COMPARISON OF LIQUIDUS AND SOLIDUS TEMPERATURES OF CONTINUOUSLY CAST STEELS DETERMINED BY DIFFERENT THERMO-ANALYTICAL METHODS

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Abstract

Thermo-analytical methods are commonly used for phase transformation temperature identification in a lot of science and industrial applications. Currently, there are most frequently methods based on very small samples analyses like a differential scanning calorimetry (DSC) and/or a differential thermal analysis (DTA) realised for various materials mostly in combination with a thermo-gravimetry (DSC/TG; DTA/TG respectively). The aim of such methods of tiny samples is to fit a transformation process without an influence of the sample mass and to get universal like conclusions. On the other hand, older direct thermal analytical method generally done on tens grams and larger samples are not so popular now excluding few applications regarding to cast iron and/or non-ferrous metals and their modifying process monitoring. However, simultaneous utilisation of both mentioned methods during determination of real steel liquidus (T_L) and solidus (T_S) temperatures leads to suppressing their individual disadvantages and enable to fit the results for such heterogeneous material like steel in the best possible way. The paper is focused on the discussion of T_L and T_S of 18 continuously cast steels analysed in the frame of No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program”. The submitted evaluation shows an importance of the parallel utilization of methods, accuracy and reproducibility of the results and also the deviations of the experimentally determined T_L and T_S and empirically calculated values of the industrial partner and values obtained by thermodynamic calculations.

Keywords: Steel, solidus temperature, liquidus temperature, thermal analysis, thermodynamic calculations

1. INTRODUCTION

Constantly increasing and strict requirements on quality of continuously cast round billets and cast steel require a comprehensive approach to solve whole process of steelmaking. To ensure of cleanliness and micro-purity of steel [1,2], the correct adjustment of the slag regime [3-5] during the secondary steel refining process plays a significant role. The assessment of strength characteristics is important for assuring the high quality of steel [6,7].

A numerical simulation also has considerable importance in steelmaking process. The implementation of simulation results [8-11] can significantly affects the quality of produced steel. Thermodynamic properties of materials, especially for casting and solidification of the steel, the solidus (T_S) and liquidus (T_L) temperature are among the most crucial parameters [11,12]. Precise knowledge of T_L is particularly important in relation to the superheat setting of steel before its casting. T_S is related with the solidification process and range of two-phase region between T_L and T_S, which by segregation phenomena is affected [13-17]. Knowledge of these critical temperatures is necessary not only for the correct setting of the technology of steel casting and proper solidification of steel, but also for precise setting of simulation conditions of steel solidification.

This paper follows the previous research in the field of thermal analysis in the frame of a project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program”. Now, it summarises the results obtained for 18 steel grades cast into round billets. The significance of parallel utilization of both presented methods of thermal analysis for an industrial practice of steel casting is evident.

2. METHODS USED FOR THE IDENTIFICATION OF SOLIDUS AND LIQUIDUS TEMPERATURES

Currently, it is possible to utilise a several dozens of thermo-analytical methods. Three of them are the most popular. In the field of thermal analysis, in the range of one half to three quarters of all professional works, these methods are employed: Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) [18-25]. Simultaneous combinations as TG/DTA and TG/DSC are often applied. In the past, Direct Thermal Analysis (direct measurement of the temperature change of the studied sample esp. under the linear cooling conditions) was also widely used [26]. This method is still applicable for measuring T_L and T_S of metallic materials.

Generally, thermal analysis (TA) [27-30] allows to monitor the changes in the study material by measuring selected physical properties in dependence on time or temperature (phase transformations, heat capacity etc.). TA methods are predominantly dynamic processes and allow to obtain information about the status change of the sample. These processes require a non-isothermal temperature regime (usually linear heating or cooling of the sample). Changes of the studied material either directly by measuring the selected physical properties or indirectly by measuring of the properties at the surrounding of the sample are determined.

A combination of two thermo-analytical methods (TA methods) - *Direct Thermal Analysis (DirTA)* and *Differential Thermal Analysis (DTA)* on two different professional systems for different sample mass (approx. 22 g, resp. 120-210 mg) for study of T_L and T_S temperatures of investigated steels were used. Results from both TA methods (T_L and T_S temperatures) and the empirical calculations and predictions by modern commercial SWs for phase transformation temperatures determining are also compared. A combination of all approaches ensures the achievement of the maximum possible correctness of the results.

