DIFFERENCES BETWEEN EXPERIMENTALLY DETERMINED AND CALCULATED LIQUIDUS AND SOLIDUS TEMPERATURES OF LARGE DIAMETER CONTINUOUSLY CAST STEEL

STROUHALOVÁ Michaela[1], GRYC Karel[1], SMETANA Bedřich[2], ZLÁ Simona[2], SOCHA Ladislav[1], MICHALEK Karel[1], KALUP Aleš[2]

[1]*VSB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Metallurgy and Foundry, and Regional Materials Science and Technology Centre, Czech Republic, EU*
michaela.strouhalova@vsb.cz, karel.gryc@vsb.cz, ladislav.socha@vsb.cz, karel.michalek@vsb.cz

[2]*VSB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Physical Chemistry and Theory of Technological Processes, and Regional Materials Science and Technology Centre, Czech Republic, EU*
bedrich.smetana@vsb.cz, simona.zla@vsb.cz, ales.kalup@vsb.cz

Abstract

The methods for determination liquidus (T_L) and solidus (T_S) temperatures in high-temperature region for selected steel grade were compared in the frame of this paper. The paper deals with discussion of the results obtained by the two different simultaneous methods of high-temperature thermal analyses (Direct Thermal Analysis and DTA) on the high-sophisticated specialized experimental systems (Netzsch STA 449 F3 Jupiter, Setaram SETSYS 18$_{TM}$). The continuously cast steel with large diameter (350 mm) was studied. Based on mentioned dynamic thermo-analytical methods the T_S and T_L temperatures under different heating/cooling conditions were determined. On large samples (approx. 21 g), the method of Direct Thermal Analysis (DirTA) in conditions of linear heating and cooling was applied. On small samples (approx. 150 mg), the experiments using Differential Thermal Analysis (DTA) under conditions of linear heating were realized. Finally, the data acquired from thermo-analytical measurements were compared with values from calculations by specialized programs (ThermoCalc and IDS software) and with liquidus temperature currently defined in practice of continuous casting of discussed steel grade.

Keywords: Steel, continuous casting, thermal analysis, thermodynamic software, liquidus and solidus temperature

1. INTRODUCTION

Metallurgical processes related to steel production are strongly connected with knowledge of the thermo-physical and thermodynamic properties of metal materials during overall process steps. Methods of thermal analyses allow studying thermo-physical and thermo-dynamic properties of metallic systems. They also describe behaviour of such systems under strictly specified conditions in dependence on time and/or temperature [1-4].

Material properties of metal systems based on iron are determined by its chemical composition, which is closely associated with the whole technological process of steelmaking. In the steelmaking practice metal alloys are produced from a liquid state - from a liquid metal. The most important phase transformations at the process of casting a liquid metal (steel casting) are connected with the process of crystallization, resp. process of own solidification - phase transformation of metal material from liquid to solid state [5]. Solidification process is decisive influenced by a type, quantity, size of defects and their distribution in the volume of the solidified metal. Moreover, the phase transformation process involves solidification of the cast steel also morphological, physical and volume changes. Interval of own solidification process of cast steel is a serious source of dangerous defects in the cast steel [6, 7]. The solidification process is connected with segregation phenomena

that significantly reduce utility properties of cast steel and the operational reliability of the final product [8-10]. From the perspective of the possibility of impacts on the quality of the cast steel (steel is multicomponent melt with wide range of non-metallic phases), the knowledge of solidification process is very important [11, 12]. Results from a study of material structure and their characteristic properties is very important from the view point of correct setting of boundary conditions for numerical modelling that is very often used for optimising modern metallurgical processes [13-15].

Specifically, for steel casting and solidification of steel, temperatures of phase transformations in high temperature region (1200-1600 °C) are important. Phase transformation temperatures, that form a boundary zone (region) of solidification process of cast steel are T_L and T_S temperatures. T_L is connected with the setting of superheat of steel before casting, while the T_S is associated with the width of two-phase zone and may indicate the effects of segregation phenomena.

