

## Identification of defect prone peritectic steel grades by analyzing the high temperature phase transformations

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### Abstract

Continuous casting of peritectic steels is often difficult and critical; bad surface quality, cracks and even breakouts may occur. Particularly, the initial solidification of peritectic steels within the mold leads to formation of surface depressions and uneven shell growth. As commercial steels are always multi-component alloys, it is necessary to take into account also the influence of alloying elements besides carbon on the peritectic phase transition. Especially for new steel grades with high Mn, Si and Al contents, there is a lack of information regarding the solidification sequence and the phase diagrams for initial solidification. Based on a comprehensive method development, the present study shows that high precious Differential Scanning Calorimetry (DSC) measurements allow a clear prediction whether an alloy is peritectic (i.e. critical to cast) or not.

### Introduction

It is well known that producing some specific steel grades by means of the continuous casting (CC) process is often difficult and critical; bad surface quality cracks and even breakouts may occur. Particularly, the formation of surface depressions during the initial solidification within the mold can be obtained at a certain range of carbon. This situation is illustrated in Figure 1a in terms of an unevenness index. It can clearly be seen that a maximum exists at approximately 0.12 wt.-%C. Depression formation further results in an uneven shell growth, coarse grains and other negative events such as the formation of hot tears.

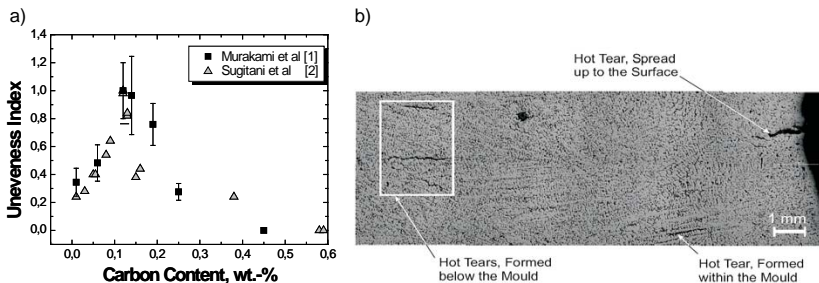


Figure 1. a) Unevenness index over the carbon content [1, 2] b) different types of hot tears as a result of a depression [3].

Figure 1b shows hot tears at different positions below a depression and represents a critical material defect which results in a significant loss of quality. The formation of hot tears in the ground of depressions is related to the air gap formation, the resulting reduced heat transfer from the mold, a thinner strand shell and the increase of stresses and strains in the solid/liquid (S/L) two phase region. These correlations are explained in detail in literature [3, 4]. The formation of depressions during the CC process is described by means of examples in [5, 6, 7, 8] and is mainly determined by the chemical composition of the melt. It is evident that steels with an equivalent carbon content between 0.09 and 0.16 clearly show a maximum of these negative phenomena. Besides the depressions, continuous casters also observe higher mold level and temperature variations within this critical carbon range.

Considering the high temperature range of the iron-carbon (Fe-C) equilibrium phase diagram, illustrated in Figure 2a, it is obvious that the above mentioned critical/specific steel grades are between the characteristic points  $C_A$  and  $C_B$ . Classifying four different carbon ranges (range I left of  $C_A$ , range II: between  $C_A$  and  $C_B$ , range III: between  $C_B$  and  $C_C$  and range IV: right of  $C_C$ ) a clearly different solidification and transformation sequence will be passed through. Table I summarizes these different transformation behaviors in the equilibrium binary Fe-C system. The specialty of the critical range II in comparison with the other three ranges is that in this case the transformation of  $\delta$ -Fe to  $\gamma$ -Fe (i.e. the peritectic phase transition) starts in the S/L two phase region and ends in the solid (see also Figure 2a).

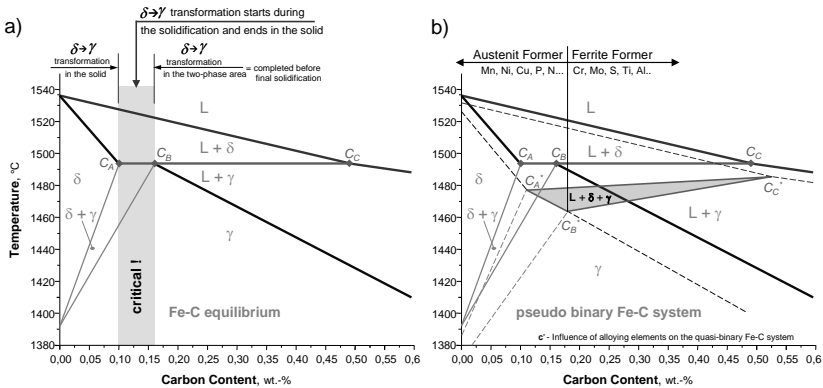


Figure 2. a) Fe-C equilibrium diagram with the critical carbon range between 0.09 and 0.16 wt.-%C and b) influence of alloying elements on the Fe-C system.

