COMPARISON OF EXPERIMENTAL AND NUMERICALLY CALCULATED THERMAL PROPERTIES OF STEELS

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Abstract

Reliable knowledge of thermo-physical properties of materials is essential for the interpretation of solidification behavior, forming, heat treatment and joining of metallic systems. It is also a precondition for precise simulation calculations of technological processes. Modeling usually requires the knowledge of temperature dependencies of three basic thermo-physical properties: heat capacity or enthalpy, density and thermal conductivity. Nowadays many software packages for thermodynamic calculations enable to calculate specific heat or enthalpy on the basis of chemical composition. However, the results of calculation must be verified experimentally. Paper deals with a problem of specific heat measurements for steels in wide temperature region, from room to solidus temperature. The method used for investigations was Differential Scanning Calorimetry (DSC), which is one of the most common used techniques of thermal analysis in the field of metallurgy. The results of calculations using FactSage with SGTE database and experimental data were compared for three steel grades. Very good agreement was obtained. On the basis of specific heat results the enthalpy changes with temperature were calculated for each steel grade. Obtained values of thermal properties depend on chemical composition and temperature. It is important to investigate the thermal properties for concrete steel grades for modeling processing or casting.

Keywords: specific heat capacity, enthalpy, DSC, metallic systems, FactSage

1. INTRODUCTION

Knowledge of thermo-physical properties has become very important for a design and optimization of industrial processes. Thermal properties supply the data basis for engineering calculations and practical application of construction parts. Most important properties that influence the results of process modeling are specific heat or enthalpy, density and thermal conductivity [1]. All of these change their values within temperature and chemical composition. There are a few software packages with thermal databases, which allow calculating thermo-physical properties of steels, ex. FactSage, ThermoCalc, MT Data, IDS. However, the results of calculations for more complex systems, such as steels, may differ from data obtained experimentally and are still poorly verified [2].

One of the fundamental thermo-physical data of materials is specific heat. Many other thermodynamic properties, such as enthalpy, entropy, and Gibbs free energy can be calculated from highly precise specific heat data. Hence, much work has been done to measure specific heat with calorimetric instruments throughout the world. The most common used technique is Differential Scanning Calorimetry (DSC) in which the heat flow from sample and from reference sample is measured as both sample and reference are subjected to the same temperature regime. In the field of metallurgy it is used for measurements of temperatures and enthalpies of phase transformations and specific heat of steels and slags [3-6]. DSC is a comparative method in which calibration must be run prior to the measurement. For specific heat measurements only temperature is calibrated, usually by melting points of pure substances.

Paper presents the results of specific heat measurements for three non-alloyed steel grades conducted for the purposes of continuous casting process modelling and enthalpies calculated on the basis of these results. Specific heat and enthalpy calculated in FactSage 6.3. using SGTE thermodynamic database is also presented

to compare. FactSage is currently very popular software for thermodynamic calculations which applies to many problems associated with metallurgy [7]. Numerical calculations were conducted for all steel grades in wide temperature range 20 - 1600 °C.

2.   THEORETICAL BACKGROUND

2.1   Specific heat

Specific heat c_p is defined as the amount of heat required to change the temperature of one gram or mole (so called molar heat capacity) of the substance by one degree:

$$c_p = \frac{1}{m} \cdot \frac{dQ}{dT}$$
(1)

Specific heat depends on temperature and slightly on grain size. General temperature dependence is described by polynomial introduced by Meyer and Kelly [8]:

$$c_p = c_1 + c_2 T + c_3 T^2 + \frac{c_4}{T^2}$$
(2)

The coefficients in the above equation are characteristic for a substance or for phase in case the material has allotropic forms. With respect to the contribution of each element to the whole specific heat and temperature dependence the following expression, called Neumann-Kopp rule, is possible:

$$c_p(T) = \sum_{i=1}^{N} x_i c_p^i(T)$$
(3)

where N is the number of alloying elements, x_i and c_p^i the weight percent and specific heat of ith element respectively.

