STUDY OF HEAT CAPACITY OF REAL STEEL GRADE

Monika ŽALUDOVÁ[a,b], Bedřich SMETANA[a,b], Simona ZLÁ[a,b], Jana DOBROVSKÁ[a,b], Silvie ROSYPALOVÁ[a,b], Aleš KALUP[a], Karel MICHALEK[a,b]

[a] *VSB-TUO, Faculty of Metallurgy and Materials Engineering (FMME), Ostrava, Czech Republic, EU, monika.zaludova@vsb.cz*

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

Abstract

Heat capacity of steels is one of the crucial thermophysical parameters used for process behaviour prediction in many applications. Heat capacity is an input variable for many thermodynamical and kinetic programs. The dependences of heat capacity on common variables (temperature, pressure,etc.) are also commonly used as the input data in software packages that are applicable in the field of applied research for simulations of technological processes. Experimental data of heat capacities can be found in literature, but it is difficult to find data for given steel (with exact chemical composition). The paper deals with the study of heat capacity of real steel grade in the low temperature region. Heat capacity of steel was obtained using DSC continuous method and laboratory system MHTC (Multi High Temperature Calorimeter). Experimentally obtained data of heat capacity were compared with calculated data of heat capacity.

Keywords: heat capacity, steel, thermal analysis, ThermoCalc, Neumann-Kopp rule

1. INTRODUCTION

Heat capacity (often called specific heat) [1, 2] and other material properties [3, 4] of alloys (metals) are crucial thermo-physical quantities for many applications. Heat capacity is an input variable for many thermo-dynamical (e.g. Thermocalc, Pandat, MT Data,...) and kinetic programs (e.g. IDS-Solidification analysis package,...). Heat capacity dependencies are also used like an input data for many programs, which are applicable in the field of applied research [5, 6], and for simulations of technological processes using calculating SW (e.g. Calcosoft, Magmasoft, Fluent...). It follows from the mentioned above that the heat capacities of materials, in our case alloys, play a very important role in the field of basic and applied research. Generally, experimental data can be found in the accessible literature, but corresponding (needed) data, for concrete alloy, can be found very seldom. The knowledge of proper values of heat capacities of alloys at the corresponding temperature can substantially contribute for addition and precision of existing databases and simulations software. The paper presents experimental and theoretical possibilities of heat capacity of steel determination in a wide temperature region (470-1500 K).

2. NEUMANN-KOPP RULE

Neumann-Kopp rule is one of the simple calculations for obtaining of heat capacities and its dependences on temperature. Molar heat capacity of solid solution formed by compounds A, B, C can be mathematically expressed according to Neumann-Kopp rule as follows:

$$C_{pm,sol.solution} = X_A C_{pm,A} + X_B C_{pm,B} + X_C C_{pm,C} \qquad (1)$$

where X is molar fraction of individual compounds and C_{pm} is molar heat capacity in J/K·mol (or its dependence on temperature) of individual compounds at constant pressure. Molar heat capacity of individual compounds can be found in literature (for example in [7]) in the form its dependence on temperature:

$$C_{pm} = a + bT + cT^{-2} \quad (2)$$

where a, b, c is constant calculated on the basis of experimental measurement of molar heat capacity at constant pressure and T is temperature in K. When using Neumann-Kopp rule it is necessary to consider not only the content of individual elements but also the phase in which the elements are and whether elements do not form compounds with other elements.

Molar heat capacity in J/K·mol was calculated using Neumann-Kopp rule. Molar heat capacity on specific heat capacity was recalculated according to the following formulae:

$$C_p = \frac{C_{pm}}{M} \quad (3)$$

where M is molar weight of sample.

Heat capacity calculated according to Neumann-Kopp rule may not be accurate. It is always necessary to verify calculated values using the experiment. Application of Neumann-Kopp rule is quick, simple and cheap way to get the values of heat capacities at absence of experimental data [8].

3. THERMOCALC

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 ThermoCalc (version 7.0.1) for calculating of heat capacity (apparent heat capacity) of real steel grade was used. Calculations were performed with use TCFE7 database [10]. Calculations using Thermocalc are more sophisticated than using Neumann-Kopp rule, nevertheless it is always necessary to verify calculated values using the experiment.

