

## IMPORTANT ASPECTS OF PHASE TRANSFORMATIONS TEMPERATURES STUDY OF STEELS BY USE OF THERMAL ANALYSIS METHODS

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### Abstract

The paper deals with the study of phase transitions temperatures (mainly solidus and liquidus) with use of different thermal analysis methods. The key thermal analysis methods are at the present days **DTA** (Differential Thermal Analysis), **DSC** (Differential Scanning Calorimetry) and “**direct**” thermal analysis (**TA**). The study presents the basic principles of these methods, characteristics, advantages and disadvantages. There are presented results from the high temperature region (above) 1000 °C with focus on the melting and solidifying region of multicomponent alloys such as steels. The paper discusses obtained results with three mentioned methods at heating/cooling process, with different loads of samples and other factors that can influence the obtained results. The evaluation of heating/cooling curves, DTA (DSC) - curves at heating and cooling is demonstrated. The obtained solidus and liquidus temperatures are compared and discussed.

**Keywords:** thermal analysis, conditions, methodology, liquidus, solidus, steel

### 1. INTRODUCTION

The better control of the entire steel production cycle - from selection of quality raw materials, through proper control of primary and secondary metallurgy processes, and finally, the optimum setting of casting and solidification conditions, is necessary for modern competitive steel making company. The refining processes, optimizing the slag regimes [1, 2] thermal and chemical homogenization of the melt [3, 4] or filtration of steel is very important to solve (continuously improve).

It is necessary (for each steel production company) to improve and optimize production processes continuously to compare favourably with other competitors. To improve and optimize the technological processes of steel production is it necessary to know, among others, the proper material data. One of many important data for steel production process are phase transition temperatures. In low temperature region are very important phase transition temperatures of e.g. eutectoid transformation,  $\alpha$  -  $\gamma$  transition etc., which are important for subsequent heat and mechanical treatment. In the high temperature region are the most important data temperatures of solidus and liquidus [5, 6], which are important mainly for setting of casting conditions.

This paper presents a short review of today used methods (DTA - Differential Thermal Analysis, DSC - Differential Scanning Calorimetry and TA - “direct” thermal analysis for obtaining of phase transition temperatures, particularly temperatures of solidus and liquidus. The critical insight to aspects of thermal analysis methods is one of the objectives of this paper. Selected characteristics of thermal analysis methods are presented. Some advantages and disadvantages of them are discussed.

## **2. THERMAL ANALYSIS**

Many dozens of years are used methods of thermal analysis in many branches for characterization of thermal behavior of materials at heating/cooling process and at isothermal conditions as well. Many important material properties are investigated: temperatures of phase transitions [5-8], latent heats of phase transitions [9], heat capacities [10], kinetic parameters, thermal stability of materials and others.

There are many factors that can influence the resulting data. The whole experimental arrangement of the tangible equipment (not modifiable by user) has its influence: furnace, type of sensors, count of thermocouples, etc. On the other hand there are conditions of performed experiments which can be very easy modified by user: heating/cooling rate, atmosphere, mass of sample, crucible, etc. Mentioned factors can substantially influence the resulting data.

Tangible equipment - arrangement, concrete method, experimental conditions can be the decisive factor for obtaining reliable data. Three today most frequently used methods (TA, DTA and DSC) with three experimental systems is possible to utilize for performing thermal analysis measurements at our working site.

### **2.1 Direct thermal analysis (TA)**

The "direct" thermal analysis [11] is based on the direct measurement of the temperature of the sample during its continuous linear heating/cooling or isothermal dwell. The result is the so called heating/cooling curve if heating/cooling is performed. Focused on phase transitions there is a deviation on heating/cooling curve from the otherwise linear curve progression during the running phase transformation in the samples. It is possible to obtain temperatures of phase transformations based on the curve deviations (e.g. liquidus and/or solidus temperatures) if the heat effect of phase transition and sensor sensitivity is large enough.

