TEMPERATURES OF SOLIDUS AND LIQUIDUS OF TOOL STEEL

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Abstract

The paper deals with the study of thermo-physical properties of real tool steel grade. The work is focused mainly on phase transition temperatures, particularly liquidus and solidus temperatures determination. These key phase transition temperatures were studied using two thermal analysis methods: “direct” thermal analysis (TA) and Differential Thermal Analysis (DTA). Temperatures of solidus and liquidus are discussed with values used for real casting process and with theoretically calculated temperatures using selected polynomial equations and by SWs, such as Thermo-Calc 2015b version with database TCFE8 and IDS (solidification analysis package). Differences between solidus and liquidus temperatures were encountered between theoretical and experimental values and values used for real casting process. Temperatures of solidus and liquidus were specified with use of thermal analysis methods. Discussion of obtained temperatures is performed with possible impact to the real casting process.

Keywords: Solidus and liquidus temperature, thermal analysis, steel

1. INTRODUCTION

It is necessary, for each steel production company, to improve and optimize production processes continuously to compare favourably with other competitors. 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 [1], is necessary for modern competitive steel making company (e.g. the refining processes, optimizing the slag regimes, thermal and chemical homogenization of the melt or filtration of steel is very important to improve).

To improve and optimize the technological processes of steel production, it is necessary to know, among others, the proper material data. One of many important data for steel production process are phase transition temperatures (from low [2] and also high temperature region [3] up to 1600 °C). In the high temperature region, there are the most important temperatures of solidus and liquidus, which are important mainly for setting of casting conditions and for a simulation (as one of crucial input quantity) of real technological processes related to steel production - modelling of casting processes using e.g. PROCAST SW [2] etc.

This paper presents results obtained by two methods of thermal analysis. Presented results (temperature of solidus T_S, liquidus T_L and peritectic transformation T_P) were obtained using TA - “direct” thermal analysis and

DTA - Differential Thermal Analysis. Experimentally obtained data were discussed and compared with results calculated using SW Thermo-Calc (ver. 2015b, TC SW) and database TCFE8 and also with results obtained using kinetic SW IDS.

2. THERMAL ANALYSIS

Thermal analysis methods are very often used methods (mainly) for characterization of materials from thermophysical and thermodynamic point of view. More about group of thermal analysis methods can be found e.g. in [4]. The principle of these methods is monitoring of sure quantity by linear heating/cooling rate, isothermal dwell or combination of both: linear heating/cooling changing with isothermal dwell [2, 4].

2.1. Direct thermal analysis (TA)

The "direct" thermal analysis [4] 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)

Differential Thermal Analysis (DTA) [2, 4] is based on the 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 curve expressing the dependence of temperature 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. If heat calibration is performed, DTA can be used for heat effects of phase transitions determination [4].

2.3. Experimental base at our working site

There are used many experimental systems for determination of phase transition 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 phase transition temperatures. These equipments are from two different manufacturers and are used in three modifications. Two of them were used for obtaining of phase transition temperatures in the region of melting: Netzsch STA 449 F3 Jupiter for direct thermal analysis (TA, S - type thermocouple) and Setaram SETSYS 18_{TM} with DTA sensor (S - type, tri-couple) for Differential thermal analysis.

3. EXPERIMENT

Samples of tool steel grade were prepared by Vítkovice Heavy Machinery a.s. **Table 1** presents chemical composition of steel grade. Samples were machined in to the desired shape for each equipment and method, then polished and cleaned by ultrasound impact in acetone. Samples were analysed in corundum crucibles in inert atmosphere of Ar (6N). Before analyses, the inner space of the furnaces was flushed by inert gas, evacuated and again filled with inert gas. Temperature calibration was performed using Ni (4N5) or Pd (5N). Corrections respected influence of heating rate and influence of mass of sample were performed.

