# THERMAL ANALYSIS OF MEDIUM-CARBON STEELS

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**Abstract**

Series of thermal analysis measurements by Differential Thermal Analysis (DTA) and Direct Thermal Analysis (TA) were performed on two real grade medium carbon steel samples in low and high temperature regions. Temperatures of eutectoid transition ($T_E$), end of α-ferrite to γ-austenite transition ($T_{\alpha\rightarrow\gamma}$), solidus ($T_S$), peritectic transition ($T_P$), liquidus ($T_L$) were determined. The stability and reproducibility of the results were verified by statistic evaluation and discussed with theoretical calculations carried out by Solidification Analysis Package (IDS) and Thermo-Calc™ (2015b, TCFE8; TC) software.

**Keywords:** Thermal analysis, steel, solidus, liquidus, heat capacity, thermo-calc, IDS

## 1. INTRODUCTION

Material science and general knowledge about thermo-physical properties of steels is getting more and more importance due to increasing pressure on steel industry to reduce price of steel to minimum. The most promising way companies choose is the reduction of costs, with particular focus on energy savings [1]. It is widely known, that production of steel is energetically demanding, therefore it is necessary to define requirements and analyse a real steel samples in detail to achieve precise and efficient process of production.

Theoretical calculations using specialised software are becoming increasingly important due to its overall efficiency. A decision cannot be made, though, based purely on calculation [1]. The accuracy of the calculation depends on used model and correct data in its databases. Lack of data or faults in databases results in unpredictable errors of calculation, and therefore it is recommended always to check the calculated results with an experimental measurement [2].

Significant thermo-physical properties of steels are, among others, temperatures of solidus, liquidus, eutectoid, peritectic and magnetic transitions [2]. The aim of this paper was to obtain these key thermo-physical data from two real steel grades by experiment and theoretical calculations, then assess the calculated and experimental data in term of reproducibility, evaluate comparability of the analytical methods used and revise substitutability of the thermal analysis by software.

## 2. ANALYTICAL METHODS AND CALCULATIONS

Thermal analysis covers a wide range of methods used to determine the physical or chemical properties of a material as it is heated, cooled or held at constant temperature. This provides analytical information on the fundamental properties of materials [5]. The experiments were carried out by two thermo-analytical methods: Differential Thermal Analysis (DTA) and Direct Thermal Analysis (TA).

Differential Thermal Analysis (DTA) is thermo-analytical method where temperature effects are studied during continuous linear heating or cooling in controlled atmosphere. The temperature of the analysed sample is

measured relative to a reference sample. A reference sample can be standard material (e.g. Pd) or an empty crucible. The result of the measurement is DTA curve [11, 12].

Direct Thermal Analysis (TA) is thermo-analytical method where direct measurement of temperature of the sample is carried out during its heating or cooling in controlled atmosphere [9].

The amount of heat involved and temperature at which these changes take place are characteristic for changes in structure of steel: Eutectoid Transition ($T_E$), End of α-Ferrite to γ-Austenite transition ($T_{\alpha\rightarrow\gamma}$), Solidus ($T_S$), Peritectic transition ($T_P$), Liquidus ($T_L$).

The theoretical calculations were performed by Thermo-Calc™ [11] (TC) and Solidification Analysis Package [14] (IDS) software. The Thermo-Calc is sophisticated software using CALPHAD approach and includes many databases, which are necessary to its calculations. The IDS software is based on kinetics and thermodynamic calculations and is utilized for the determination of temperature dependencies for thermo-physical properties of steels.

## 3. THEORETICAL CALCULATIONS

The IDS calculations (SW) reported problems with calculations, for studied steel samples, below 1000 °C due to exceeded concentration limits of some elements. Extensive tests were performed to find problematic elements, but with no success. Only limited content of most of the elements enabled calculation in this temperature region but results were incorrect and not corresponding with experimental results. For IDS calculations Sn, As, Sb were not included, because they are not defined in the IDS database and O was excluded due to defective results with high divergence to experimental values.

The Thermo-Calc calculations were performed on TC v. 2015b, using TCFE8 database. All determined elements were used for calculation, Sn, As, Sb are not defined in the TCFE8 database and were not taken into account. Oxygen was excluded due to its impact on stability of calculation in term of calculation time and results obtained.