There are a few methods to determinate specific heat, but all of them are based on one of the two principles: heat flow divided by heating rate and sample mass or comparison with a specific heat capacity of standard that is subjected to the same temperature program. Comparative methods give higher attainable accuracy, but more measurements are required, what influences longer measurement time. One of these methods is continues method in DSC. Specific heat is determined on the basis of three measurements run one after another: measurement with empty crucibles (blank curve, B), reference material (R) and sample (S). All the measurements must be performed during continuous heating between two isothermal segments. The specific heat of the sample $c_p^S(T)$ is calculated as follows [9]:

$$c_p^S(T) = c_p^R(T) \cdot \frac{m_R[DSC_S(T) - DSC_B(T)]}{m_S[DSC_R(T) - DSC_B(T)]}$$
(4)

where m_R, m_S are reference and sample masses, DSC_B, DSC_R, DSC_S are DSC signals for blank, reference and sample respectively and c_p^R is known specific heat of reference material. The accuracy of specific heat measurement is decisively dependent on the reproducibility of the blank curve measurement. Asymmetries of the measuring system can be seen as a blank curve drift. However, the drift can be corrected with a linear term (5). Correction $DSC(t)$ is calculated on the basis of DSC signals registered for concrete times t_1 and t_2 during first and second isothermal holding [9]:

$$DSC(t) = DSC(t_1) + \frac{DSC(t_2) - DSC(t_1)}{t_2 - t_1} \cdot (t - t_1) .$$ (5)

2.2 Enthalpy calculation

In many calculations enthalpy can be used instead of specific heat, as for processes going under constant pressure it is equal to the amount of exchanged heat. Enthalpy ΔH is calculated as follows:

$$\Delta H(T) = \int_{T_0}^{T} c_p(T) dT$$ (6)

In steels often first order phase transformations occur during temperature changes. As the specific heat during phase transformation cannot be defined, the enthalpy in these temperature ranges can be calculated on the basis of the new phase fraction f and the latent heat of transformation L as follows:

$$\Delta H(T) = \int_{T_0}^{T} c_p(T) dT + (1 - f)L$$ (7)

3. EXPERIMENT

3.1 Materials

Materials for investigations were 3 grades of non-alloyed steels with different chemical composition summarized in **Table 1**. Samples were cut from continuously cast slabs into roller shape with the diameter of app. 5 mm and 1 mm in height. Masses of such prepared samples were app. 150 mg.

Table 1 Chemical composition of investigated steel grades

Steel grade	Chemical composition, wt. %								
	C	Mn	Si	P	S	Cu	Cr	Ni	Mo
A	0.07	0.74	0.02	0.013	0.01	0.02	0.02	0.07	0.007
B	0.25	0.79	0.17	0.02	0.03	0.23	0.08	0.08	0.01
C	0.09	0.67	3.81	0.01	0.03	0.20	0.05	0.05	0.01

3.2 Experimental procedure

Experiments were conducted using heat flux device NETZSCH STA 449 F3 Jupiter. Temperature program used for measurements consisted of three segments: isothermal, dynamic heating with heating rate of 20 °C/min and second isothermal. The investigated temperature range was from 40 °C to the solidus temperature of each steel grade. The measurements were conducted in an inert atmosphere of helium (6N). The atmosphere was dynamic with a gas flow of 50 ml/min. Samples were inserted into Pt-Rh crucibles with lids and alumina inners to avoid reaction between steel and platinum. As a reference material α-Al_2O_3 was used since its specific heat is well covered in literature. Reference had the same shape as samples and the mass of 111 mg.

Prior to the actual measurements the one for temperature calibration were conducted using pure metals: In, Zn, Al, Ag, Au, under the same conditions as further investigations. On the bases of fusion temperatures T_{exp} of calibrating materials temperature calibration curve, shown in **Fig. 1**, was calculated.
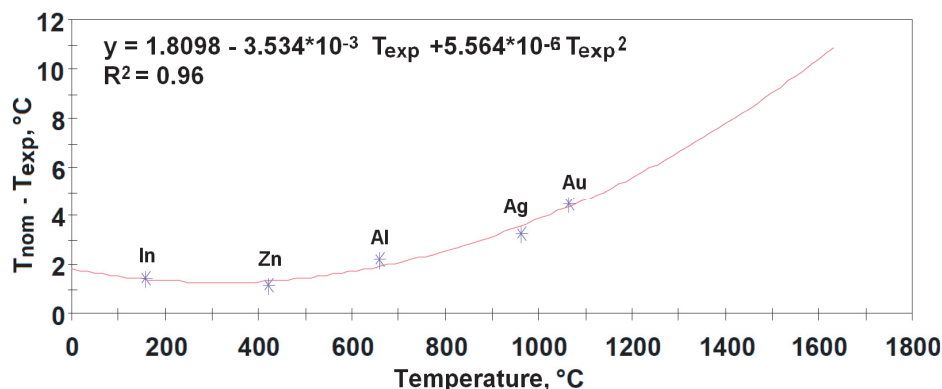
$$y = 1.8098 - 3.534 \cdot 10^{-3}\ T_{exp} + 5.564 \cdot 10^{-6}\ T_{exp}^{2}$$
$$R^2 = 0.96$$

Fig. 1 Temperature calibration curve and its equation

4.   RESULTS AND DISCUSSION

The comparison of experimental and numerically calculated specific heat of steel A is shown in **Fig. 2a**. Very good agreement was obtained in case of this steel grade. At low temperature region (up to app. 1000 °C) the relative deviation between calculated and experimental values does not exceed 3%. Above 1000 °C the relative deviation was max. 10%. The peaks, which appear on the experimental curve during phase transformations, are shifted as compared to numerical calculations. This is probably related to the fact that FactSage calculations are run for equilibrium conditions while during experiment equilibrium is never achieved. The shift of phase transformations appears for all investigated steel grades.

