DETERMINATION OF HEAT CAPACITY OF STEEL WITH USE OF THERMAL ANALYSIS AND THERMO-CALC

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Abstract

DSC method (Differential Scanning Calorimetry) is one of the thermal analysis methods which is suitable for studying the thermodynamic properties of metallic systems. In this work the heat capacities of real steel grade in the solid phase under strictly defined conditions for controlled heating were studied. The paper deals with the investigation of real steel grade in the solid phase under strictly defined conditions for controlled heating. Heat capacity of steel was obtained using high-temperature calorimeter Setaram MHTC 96 (Multi High Temperature Calorimeter) with 3D DSC sensor. Experimentally acquired heat capacity („Apparent Heat Capacities“) of real steel grade was confronted with the calculated theoretical data (software Thermo-Calc) and with data reported in the available literature.

Keywords: DSC, heat capacity, steel, thermal analysis, Thermo-Calc

1. INTRODUCTION

Methods of studying of processes related to steel production are based on knowledge of the thermodynamic properties of materials occurring in the technological processes. It is necessary to pay attention to acquisition of reliable data, which are needed for modelling of processes, for control of solidification processes, but also for improvement of process procedures and for enhancement of their efficiency. Typical necessary data are heat capacities (often called specific heats) [1], phase transition temperatures, latent heats, surface tension, interface tension [2-5] and other important data (thermal conductance, etc.). The obtained data should be used like input data for many simulation programs (simulation of the temperature and concentration fields in castings), numerical, physical models and requirements of practice (casting conditions) and they should contribute to explanation of mechanism of phase transformations of steels, which appear to be much more complex that it has been referred so far. Many of these data are accessible in the literature, but it is very often difficult to find data for a given material (with exact chemical composition), as well as for the required temperature interval. The data for given material as found in different sources of the literature sometimes even differ from each other [2].

Differential Scanning Calorimetry (DSC) presents one possibility for describing thermal behaviour of steels and for verifying theoretical data. This method makes it possible to obtain thermophysical and thermodynamic data (such as heat capacities, latent heats, ...) not only of metallic systems [3].

The purpose of this investigation was the experimental and theoretical determination of the heat capacities of real steel grade in the solid phase under strictly defined conditions for controlled heating.

2. THEORETICAL BASICS

Differential Scanning Calorimetry (DSC) is the technique in which the difference in heat flow rate (or power) to the sample and to the reference sample is monitored against time while the samples are exposed to a temperature programme. This method makes it possible to obtain heat capacities and latent heats not only of steels. Heat capacity can be expressed as heat (Q) absorbed/released by the sample (material) during its heating or cooling between the temperatures T_1 and T_2 [1, 3]: mean value of C_p at constant pressure can be expressed by the equation (1):

$$\overline{C} = \frac{Q}{T_2 - T_1} \quad (1)$$

For comparison of the values of heat capacity of different materials, it is necessary to relate this quantity to the amount of material. If the C_p is related to the (sample) mass, then the so-called specific heat capacity at constant pressure is defined. The device through which you can obtained data is a differential scanning calorimeter (DSC device) [1, 3].

Continuous method is the fastest method for C_p determination and was used for experimental measurements in this study. The scheme of the continuous method is shown in **Figure 1**.

The heat capacity determination on the basis of DSC experiment (continuous C_p method) comprises three main sequences: the first sequence is adjusted isothermal dwell, the second sequence is linear heating in the whole measured temperature interval and the third sequence is isothermal dwell at the temperature that makes it possible to cover the desired temperature interval. All the three sequences must be performed with empty crucibles (B), with the sample (S) and with the reference sample (C). Consecutively, the heat capacity can be calculated according to the following equation (2) [6-8]:

