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APPLICATION OF THERMAL ANALYSIS TESTS RESULTS IN THE NUMERICAL SIMULATIONS OF CONTINUOUS CASTING PROCESS

ZASTOSOWANIE WYNIKÓW BADAŃ ANALIZY TERMICZNEJ W OBLICZENIACH NUMERYCZNYCH PROCESÓW ODLEWANIA STALI

Measurement of thermophysical properties of steel is possible by using different thermal analysis techniques. In the field of metallurgy the most relevant methods are Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). The paper presents the results of thermophysical properties which are necessary to carry out numerical simulation of continuous casting of steel. The study was performed for two steel grades S320GD and S235JR. The main aim of the research was to determine the dependence of specific heat on temperature. On the basis of obtained results the thermal effects of phase transformations and characteristic transition temperatures were also identified. Both the specific heat of steel and thermal effects of phase transformations are included in the Fourier-Kirchhoff equation, as the material properties necessary to obtain the numerical solution. The paper presents the research methodology, analysis of results and method of determining the specific heat of steel based on the results of DSC analysis.

Keywords: thermal analysis of steel, specific heat, enthalpy of phase transitions, steel

Pomiar właściwości termofizycznych stali możliwy jest dzięki wykorzystaniu różnych technik analizy termicznej. W metalurgii najszersze zastosowanie znalazły różnicowa analiza termiczna (DTA) oraz różnicowa kalorymetria skaningowa (DSC). W pracy przedstawiono wyniki badań właściwości termofizycznych koniecznych do przeprowadzenia symulacji numerycznej procesu ciągłego odlewania stali. Badania wykonano dla dwóch gatunków stali S320GD i S235JR. Głównym celem badań było wyznaczenie funkcyjnej zależności ciepła właściwego analizowanych gatunków stali od temperatury. Na podstawie przeprowadzonych badań określono również efekty cieplne przemian fazowych oraz charakterystyczne temperatury przemian. Zarówno ciepło właściwe stali jak i efekty cieplne przemian fazowych wchodzą w skład równania Fouriera-Kirchhoffa, jako właściwości materiałowe konieczne do uzyskania rozwiązania numerycznego. W pracy przedstawiono metodykę badań, analizę uzyskanych wyników oraz sposób wyznaczania ciepła właściwego stali w oparciu wyniki analizy DSC.

1. Introduction

Numerical modelling applied to simulations of the continuous steel casting process is an important element combining scientific research with the practical application of test results under industrial conditions. The computer simulation not only enables the temperature field of the strand to be forecast, but also the thickness of the shell forming in the mould. It also allows the determination of the strand metallurgical length for the selected steel grade and the adopted cooling programme. Thanks to computer simulation we are able to test the influence of a change in the key process parameters on its final effect, without interfering in the actual process. Various variants of boundary conditions assumed in the numerical simulation, describing complex mechanisms of heat transfer between the solidifying cast strand and the environment, enable various cooling programmes to be optimised for the shell forming rate or thermal stress occurring in the cast strand [1]. ProCAST is an example of a commercial program which enables the CCS process to be modelled [2,3].

Two main problems are most often encountered when formulating a numerical model of the steel continuous casting process. The first one is the determination of the boundary conditions of heat transfer between the solidifying cast strand and its environment. The second problem concerns limited access to the database of thermophysical properties of a broad range of steel grades cast in the continuous manner.

Taking the process conditions into account, direct monitoring of its course with available measurement methods is difficult. The process conditions prevailing in the secondary cooling zone of a continuous casting machine, such as the thermal radiation of the strand cooled, as well as intensive water-air cooling causing the formation of large amounts of steam and scale covering the strand, substantially hinder the verification of the boundary conditions assumed in a numerical model. In the primary cooling zone, the strand shrinks as a result of shell crystallisation. This shrinking causes the forma-

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tion of an air gap between the mould walls and the solidifying strand. This phenomenon disturbs the steady conditions of heat transfer in the process. Consequently, the boundary conditions that are necessary to obtain the modelling result bring about simplifications to the description of the heat transfer mechanisms, which translate into the accuracy of the numerical solution obtained [4].

