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Linking up of HT-LSCM and DSC measurements to characterize phase diagrams of steels

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Abstract. The phase transformation sequence during the solidification of carbon steels strongly influences their behavior in the casting process. Therefore, most exact knowledge of the dependence of the transformation characteristics on the steel composition is of highest relevance for process and quality optimization. The influence of alloying elements like C, Mn or Si on phase transformation is well understood as far as their content is rather low. New steel grades, like high-alloyed TRIP- or TWIP-steels contain almost up to 10 wt.-% of Si and Al and 30 wt.-%Mn. The present work focuses on first results of the parallel investigation into phase transformation of Fe-Al-C alloys by means of Differential Scanning Calorimetry (DSC) and Thermo-Optical Analysis (TOA) with a High-Temperature Laser-Scanning-Confocal-Microscope (HT-LSCM). DSC is a well established method for the accurate measurement of all phase transformation temperatures accompanied by significant enthalpy changes. Due to small enthalpy changes, DSC results are limited with respect to the γ/δ -transformation. Besides dilatometry and X-ray diffraction, the optical in-situ observation of phase transformation by HT-LSCM proved to be a comprehensive method. After a short description of the methods, results for the Fe-0.4%Al-0.22%C and Fe-1.5%Al-0.22%C systems will be discussed in detail and finally compared with results from computational thermodynamics.

1. Introduction

Phase diagrams and the knowledge of phase transformations of materials represent very important information for scientists, materials engineers and process operators to understand material behavior during solidification, heat treatment and the whole further processing. Regarding steels, a special feature are the two different high-temperature phases: $\gamma(\text{fcc})$ - and $\delta(\text{bcc})$ -iron. Figure 1 illustrates the equilibrium binary Fe-C (gray thin lines) and four ranges of different transformation sequences, which are additionally summarized with a table in this figure. Steels which solidify according to the transformation sequence of range II are of special interest, because in this case the transformation of δ -Fe to γ -Fe (i.e. the peritectic phase transition $\gamma \rightarrow L+\delta$) starts in the solid-liquid two phase region and ends in the solid. It is believed that this specific transformation sequence during solidification and subsequent cooling is responsible for an increased defect appearance (such as hot tears, surface defects, depression formation and in the worst case breakouts) in the continuous casting process [1-4]. This critical range II is often characterized by a carbon content between C_A and C_B . However, since steel is always a multi-component material it is clear that pseudo binary phase diagrams must be used to understand the transformation sequence. Figure 1 schematically shows how alloying elements significantly influence the Fe-C phase diagram (green thick lines) and the position and temperature of the characteristic points C_A^* , C_B^* and C_C^* . Pseudo binary Fe-C diagrams of multi-component alloys can be calculated with commercial Gibbs minimizers (CALPHAD's approach) such as ThermoCalc (TC), FactSage (FS), MTDat, PANDAT to mention just a few examples. Using such commercial software tools, the position and temperature of the characteristic points C_A^* , C_B^* and C_C^* can be easily determined. Low alloyed steels (typical construction and engineering steel grades) and simple Cr and Ni high alloyed steels (stainless and tool-steel grades) seem to be well described in commercial thermodynamic databases.



Figure 1. Fe-C equilibrium diagram in the high temperature range.

In contrast to the above mentioned steels, however, calculated pseudo binary phase diagrams of novel steels grades which exhibit for example higher content of Mn, Si and Al (typically TRIP and TWIP steels) show partly divergent results. This can mainly be explained by a lack of trustworthy thermodynamic data. Figure 2 shows, for example, the results of calculated pseudo binary Fe-1%Si-C (left) and Fe-1%Al-C (right) diagrams using ThermoCalc 5.0 (TC) and FactSage 6.2 (FS).



Figure 2. ThermoCalc and FactSage calculation of the pseudo binary Fe-C diagram of the system Fe-1%Si-C (left) and Fe-1%Al-C (right).