This paper augments the previous works in the field of thermal analysis of industrially produced steel grades. The authors already have a lot of experience using various methods of thermal analyses, e.g. [16]. From the history of Department of Metallurgy and Foundry of VSB - Technical University of Ostrava can refer these [17]. Now, differences between experimentally determined T_L and T_S temperatures of continuously cast large diameter rounds and also their calculated T_L a T_S by specialized programs are discussed in this paper. Two different thermo-analytical methods (Direct Thermal Analysis and DTA) and two different high-sophisticated laboratory systems (Netzsch STA 449 F3 Jupiter, Setaram SETSYS 18$_{TM}$) to obtain the experimental data were used.

Besides, the method of direct thermal analysis in the study of cast iron is also used [18-20].

2. CONDITIONS OF EXPERIMENTAL MEASUREMENTS

On Netzsch STA 449 F3 Jupiter experimental apparatus, measurements of steel samples approx. 21 g by DirTA method (a direct measurement of temperature in time dependence of the studied sample during its controlled linear heating/cooling) were realised. T_L and T_S temperatures under the conditions of linear heating and cooling and also under cyclic experiments (2 heating and cooling cycles performed under the same conditions) were obtained. Setting of the measurements were as follow: in the first cycle of measurement the sample of steel was heated at high heating rate (20 °C.min^{-1}) to a temperature 1300 °C, where high-temperature region starts, then it was heated by selected heating rate 5 °C.min^{-1} (1st heating) to a temperature, at which the sample completely gone in the liquid phase (1580 °C). From this temperature it was cooled by cooling rate 5 °C.min^{-1} (1st cooling) until complete solidification (1300 °C), and subsequently in second cycle of measurement was heated again by same heating rate 5 °C.min^{-1} (2nd heating) to complete melting (1580 °C) and then cooled by cooling rate 5 °C.min^{-1} (2nd cooling).

The Setaram SETSYS 18$_{TM}$ experimental system for measurements of small steel samples approx. 150 mg with DTA method (a measurement of temperature difference between sample and reference) was also used. In this case, the T_L and T_S temperatures only under the conditions of linear heating were determined. Heating of the sample at high heating rate (30 °C.min^{-1}) from 20 to 1200 °C (eventually to 1350 °C) was carried out, after that from 1200 °C (eventually 1350 °C) to 1600 °C by heating rate 10 °C.min^{-1}. After the complete melting, a sample was cooled by same heating rate to 1100 °C and then cooled by high heating rate to ambient temperature.

Steel samples in a desired shape corresponding to each experimentally arrangement (DirTA or DTA) in corundum crucibles in the surrounding of inert atmosphere of pure argon of high purity were analysed. All experimental measurements (according to each method) under the same experimental conditions were carried out. Summary of the measurement setup is shown in **Table 1**.

Table 1 Experimental setup

Method	Experimental conditions	
Direct Thermal Analysis (DirTA)	Atmosphere: dynamic inert (Ar, purity 6N, 50 ml.min^{-1})	Temperature program: linear heating/cooling, heating/cooling rate 5 °C.min^{-1}
	TG measuring sensor (rod): "S" type thermocouple	Thermocouple: Pt/PtRh 10 %
Differential Thermal Analysis (DTA)	Atmosphere: dynamic inert (Ar, purity 6N, 2 l.hour^{-1})	Temperature program: linear heating, hearting rate 10 °C.min^{-1}
	TG/DTA measuring rod: "S" type tri-couple	Thermocouple: Pt/PtRh 10 %

Before determination T_L and T_S temperatures a number of methodological experiments (calibration experiments with standard metals) were realized. Values of temperature correction, expressing the effect of influence of experimental conditions (with respect a melting point temperatures of pure standard materials) on T_L and T_S obtained by using DirTA and DTA thermo-analytical methods were quantified.

3. RESULT AND DISCUSSION

From the series of thermal analyses experiments, T_L and T_S temperatures of samples of investigated continuously cast steel (with such content of main elements (wt.%): C = 0.2; Mn = 1.15; Si = 0.3) were determined. Experimental results (already including a correction) are discussed below.