Table 1 Chemical composition of analyzed steels, (wt.%)

Sample	C	Mn	Si	P	S	Cu	Ni	Cr	Mo	V	Ti	Al	Nb	Sn	N
(steel)	0.38	0.40	0.94	0.010	0.001	0.11	0.30	5.00	0.15	0.404	0.002	0.022	0.005	0.012	0.0100

Two equipments for thermal analysis were used for determination of phase transition temperatures (T_S, T_L and T_P; solidus, liquidus and peritectic transformation): SETARAM SETSYS 18$_{TM}$ (DTA, sample mass approx. 200 mg) and NETZSCH STA 449 F3 JUPITER (TA, sample mass approx. 22 g). Phase transition temperatures were obtained by use of DTA at heating process - heating rate was 10 °C.min^{-1} and also TA method at controlled cycling experiments - two heating runs and two cooling runs were performed; heating and cooling process at 5 °C.min^{-1}.

4. CALCULATIONS

Theoretical calculations were performed using kinetic SW IDS [3] and newest version of Thermodynamic SW Thermo-Calc [5], version 2015b and database TCFE8. Some simplifications of adopted models are presupposed for these SWs and also the basis of data needed for calculations are limited. IDS SW was used as a "black box" for calculation of obtained temperature values. Thermo-Calc SW was used for calculation of phase transition temperatures, isoplethic metastable phase diagram with variable carbon content only and property diagram expressing the amount of a phase on temperature; default phases were included for calculation.

5. RESULTS AND DISCUSSION

From experimental measurements, DTA, heating and cooling curves were obtained, **Figures 1 - 3**. Experimental phase transition temperatures are presented in **Tables 2 - 4**, theoretical values in **Table 5**.

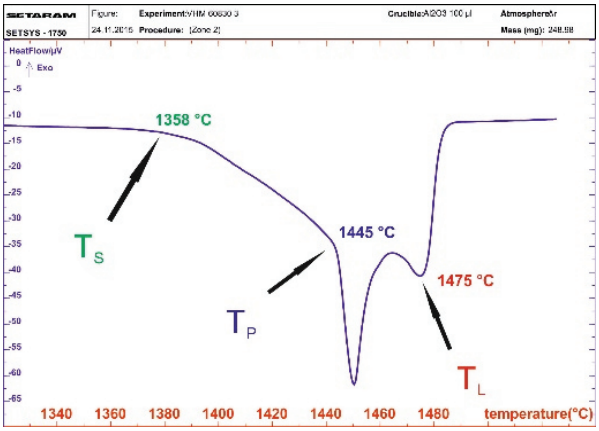

Figure 1 DTA curve of analyzed steel, heating 10 °C.min^{-1}, melting

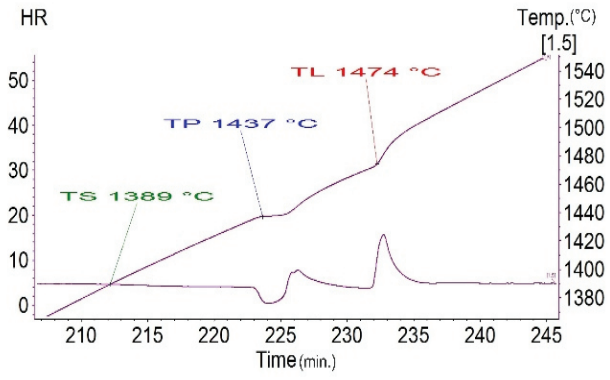

Figure 2 Heating curve of analyzed steel, heating 5 °C.min^{-1}, melting

Figure 4 shows comparison of experimentally obtained temperature intervals for solidus, liquidus and peritectic reaction with isoplethal equilibrium phase Fe-C diagram. **Figure 5** presents comparison of temperature intervals of experimentally obtained solidus, liquidus and peritectic temperatures with property diagram (amount of phases in dependence on temperature).