The results of the ThermoCalc and FactSage calculations show very good agreement (i.e. the difference in the transformation temperatures ΔT is smaller than 10 °C) in the case of Fe-1%Si-C alloy, but very contradictory results in the case of Fe-1%Al-C. In order to visualize these uncertainties with respect to Al in detail, Figure 3 shows the pseudo binary Fe-Al-0.22%C diagram, calculated with

ThermoCalc and FactSage. It can clearly be seen that already at rather low values of Al, both calculated phase diagrams are totally different. The above mentioned and illustrated disagreement, especially with respect to the results when Al is present, exemplarily shows the great need for experimental methods to evaluate thermodynamic calculations and to measure new systems on the one hand. On the other hand, however, sometimes only the knowledge of the transformation behavior and sequence is of interest (i.e. is a new steel grade between C_A^* and C_B^*). In doing so, different experimental methods can be used. The present study shows the possibilities, assets, drawbacks and limitations of two different experiments, the High-Temperature Laser-Scanning-Confocal-Microscopy (HT-LSCM) and the Differential Scanning Calorimetric (DSC) method using the example of three different alloys. These three alloys are Fe-1%Si-0.14%C, Fe-0.4%Al-0.22%C and Fe-1.5%Al-0.22%C, which are additionally illustrated in Figure 2 (left) and Figure 3.



Figure 3. Test alloys and thermodynamic calculations of the pseudo binary Fe-Al system.

2. Experimental Methods

In the following section, the two applied experimental methods are described. Prior to that it should be mentioned that the production of the necessary samples was the same in both cases: The alloys were melted in an alumina crucible from high purity raw materials with a High Frequency Remelting Furnace under argon atmosphere and were centrifugally cast in a copper mould and analyzed by emission-spectroscopy.

The High-Temperature Laser-Scanning-Confocal-Microscopy is a special kind of Thermo-Optical Analysis (TOA) which enables in situ observations of surface phenomena in liquid and solid samples up to a maximum temperature of 1650°C. Since this well established method is described in detail in the relevant literature [5-8], the present study gives just a brief overview on the experimental set-up: The right hand side of Figure 4 shows an overview of the whole facility, the left hand side shows the experimental assembling together with detailed images of the sample holder in the high-temperature furnace. This infrared furnace consists of a gold-coated chamber and has the shape of a symmetric ellipse. The heating is carried out by means of a halogen lamp which is located in the bottom focal point, whereas the crucible is in the upper focal point.

Similar to other thermal analysis methods, protective gas atmosphere (argon, quality 6.0), type-S thermocouples in the sample holders and alumina crucibles were used. In the present study, the following experimental adjustments and parameters were employed. The size of the samples was 4x4x1mm (polished, but not etched). The heating rate was 500 K/min up to a temperature of 1300 °C, subsequently an isothermal holding for 5 minutes took place being followed by a slow heating up using a heating rate of 10 K/min until everything was liquid. During the whole period of the experiment, a video was produced, where a frame rate of 60 frames per second enables the observation

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and recording of fast processes. This video was finally analyzed in detail and the results will be illustrated later in the paper.



Figure 4. HT-LSCM at the Chair of Metallurgy, Montanuniversitaet Leoben.

The Differential Scanning Calorimetric measurements record all phase transitions which can be associated with an exo- or endothermic effect (=enthalpy change). The equipment used in the study was a NETZSCH DSC with a platinum DSC sensor and type-S thermocouples. The DSC consisted of a sample and reference crucibles, which are connected by a heat flow plate both exposed, ideally, to the same heating power input by convection and radiation from the cylindrical heating oven. The measurement signal is derived from the temperature difference between the sample and reference crucible expressed in terms of a heat flow. Detailed descriptions can be found for example in [9]. The experimental set-up used in the present study was calibrated by measuring the well known melting point and enthalpy of fusion of seven high purity elements (In, Sn, Al, Ag, Au, Ni and Co). All of these measurements were carried out under the same conditions in alumina crucibles with lids under protective gas atmosphere (argon, quality 6.0). In order to achieve best equilibrium conditions, grounded steel samples with a mass of 50 mg and a controlled heating rate of 10 K/min were used. In addition, the thermal resistance and the time constants of the measurement system were corrected. Finally it should be mentioned that accurate measurements of highly reactive steels with higher amounts of Al and Si requires special attention regarding the purity of the atmosphere in the DSC and their leak tightness. For this reason, different getters are used to clean the protective gas in the oven and most importantly, the samples were heated up only once in order to measure only the virginal material.

3. Results – Thermal Analysis

First of all, the results of the DSC measurement of alloy 1 (Fe-1%Si-0.14%C) will be illustrated and discussed in detail. Thereafter, the findings of alloy 2 (Fe-0.4%Al-0.22%C) and alloy 3 (Fe-1.5%Al-0.22%C) applying both experimental methods, DSC and HT-LSCM, will be analyzed in detail and finally the determined phase transformation sequence and temperatures will be compared.

