Metallurgy, Montanuniversitaet Leoben, Franz-Josef-Straße 18, A-8700 Leoben, Austria
²voestalpine Stahl GmbH, voestalpine-Straße 1, 4020 Linz, Austria
Email: peter.presoly@unileoben.ac.at

Abstract. Reliable thermodynamic data are essential information required for the design of new steel types and are a prerequisite to effective process optimization and simulation. Moreover, it is important to know the exact temperatures at which the high-temperature phase transformations ($T_{\text{Liquid}}$, $T_{\text{Solid}}$, $T_{\text{Perit}}$, $T_{\gamma \rightarrow \delta}$) occur in order to describe the solidification sequence and to describe further processing parameters. By utilizing DTA/DSC measurements, our earlier experimental studies of selected commercial DP, TRIP and high-Mn TWIP steels, have indicated that currently commercially available databases can often not be utilised to reliably describe the behaviour and microstructural development in such complex alloy systems. Because of these ostensible deficiencies, an experimental study was undertaken in an attempt to determine the pertaining thermodynamic data to analyse the behaviour of the important five-component Fe-C-Si-Mn-Al alloy system. High purity model alloys with systematic alloy variations were prepared and utilized in order to determine the influence of individual alloying elements in this complex, but industrially important alloy system. The present study provides new validated experimental thermodynamic data and analysis of the five-component Fe-C-Si-Mn-Al system, which will allow the construction of new phase diagrams, prediction of solidification sequences and the assessment of micro-segregation.

1. Introduction and Motivation
Thermodynamic databases are widely used and have become standard tools in research, development and production control in the steel industry. With user-friendly software programs, which access these databases, complex chemical reactions and phase equilibria that occur during steelmaking operations can be calculated over wide ranges of temperature, pressure and chemical compositions. A variety of Gibbs free energy minimizing commercially software packages such as ThermoCalc, FactSage, MTDat, PANDAT, JMatPro, IDS are freely available. The reliability of the predictions made by using these programs is limited by the accuracy of the thermodynamic data underpinning the binary, ternary and quaternary sub-systems. Some of the experimental data of important binary and ternary systems are quite old and have not been sufficiently verified by modern experimental techniques. Moreover, the purity of some of the older alloys are sometimes suspect. Computational thermodynamics are usually based on the CALPHAD approach [1,2]. The CALPHAD method has the potential to enable the calculation of complex, higher alloyed systems on the basic of well-established and reliable thermodynamic data, describing binary, ternary and quaternary sub-systems.
Of specific interest in these developments is steel, the main metallic construction material and hence, thermodynamic steel databases are continuously improved. Some of the most important developments in the design of steels in the last few decades have been the concepts of high strength and ductile steels for the automotive industry. Three of these alloying concepts are Dual-Phase (DP), TRansformation Induced Plasticity (TRIP) and Twinning Induced Plasticity (TWIP) steels. These steel types are considered as a new generation of automotive steels due to the advantages of weight reduction, energy saving and safety performance of automobiles. All these steel types are based on the iron-carbon-manganese system with additions of ferrite formers such as silicon and aluminium, in addition to micro-alloying elements. This means, that the alloy matrix consists of the Fe-C-Si-Al-Mn system (in different variations, often with or without Al, or with very high Mn contents up to 25 wt.-%, for example in TWIP steels). The main differences compared to previous steel grades are the significantly higher levels of the ferrite formers Si and Al.

Apart from research on the material and product properties at lower temperature, knowledge of the high-temperature phase transformation temperatures \( T_{\text{Liquid}}, T_{\text{Solid}}, T_{\text{Perit}}, T_{\gamma \rightarrow \delta} \) plays an important role in describing initial solidification phenomena and the control of subsequent production processes. As visualized in Figure 1a four different transformation sequences (I-IV) can be distinguished in the Fe-C system, characterized by the points \( C_A, C_B, \) and \( C_C \) \[3\]. Figure 1b visualizes the strong influence of alloying elements, the effect of which can be distinguished as either austenite formers (such as Mn, Ni, Co, Cu, N...) or ferrite formers (such as Cr, Mo, W, Al, Si, Ti, V...).