Impact of phases allowed in TC calculation was tested as well. It is recommended to exclude only the phases we are certain can't be found in the sample during analysis. In this case, metastable equilibrium during experiment is achieved; therefore diamond and graphite phase was excluded. In general, restriction of one or two phases, present at some point during calculation, resulted in no effect on calculated temperatures. Only amount of phases differed. When calculation was restricted to only main phases (FCC, BCC, cementite, and liquid) the results were affected by significant error. Solidus temperature was the most affected by restriction of phases. Moreover, the calculation often became unstable and ended in range of $T_S$ point. Elimination of phases had no practical impact on length of calculation. The best results were obtained if all phases, except diamond and graphite phase, were allowed; therefore this setting was used as a default for calculation of important temperatures.

## 4. EXPERIMENT

Medium carbon steels were prepared from real steel castings. The samples were machined to a desired shape for each equipment and method, then polished and cleaned by ultrasound in acetone. The mass of sample was 23 - 25 g for TA and approximately 200 mg for DTA. The S1 sample contains 0.368 wt. % and S2 sample contains 0.646 wt. % of carbon. Description and setting of equipment is described e.g. in [15].

- Setaram SETSYS 18™ - DTA sensor (S - type tri-couple), (DTA);
- Netzsch STA 449 F3 Jupiter sensor (S-type, mono-couple), (TA).

The experiments were performed for low and high temperature region separately, to eliminate impacts of decarburization and to ensure, that all phase transitions and heat effects are easily identifiable.

The experiments were performed in corundum crucibles in inert atmosphere of Ar (6N). Heating rates were 10 °C.min$^{-1}$ (DTA) and 5 °C.min$^{-1}$ (TA). Measured temperatures were corrected on melting temperature of pure palladium (5N), on melting temperature of pure nickel (5N), on influence of the heating rate and on influence of the sample mass.

## 5. RESULTS AND DISCUSSION

Based on DTA and TA analysis results (**Figures 1 - 3**), following temperatures of phase transitions were determined: Eutectoid Transition ($T_E$), End of α-Ferrite to γ-Austenite transition ($T_{\alpha\rightarrow\gamma}$), Solidus ($T_S$), Peritectic transition ($T_P$), Liquidus ($T_L$). Experimental and also theoretical temperature values are presented in **Table 1.** Statistic evaluation of obtained experimental results was performed by mean values, standard deviation and variation coefficient. All measurements, in general, show high level of consistency and low level of variability. The standard deviation of the results does not exceed 2 degrees of Celsius and variation coefficient does not exceed 0.3 %. **Figure 1** presents DTA curves in low temperature region, and **Figure 2** presents DTA curves in high temperature region. For both figures, the curve 1 represents steel 1 and curve 2 represents steel 2. **Figure 3** presents only results obtained by heating process of steel 1 (curves 1/1, 1/2), and steel 2 (curves 2/1, 2/2).

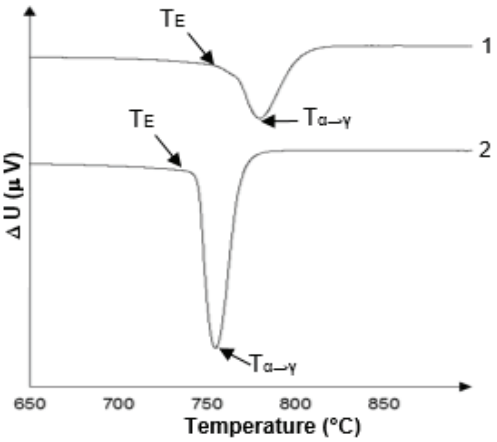


**Figure 1** DTA curves, low temperature region; steel grade 1 and 2

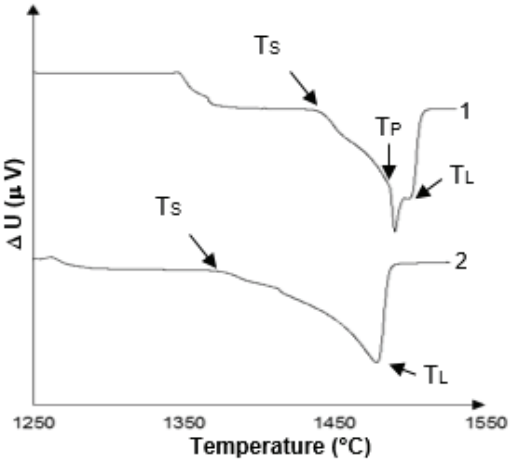


**Figure 2** DTA curves, high temperature region; steel grade 1 and 2

**Table 1** presents all measured and calculated results for both steel grades**.** Two cycles were performed, each cycle consists of heating and cooling step in high temperature region. All steps are analysed and significant temperatures are determined, but due to the high standard deviation and variation coefficient, the results from cooling step were excluded.