T_L and T_S temperatures under the linear heating/cooling conditions, and also under cyclic experiments (2 heating and cooling cycles, under the same conditions) by DirTA were acquired. Only under the linear heating conditions, T_L and T_S temperatures by DTA were determined. Experimental results (T_L and T_S from DirTA and DTA) with empirically calculated T_L and T_S temperatures (by empirical equations of industrial partner INDUSTRY) were compared. Experimental values were also predicted by modern commercial SWs IDS (Solidification Analysis Package), Computherm or Thermo-Calc (database TCFE7) by own calculations (with regard to chemical composition available).

3. RESULTS AND DISCUSSION

Completely 18 melts of 18 steel grades are discussed. T_S and T_L temperatures were experimentally determined for each steel grade by both methods of thermal analysis (DirTA and DTA). The aim of the paper is not a detail analysis of the results for individual steel grade, but to achieve a comprehensive view on the results obtained not only by DirTA and DTA thermo-analytical methods, but also based on their confrontation with T_L, resp. T_S, predicted by empirical equations used in conditions of industrial partner (INDUSTRY) and with two thermodynamic professional SWs (IDS, Computherm or Thermo-Calc). Therefore, T_S temperature by DTA under the conditions of linear cooling weren't identified. However, due to the higher sensitivity of the sensor, T_S temperature for all investigated steels by DTA, were also determined.

3.1. The analysis of the liquidus temperature

Experimentally and empirically determined T_L for analysed steel grades are summarized in **Table 1**. Experimentally captured T_L temperatures in the average form and as corrected values of the experimental conditions obtained from two correctly performed analyses are presented.

Table 1 Liquidus temperatures obtained by different methods; °C

Steel grade	DTA	dirTA		INDUSTRY	IDS	Computherm or Thermo-Calc*
	Heating	Heating	Cooling			
A	**1523**	1521	1518	1521	1521	1527
B	**1517**	1516	1511	1516	1521	1522
C	1510	**1514**	1511	1510	1517	1517*
D	**1515**	**1515**	1511	1512	1518	1518
E	1517	**1520**	1517	1517	1521	1518*
F	1511	**1515**	1512	1513	1517	1517*
G	1482	**1489**	1486	1486	1492	1493*
H	1492	**1493**	1487	1492	1497	1498*
I	**1472**	**1472**	1461	1467	1477	1477*
J	**1509**	**1509**	1505	1508	1513	1513*
K	1485	**1496**	1490	1488	1494	1494*
L	1486	**1489**	1484	1483	1492	1492*
M	1481	**1487**	1481	1480	**1487**	**1487***
N	1498	**1503**	1499	1497	1502	**1503***
O	1488	**1491**	1486	1485	**1491**	**1491***
P	1516	**1520**	1517	1516	**1520**	1527*
Q	1502	**1506**	1502	1503	1508	1508*
R	1513	**1516**	1513	1511	1515	1511*

The following approach has chosen to obtain one final T_L temperature which should be recommended as optimal T_L temperature for the adjustment of steel casting technology:

1) Presented experimental results have high degree of reproducibility and are more accurate than empirically calculated.

2) To avoid a threat (based on recommended temperatures by TA) of steel casting process, the highest T_L temperature from the three T_L experimentally determined (TA) temperatures (2x linear heating, 1x linear cooling) is recommended for each melt (grey mark and bolt font in **Table 1**).

Values got by dirTA method are selected for a final recommendation of T_L temperature from linear heating conditions for almost of all studied steel grades (also evident in **Table 1**). T_L based on linear heating DTA conditions fits the higher and final recommended value five times. Values obtained under the linear cooling and dirTA condition are lower than recommended value for each studied steel grades.

Related to the calculated T_L values, it could be stated that no one value predicted by system used for T_L prediction in the industrial conditions fits the real T_L for defined steel grades. T_L predicted by industrial partner are lower than experimentally determined ones in every studied case. However, the difference is almost up to 4 Celsius degrees. Applied thermo-dynamical SWs fits only four experimentally determined T_L and such calculated values varies in the difference interval <-5; 7> °C for all used SWs except IDS prediction for F steel grade (+28 °C difference).