Special features of this high-temperature system are the two different phases: \( \delta \)- and \( \gamma \)-iron, showing significant differences in their density due to the different crystal structures (\( \delta = \) face centred cubic / \( \gamma = \) body centred cubic) \[4\]. Steels which solidify according to the transformation sequence of range II are of special interest, because in this case the transformation from \( \delta \)-Fe to \( \gamma \)-Fe (i.e. the peritectic phase transition \( \text{L} + \delta \rightarrow \delta + \gamma \rightarrow \gamma \)) starts in the solid-liquid two phase region and ends in the solid. The specific peritectic transformation range II is implied in an increased appearance of defects (such as hot tears, surface defects, depressions, and in the worst case breakouts) in the course of the continuous casting process \[5,6\].

![Figure 1.](image-url)

**Figure 1.** a) Fe-C equilibrium diagram with the critical peritectic range and b) influence of alloying elements on the Fe-C system in the high temperature range.
2. Demand for a database development
Previous experimental studies [3,6,7] have shown that if new alloying systems are considered, the range of validity of the thermodynamic database that is being used has to be carefully evaluated in each case. Investigations of 22 steel grades from the production program of voestalpine Stahl Linz in 2013 proved that by means of thermodynamic calculations with different databases about two-thirds of the steel grades are correctly identified with respect to the transformation range I to IV. Unfortunately, this also means that up to one-third of these steels were calculated inaccurately or incorrectly [6].

A recent investigation of selected DP-, TRIP- and TWIP-steels by means of Differential thermal analysis (DTA) and Differential scanning calorimetry (DSC) measurements explicitly indicated that current calculations of phase transformations in the Fe-C-Si-Mn system need to be reassessed [7]. Specifically, measurements on TWIP steels demonstrate that there exists a huge potential for further investigations of the higher alloyed Fe-C-Si-Al-Mn system. These arguments also apply to some other high alloyed systems. The need for the measurement of these systems – despite problems with the manufacturing of the samples and the measurement itself, is evident:

a) Verification of the results of available databases for high alloyed systems,
b) Creation of reliable databases for new alloy developments

c) Use of the data for the assessment of solidification kinetics (prediction of micro-segregation and formation of primary precipitates).

One important component of this work is the focus on segregated-areas which occur at the dendritic scale during the solidification. Inter-dendritic segregation, which can be calculated by micro-segregation models, are often responsible for the formation of defects during the casting process (e.g., hot tearing) and can also negatively affect product quality (inhomogeneous microstructure, and undesirable primary precipitates). In a recent paper the use of thermodynamic databases for the calculation of micro-segregation is described in detail for the case of a TRIP steel [8]. Figure 2 shows the measured and calculated equilibrium temperature of a medium-alloyed TRIP steel containing 0.77 wt.-% Al. The DSC measurement (heating rate corrected) on the left side of Figure 2 clearly shows a large peritectic peak between the solidus and liquidus temperature, which is typical for alloys between $C_B^*$ and $C_C^*$ (transformation sequences III). The position of the alloy in a pseudo-binary Fe-C phase is visualized on the right-hand side of Figure 2. The TRIP steel under investigation is well described by the TCFE7 (ThermoCalc) and the FSstel (FactSage 6.4) databases (only the peritectic temperature is calculated marginally too high). Since the original SGTE2014 database has no thermodynamic description of the ternary Fe-C-Al system, the peritectic range and the solidus temperature are calculated too low. The calculation with a newly optimized extract of the SGTE2014 database predicts all transformation temperatures very well. Although the initial concentration (Fe-0.21%C-0.54%Si-2.12%Mn-0.77%Al) of this commercial TRIP steel is well described by both the FSstel and SGTE databases, subsequent micro-segregation calculations show significant differences [8]. Only the optimized database extract could achieve realistic results, since the Fe-C-Si-Mn-Al system (and its subsystems) has been individually improved. The following section explains the method by which this specific database was systematically further developed by means of DSC measurements.
3. Methodology to reassess thermodynamic databases