Table I. Different transformation characteristics in the Fe-C system

Range	Position	Phase sequence	Characteristics
I	left of $C_A$	$L \rightarrow L+\delta \rightarrow \delta \rightarrow \delta+\gamma \rightarrow \gamma$	primary $\delta$ -Fe solidification
II	between $C_A$ and $C_B$	$L \rightarrow L+\delta \rightarrow \delta+\gamma \rightarrow \gamma$	peritectic transformation starts during the solidification and finish in the solid
III	between $C_B$ and $C_C$	$L \rightarrow L+\delta \rightarrow L+\gamma \rightarrow \gamma$	peritectic transformation starts during the solidification finish in the L/S region
IV	right of $C_C$	$L \rightarrow L+\gamma \rightarrow \gamma$	primary $\gamma$ -Fe solidification

Furthermore, alloying elements significantly influence the phase diagrams and the position and temperature of the characteristic points  $C_A$ ,  $C_B$  and  $C_C$ . This situation is demonstrated in Figure 2b in terms of a pseudo binary Fe-C diagram. The effect of the alloying elements can be distinguished between austenite formers (like Mn, Ni, Cu, ...) and ferrite formers (like Cr, Mo, Al,...). It can also be seen that the presence of higher concentrations of alloying elements prefer the formation of a peritectic ternary region (L+ $\delta$ + $\gamma$ ). Based on the above illustrated explanations it is clear that great efforts were made in the past to describe the essential influence of alloying elements on the transformation sequence in order to identify whether a specific steel grade is within the critical range II or not.

In order to summarize the above illustrated facts it can be stated that - if the phase transformations during the solidification and the characteristic points  $C_A$  and  $C_B$  are well known-critical steel grades can be produced safely by target selection of special casting powders, cooling programs and casting speed. As commercial steels are always multi-component alloys, it is necessary to take into account also the influence of alloying elements besides carbon on the peritectic phase transition and the position of  $C_A$  and  $C_B$ . Hence, great efforts were made in the past to describe the influence of alloying elements on this critical range. However, for new steel grades (e.g. high alloyed Fe-C-Mn-Al-Si steels, like TRIP- and TWIP-steels) there is a lack of information about the position of the alloy within the Fe-C phase diagram (i.e. the sequence of transformation characteristics). Therefore, new investigations are essential to find out in a first approach (user-oriented for the process management of the CC process) whether a new steel grade is within the critical range (i.e. between  $C_A$  and  $C_B$ ) and in a second approach (fundamental) to characterize the transformation behavior in detail and systematically. This question goes hand in hand with the search for a reliable and simple laboratory method. In the present study a DSC method is used.

In the following sections, first different calculation methods to characterize peritectic steel grades are summarized. Secondly, the potential of DSC measurements to characterize the different transformation characteristics will be illustrated. And lastly, the application of the above described approaches to identify a new steel grade will be done using the example of a new Fe - 0.22wt.-%C - 2wt.-%Al alloy. It will be demonstrated why one DSC measurement is sufficient to determine the transformation characteristics and in this regard whether an unknown steel grade is in range I, II (critical), III or IV. This will be carried out by illustrating and discussing the measured DSC signal.

### Calculation methods to characterize peritectic steel grades

In the following, four different methods to calculate the influence of alloying elements on transformation characteristics are summarized. All these methods are more or less simple tools to characterize peritectic steel grades only on the basis of the alloy composition.

#### a) Carbon equivalent calculations

The simplest method are various formulas to calculate an equivalent carbon content ( $C_P$ ) by the addition of different alloying elements ( $C_i$ ) with weighted coefficients ( $X_i$ ), whereas austenite formers are always positively weighted and ferrite formers negatively. If the calculated value of  $C_P$  is between 0.09 and 0.16 (=  $C_A$  and  $C_B$  in the binary Fe-C system) the steel is considered as critical.  $C_P$ -formulas were published by several authors [8, 9, 10] and can be written as:

$$C_P = C_C + \sum_{i=1}^{i=n} X_i * C_i \quad \text{for example: } C_P = [\%C] + X_{Mn} * [\%Mn] - X_{Si} * [\%Si] + \dots$$

Such additive  $C_P$ -formulas often originated from operational observations and describe well simple low alloyed steels. However, such simple approaches cannot consider the interaction

between the different elements and are only valid for a very limited concentration range. For complex steels grades such formulas are not useful or even calculate unrealistic (negative) or wrong values, moreover the distance between  $C_A$  and  $C_B$  is fixed with 0.06 wt.-%C and cannot diverge.