3.1. Direct Thermal Analysis vs. DTA results

Temperatures of T_L and T_S for both cycles of heating (H1; H2) and cooling (C1; C2) of steel samples from the evaluation of heating and cooling curves in the high temperature region were obtained (**Table 2**).

Table 2 DirTA: Experimentally determined liquidus and solidus temperatures

Sample	T_L; °C	T_S; °C
1 H1	1510	1471
1 C1	1505	1462
1 H2	1511	1471
1 C2	1505	1459
2 H1	1509	1463
2 C1	1501	1459
2 H2	1507	1467
2 C2	1500	1459
Mean Value	**1506**	**1464**
Std. deviation	3.6	4.9

From the DirTA measurements, T_L temperatures at the range interval from 1500 to 1511 °C were read. T_S temperatures were identified at the interval range from 1459 to 1471 °C. In contrast with DTA phase transformation temperatures (**Table 3**), DirTA results show a higher variability of T_L and T_S. Difference between maximum and minimum T_L from DirTA analyses is 11 °C, for T_S it is 12 °C. DTA analyses refer a minimal

degree of variability for T_L and T_S temperatures read from DTA curves. Differences between DirTA and DTA are for T_L, resp. T_S mean values 3 °C, resp. 15 °C.

Table 3 DTA: Experimentally determined liquidus and solidus temperatures

Sample	T_L; °C	T_S; °C
1	1509	1479
2	1509	1479
3	1508	1479
Mean Value	**1509**	**1479**
Std. deviation	0.26	0.34

In previous **Table 2**, T_L and T_S temperatures from DirTA analyses from both modes (linear heating and cooling) were presented. To acquire more accurate idea of the achieved results, evaluation of the heating and cooling mode separately is relevant. Generally, a cooling mode is influenced by the supercooling of the studied sample. Supercooling is affecting the solidification process of large samples too. T_L and T_S temperatures obtained under the cooling conditions are usually lower than such temperatures obtained by the mode of linear heating and they can distort the results (T_L and T_S mean values). Evaluation of DirTA results for each mode separately is summarized in **Table 4**, **Table 5**. Acquired difference between the temperatures from linear heating mode and under the cooling conditions can also be caused by different mechanisms of phase transformation (melting and solidification of the sample runs differently).

Table 4 DirTA: Experimental T_L and T_S temperatures from linear heating mode

Sample	T_L; °C	T_S; °C
1 H1*	1510	1471
1 H2*	1511	1471
2 H1*	1509	1463
2 H2*	1507	1467
Mean Value	**1509**	**1468**
Std. deviation	1.2	3.2

Table 5 DirTA Experimental T_L and T_S temperatures from linear cooling mode

Sample	T_L; °C	T_S; °C
1 C1**	1505	1462
1 C2**	1505	1459
2 C1**	1501	1459
2 C2**	1507	1467
Mean Value	**1505**	**1462**
Std. deviation	2.2	3.4

Furthermore, differences between experimental temperatures obtained by different thermo-analytical methods (DirTA, DTA), resp. in heating mode or cooling mode may be caused by the experimental arrangement and

experimental conditions of experiments. Each method and arrangement mode has its advantages and disadvantages at the same time. Differences may be also cause by insufficient contact of the sample with the crucible. A proper contact of surface of the sample with surface of crucible is the most important. Specifically, a contact of steel with crucible thus indirectly with the thermocouple in cyclic experiments during the repetitive melting of sample may be changed.

Some differences could be caused by procedure of evaluation of temperature curves: insufficient diversions of the curves; absence of a sharp deflection of curves in the moment of the beginning of phase transformation of the sample. Moreover, some phase transformation occurs very slowly. Sample absorbs/releases small quantity of heat per unit of time and small temperature change occurs. It leads to a relatively small thermal effect at the beginning of the transformation of the sample may not be detected.

3.2. Theoretically vs. experimentally determined temperatures

Experimentally determined T_L and T_S temperatures were also compared with the theoretically calculated temperatures by IDS and ThermoCalc software and T_L temperatures from industrial partner (**Table 6**, **Figure 1**, **Figure 2**). $T_{L(1)}$ and $T_{L(2)}$ temperatures represents values based on own calculations/equations in real steel plant conditions of industrial partner.