### **2.2 Differential thermal analysis (DTA) and Differential scanning calorimetry (DSC)**

The Differential Thermal Analysis (DTA) [11] and/or the Differential Scanning Calorimetry (DSC) [11] are methods based on the same principle. The principle of these methods is based on measurement of the temperature difference between the measured sample and reference. Reference can be an empty reference crucible or reference crucible with a standard material. The sample and reference are subjected to the same settings of temperature program of the continuous linear heating/cooling (in special cases isothermal dwell). The result is the DTA (DSC) curve expressing the dependence of temperature difference (if calibration with respect to the heat performed the heat fluxes difference) between the measured sample and reference. If there is on-going any phase transformation in the sample, there is a deflection from the baseline (peak is formed). It is possible to obtain the temperatures of phase transformations by interpretation of such peaks for given experimental conditions and many other parameters.

### **2.3 Experimental base used at our working site**

There are used many experimental systems for determination of solidus and liquidus temperatures of many materials included steels also: Setaram, Netzsch, Mettler, TA Instruments and others.

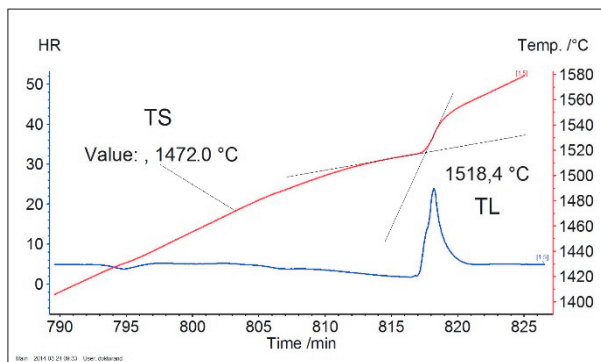
There are three devices at our working site that can be used for obtaining of solidus and liquidus temperatures. These apparatuses are from two different manufacturers and are used in three modifications. Netzsch STA 449 F3 Jupiter is used for direct thermal analysis (TA, S - type thermocouple), Setaram SETSYS is used with DTA sensor (S - type tri-couple) and Setaram MHTC (Multi High Temperature Calorimeter) is equipped with 3D DSC sensor (B - type). More specific information about these apparatuses can be found in [9].

### 3. EXPERIMENT

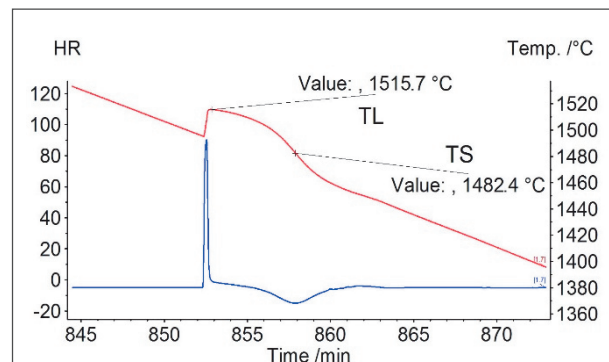
Steel samples (low carbon steel: with approximately 0.08 wt.% C and 0.6 wt. % Mn) were prepared from real steel castings delivered from ArcelorMittal Ostrava a.s. Samples were machined in to the desired shape for each equipment and method, then polished and cleaned by ultrasound impact in acetone. The mass was: 23 - 25 g for TA, around 1.2 g for 3D DSC and approximately 180 mg for DTA. Experiments were performed at five different heating/cooling rates by TA (1, 5, 10, 15 and 20 °C·min<sup>-1</sup>), at one heating rate using MHTC (5 °C·min<sup>-1</sup>) and DTA (10 °C·min<sup>-1</sup>). Temperature calibration was performed using pure nickel (5N) and its standard melting temperature 1455 °C. Selected results: heating/cooling curves, DTA and DSC curves are presented on **Figs. 1-6**. Experiments were performed in corundum crucibles in inert atmosphere of Ar (6N). Different heating/cooling conditions were not performed with these steel samples using DTA and DSC. Experiments demonstrating the influence of heating/cooling rate on shift of temperatures of liquidus and solidus (with samples analysed by 3D DSC and DTA) were partially published in [5, 12]. In addition to that the study of influence of mass of sample using 3D DSC and DTA was performed earlier as well [12]. Temperatures of solidus and liquidus obtained using 3D DSC and DTA were corrected besides correction with respect to the melting point of pure nickel on influence of heating rate and influence of mass of sample.