**b) Calculation model from Kagawa and Okamoto**

The approach by Kagawa and Okamoto [11] is the first study, where the direct influence of alloying elements on the critical points  $C_A$ ,  $C_B$ ,  $C_C$  is considered. The model is based on coefficients reflecting the shift in the temperatures ( $\Delta T_{CA}$ ,  $\Delta T_{CB}$ ,  $\Delta T_{CC}$ ) and concentration ( $\Delta C_{CA}$ ,  $\Delta C_{CB}$ ,  $\Delta C_{CC}$ ) of the critical points for each element. With this information even full pseudo-binary Fe-C equilibria with all high temperature phase transformations can be calculated, as well as the concentrations and temperatures of  $C_A^*$ ,  $C_B^*$  and  $C_C^*$ , like in Figure 2b.

This more comprehensive model can consider the different effects of third elements on the critical points, particularly the distance between  $C_A$  and  $C_B$  (= range II) can expand. However, it only considers the effect of individual alloying elements without the interaction between the different elements. In addition the published coefficients are also only responsible for a very limited concentration range and no coefficients for aluminum are available.

**c) Peritectic Predictor Equations from Blazek et al.**

The peritectic predictor equations are two formulas respectively for  $C_A$  and  $C_B$  and were published by Blazek et al. [12]:

$$C_A = 0.0896 + 0.0458 * Al - 0.0205 * Mn - 0.0077 * Si + 0.0223 * Al^2 - 0.0239 * Ni + 0.0106 * Mo + 0.0134 * V - 0.0032 * Cr + 0.00059 * Cr^2 + 0.0197 * W$$

$$C_B = 0.1967 + 0.0036 * Al - 0.0316 * Mn - 0.0103 * Si + 0.1411 * Al^2 + 0.05 * Al * Si - 0.0401 * Ni + 0.03255 * Mo + 0.0603 * V + 0.0024 * Cr + 0.00142 * Cr^2 - 0.00059 * Cr * Ni + 0.0266 * W$$

These formulas are based on a comprehensive regression study of the influence of alloying elements on the critical points  $C_A$  and  $C_B$ , using the commercial thermodynamic software ThermoCalc within a certain concentration range (e.g. Mn, Si, Al up to maximum 2 wt.-%). The formulas are similar to  $C_p$ -formulas, whereas austenite formers and ferrite formers (with exception of silicon) are each rated negatively and positively. A great advantage in comparison to previous  $C_p$ -formulas is that  $C_A$  and  $C_B$  are given separately and also the partial interaction of selected elements such as Al\*Si and Ni\*Cr is considered. The point  $C_C$  is not considered and the determination of transformation temperatures is not possible.

**d) Calphad method – Gibbs Minimizer**

The most comprehensive method is the numerical calculation of multi-component phase diagrams using the CALPHAD's approach which considers all (known) interactions. There are different commercial Gibbs minimizers on the market such as ThermoCalc, FactSage, MTDat, PANDAT and so on. All these programs allow calculating "everything" - all phase transformations for all compositions, but even this can be dangerous, since all these calculations are only as good as the underlying databases, which are based exclusively on existing - previously investigated - systems.

For typical low alloyed Fe-C-Si-Mn steels (e.g. with 0.3 wt.-%Si and 1.5 wt.-%Mn) all four different methods agree very well. Even simple  $C_p$  calculations excellently describe these typical structural steels. For more alloying elements, method c) and d) are recommended. Higher alloyed

complex steel grades (e.g. TRIP- and TWIP-steels) can only be handled by the Calphad method, however the scope and quality of the used thermodynamic databases need to be proved.

**Experimental method - the Differential Scanning Calorimetric (DSC)**

DSC measurements are an excellent method which record all transitions associated with an exo- or endothermic effect (= enthalpy change). With a very high accuracy almost all important phase transformations in steels can be measured. The equipment used in the study was a NETZSCH STA409PG *Luxx* (simultaneous thermal analyzer, Selb, Germany) with a platinum DSC sensor and type S thermocouples as shown in Figure 3. The Pt/Pt10%Rh thermocouples of the DSC sensor were calibrated at the melting points of 7 high purity elements (In, Sn, Al, Ag, Au, Ni, Co). All measurements were carried out under the same conditions in alumina crucibles with lids under protective gas atmosphere (argon, quality 6.0) during controlled heating up to 1550°C. In order to achieve best equilibrium conditions, special polished samples with a maximum mass of 50mg and a heating rate of 10K/min were used, in addition the plant influence on the DSC signal was corrected by an extra calculation with the Netzsch Programm Correct2 [13]. Precisely the investigation of highly reactive steels with larger amounts of Al and Si requires special attention regarding the purity of the atmosphere in the DSC. In order to achieve the best results four different getters are used to clean the protective gas in the oven, moreover the samples are heated only one time, to measure only the virginal material.