4. MATERIAL

Low-carbon steel (ČSN 41 1353: 1983) was chosen as experimental material. Sample was cylindrical in shape, 5 mm in diameter and 11 mm in height, with mass about 1700 mg. Sample was brushed to remove possible oxidation layer, then in acetone by simultaneous ultrasound impact was cleaned.

5. EXPERIMENTAL EQUIPMENTS AND CONDITIONS

Laboratory system for thermal analysis Setaram MHTC 96, measuring rod **3D DSC** and thermocouple of the type „B“ (PtRh 6%/ PtRh 30%) were used for obtaining of heat capacity. The thermocouple consists of 20 thermocouple connections, which surround the crucible walls (**3D DSC** sensor). The sample was analysed in corundum sleeves inserted into platinum crucibles with volume of 400 μl. Dynamic atmosphere of He (purity 6N) was maintained in the furnace during analysis in order to protect the sample against oxidation.

The experiment was consisted in performing three measurements with two cells: the measurement and the reference cells. (An empty platinum crucible with corundum sleeve was in reference cell in all measuring.) The first measuring was done with the empty platinum crucible with corundum sleeve (blank), the second measuring with mass m_s of steel sample in crucible in measuring cell and the third measuring with mass m_c of reference sample of corundum with a known heat capacity C_{pc} in crucible in measuring cell. The heat capacity was determined on the basis of adjusted isothermal holding at 420 K, linear heating 10 K/min in the whole measured temperature interval and isothermal holding at the temperature 1570 K. In **Fig. 1** is given scheme measuring by continuous method for calculating capacity. Each measurement was performed four times. Despite the fact that this method measuring of capacity is fast, measurement is time consuming.

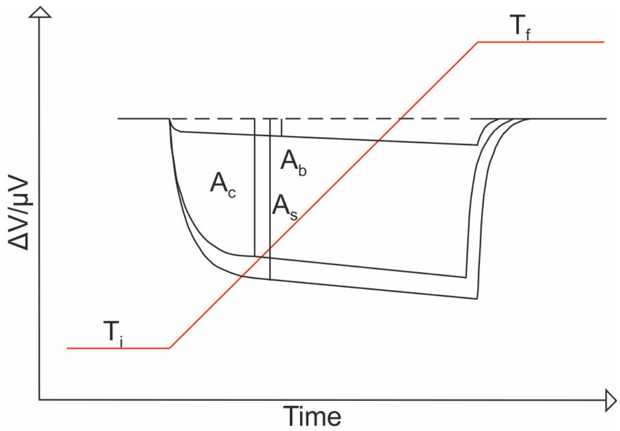

Fig. 1 Scheme of continuous method

Consecutively, the heat capacity can be calculated according to the following formulae [11]:

$$C_p = C_{pc} \frac{m_c (A_s - A_b)}{m_s (A_c - A_b)} \tag{4}$$

where, A_b, A_s, Ac in μV 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.

6. RESULTS AND DISSCUSION

Apparent heat capacity was obtained on the basis of evaluation of DSC curves. Curves obtained from all measurements were compared each other. Standard deviation was lower than 1 %.

Experimental results and calculated values were compared and discussed. The comparison presents **Fig. 2**. **Fig. 2** shows dependences of steel C_p in selected temperature interval (473-1523 K). Apparent heat capacity (C_p with contribution of transformation) was obtained using experiment and calculation in thermodynamic software ThermoCalc. Heat capacity using Neumann-Kopp rule was obtained.

Very good agreement of experimental values with values calculated using ThermoCalc was achieved in the temperature region 470-980 K. The relative deviation does not exceed 2.6 %. Good agreement of experimental values with values calculated using ThermoCalc was achieved in the temperature region 1210-1500 K also. The relative deviation does not exceed 4.5 %. Heat capacity values significantly differ between temperatures 980-1210 K due to taking place transformation. (The first thermal effect corresponds to eutectoid phase transformation, second corresponds to the change of magnetic properties and third corresponds to the alpha-gamma phase transformation.) It is impossible experimentally obtain heat capacity of phase transformation. It is possible to obtained apparent heat capacity, which contains thermal effect of transformation. Experimentally obtained and calculated apparent heat capacities have a similar behaviour. Thermal effects on the experimental curve are shifted to the higher temperature. It can be probably explained by simplifications and limitations that are implemented in the calculation model or dynamics of the process and by detection capabilities of instruments [12]. Heat capacity was experimentally obtained at heating rate 10 K/min, while ThermoCalc calculated heat capacity at equilibrium conditions.