The left hand side of Figure 5 shows a typical result of a DSC measurement (alloy 1: Fe-1%Si-0.14%C), whereas the illustrated curve (DSC-signal^{corr}), i.e. the measured heat flow, is adjusted by the influence of the heating rate, sample mass, crucible and the DSC-sensor configuration. In doing so, this signal correction procedure identifies the determined temperatures as equilibrium transformation temperatures. This was done by using a commercial software tool [10] and applies for all illustrated curves in the following section. Additionally, the transformation temperatures and subsequently the present phases are illustrated in the diagram. This correlation of the possibly appearing phases is not trivial and will be discussed below:

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Figure 5. DSC measurements of alloy 1 (Fe-1%Si-0.14%C).

Since phase transformations are always associated with a change in enthalpy (i.e. heat will be released or consumed) and the DSC method allows the measurement of the heat flow, an occurring phase transformation causes a deviation of the horizontal baseline. The first deviation which can be seen in Figure 5 takes place at 1443 °C. However, only a very small deviation of the heat flow can be observed which points to a transformation of very small enthalpy changes. With respect to even possible phase transitions in the high temperature range (T > 1200 °C) of steels, this is typical when austenite starts to transform δ -ferrite ($\gamma \rightarrow \gamma + \delta$). Hence, the temperature of 1443 °C was identified as $T_{\gamma \to \gamma + \delta}$. The larger the temperature range of the two phase region ($\gamma + \delta$), the smaller is the heat flow per unit of time. Consequently the $\gamma \rightarrow \delta$ transformation is hardly measurable. At 1472.7 °C a very sharp peak appears which is followed by a typical melting peak of an alloy. These peaks can be associated with the peritectic phase transformation $(\gamma \rightarrow L + \delta)$ temperature, T_{Perit} and the liquidus temperature T_{Liquid}. The sharp increase is not only due to the enthalpy change caused by the peritectic transition but also due to fact that this peritectic peak coincides with the solidus temperature. Hence, this is a clear criterion of an alloy situated between C_A and C_B (= range II). Alloys which are situated between C_B and C_C show clearly different characteristics, because the solidus temperature is lower than the peritectic temperature. Thus, the deviation from the baseline due to the melting process is followed by a sharp increase due to the peritectic transition.

Finally, the determined phase transformation temperatures are incorporated in the Fe-1%Si-C pseudo binary phase diagram, illustrated on the right hand side of Figure 5. It can be seen that the determined transformation temperatures of alloy 1 are in very good agreement (Δ T is smaller than 10 °C) with the results of the TC and FS calculation. A large number of DSC measurements in the system Fe-Si-C and Fe-Si-Mn-C showed that the standard deviation of the measurement of solid-solid transitions is ⁺/.5 °C and of solid-liquid transitions ⁺/.2 °C. Therefore, DSC measurements, which are very well reproducible, can be used as a benchmark.

As indicated in the introduction, the thermodynamic calculations of the ternary system Fe-Al-C are very contradictory. In order to shed light on the matter, first investigations were conducted using the HT-LSCM method. Figure 6 shows selected pictures of alloy 2 (Fe-0.4%Al-0.22%C). At 1440 °C (A2-I) shows a pure austenitic microstructure whereas a significant grain coarsening can be observed in the video. Subimage A2-II shows this grain growth in terms of a consumption of a smaller grain. Melting of the sample typically starts at the grain boundary at a temperature of 1480 °C (A2-III), which can be identified very clearly by a moving liquid phase on the surface of the sample. With further heating the melt spreads over the whole surface (A2-IV). As a result, it is not possible to determine the liquidus temperature as well as further transformations such as the peritectic. However, since the first detected phase transformation is $\gamma \rightarrow L+\gamma$, alloy 2 is situated either between C_B and C_C (range III) or even higher than C_C (range IV). Both thermodynamic software tools predict the following transformation sequence for alloy 2: $\gamma \rightarrow L+\gamma \rightarrow L+\delta \rightarrow L$ (= range III, see also Figure 3).

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A2-IV: (γ+) L **Figure 6.** HTLSCM result of alloy 2 (Fe-0.4%Al-0.22%C).



A3-I: 100% γ-grains



A3-II: δ-formation



A3-III: γ+δ



A3-IV: $\gamma + \delta \rightarrow L + \delta$

Figure 7. HTLSCM result of alloy 3 (Fe-1.5%Al-0.22%C).