The most important step for database optimization is the identification of the affected subsystem which needs to be reassessed. Therefore, it is important to understand the construction of a CALPHAD database, which is illustrated in Figure 3. The Gibbs Energy $G^\varphi$ of each phase $\varphi$ consists of three terms; $G^\varphi_{\text{ideal}}$ describes the standard Gibbs energy of a mechanical mixture of the constituents of the phase, $G^\varphi_{\text{excess}}$ describes the entropy of mixing an ideal solution and $G^\varphi_{\text{impurities}}$ describes the so-called excess term. Based on experimental data, the excess term $G^\varphi_{\text{impurities}}$ is assessed to describe the interactions of the elements with each other and therefore the "real behaviour". In order to perform calculations in a five-component system, knowledge of 5 quaternary subsystems, 10 ternary subsystems and 10 binary subsystems are required. It is especially important to verify the sub-systems in the Fe-rich corner of the alloy system. Complex multi-component alloys and commercial steels cannot be used for database optimization, since the different interactions of the alloying elements overlap each other. Furthermore, undesirable trace elements in commercial steels negatively affect the determination of the equilibrium phase transformation temperatures by the formation of low melting phases. Consequently, high purity model alloys, with systematic alloy variations were used in the present investigation in order to determine the influence of specific alloying elements on the selected subsystems.

$$G^\varphi = G^\varphi_{\text{ideal}} + G^\varphi_{\text{excess}} + G^\varphi_{\text{impurities}}$$

**Figure 3.** CALPHAD methodology [2].
In a previous study the need for a systematic reassessment of the quaternary Fe-C-Si-Mn system was clearly identified [7]. Since silicon and manganese are most important alloying elements, the description of their interaction is of fundamental importance and because interaction between alloying elements are stronger at higher concentrations, 2%Si and 2%Mn additions were chosen for further investigation. The test program with six alloys is visualized in Figure 4, whereby alloy III has been already investigated [7] and was clearly identified as peritectic (range II, between $C_a^*$ and $C_b^*$). This finding makes the whole investigation very exciting, since all calculations (TCFE7, FSstel, SGTE2014) provides nearly identical results, predicting the peritectic range II at significantly lower carbon contents.

On the right-hand side of Figure 4 the production of model alloys is illustrated. All Fe-C-2%Si-2%Mn model alloys (about 60g) were produced from high-purity raw-materials in an alumina crucible with a high-frequency re-melting and spin-casting machine under an argon atmosphere. The samples were very homogeneous due to the inductive melting, the spin casting and the rapid solidification in a copper mould. Chemical analyses were carried out by emission-spectroscopy and in addition, the carbon content was analysed by LECO combustion analysis since this method is more accurate.

![Figure 4. Fe-C-2%Si-2%Mn test program and the production of model alloys.](image)

To assess the high temperature phase transformations ($T_{\text{Liquids}}$, $T_{\text{Solid}}$, $T_{\text{Perit}}$, $T_{\text{Fe(III)}}$) DSC measurements were carried out under equilibrium conditions as described earlier [3,6]. The equipment used in that study was a NETZSCH DSC404F1 Pegasus with a Rhodium-furnace and a platinum DSC sensor with type-S thermocouples and Al$_2$O$_3$ sample cups. The experimental set-up was calibrated by measuring the well-known melting points of high purity In, Bi, Al, Ag, Au, Ni, and Co. In order to achieve the best equilibrium conditions, 50 mg samples and a heating rate of 10 K/minutes were used. In addition, the heating rate affected DSC measurements were corrected by the NETZSCH Tau-R software [9] regarding the thermal resistance and the time constants of the DSC sensor.
Figure 5. Fist measurement results of the Fe-C-2%Si-2%Mn.