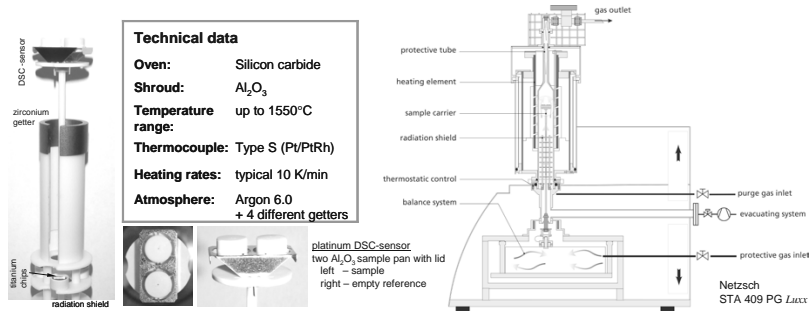


Figure 3. Layout of a NETZSCH STA409PG with a high temperature DSC sensor.

In Figure 4, three different DSC measurements with different carbon contents from the well known Fe-C-Si system are compiled. All the process relevant transformation characteristics from Table 1 show a unique DSC signal during melting. The DSC signal from alloys left of  $C_A$  (rang I - primary  $\delta$ -Fe solidification) and alloys right of  $C_C$  (range IV - primary  $\gamma$ -Fe solidification) show similar characteristics, except the width of the two-phase S/L-region which is much wider at higher carbon contents.

Only alloys between  $C_A$  and  $C_B$  (range II) exhibit - due to the peritectic phase transformation - a separate characteristic sharp peak, which coincides with the solidus temperature, visualized in Figure 4, alloy II. Referring to Figure 1a, steels with 0.12 wt.-%C (= between  $C_A$  and  $C_A$ ) are most critical. Only these peritectic steel grades exhibit this unique sharp peak, which can be clearly determined by means of DSC measurement. Beside these clear YES/NO criterion for peritectic steels, also all relevant transition temperatures ( $T_{\gamma-\delta}$ ,  $T_{Solid}$ ,  $T_{Perit.}$ ,  $T_{Liquid}$ ) can be measured and used to validate or to asses full phase diagrams. The Fe-C-Si system was chosen consciously, because it is well described in literature [14, 15]. The quality of the ThermoCalc

[16] calculation of the pseudo binary phase Fe – 1wt.-%Si – C diagram can be confirmed by the DSC measurements.

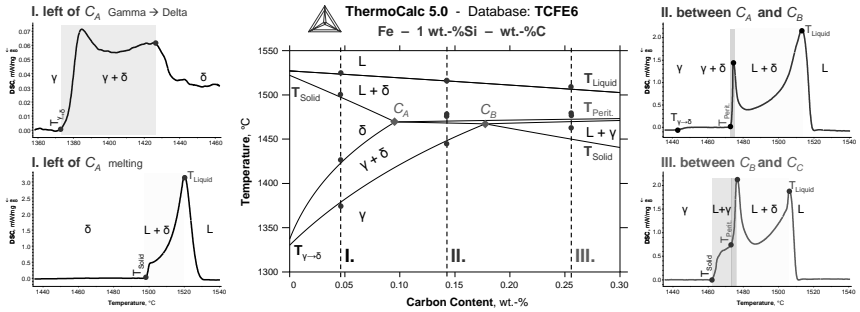


Figure 4. Characteristic DSC-signals from the well known Fe-C-Si system

### Results

In order to demonstrate the potential of the DSC method for characterizing new alloying systems, a model alloy with the composition of Fe – 0.22wt.-%C – 2wt.-%Al, as shown in Figure 5, will be explained in detail. This steel with 2wt.-%Al was chosen purposely, because the two commercial thermodynamic programs ThermoCalc [16] and FactSage [17] show very different results. The alloy for the DSC measurement was melted in an alumina crucible with a High Frequency Remelting Furnace (HRF) under argon atmosphere from high purity raw materials and was centrifugally cast in a copper mold and analyzed by emission-spectroscopy.