The second problem that is encountered during continuous steel casting process modelling is limited access to the thermophysical data of the steel; in the numerical model this defines the material behavior during the solidification. Taking the large number of steel grades cast in CCS machines into account, the availability of reference data on analysis of the thermal properties of steel is very limited. However, it is not possible to make a comprehensive and useful simulation of the CCS process when the basic material data of the steel is unknown. The basic equation that is solved in the numerical simulation of the CCS process is the Fourier-Kirchoff equation (1), containing a set of key thermophysical data for steel, which is defined as the material model.

$$\left[\frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y}\left(\lambda \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z}\left(\lambda \frac{\partial T}{\partial z} \right) \right] + \dot{q}_v = \rho(T)\, c_p(T) \frac{\partial T}{\partial \tau}$$

(1)

where:

λ – thermal conductivity,

ρ – density,

c_p – specific heat,

$\dot{q}_v$ – internal heat source such as latent heat of phase transformations.

The material model consists of a few parameters such as specific heat, viscosity, density and heat conductivity. In a numerical model it is particularly significant to precisely determine the heat conductivity and the specific heat as they are key during the description of heat transfer by conduction – a dominating heat transfer mechanism in the process of continuous casting of steel. From the perspective of process modelling, it is also vital to know the Liquidus and Solidus temperatures that are characteristic of the chosen steel grade, and the phase transition enthalpy, complementing the thermal balance of the solidifying strand.

Due to the small quantity of reference data, in some cases the thermophysical steel data that is necessary for calculations may be generated by applying programs for thermodynamic computing such as FactSage or ThermoCalc [5]. However, for the ProCAST program the availability of data depends on the thermodynamic database at hand, and determines arbitrary adoption of one of three steel crystallisation models – Scheil, Lever or Back Diffusion. Due to the crystallisation mechanism and the occurring segregation of components, the most appropriate model for steel is the Back Diffusion model, yet its application requires that the strand cooling rate is known. Depending on the selected crystallisation model, the calculated Solidus temperatures in the case of ThermoCalc used by ProCAST differ even by a few tens of degrees.

Taking into account the accuracy of the numerical solution, actual values of the thermophysical properties of the steel should be considered in simulation of CCS process. Required thermophysical properties can be obtained experimentally using the methods of thermal analysis.

2. Test material and research methodology

Two steel grades cast with a continuous casting machine for long products were selected for an analysis of thermophysical properties. The chemical composition of the selected steel grades is presented in Table 1. The grades analysed have similar chemical compositions, which allowed verification of repetitiveness of the test results obtained. The test samples were cut from the cast strands after the completed casting process. The dimensions of the prepared samples were: diameter 5 mm, height about 1 mm, weight about 150mg.

TABLE 1

The chemical composition of the analyzed steels

Steel grade	Chemical composition, %								
	C	Mn	Si	P	S	Cu	Cr	Ni	Mo
S320GD	0,070	0,740	0,020	0,013	0,010	0,020	0,020	0,070	0,007
S235JR	0,080	0,520	<0,005	0,015	0,014	0,030	0,007	0,007	<0,005

Differential scanning calorimetry (DSC) was used to measure the thermophysical properties of the selected steel grades [6]. Out of the available methods of thermal analysis, the DSC method and differential thermal analysis (DTA) are the methods that are most often applied in metallurgy [5,7-9]. The DTA analysis is used for identification of phase transition temperatures in steels, e.g. the solidification or melting temperature, examination of the transformed phase fraction, or measurement of the Solidus and Liquidus temperatures. The DSC method additionally allows determining a parameter which is essential from a thermal balance perspective, namely the phase transition heat, in particular the steel solidification heat, characterised by the highest exothermic effect relative to other transformations occurring in steel.