3.2. The analysis of the solidus temperature

Solidus temperature appears to be less significant than T_L in the operational conditions of steelmaking. However, its importance can't be ignored, especially in the content of internal quality influencing. The main reason is that in the two-phase region between T_L and T_S temperatures, the conditions supporting a number of processes with a negative impact on the quality of cast steel exist. Correct setting of T_S and T_L temperatures can significantly affects the results of numerical simulations whose are necessary to recommended interventions to optimise the casting process. T_S temperatures are summarized in **Table 2**.

Table 2 Solidus temperatures obtained by different methods; °C

Steel grade	DTA	dirTA		IDS	Computherm or Thermo-Calc*
	Heating	Heating	Cooling		
A	1,492	**1,484**	**1,484**	1,485	1,490
B	1,488	1,482	**1,469**	1,482	1,490
C	1,485	1,478	**1,467**	1,477	1,457*
D	1,489	1,482	**1,469**	1,477	1,486
E	1,489	1,482	**1,471**	1,483	1,469*
F	1,472	1,479	**1,463**	1,418	1,476*
G	**1,422**	1,424	1,453	1,418	1,409*
H	**1,430**	1,435	1,439	1,437	-
I	1,463	**1,372**	1,433	1,383	1,366*
J	1,479	1,468	**1,462**	1,471	1,424*
K	**1,418**	1,430	1,449	1,421	1,405*
L	**1,418**	1,419	1,440	1,424	-
M	**1,415**	**1,415**	1,440	1,413	-
N	**1,447**	1,449	1,451	1,446	1,449*
O	**1,426**	**1,426**	1,443	1,422	1,398*
P	**1,450**	1,464	1,473	1,484	1,485*
Q	1,462	1,453	**1,444**	1,447	1,427*
R	1,479	1,480	**1,461**	1,480	-

As the final recommended T_S (from TA analysis) for practical use in conditions of industrial partner, the lowest values (grey mark and bolt font in **Table 2**) were selected in accordance with the above approach. Unlike previously discussed T_L and **Table 1**, the more variable distribution of the final recommended solidus temperatures is evident. No one method is dominant; this highlights the positive impact of different methods and the mass of sample usage on a proper selection of crucial temperatures for one steel grade. Generally known difficulties with the correct identification of T_S are obviously also based on the fact that no SW's predicted values fit the experimentally determined and selected T_S. Data related to T_S from industrial partner were not delivered for comparison. It was not possible to calculate all T_S by SW due to specific limitations.

The **Table 3** with divergences from the final recommended T_S obtained by different methods underlining the difficulties with T_S determination given by the non-uniformity of steel behaviour during solidification including varying conditions on the one side and also given by complicated numerical describing of all mechanisms related to the nucleation and solidification of such heterogeneous and multi-component material like steel.

Table 3 Divergences from the final recommended T_S obtained by different methods; °C

Steel grade	DTA	dirTA		IDS	Computherm or Thermo-Calc*
	Heating	Heating	Cooling		
A	8	**0**	**0**	1	6
B	19	13	**0**	13	21
C	18	11	**0**	10	-10*
D	20	13	**0**	8	17
E	18	11	**0**	12	2*
F	9	16	**0**	-45	13*
G	**0**	2	31	-4	-13*
H	**0**	5	9	7	-
I	91	**0**	61	11	-6*
J	17	6	**0**	9	-38*
K	**0**	12	31	3	-13*
L	**0**	1	22	6	-
M	**0**	**0**	25	-2	-
N	**0**	2	4	-1	2*
O	**0**	**0**	17	-4	-28*
P	**0**	14	23	34	35*
Q	18	9	**0**	3	-17*
R	18	19	**0**	19	-

Furthermore, it is also possible to observe that divergences of T_S temperature obtained by different methods from the final recommended values (**Table 3**) are more pronounced (usually in the order of tens of degrees of Celsius for individual melts) than in the case of T_L identification. However, there are steel grades where these differences are less than 10 °C. Due to the procedure of recommendation of final T_S temperatures - recommended T_S values are always lower than other thermal analysis methods' results. With the use of thermodynamic SWs, some calculated values were higher, other lower than the final recommended T_S obtained based on thermal analysis methods.

