LIQUIDUS, SOLIDUS AND OTHER PHASE TRANSITION TEMPERATURES AND HEAT CAPACITY OF LOW CARBON STEEL

SMETANA Bedřich[1,2], ZLÁ Simona[1,2], KAWULOKOVÁ Monika[1,2], KALUP Aleš[1], GRYC Karel[1,2], MARTINÍK Ondřej[1], DOSTÁL Petr[1], FRANCOVÁ Hana[1], DOBROVSKÁ Jana[1,2], MICHALEK Karel[1,2], STROUHALOVÁ Michaela[1,2], VÁLEK Ladislav[3]

[1] VSB - Technical University of Ostrava (VSB-TUO), Faculty of Metallurgy and Materials Engineering (FMME), Ostrava, Czech Republic, EU, bedrich.smetana@vsb.cz

[2] Regional Materials Science and Technology Centre (RMSTC), Laboratory for Modelling of Processes in the Liquid and Solid Phases, Ostrava, Czech Republic, EU, bedrich.smetana@vsb.cz

[3] ArcelorMittal Ostrava a.s., Research, Ostrava, Czech Republic, EU, ladislav.valek@arcelormittal.com

Abstract

The paper deals with the study of thermo-physical properties of selected real steel grade. The work is focused mainly on phase transition temperatures and heat capacities, particularly liquidus and solidus temperatures, eutectoid transition, alfa-gamma and magnetic transition. Different thermal analysis methods were used for obtaining of experimental data: "direct" thermal analysis (TA), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). Theoretical study of analysed steel grades was performed using IDS SW (Solidification Analysis Package) and thermodynamic SW Thermo-Calc with database TCFE7. Experimental and theoretical data were compared and discussed.

Keywords: Thermal analysis, steel, solidus, liquidus, eutectoid transition, alfa-gamma and magnetic transition, heat capacity

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, is necessary for modern competitive steel making company (e.g. the refining processes, optimizing the slag regimes [1] thermal and chemical homogenization of the melt [2] or filtration of steel is very important to improve).

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 (from low and also high temperature region up to 1600 °C). In low temperature region are very important phase transition temperatures of e.g. eutectoid transformation, α - γ transition, temperature of Curie point etc., which are important for subsequent heat and mechanical treatment [3, 4]. In the high temperature region are the most important temperatures of solidus and liquidus [5-7], which are important mainly for setting of casting conditions. Except of transition temperatures play the key role also heat capacity [8] and latent heats [9]. Heat capacity and latent heat is important mainly as an input quantity for simulation of real technological processes related to steel production, for SWs like PROCAST [8] etc.

This paper presents results obtained by selected methods of thermal analysis: phase transition temperatures and heat capacity. Presented results were obtained using TA - "direct" thermal analysis, DTA - Differential Thermal Analysis and DSC - Differential Scanning Calorimetry. Experimentally obtained data were compared with results obtained using SW Thermo-Calc (TC SW) and database TCFE7 and also with results obtained 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 [10, 11]. The principle (frequently) 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 [10, 11].

2.1. Differential thermal analysis (DTA) and Differential scanning calorimetry (DSC)

The Differential Thermal Analysis (DTA) [10] and/or the Differential Scanning Calorimetry (DSC) [10] are methods based on the same principle. The principle of these methods 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 (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. If heat calibration is performed, DTA and DSC can be used for latent heats of phase transitions determination [12].

If DSC considered than it is possible by the alternation of linear heating with isothermal dwell to obtain heat capacities (C_p). In the case of DSC two methods can be used: "continuous" or "stepped" method of C_p determination. More about these two methods can be found in e.g. [11, 12]

2.2. Direct thermal analysis (TA)

The "direct" thermal analysis [10] 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.

2.3. Experimental base used at our working site

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

There are three devices at our working site [11] that can be used for obtaining of phase transition temperatures and heat capacities. These equipments 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 equipments can be found in e.g.: [11].

3. EXPERIMENT

Samples of peritectic steel grade were prepared from billets continuously cast on billet caster in ArcelorMittal Ostrava, a.s. Production data as chemical composition of steel grade, speed of casting, steel temperature in tundish, etc. has been collected for next possible evaluation. 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) or He (6N). Before analyses was the inner space of the furnaces flushed by inert gas, evacuated and again filled with inert gas. Temperature calibration was performed using Al (5N) and Ag (5N) in low temperature region and Ni (4N5) or Pd (5N) in high temperature region. Corrections respected influence of heating rate and influence of mass of sample were performed. Heat capacity measurements with Pt (3N5) as a standard were performed.