In **Fig. 2b** enthalpy calculated using SGTE database and calculated on the basis of experimental specific heat according to equation (6) for steel A is shown. Excellent agreement was obtained in whole investigated temperature range.
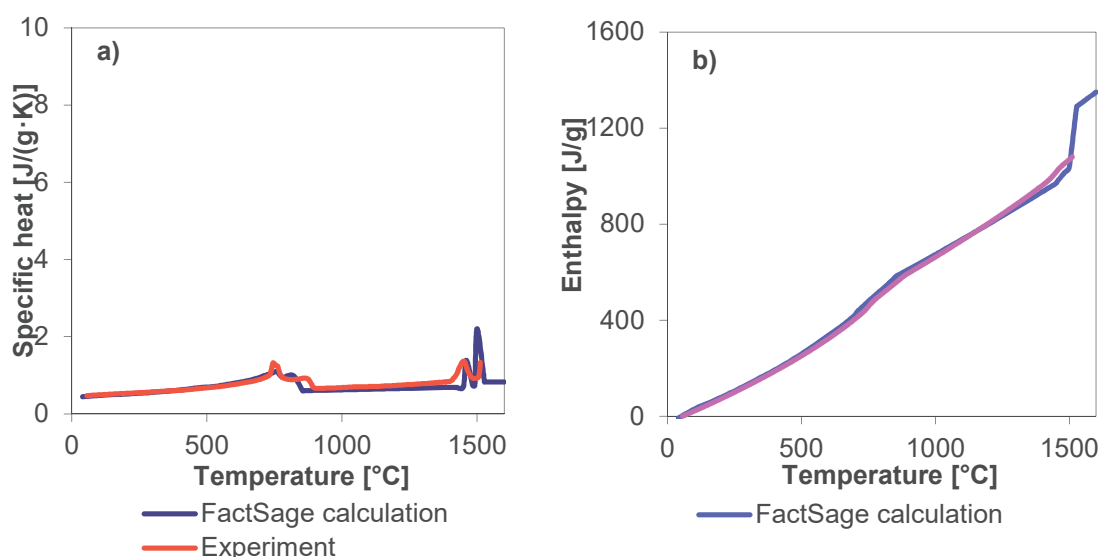

Fig. 2 Comparison of experimental and calculated specific heat of steel A (a), enthalpy of steel A (b)

The results for steel B are presented in **Fig. 3**. At low temperature region good agreement was obtained with the maximum relative deviation of 3%. However, at high temperatures there are significant differences in experimental and calculated specific heat values (see **Fig. 3a**) and as a result, in enthalpy values (see **Fig. 3b**). Similar tendency shows the result for steel C shown in **Fig. 4**. Steel C is ferritic steel with high amount