The DSC analysis consists in measurement of the difference in heat fluxes, recorded for the sample analysed and the reference sample. During the measurement, both the sample and the reference material, are subjected to the effect of the same temperature programme, determining the temperature change rate during the analysis. In the reference material used in the tests, within the assumed temperature range, no structural changes should occur. Analysis of the recorded change in the heat fluxes from reference material and steel sample allows identification of phase transitions in the steel [8]. In practice, as the measurement is performed under isobaric conditions, the recorded difference in heat fluxes corresponds to enthalpy changes as a function of temperature, whereas the peak areas correspond to the heat of phase transitions occurring in the steel.

The measurement of phase transition enthalpy by differential scanning calorimetry is performed in two stages. The first one is a recording of the baseline. The measurement for an empty crucible is performed. This activity is repeated several times in order to obtain a stable and repeatable line. Next the measurement for the sample is performed under the same conditions. The DSC curve which serves as the basis for the measurement of transition enthalpy is determined as the difference of signals for the sample and the baseline. At the time of transition, depending on its nature, a disturbance called either

endo- or exothermic peak appears on the DSC curve. The peak area corresponds to the recorded change in enthalpy ΔH (2) [10].

$$\Delta H = \frac{1}{m_S \cdot E} \int_{T_1}^{T_2} [(DSC_S(T) - DSC_B(T)] \, dT \qquad (2)$$

where:

m_s – mass of sample, [g]

DSC_S – signal value for the sample, [V·s]

DSC_B – signal value for the baseline, [V·s]

E – calibration factor of heat exchanged, [V/W]

The heat of phase transitions is included in the F-K equation (1) as parameter $\dot{q}_v$, or the internal heat source.

Application of the DSC-cp carrier in thermal analysis tests, which is adjusted to analyse the variability of the specific heat, allows a determination of the dependence of this parameter on temperature. The requirements concerning the specific heat measurement with the DSC method at continuous heating are described in standards ASTM E 1269, ISO 11357-4 and DIN 51007. All three standards require using the same temperature programme consisting of three segments: isothermal holding, heating at a constant rate and isothermal holding once again. Such a programme is applied for three measurements, which should be performed directly in sequence under identical measurement conditions: the baseline measurement, the measurement of a reference material with known specific heat (most often α-Al$_2$O$_3$), the measurement for the sample. The dependence of the specific heat on temperature is calculated based on formula (3):

$$c_p^S(T) = c_p^R(T) \cdot \frac{m_R(DSC_S(T) - DSC_B(T))}{m_S(DSC_R(T) - DSC_B(T))} \qquad (3)$$

where:

DSC_B, DSC_R, DSC_S – signals corresponding to the effects of heat registered respectively for the baseline sample and the reference material, [V]

m_R, m_S – masses of the reference material and samples, [g]

c_p^R – specific heat of the reference material, [J·g^{-1}·K^{-1}]

Standard DIN 51007 used in the presented tests additionally introduces a linear adjustment (4) with the aim of eliminating the baseline drift [10].

$$DSC_{DIN}(t) = DSC(t_1) + \frac{DSC(t_2) - DSC(t_1)}{t_2 - t_1} \cdot (t - t_1) \qquad (4)$$

This adjustment is determined on the basis of the DSC signal values at times t$_1$ and t$_2$ of isothermal segments of the temperature programme.

3. Test result analysis

The DSC tests and specific heat tests were carried out with a heat flux NETZSCH STA 449 F3 Jupiter calorimeter. This device allows conducting DSC measurements at temperatures ranging from room temperature to 1650°C, with scanning rates of 0.01-50°C/min. The DSC analysis sensitivity is 1 μW.

3.1. The determination of phase transition temperatures and thermal effects of transitions

The tests of melting temperatures and enthalpies were carried out in a dynamic helium 6N atmosphere. The samples were placed in crucibles made of Al$_2$O$_3$, the reference sample was an empty crucible. The test was conducted with a heating rate of 10°C/min from room temperature to the temperature at which the sample completely melted. Before starting the actual tests, the temperature was calibrated and the exchanged heat was calibrated within the whole measurement range of the instrument. The temperature calibration was performed based on the melting temperatures, and the calibration of the exchanged heat on the basis of melting enthalpy of pure elements such as In, Zn, Al, Ag, Au.