Table 6 Experimentally determined and theoretically calculated temperatures

DirTA		DTA		IDS		ThermoCalc		Industry	
T_L; °C	T_S; °C	T_L; °C	T_S; °C	T_L; °C	T_S; °C	T_L; °C	T_S; °C	$T_{L(1)}$; °C	$T_{L(2)}$; °C
1506	1464	1509	1479	1513	1471	1513	1424	1508	1510

Experimentally obtained T_L temperatures (mean values: 1506 °C according DirTA; 1509 °C according DTA) achieve lower temperatures than theoretically calculated T_L by IDS and ThermoCalc. Maximum difference there is 7 °C. T_L temperature from DirTA is lower than $T_{L(1)}$ (2 °C) and $T_{L(2)}$ (4 °C) calculations from industrial partner, while DTA T_L temperature is located in the interval of $T_{L(1)}$ and $T_{L(2)}$. T_S temperature (1464 °C) determined by DirTA analyses is located in the interval range of theoretical determined T_S temperatures: 1424 - 1471 °C. Ts temperature from ThermoCalc is not displayed due to its very low value in **Figure 2**. T_S from DTA analyses (1479 °C) is higher than the theoretically calculated T_S temperature.

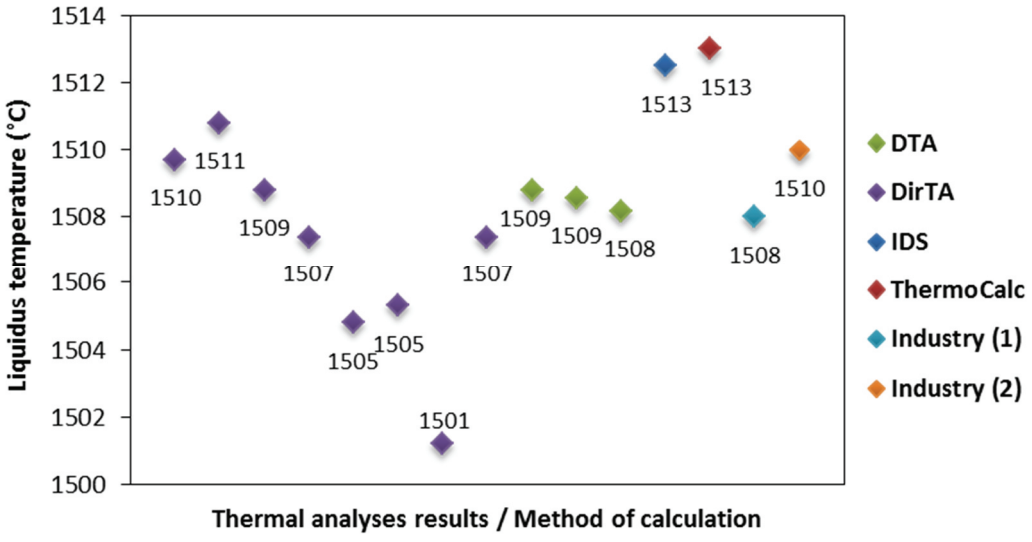

Figure 1 Liquidus temperatures of studied steel determined by different methods

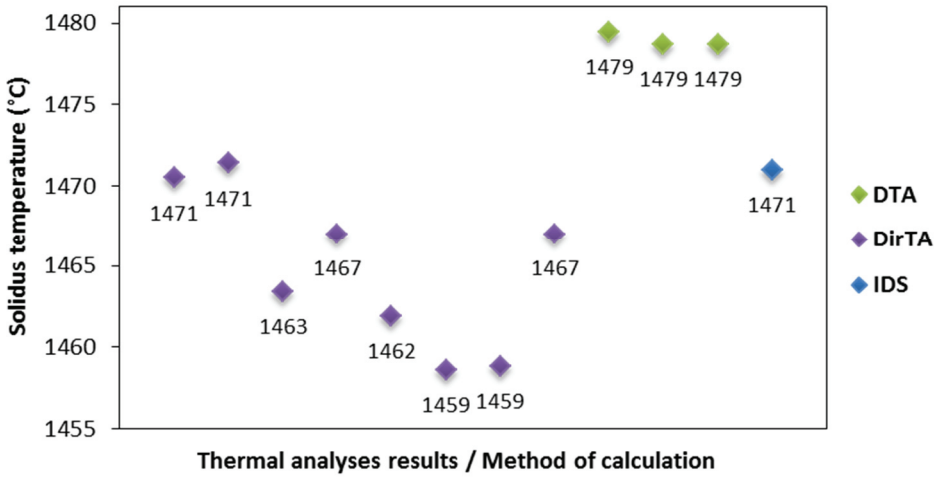

Figure 2 Solidus temperatures of studied steel determined by different methods

Differences between experimental and theoretical values may be caused just by software (calculation method, simplifying assumptions, inability to inclusion of all elements to the calculation) and its databases (absence or deficiency of required input data, incorrect data). Moreover, the differences may be caused by a chemical, phase and structural heterogeneity of the sample, the inappropriate preparation of the sample or wrong adjustment of methodology of experiments. To minimize the negative impact of incorrect adjustment of methodology a number of methodological measurements were performed.

4. CONCLUSION

Paper was devoted to the determination of liquidus (T_L) and solidus (T_S) temperatures of large diameter continuously casting steel. In this work, the possibilities of measurement of these high-temperature phase transformation temperatures (as one of the most crucial parameters for setting of continuous casting process) using a different experimentally arrangement and heating/cooling conditions of different thermo-analytical methods (Direct Thermal Analysis and Differential Thermal Analysis) were presented. Based on chemical composition