LATENT HEATS OF MELTING AND SOLIDIFYING OF REAL STEEL GRADES

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Abstract

The paper deals with the study of latent heats of melting and solidifying of real steel grades. Two real steel grades were investigated and values of latent heats of melting and solidifying were obtained. Latent heats are very important quantities for thermodynamic and kinetic modelling. These data are also valuable for many SWs used for technological processes modelling. The obtained data can serve for the addition and enhancement of many thermodynamic databases. Latent heats of phase transformations were obtained using DSC method (Differential Scanning Calorimetry). Setaram MHTC (Multi High Temperature Calorimeter) Line 96 equipped with 3D DSC sensor was used for measurements. Controlled heating/cooling of alloys was conducted at the rate of 5 K·min^{-1}. Comparison and discussion of experimental and calculated (IDS, Thermo-Calc) data was performed, too.

Keywords: Latent heat, DSC, Thermo-Calc, IDS

1. INTRODUCTION

Structure and properties of steel alloys is still object of extensive research [1, 2]. Unfortunately, a lack of experimental data about these systems still persists. Some information can be found in the literature, but these data are usually incomplete [3]. Moreover the presented data mentioned in the literature [4, 5] differ. Due to necessity to use exact experimental data as an input data for many simulation programs, numerical or physical models [6] and requirements of practice (e.g. casting, welding, solidification), an investigation of multicomponent steel alloys is still highly topical theme.

Missing data, such as temperatures of solidus (T_S), temperatures of liquidus (T_L), heat capacity (C_p) and others can be obtained using thermal analysis measurements [7]. The DTA (Differential Thermal Analysis) is one of the possible methods. Another common method is the DSC (Differential Scanning Calorimetry, 2D and/or 3D). The isothermal methods, "DROP" calorimetry, are very often used for obtaining of studied quantities as well.

Also, missing data can be calculated using simulation programs. As for all calculations, it is necessary to validate its results with exact experimental data, e.g. density, enthalpy, heat capacity [8] and other important material data [9]. It is also suitable to support these data by structural and phase analysis.

2. EXPERIMENTAL

Real steel samples were supplied by ArcelorMittal Ostrava, a. s. The first sample represents low carbon steel grade with content of silicon 0.2 wt %. The second sample has been prepared from GOES (Grain Oriented Steel Grade). This is low carbon steel with content of Si about 3 wt %. These samples have been prepared from continuously cast slab sample.

Samples were ground up and washed in acetone under ultrasound before measurement. Experimental values of latent heats and temperatures of solidus T_S and liquidus T_L were obtained in alumina crucibles under inert atmosphere of He (99.9999 %) using SETARAM **MHTC 96** (Multi High Temperature Calorimeter, Line 96) device with 3D DSC sensor. Properties of this device are shown in **Table 1**.

Table 1 Characteristics of SETARAM MHTC 96 device

Quality	Setaram MHTC 96
Methods	hf-DSC (heat flux DSC), DROP
Temperature	from 20 to 1600 °C
Heating rate	from 0.001 to 99 K·min^{-1} (according to manufacturer)
Temperature program	linear heating/cooling, isothermal measurements
Sample mass	DSC: up to 2.5 g DROP: up to 30 g
Atmosphere	vacuum, inert, reactive (oxidative/reductive)
Type of Cp sensor	3D DSC sensor

2.1. Measurements of latent heat of melting/solidifying

Latent heats were obtained using MHTC 96 and B-type 3D hf-DSC (heat flux DSC) sensor, which provides better detection of absorbed/released heat against 2D sensor (**Fig. 1**). The enthalpy calibration, which has to be done with respect to the studied temperature range, analysed material and experimental conditions, was performed by relation of heat effect of sample to the generally accepted value of heat effect of reference.
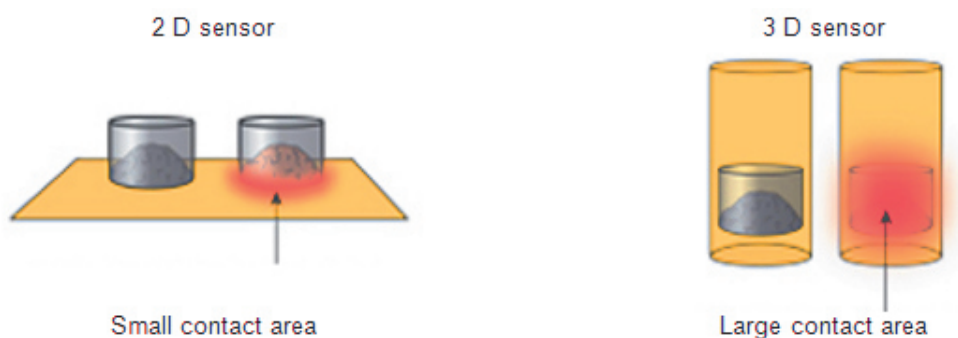

Fig. 1 Comparison of 2D and 3D sensor.