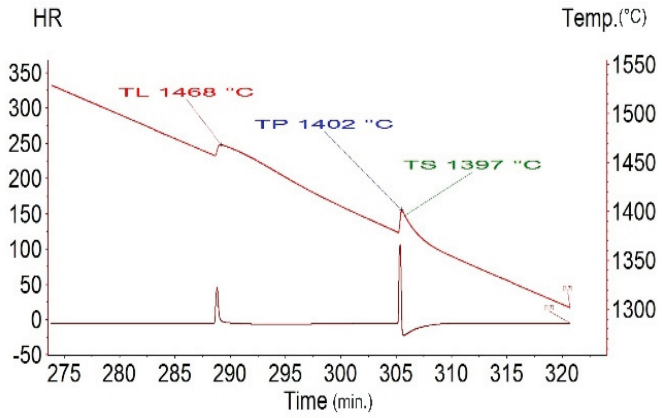

Figure 3 Cooling curve of analyzed steel, cooling 5 °C.min^{-1}, solidification

5.1. Temperature of solidus, T_S

Temperature of solidus obtained by DTA is 1365 °C, by TA (heating) 1389 °C and by cooling regime also 1389 °C. Temperature range of detected solidus temperature is 24 °C (1365-1389). Solidus temperature calculated using IDS SW is 1382 °C, by TC SW 1404 °C and according to the VHM relation used for technological purpose 1354 °C. Theoretical range for solidus temperature is 1354-1404 °C, that is the range of 50 °C - twice higher than experimental range. Experimental solidus temperature range is also compared with theoretically calculated phase diagram and property diagram, see **Figures 4** and **5.** There are very often differences between solidus temperatures obtained experimentally and also theoretically. The differences are usual in order of dozens of degrees of Celsius [3]. If the experimental values considered that is the problem especially with relatively slow melting process start (low amount of heat is absorbed by sample) - there are very often problems with proper start of melting process determination, especially by direct thermal analysis (TA). Also the theoretical values calculated from polynomial relations or using special SWs relatively differ from each other, because the basis is in the earlier experimental values (not so proper data are known like for e.g. liquidus temperatures).

Table 2 Experimental liquidus (T_L), solidus (T_S) and peritectic transformation (T_P) temperatures, DTA, heating

Sample	T_S	T_P	T_L
	(°C)		
run 1	1358	1447	1465
run 2	1360	1447	1465
run 3	1377	1449	1466
Mean value	**1365**	**1447**	**1465**
St. deviation	8	1	0
Var. coeff. (%)	0.62	0.06	0.03

Table 3 Experimental liquidus (T_L), solidus (T_S) and peritectic transformation (T_P) temperatures, TA, heating

Sample	T_S	T_P	T_L
	(°C)		
2_1 H1*	-	-	-
2_1 H2*	-	-	-
2_2 H1*	1385	1444	1477
2_2 H2*	1393	1443	1478
Mean value	**1389**	**1444**	**1478**
St. deviation	4	1	1
Var. coeff. (%)	0.29	0.03	0.03
* Heating			

5.2. Temperature of peritectic transformation, T_P

The start of peritectic transformation temperature (T_P) is at 1447 °C (DTA), 1444 °C (TA, heating) and 1390 °C (TA, cooling). Very good agreement was achieved at heating process for start of peritectic transformation. In

case of cooling relatively high shift to lower temperatures was observed (undercooling often can occur connected with nucleation difficulties). The solidus temperature at cooling is then very close to T_P (if high undercooling takes place). So, the value of T_P seems not to be a representative value. Theoretical value calculated using TC SW is 1455 °C and is about 8 (11) degreeses higher than experimentally obtained and T_P value calculated by IDS SW is 1441 °C and is only about 3 °C (6 °C) lower than experimental values. Experimentally obtained peritectic transformation range is also compared with calculated phase diagram and property diagram, see **Figures 4** and **5.**

5.3. Temperature of liquidus, T_L

Temperatures of liquidus are of a large importance mainly in connection with adjusting the casting temperature at real technological process. The results of thermal analysis of investigated steel lead to obtaining of liquidus temperature T_L. Theoretical calculations were performed also with IDS, Thermocalc and empirical equation (VHM). Experimental liquidus temperature range is compared with calculated phase and property diagram, **Figures 4** and **5**.

Table 4 Experimental liquidus (T_L), solidus (T_S) and peritectic transformation (T_P) temperatures, TA, cooling

Sample	T_S	T_P	T_L
	(°C)		
2_1 C1**	1390	1390	1467
2_1 C2**	1381	1382	1468
2_2 C1**	1384	1385	1469
2_2 C2**	1402	1402	1468
Mean value	**1389**	**1390**	**1468**
St. deviation	8	7	1
Var. coeff. (%)	0.58	0.53	0.04
** Cooling			

Table 5 Theoretical liquidus (T_L), solidus (T_S) and peritectic transformation (T_P) temperatures

Sample	IDS[1]			ThermoCalc[2]			VHM[3]	
	Equilibrium							
	T_S	T_P	T_L	T_S	T_P	T_L	T_S	T_L
	(°C)							
	1382	**1441**	**1474**	**1404**	**1455**	**1482**	**1354**	**1493**
[1] SW Solidification analysis package: elements not included for calculation: Sn, As, Sb, Ce, H a O.								
[2] SW ThermoCalc: elements not included for calculation: Sn.								
[3] Vítkovice Heavy Machinery, a.s. calculation (empirical relation), not. incl.: Ti, Nb, N, As a W.								