of investigated steel, the theoretically calculations of liquidus and solidus by specialised software (IDS database, ThermoCalc) were realised and discussed. Finally, experimentally and theoretically temperatures were compared with values currently used in real steel plant conditions. The acquired data will be used for optimizing the conditions of numerical simulation (setting of boundary conditions in simulation calculations ProCast) and also to optimize of the current technology of continuous casting and solidification of studied round billet steel. Application possibilities of use different thermo-analytical methods and experimentally systems can extend reproducibility of experimental results and also verify the methodology of both thermo-analytical methods to correct determining the high temperature phase transformation temperatures of real steels.

ACKNOWLEDGEMENTS

The work was carried out in the frame of project No. TA03011277 "Research and development in the field of numerical and material analysis of steel solidification with application output in the optimization of the continuous casting technology at innovative dimensions of billets" solved with the financial support of TA CR.

This paper was created in the frame of the project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic.

This work was carried out in the support of the project of "Student Grant Competition" numbers SP2016/89 and SP2016/103.

REFERENCES

[1] GALLAGHER, P., K. Handbook of Thermal Analysis and Calorimetry: Principles and Practice. Volume 1. First edition, 1998. Second impression 2003. Amsterdam: Elsevier, 2003. ISBN 0-444-82085-X.

[2] BROWN, M., E. Handbook of Thermal Analysis and Calorimetry. Volume 1. Amsterodam: Elsevier, 1998. 722 s. ISBN 8053-9599.

[3] BOETTINGER, W. J., KATTNER, U. R., MOON, K., PEREPECZKO, J. H. DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing. Special Publication 960-15. Washington: National Institute of Standards and Technology, 2006. 90 s.

[4] HATAKEYAMA, T., ZHENHAI, L. Handbook of thermal analysis. U.K. : Wiley, 1998. 452 s. ISBN 0-471-98363-2.

[5] FLEMINGS, M. C. Solidification Processing. METALLURGICAL TRANSACTIONS B. 1974, vo. 5, no. 10, p. 2121-2134. ISSN: 1543-1916.

[6] BECKER, W. T., SHIPLEY, R. J. ASM handbook: Failure Analysis and Prevention. Volume 1. USA: American Technical Publishers Ltd., 2002. 1164 p. ISBN: 978-0-87170-704-8.