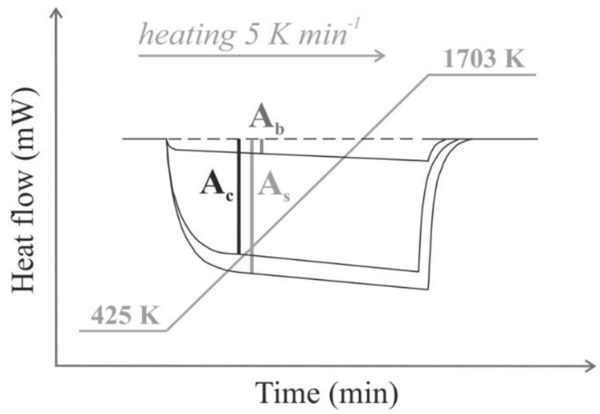


Figure 1 Scheme of continuous Cp method

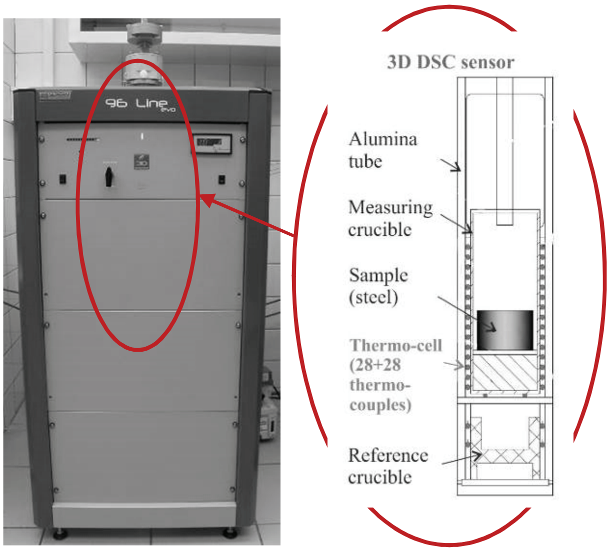
$$C_p = C_{pc} \frac{m_c (A_s - A_b)}{m_s (A_c - A_b)} \quad (2)$$

where, A_b, A_s, A_c in mW are segments corresponding to the heat effects detected for blank (measurement with empty crucibles), measurement with sample and reference sample, C_{pc} in J/K·g is the heat capacity of reference sample, C_p in J/K·g is the heat capacity of measured sample, m_s in mg and m_c in mg are masses of sample and reference sample.

3. EXPERIMENT

3.1. Equipment, material and conditions

Heat capacity ("apparent heat capacity"- the heat capacity including the latent heat of the phase transition) of the low-carbon steel was acquired with use of experimental laboratory equipment for thermal analysis Setaram MHTC 96 (Multi High Temperature Calorimeter [8], **Figure 2**), measuring rod 3D DSC (drop sensor, **Figure 2**) and thermocouple of the type „B" (PtRh 6 %/PtRh 30 %) were used for obtaining of heat capacity. The thermocouple consists of 28 thermocouple connections, which surround the crucible walls and bottom (3D DSC sensor). DSC method was used for the purposes of measurement of heat capacity of steel. The sample was analysed in corundum crucible with volume of 5 300 µl. Dynamic atmosphere of He (purity 6N) was maintained during analysis in order to protect the sample against oxidation. Helium is more suitable for obtaining the Cp values using scanning methods because of its substantially higher thermal conductivity in comparison with argon (Ar).



Experimental possibilities	Setaram MHTC 96
experimental methods	hf-DSC ("Continous" and "Stepwise" method); drop; DSC
temperature range	+ 20°C to + 1600°C
heating/cooling rate	0.001 to 99 °C/min
temperature programs	linear heating/cooling; isothermal holding; cycling
sample mass	hf-DSC up to 2.5 g
	DROP up to 30 g
atmosphere	vacuum; inert; reactive
type of Cp sensor	3D DSC sensor

Figure 2 Laboratory equipment Setaram MHTC 96 with measuring rod/drop sensor 3D DSC, experimental possibilities

Low-carbon steel (approx. 0.186 wt % of C, 1.310 wt % of Mn, 0.184 wt % of Si) was chosen as experimental material. Sample was cylindrical in shape, 14 mm in diameter and 10 mm in height, with mass about 13 g. Sample was brushed to remove possible oxidation layer, then in acetone by simultaneous ultrasound impact was cleaned.