The test results of the DSC analysis for steels S320GD and S235JR are presented in Fig. 1 and Fig. 2 respectively. Endothermic peaks that are characteristic of steels, marked as A, B, C, D, can be observed on the DSC curves. They are related to phase transitions occurring in the steel grades analysed. The results of the DSC analysis for steel S320GD that are presented in Fig. 1 allow identification of phase transition temperature and phase transition thermal effects. Labels of phase transitions applied in Fig. 1 respectively correspond to: A – magnetic transformation, B – transformation of ferrite into austenite, C – formation of high temperature ferrite, D – melting. The magnetic transformation A is a second-order transition, consisting in a change in the magnetic properties of the steel. As a result of the magnetic transformation, the specific heat value changes, however no thermal effects relevant for the process modelling occur.
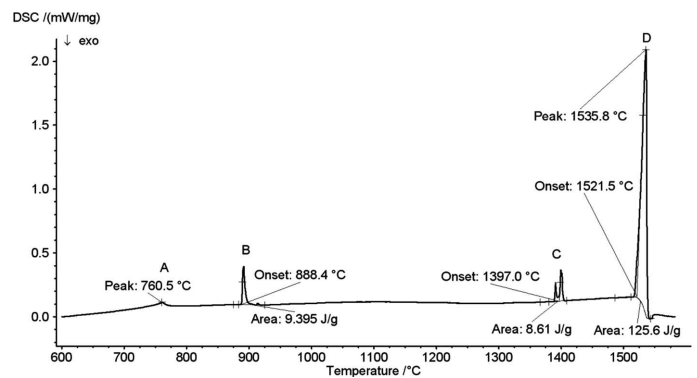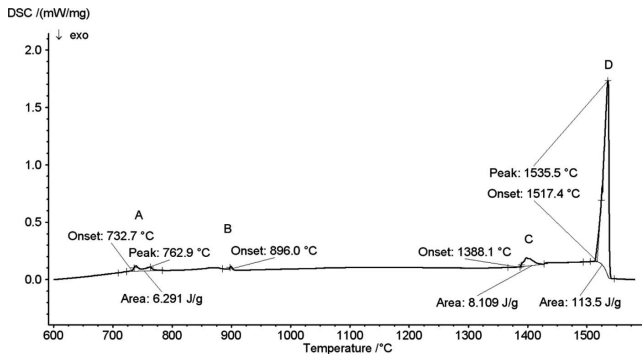

Fig. 1. DSC analysis of steel S320GD. The recorded temperatures of phase transitions and the enthalpy change. A – magnetic transformation, B – transformation of ferrite into austenite, C – formation of high temperature ferrite, D – melting

Points marked in Fig. 2 correspond to the phase transitions identified in the test that occur in steel S235JR. Labels in Fig. 2 correspond to the following phase transitions: A – combined eutectoid (732.7°C) and magnetic (762.9°C) transformation peak, B – transformation of ferrite into austenite, C – formation of high temperature ferrite, D – melting. As the thermal effect related to the transformation of ferrite into austenite was very small, the thermal effect of this transformation was not determined. The obtained test results are presented in Table 2.