The results of the HT-LSCM investigations of alloy 3 are illustrated in Figure 7, which show a transformation sequence of $\gamma \rightarrow \gamma + \delta \rightarrow L + \delta \rightarrow L$ (= range II). In the observed high temperature range (1300-1420 °C) the microstructure consists of 100% γ -grains (A3-I) which shows also a grain growth similar to alloy 2. At 1430°C the formation of δ -ferrite starts at the γ grain boundaries and tipple points (A3-II). With further heating the phase fraction of the δ phase increases, while the γ phase decreases (A3-III). Only 2°C higher, the peritectic phase transformation occurs immediately (A3-IV). The δ phase remains, while at first only the former γ phase is liquid. With further heating the residual δ phase melts and the liquid phase spreads over the whole surface as described also for alloy 2. The experimentally determined transformation sequence can be summarized by $\gamma \rightarrow \gamma + \delta \rightarrow L + \delta \rightarrow L$ (= range II). For alloy 3 the calculated transformation sequence according to TC is $\gamma \rightarrow \gamma + \delta \rightarrow L + \delta \rightarrow L$ (range II). According to FS it is $\gamma \rightarrow \gamma + \delta \rightarrow L + \delta \rightarrow L$ (range I). Hence, TC describes the results of the HT-LSCM measurements of alloy 3 better than FS.

However, it can already be pointed out that the HT-LSCM method can not be used to determine transformation temperatures precisely. Therefore, DSC measurements of alloy 2 and 3 were performed additionally. Figure 8 shows the results from these measurements with the subsequently assigned phases carried out in a similar way as described by alloy 2. Furthermore, the positions of the HT-LSCM pictures are marked in the diagrams (black arrows). The DSC trials demonstrate a transformation sequence of $\gamma \rightarrow L + \gamma \rightarrow L + \delta \rightarrow L$ (= range III) of alloy 2 and $\gamma \rightarrow \gamma + \delta \rightarrow L + \delta \rightarrow L$ (= range II) of alloy 3. These results clearly support the findings of the HT-LSCM observations, viz. an accordance of the experimentally determined transformation sequence with the calculated one using TC.



Figure 8. DSC measurements of the aluminium alloys 2 and 3 with 0.22%C.

Figure 9 represents a summarization of the thermodynamic calculations with the results from DSC measurements (red points) and the HT-LSCM method (black arrows). It is clearly noticeable that the HT-LSCM observations and the DSC measurements fit very well together and the DSC results confirm the HT-LSCM predictions on the transformation sequence. However, in order to determine transformation temperatures, the DSC method must be preferred. Comparing these values with the calculations, it can be stated that both software tools achieve a good accordance at alloy 2 (Fe-0.4%Al-0.22%C). However, considering alloy 3 (Fe-1.5%Al-0.22%C), only TC predicts the measured transformation sequence. With the exception of T_{Liquid} , the calculated transformation temperatures, using both software tools, significantly differ from the experimentally determined values.

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Figure 9. Compilation of the thermodynamic calculations with the measurements results.

4. Summary and Outlook

The present study has shown that there is a lack of inconsistent thermodynamic data, for example for newly developed steel grades with a higher amount of Al. As a result, experimental methods are necessary to advance these thermodynamic data in terms of phase diagrams. Therefore, the present study illustrates and discusses the high temperature phase transformations of three different alloys using two laboratory methods, the Differential Scanning Calorimetry (DSC) and the High-Temperature Laser-Scanning-Confocal-Microscope (HT-LSCM). It could be shown that DSC measurements are a perfect method to measure the solidus, peritectic and liquidus temperatures with high accuracy. Furthermore, the transformation sequence can directly be deduced from the characteristics of the measured DSC signal. HT-LSCM investigations enable a direct observation (Thermo-Optical Analysis) of the microstructure and the transformation behavior up to the melting point. Both methods complement each other perfectly:

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- Measuring the $\gamma \rightarrow \delta$ transformation (generally solid-solid transformations with small enthalpy changes) by means of DSC is difficult, but works very well by applying the HT-LSCM method.
- DSC is an excellent method to determine the hyperperitectic and/or the liquidus temperature. This can not easily be realized using HT-LSCM, at least during the heating stage. However, applying the concentric solidification method [7], the HT-LSCM represents a perfect laboratory to investigate the peritectic reaction and transformation.
- Although the temperature measurements are calibrated in both cases, DSC measurements are the most suitable method to determine phase transformation temperatures with high accuracy. In contrast to determining phase transformation temperatures, the HT-LSCM is predominant when investigating grain growth, solidification, sub-cooling and time-temperature-transformations (kinetic studies).

The combination of both methods is a powerful tool and enables the determination of phase diagrams, especially in the high temperature range. This will be realized in ongoing and future research activities with a strong focus on steel in combination with alloying elements which are not well described at higher contents (e.g. Al > 0.1% and combinations of Al with Si, Mn in steels).

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