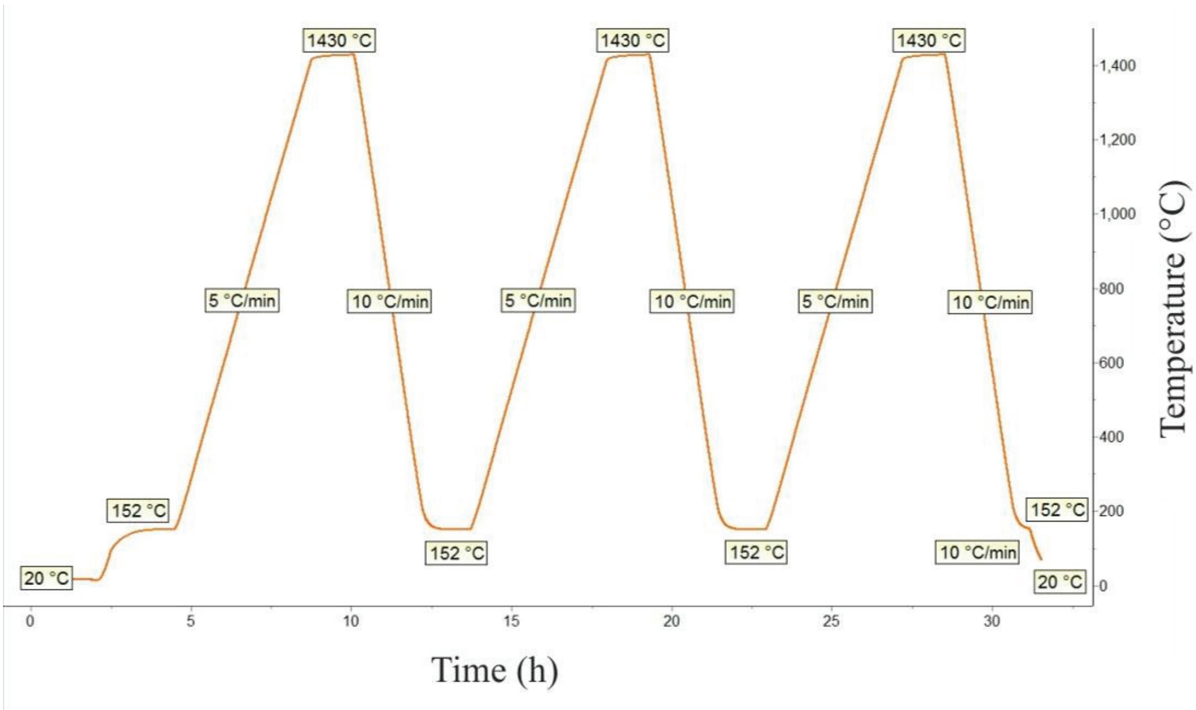


Figure 3 Temperature program for measurement of “apparent heat capacities” (MHTC 96)

The experiment was consisted in performing three measurements. The first measuring was done with the empty corundum crucible (blank), the second measuring with mass m_s of steel sample and the third measuring with mass m_c of reference sample (Pt, 3N5) with a known heat capacity C_{pc}. The measurement with the empty corundum crucible (blank) was done according to the temperature program (**Figure 3**). The measurement with the steel sample and reference (Pt) were done in the same way. The heat capacity was determined on the basis of adjusted isothermal holding at 425 K, linear heating 5 K/min in the whole measured temperature interval and isothermal holding at the temperature 1 703 K (**Figures 1 and 3**). Each measurement was performed three times (**Figure 3**). Despite the fact that this method measuring of capacity is fast, measurement is time consuming.

4. CALCULATIONS (SOFTWARE THERMO-CALC)

Software Thermo-Calc (SW TC) is a flexible software and database package for all kinds of phase equilibrium, phase diagram and phase transformation calculations and thermodynamic assessments. This thermodynamic software is based on CALPHAD method. CALPHAD method enables to prediction of phase composition of multicomponent system by utilizing thermodynamical parameters of subsystem (experimentally obtained phase and thermodynamical data of lower order system). CALPHAD method enables (besides calculation of equilibrium) to calculation a lot of thermodynamical parameters [9]. In this work software Thermo-Calc (SW TC) for calculating of heat capacity (apparent heat capacity) of real steel grade was used. Calculations were performed with use of TCFE7 database [10]. Calculations using Thermo-Calc are more sophisticated than using Neumann-Kopp rule, nevertheless it is always necessary to verify calculated values using the experiment.

5. RESULTS AND DISSCUSION

Apparent heat capacity (Cp in J/K·g) of real steel grade was obtained on the basis of evaluation of DSC curves. Experimentally obtained and calculated values of apparent heat capacity of steel are graphically presented in **Figure 4**. The resulting value of heat capacity dependence (**Figure 4**, “experiment”) was obtained from three measurements. Curves obtained from all measurements were compared each other. Standard deviation of three replicates was lower than 1 %.