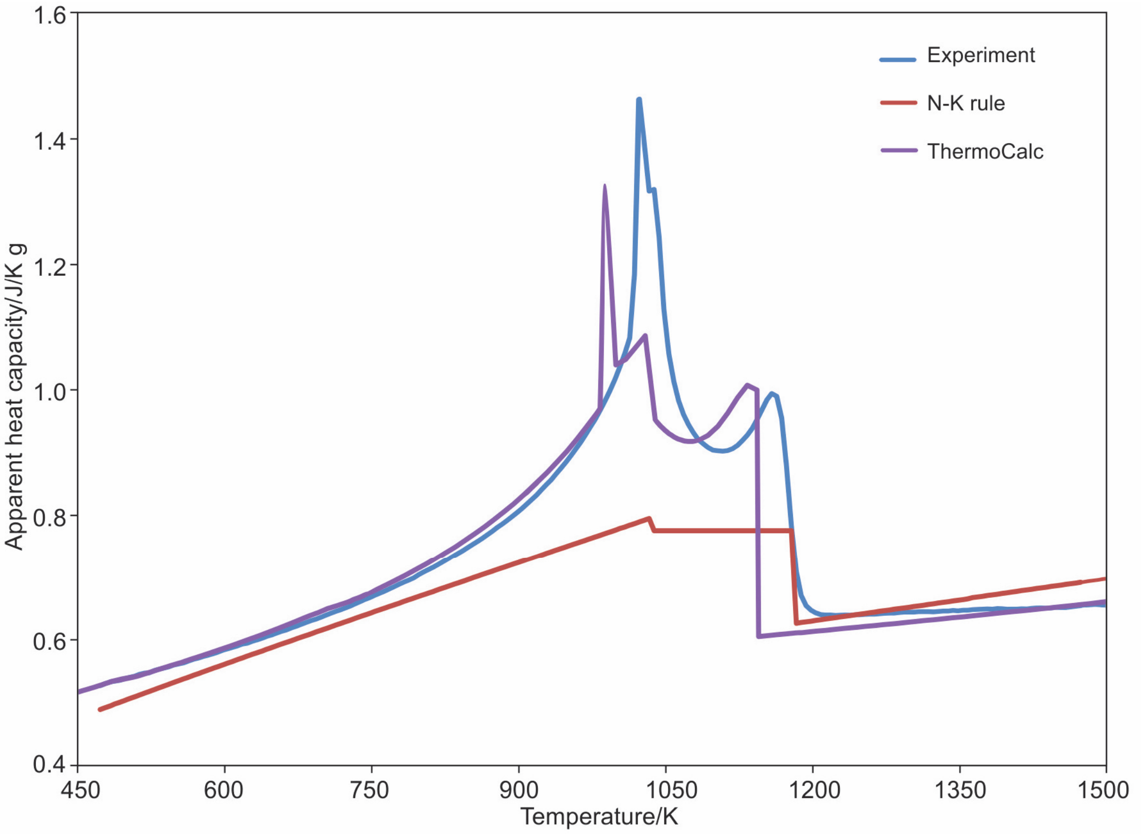

Fig. 2 Comparison of C_p dependencies, experimental and calculated values

Heat capacity was calculated using Neumann-Kopp rule (no apparent heat capacity). From this reason significant difference between experimental and calculated values was observed. But the relatively good agreement was achieved in the temperature region 470-890 K (The relative deviation does not exceed 9.5%.) and 1208-1500 K (The relative deviation does not exceed 7 %.).