### 4. RESULTS AND DISCUSSION

Based on the curves evaluation the temperatures of solidus  $T_S$  and liquidus  $T_L$  were derived for all the performed experiments. Only selected curves: for heating and cooling rate 5 °C·min<sup>-1</sup> are presented, **Figs. 1-6**. The results obtained for the same heating and cooling rate slightly differ. That fact is caused mainly due to the arrangement of the equipment alone, sample mass, sensitivity of sensors used and from other aspects (inhomogeneous temperature field, releasing/absorbtion of latent heat during running phase transition, change of chemical composition - possible decarburisation, contact of sample with sensor-crucible,...). Furthermore, the evaluation of obtained curves can be in some cases very difficult (overlapping of heat effect, not sharp deviation from base line,...), see **Figs. 1-6**.



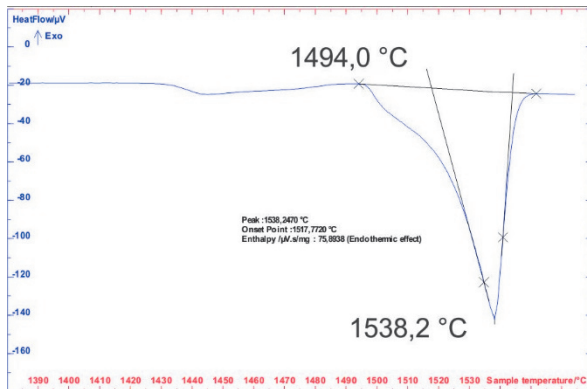
**Fig. 1** Heating curve, TA, 5 °C·min., Netzsch STA 449 F3 Jupiter



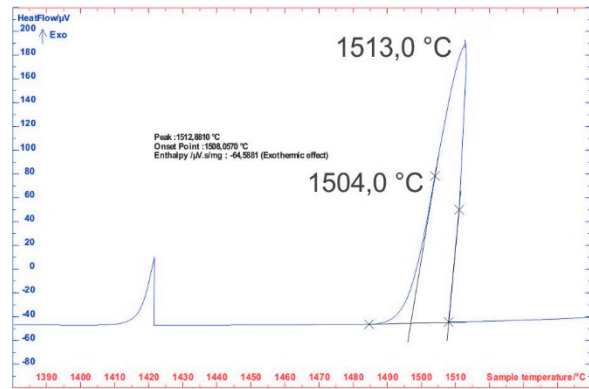
**Fig. 2** Cooling curve, TA, 5 °C·min., Netzsch STA 449 F3 Jupiter

Temperatures of phase transitions were evaluated also for other heating and cooling rates (TA) according to the generally accepted methodology modified for multicomponent systems. **Table 1** presents experimental values of temperatures obtained by all three different methods (by TA corrected to melting point of pure nickel only, 5N) and different heating and cooling rates.

Among others were phase transition temperatures calculated with use of thermodynamic and kinetic SW (Thermocalc, Computherm, IDS and calculation relation used in ArcelorMittal Ostrava a.s., **Table 2**.