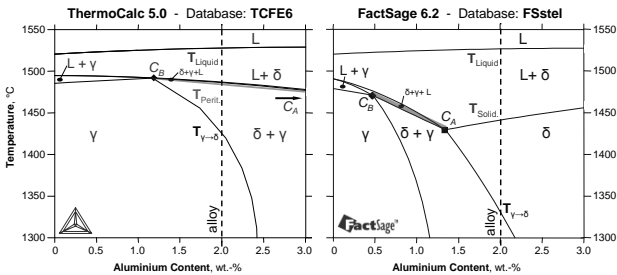


Figure 5. Thermodynamic calculations of a pseudo binary Fe – 0.22 wt.-%C – wt.-%Al system [16, 17]

The mathematical approaches, presented in the introduction, provide very different results for the mentioned Fe – 0.22wt.-%C – 2wt.-%Al alloy, summarized in Table 2. A single DSC measurement, shown in Figure 6a, demonstrates very clearly the transformation characteristics of this new alloy. The investigated alloy is definitely peritectic, identified by the unique sharp peak, which only occurs at alloys between  $C_A$  and  $C_A$ , see also the comparison with Figure 6b where the alloy is also peritectic. This new alloy is therefore also in the critical range II, and has to be

handled with special care during CC. Besides this important information, the DSC measurement shows that the transformation temperature calculated with ThermoCalc (range II – correct) is too high and that the FactSage calculations (range I) and the Peritectic Predictor Equations from Blazek (range I) show different transformation characteristics. Further DSC measurements in the system Fe-C-Al are necessary to perform a serious assessment and to determine the exact position of the critical points  $n_{C_A}$  and  $C_B$ .

Table 2. Results of the different prediction models.

<p><b>a) Carbon equivalent calculations</b>          Cannot handle alloys with aluminum.          If only the carbon content of 0.22 wt.-%C is considered, the alloy would be in range III.</p>
<p><b>b) Calculation model from Kagawa and Okamoto</b>          Cannot handle alloys with aluminum, the pure Fe-C alloy would be in range III.</p>
<p><b>c) Peritectic Predictor Equations from Blazek et. al.</b>          Calculates for the mentioned alloy for <math>C_A = 0.27</math> and <math>C_B = 0.77</math>.          That means that the model alloy with 0.22 wt.-%C is left of <math>C_A</math>, in range I and not peritectic.</p>
<p><b>d) Calphad method – Gibbs Minimizer</b>          regarding the ThermoCalc [16] calculation, range II with a peritectic temperature of 1486,6°C          regarding the FactSage [17] calculation, range I with a solidus temperature of 1440,5°C</p>

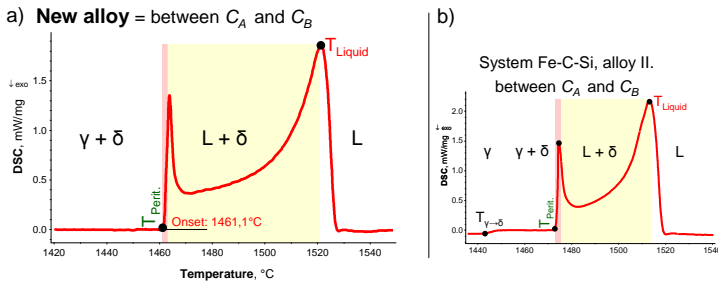


Figure 6. a) Measured DSC signal of the ternary alloy iron with 0.22wt.-%C and 2wt.-%Al, b) DSC signal from Figure 4, alloy II in detail.

### Summary and Outlook

Thermodynamic considerations are essential to categorize steels (range I – IV) for the CC-process. In addition to all mathematical approaches (simple formulas or elaborate computer programs) real measurements are essential to categorize new steel grades (especially high Fe-C-Mn-Al-Si steels). DSC measurements are an excellent method which record all transitions associated with an exo or endothermic effect (= enthalpy change) and allow to investigate:

- peritectic alloys (between  $C_A$  and  $C_B$ , range II), which are critical to cast
- transformation characteristics (= position regarding  $C_A$ ,  $C_B$  and  $C_C$ ) and almost all transformation temperatures can be determined with very high accuracy.
- DSC measurements can be used to evaluate thermodynamic programs. With systematic investigations new phase diagrams and even the exact position of  $C_A$ ,  $C_B$  and  $C_C$  can be assessed.

With one DSC trial, it can be analyzed whether new unknown alloys are peritectic or not. This essential information (YES/NO) helps to improve the process management of the continuous casting process and to ensure a high product quality.

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