of silicon. Huge differences obtained especially in enthalpy values indicate the influence of higher silicon content on numerical calculations at higher temperatures. Greater differences at high temperatures on the one hand may be a result of lower accuracy of DSC continues method. Further investigations for the high temperature region are needed, for example with the use of DSC stepwise method. On the other hand the thermodinamical data included in SGTE database may be insufficient to calculate specific heat capacity with satisfying accuracy.
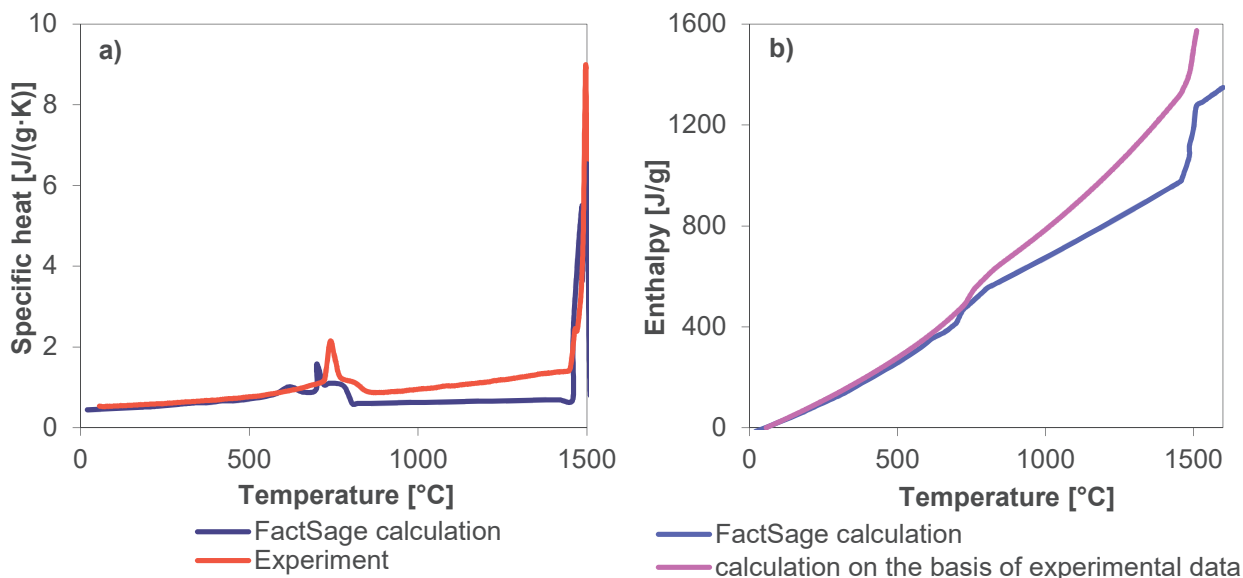

Fig. 3 Comparison of experimental and calculated specific heat of steel B (a), enthalpy of steel B (b)
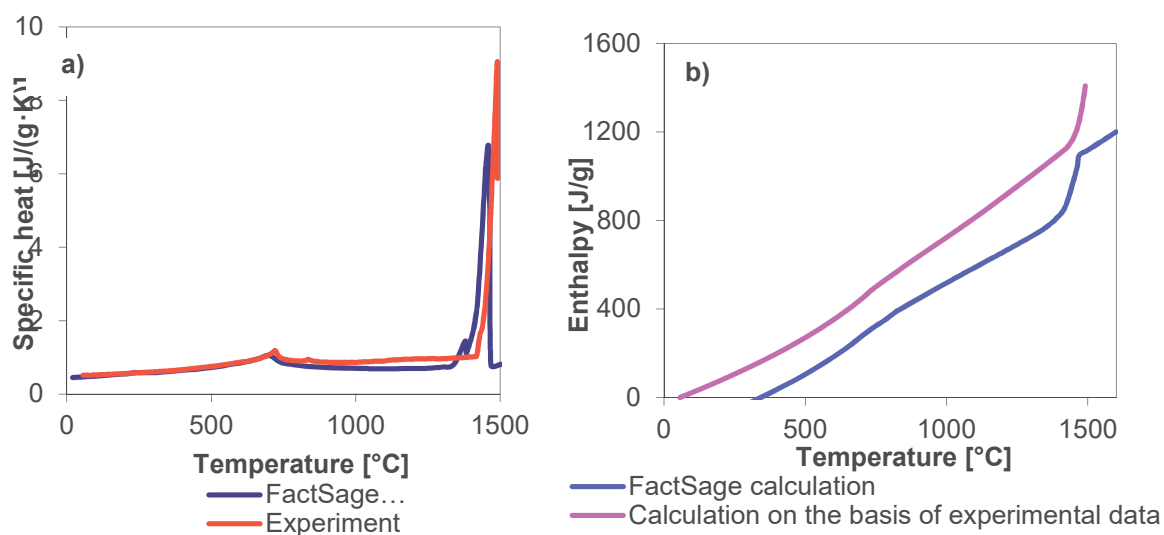

Fig. 4 Comparison of experimental and calculated specific heat of steel C (a), enthalpy of steel C (b)

In case of all steel grades the values of specific heat for steels are higher than the values reported for pure iron [4]. That indicates other elements (C, Mn, Si), when added to iron, cause increase of specific heat values.

CONCLUSION

Specific heat of three different steel grades was measured using the continuous method in differential scanning calorimetry. On the basis of measurement results the enthalpy was calculated. Both specific heat and enthalpy was also calculated using SGTE database in FactSage. Comparison of the results reviled very good agreement, especially at low temperature range. At high temperature region for steels with higher amount of alloying elements significant differences were observed. For this reason further investigation are planned on the determination of the thermal properties of real steel grades.

Specific heat and enthalpy are crucial thermo-physical quantities for many applications. Proper values of specific heat or enthalpy are used in many thermodynamical and kinetic software and can play crucial role in modeling of steel casting and processing.

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