Enthalpy of the sample was computed according to the equation (1):

$$\Delta H_{sample} = \frac{\Delta H_{reference}}{S_{reference}} \cdot S_{sample} \tag{1}$$

$\Delta H_{reference}$ - generally accepted heat of fusion of reference, S - heat effect (peak area) of fusion/solidification of reference and sample.

Pure nickel (99,999 %) was used as a reference. Samples of steels were machined in to the shape of cylinders with a diameter about 5 mm and 8 mm in height, so their mass was approximately 1.2 g. The heating/cooling rate was 5 K·min^{-1} for both steels and nickel.

2.2. Measurements of temperatures of solidus T_S and liquidus T_L

Temperatures of solidus T_S and liquidus T_L were obtained with use of the same device and with the same temperature program as for measuring of latent heat. The continuous mode was used for the detection of phase transitions and their heat effects, linear regime of heating and cooling was realised.

Measured temperatures of solidus T_S and liquidus T_L were evaluated according to general methodology modified for multicomponent systems at our working site. Connections with respect to experimental conditions were also performed [10].

2.3. Calculations

In addition to experimental measurements, latent heats and temperatures of solidus T_S and liquidus T_L were calculated using IDS/software (Solidification Analysis Package) [11] and Thermo-Calc 3.1 [12]. As for all simulations and calculations, obtained results have to be compared with measured values and this comparison was also done.

IDS software needs chemical composition (in mass %) of samples and cooling rate as an input parameters and then it will calculate temperatures of phase transformation. Because of its limitations with respect to the composition [13], some elements had to be excluded (V, Ti, B, Nb, Sn, Al, N and O) from chemical composition. The cooling rate was set to 0 K·min^{-1} (equilibrium state), so the results can be compared with Thermo-Calc, which allows calculations only at the equilibrium state.

Thermo-Calc software package uses CALPHAD method for its calculations. This software includes many databases, which are optimized for different types of calculations and have included different elements. For steels, the recommended database is TCFE7 (so called "Fe-based alloys"). Unfortunately, the Sn element is not included in TCFE7 database, so it was necessary to use another database. The chosen SSOL5 (so called "general alloys") database has included all elements contained in the samples.

Thermo-Calc allows adding and excluding phases in its calculations. In this paper, only default setting with no changes in phases addition/exclusion was used (the "black box" mode).

3. RESULTS AND DISCUSSION

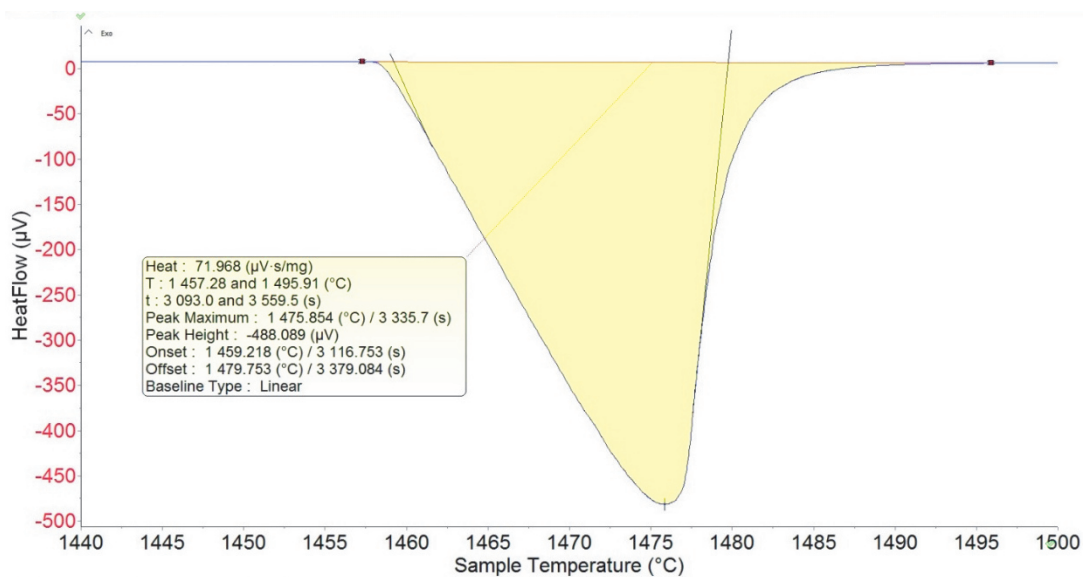Temperature was calibrated to melting points of nickel, heat effects were calibrated to pure nickel (99.9999 %, **Fig. 2**).