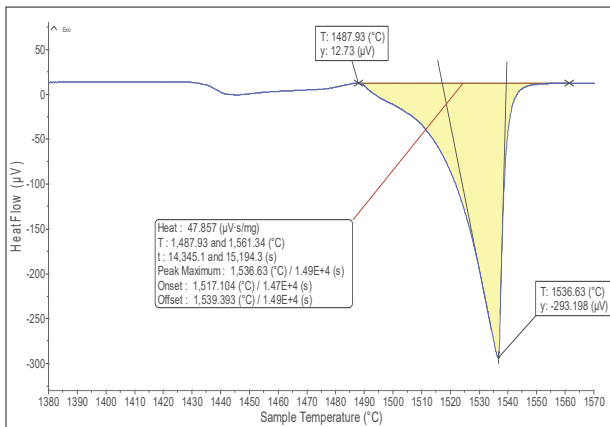


**Fig. 3** DTA curve, heating 5 °C·min.<sup>-1</sup>, Setaram SETSYS 18<sup>TM</sup>

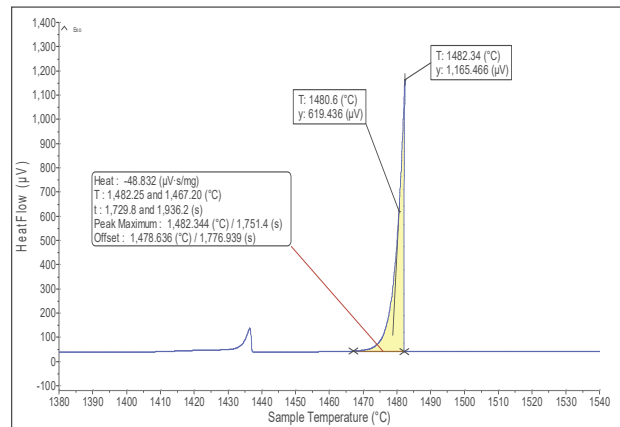


**Fig. 4** DTA curve, cooling 5 °C·min.<sup>-1</sup>, Setaram SETSYS 18<sup>TM</sup>

**Table 1** presents also temperature values obtained for DTA and DSC, but only for heating (small samples). The main reason is as follows. Due to a difficulties with origination of the first critical nuclei at the cooling process, mainly by using small samples, the values could be sometimes not representative (it is possible to obtain for some conditions of cooling different values - in some cases dozen of degrees). Different degree of undercooling can be encountered.



**Fig. 5** DSC curve, heating 5 °C·min.<sup>-1</sup>, Setaram MHTC



**Fig. 6** DSC curve, cooling 5 °C·min.<sup>-1</sup>, Setaram MHTC

Temperatures of solidus obtained at heating by TA are almost the same for each heating rate (mean value is 1479 °C). Mean value is lower than mean value obtained for cooling process. For lower cooling rates is  $T_s$  higher at cooling process (below 10 °C·min<sup>-1</sup>). For 10 °C·min<sup>-1</sup> is the same. For higher cooling rates are  $T_s$  lower than obtained at heating (above 10 °C·min<sup>-1</sup>). The maximum difference in case of  $T_s$  is 13 °C (calculated from mean values and considering heating and cooling also). It seems that solidus temperature is relatively strongly dependent on cooling rate. Calculated values of solidus are very close to the experimental values, maximum deviation is 11 °C (temperatures of solidus very often differ if compared results from different experiments, if compared experimental results and calculations - differences can be in order of dozens of degrees).

Temperatures of liquidus obtained by TA at heating are slightly higher than the values obtained by cooling, that was observed also by [13]. It was achieved excellent agreement between experimental values and also between experimental and calculated values. The maximum difference between presented values is 4 °C.

**Table 1** Experimental temperatures of solidus  $T_s$  and liquidus  $T_L$ 

|                      | TA      |             |             |         |             |             | 3D DSC  |             |             | DTA   |             |             |
|----------------------|---------|-------------|-------------|---------|-------------|-------------|---------|-------------|-------------|-------|-------------|-------------|
|                      | Heating |             |             | Cooling |             |             | Heating |             |             |       |             |             |
|                      | Rate*   | $T_s$       | $T_L$       | Rate*   | $T_s$       | $T_L$       | Rate*   | $T_s$       | $T_L$       | Rate* | $T_s$       | $T_L$       |
|                      |         | (°C)        |             |         | (°C)        |             |         | (°C)        |             |       | (°C)        |             |
| STEEL                | 1       | 1478        | 1524        | 1       | 1509        | 1523        | 5       | 1487        | 1523        | 10    | 1493        | 1523        |
|                      | 5       | 1479        | 1525        | 5       | 1489        | 1523        |         | 1486        | 1522        |       | 1491        | 1522        |
|                      | 10      | 1479        | 1525        | 10      | 1479        | 1521        |         | 1486        | 1523        |       | 1494        | 1524        |
|                      | 15      | 1479        | 1525        | 15      | 1474        | 1521        |         | 1486        | 1522        |       | 1492        | 1524        |
|                      | 20      | 1480        | 1525        | 20      | 1470        | 1520        |         | -           | -           |       | 1491        | 1523        |
| Mean Value           |         | <b>1479</b> | <b>1525</b> |         | <b>1484</b> | <b>1522</b> |         | <b>1486</b> | <b>1523</b> |       | <b>1492</b> | <b>1523</b> |
| Mean Deviation       |         | 0,7         | 0,5         |         | 13,8        | 1,2         |         | 0,4         | 0,5         |       | 1,2         | 0,7         |
| Variation Coeff. (%) |         | 0,05        | 0,03        |         | 0,93        | 0,08        |         | 0,03        | 0,03        |       | 0,08        | 0,05        |