The newly measured phase transformations are shown in Figure 5 as coloured dots, which are connected with simple lines so as to illustrate the new interfaces. The liquidus line can be determined very accurately since regression analysis shows a correlation of 98%. The newly determined phase transformations are in stark contrast to the calculated phase diagram using database SGTE2014. This simple comparison clearly shows that the delta-ferrite range is significantly larger than predicted by SGTE2014. A higher solidus temperature (T\textsubscript{Solid}\textsuperscript{γ}) is predicted, the gamma-to-delta phase transformation occurs at much higher carbon content and lower temperatures (T\textsubscript{γ\rightarrowδ}) and the peritectic range (range II) occurs at higher carbon content. These results imply that silicon is a much stronger ferrite stabilizer for this system than calculated by SGTE2014. Furthermore, the liquidus temperature and the solidus temperature in the gamma range are higher than calculated by SGTE2014. The peritectic temperature, however, is clearly reduced in comparison to the by SGTE2014 calculation.

The current investigation demonstrates that by the use of model alloys (alloy variation) and DSC measurements, complete phase diagrams can be reassessed. In this case, however, six model alloys proved to be not enough to accurately predict the peritectic range and the points of interest C\textsubscript{γ} and C\textsubscript{δ}. It was difficult to determine the γ\rightarrowδ phase transformation by using the current DSC-setup (50mg samples), due to the wide range of the γ+δ two-phase region and the resulting low enthalpy change. Therefore, further investigation of this solid-solid transition is of the essence.

The compilation in Figure 5 also shows that the biggest differences between the new measurements and the calculation with SGTE2014 occur at very low carbon concentrations. This finding clearly indicates that it is not only the Fe-C-Si-Mn system affected, but also the ternary Fe-Si-Mn system. Based on this result, carbon free Fe-Si-Mn alloys were prepared. In addition to the Fe-C-2%Mn-2%Si system, other quaternary combinations (high/low - Si/Mn) were studied, using the same method as described above, as part of a continuing comprehensive test program. Particularly important are Si-Mn combinations with higher Mn contents since steels of industrial importance are alloyed with significantly more Mn than Si and because Mn segregates much stronger than Si.
In addition to these experimental findings, an analysis of the thermodynamic databases (TCFE7, FSstel and SGTE2014) indicates that no thermodynamic description of the quaternary Fe-C-Si-Mn system is included. Therefore, the reason for the divergent calculations must be in an associated subsystem. The ternary Fe-C-Mn system (source [10]) appears well described, however, the ternary Fe-C-Si (source [11,12]) system shows a need for improvement according a previous study [7]. However, the deviations in the Fe-C-Si system are too small to explain the large discrepancies in the quaternary system. Therefore, the ternary Fe-Si-Mn system [Fe-Mn-Si: Va] (source [13]) has to be considered, since this system is particularly responsible for the low carbon region of the Fe-C-Si-Mn system, as visualized in Figure 5. It is perhaps also necessary to re-assess the binary Si-Mn subsystem, which describes the interaction of these important ferrite and austenite formers. This binary system was recently reassessed by Paek [14] and Zheng [15] and is visualized in Figure 6.

![Figure 6. Reassessments of the binary Mn-Si system [14,15].](image)

It is important to note that the data contained in these new publications have not yet been implemented in the databases. Both authors predicted similar phase diagrams, using the data of Voegel [16], which was more than 80 years ago. Hence, it would be instructive to repeat and verify these results, especially the $\delta \leftrightarrow \gamma$ transition and the peritectic range, as shown by the red circle in Figure 6. Further justification for continuing these studies are found in the suspicion that silicon is a strong ferrite (bcc) stabilizer, as indicated in the binary Si-Mn phase diagram, the dearth of published experimental measurements, especially with respect to the $\gamma \rightarrow \delta$ phase transformation and the sometimes very old raw data.