For determination of phase transition temperatures (T_S, T_L, T_{EUT}, T_C, $T_{\alpha \to \gamma, E}$; solidus, liquidus, eutectoid, Curie and alfa-gamma-Ae$_3$ temperatures) of studies steel grade were used two equipments for thermal analysis: SETARAM SETSYS 18$_{TM}$ (DTA, sample mass approx. 200 mg) and NETZSCH STA 449 F3 JUPITER (TA, sample mass approx. 22 g). With Setaram setsys 18$_{TM}$ were obtained temperatures from low and also high temperature region. Using NETZSCH STA 449 F3 JUPITER were obtained phase transition temperatures from high temperature region. Phase transition temperatures by use of DTA were obtained at heating process - heating rate was 10 °C.min^{-1} in high- and 5 °C.min^{-1} in low-temperature region. Phase transitions in high temperature region were determined also with TA method at controlled cycling experiments - two heating runs and two cooling runs were performed; heating and cooling process at 5 °C.min^{-1} and 3 °C.min^{-1} was performed.

Multi High Temperature Calorimeter Line 96 was used for C_p determination. Continuous DSC method and 3D DSC senzor (B-type thermocouples, sample mass approx. 13 mg) was used for C_p measurement. Alternating temperature program was set up. Isothermal dwell was hold at 150 °C then followed heating of sample by heating rate of 5 °C.min^{-1} up to 1400 °C followed by isothermal dwell at 1400 °C. The steel sample was then cooled to 150 °C by 10 °C.min^{-1}. The second and then the third cycle followed at the same conditions. These procedures of three cycles were performed as the blank, measurement with Pt standard and with sample alone. From these three different measurements, each including three cycles, was evaluated C_p (mean value of C_p from 1st, 2nd and 3rd heating run). Values of C_p were obtained at heating process. The so called apparent heat capacity was derived (in C_p are included also latent heats of phase transitions).

4. CALCULATIONS

Theoretical calculations were performed using kinetic SW IDS [13] and Thermodynamic SW Thermo-Calc [14]. 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 and also for C_p (apparent heat capacity). With TC SW was used TCFE7 database and only BCC, FCC, CEMENTITE and LIQUID phase were considered for calculation.

5. RESULTS AND DISCUSION

Experimental phase transition temperatures from high temperature region are presented in **Table 1**, theoretical values in **Table 2**. **Table 3** presents experimental and also theoretical values of phase transition temperatures from low temperature region. Comparison of experimental and calculated apparent heat capacity is shown on **Fig. 1**.

5.1. Temperatures of phase transitions

Temperatures of liquidus (T_L) are almost the same in the case of heating process. If focused on cooling process, T_L are slightly lower (undercooling of samples) than values obtained at heating. Theoretical (IDS, Computherm, Thermo-Calc) values of liquidus are about few degrees higher than experimental values except of values calculated by steel plant producer, **Table 2**.

In the case of solidus temperatures (T_S) the differences are bigger, see values obtained by TA and DTA, also heating and cooling (differences up to 20 °C). The lowest theoretical value of T_S was obtained by IDS. All theoretical values (1477-1486 °C) are in the interval of experimental values of T_S (1469-1489 °C).

Table 1 Experimental liquidus (T_L) and solidus (T_S) temperatures, TA and DTA.

Method	Steel sample	Experimental values							
		Regime - Regime Rate							
		H*		C**		H*		C**	
		1.				2.			
		5°C.min⁻¹				3°C.min⁻¹			
		T_S	T_L	T_S	T_L	T_S	T_L	T_S	T_L
TA[1]	1	**1481**	**1515**	**1467**	**1512**	**1481**	**1515**	**1471**	**1510**
	2	**1481**	**1516**	**1469**	**1510**	**1484**	**1515**	**1470**	**1510**
DTA[2]	3	1490	1514						
	4	1488	1516	-	-	-	-	-	-
	5	1488	1514						
Statistics	Mean value (DTA)	**1489**	**1515**	[1]TA - "Direct Thermal Analysis", *H - heating,					
	Standard deviation (DTA)	0.9	0.9	**C - cooling.					
	Variation coefficient (DTA)	0.06	0.06	[2]DTA - Differential Thermal Analysis.					

Eutectoid transformation was detected by DTA analysis and corresponding transition temperature was determined (T_{EUT}). Also Curie temperature (T_C) and alfa-gamma transition termination ($T_{\alpha \to \gamma,E}$) temperatures were evaluated from DTA curves. Summary of experimental and calculated (T_{EUT} and Ae_3 - equilibrium temperature A_3) values of these temperatures presents **Table 3**.

Table 2 Theoretical liquidus (T_L) and solidus (T_S) temperatures.

Theoretical values							
IDS[1]		Computherm[2]		Thermo-Calc[3]		Steel Plant Producer	
Equilibrium values							
T_S	T_L	T_S	T_L	T_S	T_L	T_L	
1477	1518	1486	1518	1484	1519	1512	1513
[1] SW IDS, el. not included in to the calculation: V, Ti, B, Nb, Sn, Al_rozp., N_spal., O_spal.							
[2] Thermodynamic SW Computherm, el. not included in to the calculation: B, Sn, Al_rozp., N, O.							
[3] Thermodynamic SW Thermo-Calc, el. not included in to the calculation: B, Sn, Al_rozp., N, O.							