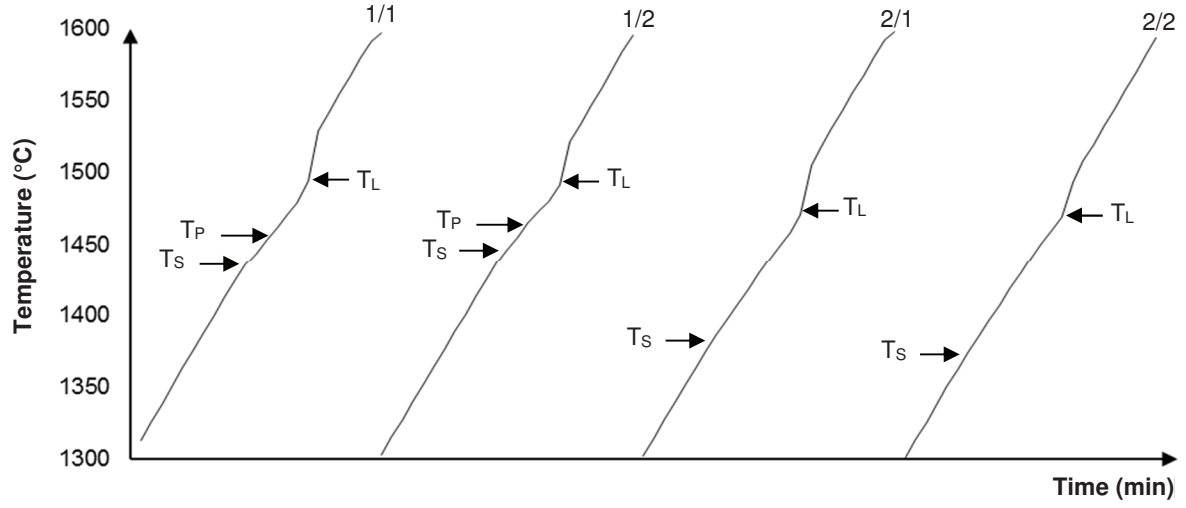


**Figure 3** TA heating curves; steel/cycle; steel grade 1 and 2; 1st and 2nd cycle

Theoretical calculations were focused on determination of all experimental temperatures obtained by DTA and TA. Calculations in high temperature region corresponded with experimental results. The low temperature region was calculated only by TC software.

**Table 1** Experimental and calculated results (°C)

| Method | Evaluation | sample S1 | | | | | | sample S2 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $T_E$ | $T_{\alpha\rightarrow\gamma}$ | $T_S$ | $T_P$ | $T_L$ | | $T_E$ | $T_{\alpha\rightarrow\gamma}$ | $T_S$ | $T_L$ |
| **TC** | | 729 | 781 | 1440 | 1486 | 1487 | | 717 | 739 | 1381 | 1478 |
| | | | | | | | | | | | |
| **IDS** | | | | 1437 | 1484 | 1497 | | | | 1383 | 1477 |
| | | | | | | | | | | | |
| **DTA** | Mean Value | 758 | 782 | 1431 | 1489 | 1492 | | 746 | 757 | 1363 | 1472 |
| | Standard Deviation | 1 | 0 | 1 | 0 | 1 | | 1 | 2 | 1 | 0 |
| | Variation Coefficient (%) | 0.12 | 0.00 | 0.09 | 0.00 | 0.08 | | 0.13 | 0.27 | 0.06 | 0.03 |
| | | | | | | | | | | | |
| **TA** | Mean Value | | | 1435 | 1479 | 1493 | | | | 1372 | 1472 |
| | Standard Deviation | | | 2 | 0 | 0 | | | | 1 | 1 |
| | Variation Coefficient (%) | | | 0.11 | 0.00 | 0.03 | | | | 0.06 | 0.03 |

### 5.1. Low temperature region

For the low temperature region two important transition temperatures $T_E$ and $T_{\alpha\rightarrow\gamma}$ were evaluated. The experiments in low temperature range were performed by DTA method only, because the TA method is not suitable for measurements in low temperature region due to the lower distinctiveness of the temperature effects on the heating or cooling curve. The temperature of magnetic transition (Currie Temperature) was not possible to determine, heat effects of phase transitions covered completely each other.