In addition to the systematic studies of the Fe-C-Si-Mn system, identical studies (experimental and literature reviews) were carried out for the Fe-C-Si-Al and Fe-Mn-Al-C systems. Only by following the careful experimental procedure, outlined above, is it possible to assess the multicomponent Fe-C-Si-Al-Mn system. By utilizing the comprehensive newly developed experimental techniques; an extract from the SGTE2014 database is further developed and optimized by using the OptiSage tool, an integral part of the program FactSage. Moreover, by the use of the verified thermodynamic data developed in this study, new phase diagrams can be predicted, micro-segregation can be better analysed and calculations can be made with respect to the sequence of solidification [8]. In conclusion, it should be emphasized that it is only possible to calculate the solute enrichment of the TRIP steel, shown in Figure 3, by the use of the newly, improved databases outlined in this study. Even if it were possible to describe the initial elemental distributions in the Fe-0.2%C-0.5%Si-2%Mn-0.8%Al system by the use of existing databases, it is not possible to predict the consequences of micro-segregation where the individual concentrations might be close to $\sim 1\%$C, $\sim 1-2\%$Si, $\sim 4-6\%$Mn, $\sim 0.6\%$Al (Al segregates negative) respectively (which are significantly different from the initial concentrations).
4. Summary and Outlook
The current study illustrates the importance of experimental thermodynamic investigations for the re-assessment of selected Fe-base systems. The current study clearly shows that the actual thermodynamic calculations of the quaternary Fe-C-Si-Mn system provide sufficient justification for further improvement. A very important finding is that in the Fe-C-Si-Mn system, which is one of the most industrially important alloy systems for the design of high strength and high ductility steels, the position of the peritectic range should be at higher carbon content and the δ-region should be larger (bcc more stable) than predicted by existing thermodynamic databases.

The methodology to re-assess thermodynamic databases by means of self-constructed phase diagrams is highly efficient, especially if the alloy production, the sample manufacture, the DSC measurements, the construction of phase diagrams and the database optimization takes place within the same research group. By the systematic approach taken in this study and the use of high purity model alloys, it has been possible to identify relevant subsystems and their interactions. The CALPHAD method has the potential to calculate complex highly alloyed systems by using well investigated and secured binary, ternary and quaternary subsystems. Once if this thermodynamic data are available, new phase diagrams can be composed, micro-segregation can be quantified and calculations can made of the sequence of solidification events.

5. Acknowledgement
Financial support by the Austrian Federal Government (in particular from Bundesministerium für Verkehr, Innovation und Technologie and Bundesministerium für Wirtschaft, Familie und Jugend) represented by Österreichische Forschungsförderungsgesellschaft mbH and the Styrian and the Tyrolean Provincial Government, represented by Steirische Wirtschaftsförderungsgesellschaft mbH and Standortagentur Tirol, within the framework of the COMET Funding Programme is gratefully acknowledged. This work is part of the ongoing K2-MPPE project A4.18.

6. References
[1] Jung, I-H 2010 Calphad 34 332.
[2] Lukas H L, Fries S G and Sundman B 2007 Computational Thermodynamics - The Calphad Method, Cambridge University Press, New York.
[3] Presoly P, Prier R Bernhard C 2013 Metallurgical and Materials Transactions 44A 5377.
[4] Jablonka A, Harste H and Schwerdtfeger K 1991 Steel Research 62 24.
[5] Xia G, Bernhard C, Ilie S and Fürst W 2008 6th ECCC (Riccione, Italy).
[6] Presoly P, Xia G, Reisinger P and Bernhard C 2014 BHM 159 430.
[7] Presoly P and Bernhard C 2015 LMPC2015 (Leoben, Austria).
[8] You D, Bernhard C, Michelic S, Wieser G and Presoly P 2015 MPPE2015 (Leoben, Austria) – in press.
[9] Software: NETZSCH Tau-R Kalibration, Version 6, Netzsch-Gerätebau, 2012.
[10] Huang W 1990 Metallurgical and Materials Transactions A21 2115.
[11] Lacaze J and Sundman B 1991 Metallurgical and Materials Transactions 22A 2211.
[12] Miettinen J and Hallsted B 1998 Calphad 22 231.
[13] Forsberg A and Agren J 1993 Journal of Phase Equilibria 14 354.
[14] Paek K M, Pak J J and Kang Y B 2014 Calphad 46 92.
[15] Zheng W, Lu X G, He Y, Cui Y and Li L 2015 Journal of Alloys and Compounds 632 661.
[16] Vogel R and Bedarff H 1933 Arch. Eisenhüttenwesen 7 423.