3.3. Analysis of two-phase region between T_L and T_S

To illustrate an importance of proper determination of T_S was further proceeded to compare the temperature interval between the two-phase region between T_L and T_S (**Table 4**).

Values of the temperature interval from T_L to T_S recommended by the thermal analysis in column TA in **Table 4** can be registered. Temperature intervals achieved by each other type of prediction (IDS; Computherm or Thermo-Calc) in the next three columns are demonstrated. The last three columns show values of the differences between the values of Thermal Analysis (TA) and values of the intervals obtained by the SW's calculations/predictions.

Conclusively, differences in the prediction of the two-phase temperature interval for individual steel grades within the individual prediction method exist. The range of the temperature interval of two-phase region identified by the TA methods, as well as SW's predicted values, is in the order of tens or hundreds of degrees of Celsius.

When comparing the temperature intervals of the range of the two-phase region, determined by the empirical calculations, it is possible to find close temperature intervals and conversely wider temperature intervals than were experimentally determined by TA methods (**Table 4**). Ranges of two-phase regions from SWs were predicted in some cases close in other ones they were wider than determined by TA methods.

Table 4 Range of two-phase temperature intervals for individual steel grades by the use of different methods of their identification and divergences of calculated range against experimentally determined range; °C

Steel grade	TA	IDS	Computherm or Thermo-Calc*	Divergences from TA values	
				IDS	Computherm or Thermo-Calc*
A	31	36	37	5	6
B	29	39	32	10	3
C	29	40	60	11	31
D	26	41	32	15	6
E	31	38	49	7	18
F	36	99	41	63	5
G	36	74	84	38	48
H	54	60	-	6	-
I	100	94	111	-6	11
J	30	42	89	12	59
K	47	73	89	26	42
L	49	68	-	19	-
M	47	74	-	27	-
N	52	56	54	4	2
O	48	69	93	21	45
P	47	36	42	-11	-5
Q	44	61	81	17	37
R	36	35	-	-1	-

4. CONCLUSION

The paper presented results of determination of liquidus and solidus temperatures for various steel grades cast into the round billets by different methods. Two methods of thermal analysis were employed. On Netzsch STA 449 F3 Jupiter experimental system, method of direct thermal analysis (dirTA) was applied. Steel samples by Differential Thermal Analysis (DTA) were analysed by Setaram SETSYS 18$_{TM}$ experimental system. Results of thermal analysis methods with the predictions of the solidus and liquidus temperatures calculated by sophisticated programs Computherm or Thermo-Calc and IDS were compared.

Acquired knowledge can be summarised as follows:

1) Because the real analysis performed using standardized methods on real samples, not by means of empirical calculations, T_L and T_S temperatures obtained by thermal analysis methods were selected for further evaluation.

2) It is obvious, that the parallel application of different methods of thermal analysis and different mass of the steel samples makes it possible to compare the results of these analyses and then recommend the more critical and proper T_L and T_S values.
3) Divergences between T_L temperatures for individual steel grades across the different used methods of prediction as were compared were generally less problematic that T_S determination. However, these divergences can’t be generally considered insignificant even in the case of T_L.
4) Temperature ranges from T_L to T_S in most cases show significant differences depending on the choice of the used method of prediction. Here, the impact of choosing the final recommended T_L and T_S is the most significant.

These findings indicate that the problematic of verification of T_L and T_S temperatures requires a comprehensive approach using multiple methods of solution. More significant differences against calculations can be expected especially for special steels grades with a different content of carbon and/or alloying elements. Finally, the operational experiments in real plant conditions should be proceeded to adjustment of the casting technology to gain savings not only in the field of superheat temperature of steel before casting but also for better prediction of two-phase zone and cooling zone setting.

Furthermore, it is appropriate to implement measured results into numerical simulations focused on the optimization of steel casting technology and solidification of the steel. It should lead to more accurate results corresponding to real conditions.

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