\*heating or cooling rate in °C.min<sup>-1</sup>

To obtain reliable phase transition temperatures is a difficult task. Many authors do that, but don't take in to the consideration the whole arrangement of the equipment and conditions, from which can arise differences, others do that reliable but have only one method and equipment. It is necessary to think about temperature fields in samples (large vs. small samples; the colder parts of samples are heated by warmer and vice versa; these effects arise mainly if larger sample are used [14]), it is necessary to consider detection limits of sensors, it is necessary to take in to the consideration that different alloys - especially multicomponent systems like steels can behave in the different manner, it is necessary to consider possible change of chemical composition in some cases. The amount of latent heat absorbed/released during phase transition has also its significant influence on the possible detection of phase transition temperatures.

**Table 2** Calculated temperatures of solidus  $T_s$  and liquidus  $T_L$ 

| STEEL | Thermocalc <sup>1</sup> |       | IDS <sup>2</sup> |       |                      |       | Computherm <sup>3</sup> |       | AMO <sup>4</sup> |       |
|-------|-------------------------|-------|------------------|-------|----------------------|-------|-------------------------|-------|------------------|-------|
|       | Equilibrium             |       | Equilibrium      |       | Cooling 0.01 °C/min. |       | Equilibrium             |       | -                |       |
|       | $T_s$                   | $T_L$ | $T_s$            | $T_L$ | $T_s$                | $T_L$ | $T_s$                   | $T_L$ | $T_s$            | $T_L$ |
|       | 1480                    | 1525  | 1485             | 1525  | 1485                 | 1525  | 1490                    | 1527  | -                | 1521  |

<sup>1</sup>SW Thermocalc ver. 3.1, database TCFE7.  
<sup>2</sup>SW Solidification analysis package, not included following elements: V, Ti, B, Nb, Sn, Al, N, O.  
<sup>3</sup>SW Computherm, not included following elements: B, Sn, Al, N, O.  
<sup>4</sup>ArcelorMittal Ostrava a.s. calculation.

It is possible to conclude (on the basis of our long term experiences) that differences between solidus temperatures obtained using different equipments and methods or with calculation and modelling results can differ substantially in comparison with temperatures of liquidus. If compared temperatures of solidus the differences are often in the order of dozens of degrees. If compared temperatures of liquidus the differences are often in order of degrees (relatively high differences are not unusual). These differences arise mainly from above mentioned factors that can substantially influence the mechanisms of phase transitions also.

## CONCLUSIONS

In this work were presented possibilities of measurement of solidus and liquidus temperatures using our three measurement systems Netzsch STA 449 F3 Jupiter, Setaram SETSYS 18™ and Setaram MHTC in different

arrangement. Three different amounts of samples were analysed, different heating and cooling rates. Some factors having influence on obtained quantities were discussed. For solidus temperature were observed higher differences (up to 13 °C) in case of temperatures of liquidus was achieved excellent agreement. The following work at our working site will continue in this research area, because of the necessity to obtain proper data and consequently it gives the possibility to optimize technological process of con-casting in the conditions of ArcelorMittal Ostrava a.s.

## ACKNOWLEDGEMENTS

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