The DTA method for steel 1 presents average $T_E$ = 758±1 °C and $T_{\alpha\rightarrow\gamma}$ = 782 °C. The calculated results for steel 1 $T_E$ = 729 °C and $T_{\alpha\rightarrow\gamma}$ = 781°C. For steel 2 the average $T_E$ = 746±1 °C and $T_{\alpha\rightarrow\gamma}$ = 757±2 °C. In comparison with calculated results $T_E$ = 717 °C and $T_{\alpha\rightarrow\gamma}$ = 739°C.

The calculated eutectoid transition of steel 1 is about 29 °C below the measured value, which is the same difference as for steel 2. The end of α-ferrite to γ-austenite transition for steel 1 is only 1 °C below the measured value, while for steel 2 the difference is 18 °C.

### 5.2. High temperature region

In the high temperature region three transition temperatures $T_S$, $T_P$ and $T_L$ for steel 1 were obtained, while only $T_S$ and $T_L$ for steel 2. Peritectic transition was not observed in the steel 2. Also SWs calculations (IDS and TC) confirmed this fact.

On the basis of DTA method the following transition temperatures were determined for steel 1: $T_S$ = 1431±1 °C, $T_P$ = 1489 °C and $T_L$ = 1492±1 °C. By TA method were determined: $T_S$ = 1435±2 °C, $T_P$ = 1479 °C and $T_L$ = 1493 °C. Using IDS and TC were calculated: $T_S$ = 1437 °C, $T_P$ = 1484 °C, $T_L$ = 1497 °C and $T_S$ = 1440 °C, $T_P$ = 1486 °C and $T_L$ = 1487 °C.

On the basis of DTA method the following transition temperatures were determined for steel 2: $T_S$ = 1363±1 °C and $T_L$ = 1472 °C. By TA method were determined: $T_S$ = 1372±1 °C and $T_L$ = 1472±1 °C. Using IDS and TC were calculated: $T_S$ = 1383 °C, $T_L$ = 1477 °C and $T_S$ = 1381 °C, $T_L$ = 1478 °C.

The results in high temperature region are less clear than in the low temperature region. Both methods, the DTA and TA report high level of consistency with each other, the difference between all corresponding

temperatures is below or equal to 10. In fact, the liquidus difference for both steel grades is below or equal to 1. Therefore it can be assumed, that the both methods are comparable and the results are reliable and reproducible.

As for the software, it is not possible to determine the one more precise or closer to the measured results. In case of solidus, the TC presents better agreement for steel 2 and worse agreement to steel 1 compared to IDS. Also the calculated results of solidus by TC and IDS show lower deviation from TA than DTA for both steel grades.

In comparison with measured values of $T_L$, the calculated results of steel 1 by TC are about 5 °C below the measured value, while 5 °C above by IDS. This is the only case, where the software differed more than 3 °C from each other, if the software reached result at all, or the result was obviously faulty. The calculated $T_P$ of steel 1 is 3 °C below measured value.

The differences of theoretical and experimental values could be caused by Thermo-Calc calculation due to elements restriction (excluded O, Sn, As, Sb) and equilibrium state of all calculated values. Experimental values are obtained from measurement with real steel and all measurements are not in complete equilibrium. Also, the difference of heat conductivity of the reference and the sample can be reflected in shifted transition temperatures, because the sensors are located on the surface of the crucible or the sample, where temperature can be exceeding real transition temperature, while most of the samples volume is yet below the transition temperature.

## 6. CONCLUSION

Thermal analysis of two real medium carbon steel samples was performed. Phase transition temperatures were obtained for concrete steels and new original experimental data were obtained. Obtained results (temperatures $T_E$, $T_{\alpha\rightarrow\gamma}$, $T_S$, $T_P$ and $T_L$) were precised, compared and verified with theoretical calculations performed using TC and IDS software. Only the DTA method was used for measurement in low temperature region and only using TC was it possible to calculate and verify experimental results from low temperature region.

It is not possible to determine the one more precise software or the one closer to the measured results. The calculated solidus results by TC and IDS show lower deviation from TA than DTA for both steel grades. Besides one case, the software differed less or equal to 3 °C from each other. The TC is considered more versatile. The theoretical calculations by Thermo-Calc SW and IDS SW are providing, in some cases, relatively good calculation results, but it is always vital to check the data with an experiment.

All experimental values, in general, show high level of consistency and low level of variability. The standard deviation of the results did not exceed 2 degrees and variation coefficient did not exceed 0.3 %. It was shown that both thermo-analytical methods used are set correctly; the results are reproducible and comparable. Obtained experimental temperatures by the thermal analysis will be used to optimize production and processing of analysed steel grades.

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