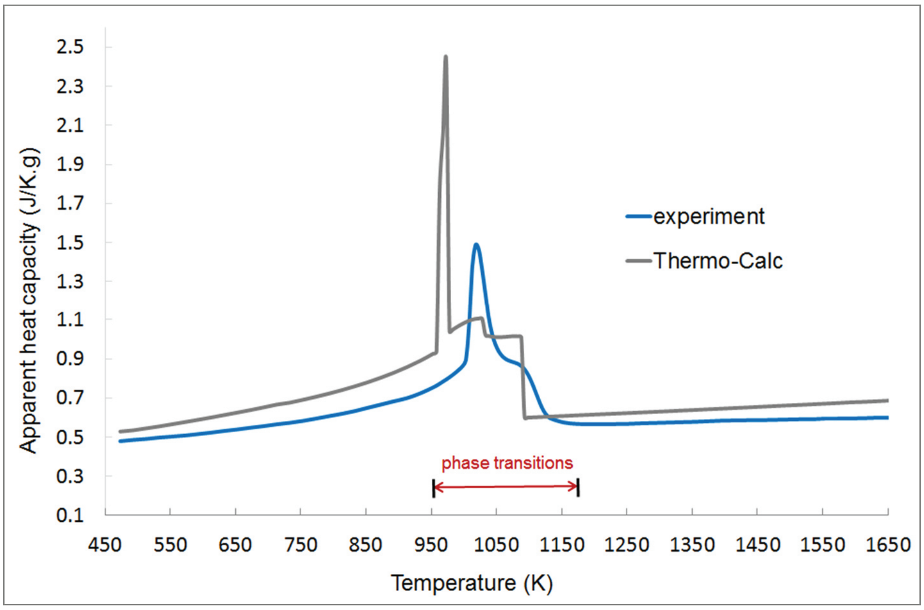


Figure 4 Comparison of C_p dependencies, experimental and calculated values

Experimental results and calculated values (SW TC) were compared and discussed. The comparison presents **Figure 4**. **Figure 4** shows dependences of apparent heat capacity (Cp including the latent heat of the phase transition) of steel in selected temperature interval (470-1 650 K).

The experimentally obtained Cp values (on the basis of three measurements) are close to the values calculated using the SW Thermo-Calc in the temperature interval of 470-950 K. Good agreement of experimental values with values calculated using Thermo-Calc was achieved in the temperature region 1170-1 650 K also. The Cp dependence trends are the same. Heat capacity values significantly differ between temperatures of 950-1 170 K because of running phase transitions. The first thermal effect (**Figure 4**, “Thermo-Calc”; from the left side) corresponds to eutectoid phase transition, second corresponds to the change of magnetic properties and third corresponds to the alpha-gamma phase transition. Experiment (**Figure 4**) shows two thermal effects on the curve and calculation shows three thermal effects. Thermal effects correspond to the change of magnetic properties and to the alpha-gamma phase transition are shifted and overlap one another.

Temperatures of the phase transitions (the experimental curve) are shifted to the higher temperature. Differences between the experimentally obtained and calculated values can be probably explained by simplifications and limitations that are implemented in the calculation models or dynamics of the process and by detection capabilities of instruments. The calculating relations and models are also often derived on the basis of experimental data (that are at present insufficient) and theoretical assumptions, which are valid most often for a certain interval of chemical composition [2, 3]. Heat capacity was experimentally obtained at heating rate 5 K/min (no equilibrium conditions), while Thermo-Calc calculated heat capacity at equilibrium conditions.

6. CONCLUSION

In the presented work apparent heat capacity of real steel grade in the low temperature region was experimentally investigated. Heat capacity of steel was obtained using DSC continuous method (Multi High Temperature Calorimeter). Experimental measurements were performed to obtain our own data of the temperature dependence of Cp on the temperature for the real steel grade. The good agreement was achieved in the temperatures regions without phase transition (ca. 470-950 K and ca. 1 170-1 650 K). Although utilisation of the calculation SW is very comfortable and fast, this procedure is mostly based on theoretical assumptions, limitations and approximations connected with the composition of the alloy, temperature interval, calculation model limitations and others. Values of Cp are mostly calculated only with respect to the chemical composition, but the Cp value (dependence) may be influenced by structure, phases present in the sample and influence of the deformational state. Therefore, the best way to obtain proper data for the system under investigation is by carrying out an experiment.

The experimentally obtained value of heat capacity will be used as input data for mathematical and physical models (eg. Magmasoft, Procast) and will also be used for optimum setting of casting conditions during real casting of steel.

ACKNOWLEDGEMENTS

This paper was created on the Faculty of Metallurgy and Materials Engineering in the Project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic, TAČR project Nos. TA03011277 and TA04010035 and student projects SP2016/90 and SP2016/103.

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