Temperature of start of gamma formation (FCC-phase formation) T_{EUT} is 737 °C and is about 28 °C higher than calculated by Thermo-Calc. Temperature of Curie point T_C is 762 °C. Theoretical value of T_C was not possible to calculate using IDS and was not calculated by Thermo-Calc SW.

Table 3 Experimental and theoretical temperatures, T_{EUT}, T_C, $T_{\alpha \to \gamma,E}$, Ae_3.

Method	Steel sample	Experimental values			Theoretical values		
		T_{EUT}	T_C	$T_{\alpha \to \gamma,E}$	IDS[1]	Thermo-Calc[2]	
		(°C)	(°C)	(°C)	Ae_3		T_{EUT}
DTA	6	737	762	836			
	7	737	762	836	**835**	**840**	**709**
	8	737	762	834			
Statistics	Mean value	**737**	**762**	**835**	[1] SW IDS, el. not included in to the calculation:		
	Standard deviation	0	0	1	V, Ti, B, Nb, Sn, Alrozp., Nspal., Ospal.		
	Variation coefficient	0.02	0.02	0.12	[3] el. not incl. in to the calc.: B, Sn, Al_rozp., N, O.		

Very good agreement (as in the case of T$_L$) was achieved in the case of termination of FCC-phase creation (end of alfa-gamma transition). Experimental value is 835 °C, calculated (Ae$_3$) by IDS 835 °C and by Thermo-Calc 840 °C.

5.2. Apparent heat capacity

Apparent heat capacity is presented on **Fig. 1**. Experimental and theoretical values are compared in the temperature region between 200-1400 °C. Heat capacities have the same trend and are close to each other in the temperature region from 200-700 °C. Theoretical values demonstrate steeper grow trend in this temperature region. Between 700-900 °C there are taking place phase transitions, discussed above (curve expressing C$_p$ is in fact "reversed" DSC curve and of course phase transition temperatures is possible to derive like in the case of DTA, resulting temperatures shown in **Tables 1** and **3**). There are visible some differences in the heat effects progress, but all mentioned phase transitions are visible with smaller or greater shift. Above the temperature 900 °C show C$_p$ values (theoretical and experimental) same trend. Theoretical values are slightly shifted to higher values.
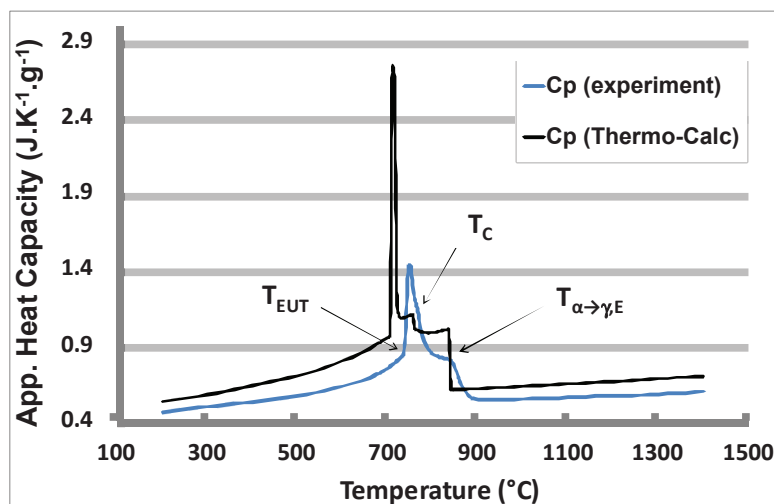

Fig. 1 Comparison of experimental and calculated (TC SW) values of apparent heat capacity.

Differences between experimental and theoretical values (in case of phase transition temperatures and heat capacities also) could be with high probability caused by calculation alone or/and by experiment alone. Calculated values correspond to the equilibrium state with only selected phases (FCC, BCC, Fe$_3$C and liquid) and incomplete chemical composition. Contrary to that experimental values have not to correspond fully to the equilibrium state. But, it can be said, that the real sample is analyzed (whole chemical composition and all phases are included). More about calculations and simulations could be found e.g. [12].

6. CONCLUSIONS

Liquidus, solidus and other phase transition temperatures were obtained experimentally and theoretically. In some cases quite good agreement was achieved e.g.: in case of liquidus temperature and in case of termination of alfa-gamma transition (Ae$_3$ temperature). Apparent heat capacity was also measured and calculated. Same trends in dependence on temperature were observed for experimental and theoretical values, mild shift of experimental values to the higher values was observed and also the shift of phase transitions is visible. It is presupposed that experimental values will be discussed for next implementation in to the real technological process directly (e.g.: T$_L$) or via a simulation and subsequently optimization of real casting process.

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