Although utilisation of the calculation (SW ThermoCalc, Neumann-Kopp rule) is very comfortable and fast, this procedure is mostly based on the theoretical assumptions, limitations and approximations connected with the composition of the alloy, temperature interval, calculation model limitations and others. Cp values are mostly calculated only with respect to the chemical composition, but the Cp values may be influenced by structure, phases present in the sample and influence of the deformational state. Therefore, the best way to obtain heat capacity for the sample is by carrying out an experiment.

CONCLUSION

The paper presents the study of heat capacity of real steel grade in the low temperature region. Heat capacity of steel was obtained using DSC continuous method (Multi High Temperature Calorimeter). Experimentally obtained data of heat capacity were compared with values of heat capacity calculated using ThermoCalc and Neumann-Kopp rule.

Apparent heat capacity was obtained on the basis of experiment and calculated by ThermoCalc. Heat capacity was calculated using Neumann-Kopp rule. Experimentally obtained data of heat capacity were compared with calculated data of heat capacity. The good agreement was achieved in the temperatures regions without phase transformation (ca. 470-900 K and ca. 1210-1500 K).

Although utilisation of the calculations is very comfortable and fast, but the best way to obtain proper data for the system under investigation is by carrying out an experiment.

Obtained results will be in the frame of project TAČR č. TA03011277 used for numerical simulations and for setting of control system of continuous casting.

ACKNOWLEDGEMENTS

This paper was created in the frame of the project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic and the project of Technology Agency of the Czech Republic No. TA 03011277 and the student project SGS (SP2014/62).

REFERENCES

[1] JEYAGANESH, B., et al. A Study on the Effect of Thermal Ageing on the Specific-Heat Characteristics of 9Cr-1Mo-0.1C (mass %) Steel. *Inter. J. Thermophysics*, 30. 2, 2009, 619-634.

[2] SMETANA, B., et al. Possibilities of heat capacity measurement of metallic systems. In *METAL 2011: Proceedings of 20th Inter. Metallurgical and Materials Conference (METAL2011), 2011, Brno. Ed.* TANGER, s r.o. Ostrava, 2011, 462-467.

[3] GRYC, K., et al. Thermal Analysis of High Temperature phase Transformation of Steel. *Metalurgija*, 52, 4, 2013, 445-448.

[4] GRYC, K., et al. Determination of the Solidus and Liquidus Temperatures of the Real-Steel Grades with Dynamic Thermal-Analysis Methods. *Materiali in Tehnologije*, 47, 5, 2013, 569-575.

[5] TKADLEČKOVÁ, M., et al. Setting a Numerical Simulation of Filling and Solidification of Heavy Steel Ingots Based on Real Casting Conditions. *Materiali in Tehnologije*, 46, 4, 2012, 399-402.

[6] SMETANA, B., et al. Experimental Verification of Hematite Ingot Mould Heat Capacity and its Direct Utilisation in Simulation of Casting Process. *J. Thermal Analysis and Calorimetry*, 112, 1, 2013, 473-480.

[7] KOMOROVÁ, L., IMRIŠ, I. Termodynamika v hutníctve. 1st ed. Bratislava: Alfa, 1990. 296 p.

[8] LAŠČEK, M. Špecifická Tepelná Kapacita Austenitickej Chrómniklovej Ocele 1Cr18Ni9. *Acta Metall. Slov.*, 14, 1, 2008, 34 - 49.

[9] ZHAO, G.W., et al. ThermoCalc-based Numerical Computations for Temperature, Fraction of Solid Phase and Composition Couplings in Alloy Solidification. *Int. J.Mater. Res.*, 99, 6, 2008, 680-688.

[10] Thermo-Calc Software TCFE7 Steels/Fe-alloys database version 7, *http://www.thermocalc.com* (Accessed 23 Aug 2013)

[11] *TG and MHTC manual version*. France: Setaram, 2009. p. 121.

[12] ŽALUDOVÁ, M., et al. Study of DTA Method Experimental Conditions and of Their Influence on Obtained Data of Metallic Systems. In *METAL 2012: Proceedings of 21th International Metallurgical and Materials Conference (METAL2011), Brno, Ed.* TANGER, s r.o. Ostrava, 2012, 640-645.