Temperature of liquidus obtained by DTA is 1465 °C, by TA (heating) 1478 °C and by TA (cooling) 1468 °C. The difference between DTA and TA (cooling) results is 3 °C (very good agreement). If compared values with TA (heating) the differences are 13 (10) °C. Theoretical value obtained by IDS is 1474 °C, by TC SW 1482 °C and by relation used by industrial partner 1493 °C. Theoretical values are substantially higher than experimental, including the value used for real casting process. The higher difference is between 1465 °C (DTA) and 1493 °C (VHM) - difference 28 °C.

This fact could have a large importance in case of casting and subsequent solidification of steel into the ingots (segregation, porosity,…, economic aspects also,…). The real experimental values, if considered DTA and TA (heating/cooling), are about 15-28 °C lower. From this point of view the adjusting of casting temperature should be modified according to the new findings related to liquidus temperature (but it has to be done very carefully). Temperatures of liquidus, peritectic reaction and solidus were more specified for investigated tool steel.

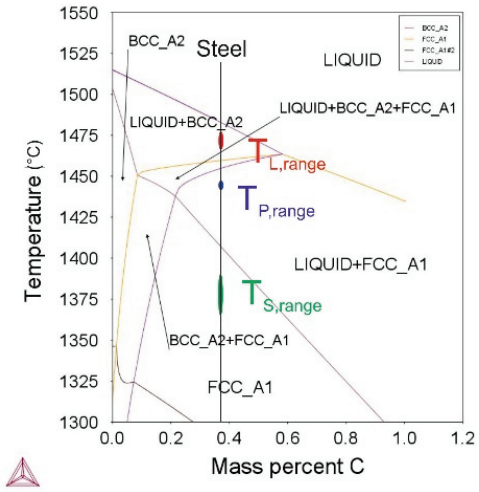

Figure 4 Comparison of experimental ranges of liquidus, solidus and peritectic transformation

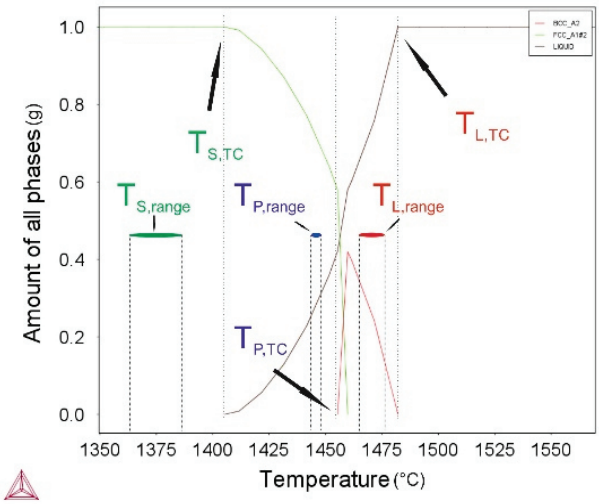

Figure 5 Comparison of experimental ranges of liquidus, solidus and peritectic transformation

6. CONCLUSIONS

Liquidus (T_L) and solidus (T_S) temperatures and also temperature of start of peritectic transformation (T_P) were obtained experimentally and theoretically and consequently discussed and compared. Phase transition temperatures for investigated tool steel were specified. It is evident that experimentally obtained phase transition temperatures (obtained by DTA and TA) are lower than calculated. The widest temperature region was observed for temperature of solidus, lowest for start of peritectic transformation and mild for temperature of liquidus. The most important value is temperature of liquidus. There were observed relatively mild differences between experimental values. It is presupposed that experimental values of T_L (1465; 1468) will be discussed for next implementation into the real technological process directly or via a simulation and subsequently optimization of real casting process.

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