Fig. 2 Heat effect of melting of pure nickel

3.1. Latent heat

Generally accepted value of melting heat of nickel is 309 J·g⁻¹ [14]. Latent heats of melting/solidifying computed according to the equation (1) and calculated latent heats are given in **Table 2**. Values of latent heats obtained using Thermo-Calc were computed from its enthalpies (**Fig. 3**).

Bigger difference (6.3 J·g⁻¹) between latent heats of melting and solidifying for the first sample of steel is probably due to undercooling of the steel sample (different heat capacities for undercooled melt and solid state [15]). Latent heats of fusion computed via IDS are lower than latent heat of solidifying obtained on MHTC 96, difference is 14 J·g⁻¹ and 16 J·g⁻¹, respectively.
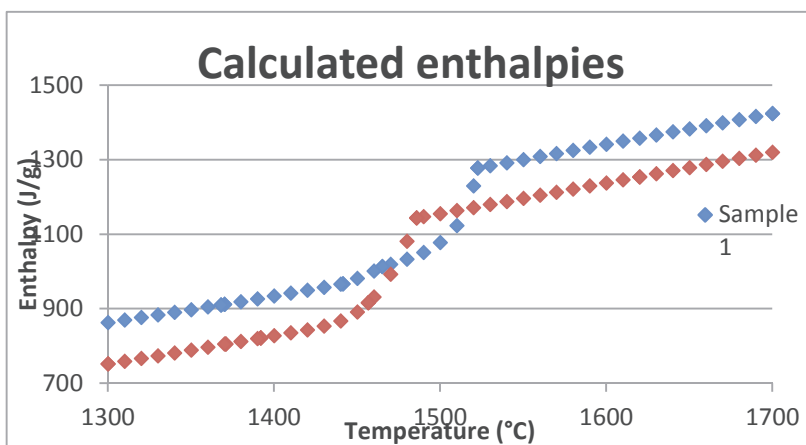
Thermo-Calc allows calculations only in the equilibrium state, but latent heat calculated with this software is between experimental values of latent

Fig. 3 Enthalpies calculated using Thermo-Calc.

heat for the first steel. For the second steel, difference between measured latent heats and latent heat calculated with Thermo-Calc is higher, because of high amount of silicon in this steel sample (cc 3.1 wt %). Increasing amount of silicon rises the difference between measured and calculated values, as it was described earlier [16]. According to available information from the literature, silicon in steel probably increases the latent heat, of melting/solidifying of steel, but detailed study focused to this phenomenon is missing.

Table 2 Latent heats (in J·g⁻¹)

Sample	MHTC 96		IDS	Thermo-Calc
	melting	solidifying		
1	246.7 ± 1.2	253.0 ± 1.3	239	251.4
2	258.2 ± 1.7	256.8 ± 1.1	241	247.3

3.2. Temperature of solidus T_S and liquidus T_L

Observed and calculated temperatures of solidus T_S and liquidus T_L are given in **Table 3**. Both observed temperatures are from heating only.

Table 3 Temperatures of solidus T_S and liquidus T_L (in °C)

Sample	MHTC 96		IDS		Thermo-Calc	
	T_S	T_L	T_S	T_L	T_S	T_L
1	1486.3 ± 0.4	1522.5 ± 0.5	1485	1525	1465.1	1522.5
2	1463.7 ± 0.6	1489.2 ± 0.5	1439	1490	1456.6	1485.6

The IDS software gives value of temperature of solidus T_S closer to experimental value for the first steel sample (difference is only 1 °C) than Thermo-Calc (difference is 21 °C), but for the second steel sample was Thermo-Calc´s value closer to experimental values than IDS (difference is 7 °C and 25 °C, respectively). Computed

temperatures of liquidus T_L are in good agreement with experimentally observed values; difference between measured and calculated values is less than 4 °C for both samples and both software.

CONCLUSIONS

Latent heats computed with IDS are in good agreement with measured latent heats of solidification. Latent heat computed using Thermo-Calc gives excellent agreement with measured data for the first steel. For the second steel, latent heat computed with Thermo-Calc is approximately 10 J·g^{-1} lower than measured latent heats. Latent heats of melting and solidifying differ for the first sample, so the steel was probably undercooled.

Thermo-Calc computed temperature of solidus T_S a little bit closer to measured values than IDS. Recalculation of Thermo-Calc´s results with improved setting of phases could give even better result. Temperature of liquidus T_L computed using IDS and Thermo-Calc are very close to each other for both samples and they are in great agreement with measured temperatures of liquidus T_L.