[7] BRIMACOMBE, J. K. Empowerment with knowledge - toward the intelligent mold for the continuous casting of steel billets. METALLURGICAL TRANSACTIONS B. 1993, vol. 24, no. 6, p. 917-935. ISSN: 1543-1916.

[8] GHOSH. A. Segregation in cast products. SÄDHANÄ. 2001, vol. 26, p. 5-24.

[9] WON, Y., THOMAS, B. G. Simple model of microsegregation during solidification of steels. METALLURGICAL AND MATERIALS TRANSACTIONS A. 2001, vol. 32, no. 7, p. 1755-1767. ISSN: 1543-1940.

[10] COMMISSION OF THE EUROPEAN COMMUNITIES. TECHNICAL STEEL RESEARCH. Segregation and phase distribution during solidification of carbon, alloy and stainless steels. Luxembourg: Office for Official Publications of the European Communities, 1991. 260 p. ISBN 92-826-0518-3.

[11] DOBROVSKÁ, J., SMETANA, B., DOBROVSKÁ, V., STRÁNSKÝ, K. FRANCOVÁ, H., ŽALUDOVÁ, M. Influence of Segregation Processes on Solidification Temperature of Steels. In METAL 2013: 22nd International Conference on Metallurgy and Materials. Ostrava: TANGER, 2013, pp. 1694-1699.

[12] DOBROVSKÁ, J., SMETANA, B., FRANCOVÁ, H., JONŠTA, Z. The influence of heating/cooling rate on transformation temperatures of Co-base alloy. Materials Science Forum, 2014, vol. 782, pp. 453-456.

[13] TKADLEČKOVÁ, M., VÁLEK, L., SOCHA, L., SATERNUS, M., PIEPRZYCA, J., MERDER, T., MICHALEK, K., KOVÁČ, M. Study Of Solidification Of Continuously Cast Steel Round Billets Using Numerical Modelling. ARCHIVES OF METALLURGY AND MATERIALS, 2016, vol. 61, no. 1, pp- 221-226.

[14] ŠTĚTINA, J., KLIMEŠ, L., MAUDER, T., KAVIČKA, F. Final- structure prediction of continuously cast billets. MATERIALI IN TEHNOLOGIJE. 2012, vol. 46, no. 2, p. 155-160. ISSN: 1580- 2949.

[15] ZHANG, Q., WANG, X. Numerical simulation of influence of casting speed variation on surface fluctuation of molten steel in mold. JOURNAL OF IRON AND STEEL RESEARCH, INTERNATIONAL. 2010, vol. 17, no. 8, p. 15-19. ISSN: 1006-706X.

[16] GRYC, K., SMETANA, B., ŽALUDOVÁ, M., MICHALEK, K., TKADEČKOVÁ, M., DOBROVSKÁ, J., SOCHA, L., VÁLEK, L., PACHLOPNÍK, R. Thermal analysis of high temperature phase transformations of steel. METALURGIJA, 2013, vol. 52, no. 4, pp. 445-448.

[17] BAŽAN, J., SALVA, O., MICHALÍK, Z., MILATOVÁ, J. Stanovení teplot likvidu a solidu ocelí. HUTNICKÉ LISTY. 1991, roč. XLIV, č. 11/12, s. 18 - 22. ISSN 0018-8069.

[18] STEFANESCU, D. M. Thermal analysis theory and applications in metalcasting. INTERNATIONAL JOURNAL OF METALCASTING. 2015, vol. 9, no. 1. p. 7-22. ISSN: 2163-3193.

[19] BANDA, W., GEORGALLI, G. A., LANG, C. B., EKSTEEN, J. J. Liquidus Temperature Determination of the Fe-Co-Cu System in the Fe-rich Corner by Thermal Analysis. JOURNAL OF ALLOYS AND COMPOUNDS. 2008, vol. 461, no. 1/2, p. 178-182. ISSN: 0925-8388.

[20] MONROE, R; BATES, C. E. Thermal analysis of ductile iron samples for graphite shape prediction. AFS TRANSACTIONS. 1982, vol. 90, p. 307-311.