It is assumed that obtained experimental values will be possible to use in optimization of real casting process (after performed simulations), but it would be very useful also, due to an insufficient experimental and theoretical data in the accessible literature in case of phase transitions, to perform more significant experiments.

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REFERENCES

[1]   ŽALUDOVÁ, M., SMETANA, B., ZLÁ, S., DOBROVSKÁ, J., VODÁREK V., KONEČNÁ K., MATĚJKA, V., MATĚJKOVÁ, P. Experimental study of Fe-C-O based system below 1000 °C. *J. Thermal Anal.Calorimetry*, 112, 2013, 465-471.

[2]   ŽALUDOVÁ, M., SMETANA, B., ZLÁ, S., DOBROVSKÁ, J., WATSON, A., VONTOROVÁ, J., ROSYPALOVÁ, S., KUKUTSCHOVÁ, J., CAGALA, M. Experimental study of Fe-C-O based system above 1000 °C. *J.Thermal Anal.Calorimetry*,111, 2013, 1203-1210.

[3]   CARLSON, K. D., BECKERMANN, C. Determination of solid fraction-temperature relation and latent heat using full scale casting experiments: application to corrosion resistant steels and nickel based alloys. *Int. J.Cast Met. Res.*, 25, 2012, 75-92.

[4]   MICHALEK, K., GRYC, K., TKADLECKOVA, M., BOCEK, D. Model study of tundish steel intermixing and operational verification. *Arch. Metal. Mater., 57,* 2012, 291-296.

[5]   SMETANA, B., ZLÁ, S., ŽALUDOVÁ, M., DOBROVSKÁ, J., KOZELSKÝ, P. Application of High Temperature DTA to Micro-Alloyed Steels. *Metalurgija*, 51, 2012, p. 121-124.

[6]   TKADLEČKOVÁ, M., MACHOVCAK, P., GRYC, K., KLUS, P., MICHALEK, K., SOCHA, L., KOVAC, M. Setting a numeric simulation of filling and solidification of heavy steel ingots based on real casting conditions. *Materiali In Tehnologije,* 46, 2012, 399-402.

[7]   GALLAGHER, P. K. *Handbook of thermal analysis and calorimetry: principles and practice*. Elsevier, 2003. p. 675, ISBN 0080539599.

[8]   SMETANA, B., ŽALUDOVÁ M., TKADLEČKOVÁ, M., DOBROVSKÁ, J., ZLÁ, S., GRYC, K., KLUS, P., MICHALEK, K., MACHOVČÁK, P, ŘEHÁČKOVÁ, L. Experimental verification of hematite ingot mould heat capacity and its direct utilisation in simulation of casting proces. *J. Thermal Anal. Calorimetry, 112,* 2013, 473-480.

[9]   GRYC, K., STRÁNSKÝ, K., MICHALEK, K., WINKLER, Z., MORÁVKA, J., TKADLEČKOVÁ, M., SOCHA, L., BAŽAN, J., DOBROVSKÁ, J., ZLÁ, S. A study of the high-temperature interaction between synthetic slag and steel. *Materiali In Tehnologije, 46,* 2012, 291-296.

[10]   ZLÁ, S., DOBROVSKÁ, J., SMETANA, B., ŽALUDOVÁ, M., VODÁREK, V., KONEČNÁ, K. Thermophysical and structural study of IN 792-5A nickel based superalloy. *Metalurgija*, 51, 2012, 83-86.

[11]   MIETTINEN, J. Calculation of solidification-related thermophysical properties for steels. *Metall. Mater. Trans., 28B,* 1996, 281-297.

[12]   ANDERSSON, J. O., HELANDER, T., HÖGLUND, L., SHI, P. F., SUNDMAN, B. Thermo-Calc and DICTRA, Computational tools for materials science. *Calphad*, 26, 2002, 273-312.

[13]   ŠMRHA, L. *Solidification and crystallization of steel ingots*. 1. ed. Praha: SNTL, 1983.

[14]   CARVILL, J. *Mechanical Engineers Data Handbook*, Elsevier, 1994, ISBN 9780750619608.

[15]   BARTH, M., JOO, F., WEI, B., HERLACH, D. M. Measurement of the enthalpy and specific heat of undercooled nickel and iron melts. *J. Non-Crystall. Solids,156-158,* 1993, 398-401.

[16]   DJURDJEVIC, M. B., FRANCIS, R., SOKOLOWSKI, J. H., EMADI, D., SAHOO, M. Comparison of different analytical methods for the calculation of latent heat of solidification of 3XX aluminum alloys. *Mater. Sci. Eng., 386A,* 2004, 277-283.