TABLE 2

The recorded temperatures of phase transitions and the enthalpy change for steel

Steel grade	T_A, [°C]	ΔH_A, [J/g]	T_B, [°C]	ΔH_B, [J/g]	T_C, [°C]	ΔH_C, [J/g]	$T_{D\ Solidus}$, [— °C]	ΔH_D, [J/g]	Liquidus, [°C]
S320GD	760.5	-	888.4	9.4	1397.0	8.6	1521.5	125.6	1535.8
S235JR	732.7	6.3	896.0	-	1388.1	8.1	1517.4	113.5	1535.5

Fig. 2. DSC analysis of steel S235JR. The recorded temperatures of phase transitions and the enthalpy change. A – combined eutectoid (732.7°C) and magnetic (762.9°C) transformation peak, B – transformation of ferrite into austenite, C – formation of high temperature ferrite, D – melting

The beginning of melting of the sample labelled in Fig. 1 and 2 as D was assumed the Solidus temperature. For steel S320GD the Solidus temperature was 1521.5°C, for steel S235JR it was 1517.4°C. To compare, the Solidus temperature in the ProCAST software was determined. The software used the ThermoCalc thermodynamic databases for steel S320GD applying the Scheil and Lever models; the results were 1425°C and 1489°C respectively. Similar discrepancies in the value of the Solidus temperature concerned steel grade S235JR. The Solidus temperatures computed with the Scheil and Lever models were 1417°C and 1487°C respectively.

The Liquidus temperature was determined on the basis of the temperature of transformation peak D, related to sample melting. It was 1535.8°C, and 1535.5°C for steels S320GD and S235JR respectively. The information on the Liquidus temperature from the ProCAST thermodynamic database for both steel grades did not diverge significantly from the value determined experimentally and was 1528°C.

The heat of transformation related to sample melting ΔH_D was 125.6 [J·g^{-1}] and 113.5 [J·g^{-1}] for steels S320GD and S235JR respectively. The phase transition temperatures and the thermal effects of the transformations were determined during sample heating. It was assumed that the temperatures of individual phase transitions corresponded to the temperatures recorded during cooling. From the perspective of process modelling, it is essential to know the transition enthalpies, and that their values both at the heating and cooling of a sample are the same. Only the phase transition temperatures may shift during sample cooling, due to the supercooling occurring in the sample.

3.2. Determining the dependence of steel specific heat on temperature

The tests of specific heat were conducted from the temperature of 40°C to the Solidus temperature of each steel grade. The samples were placed in Pt-Rh crucibles with lids and Al_2O_3 liner which prevented reactions between the crucible material and the steel. The crucibles were placed on sapphire pads, to prevent the crucibles sticking to the carrier. The reference crucible remained empty during each test. The tests were conducted in helium 6N atmosphere with a gas flow rate of 50 ml/min. The temperature programme consisted of three segments: isothermal holding at 40°C, continuous heating at a rate of 20°C/min and subsequent isothermal holding at a temperature close to the Solidus temperature. Such a temperature program was applied to 3 measurements necessary to compute specific heat: the measurement for empty crucibles (blank curve, baseline), the measurement for the reference and for the sample tested. A disc-shaped sapphire sample with a weight of 111mg was used as the reference material for the measurement of specific heat. The shape and weight of the selected material corresponded to the mass and dimensions of steel samples prepared for the tests. The dependence of specific heat as a function of temperature for the steels S320GD and S235JR determined in the tests is presented in Fig. 3 and Fig. 4. The dotted line shows the course of changes of specific heat within the phase transition range.
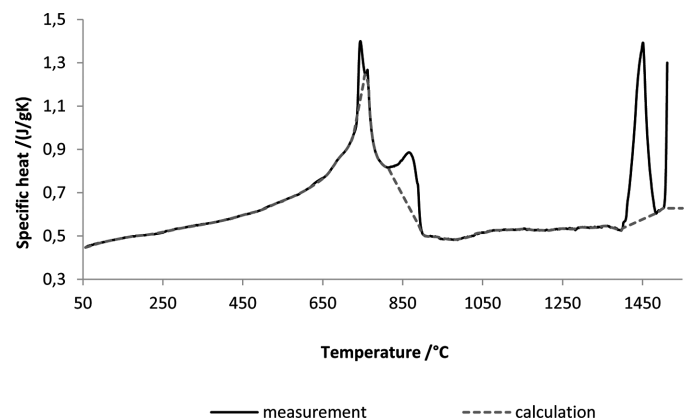

Fig. 3. Dependence of specific heat on temperature for steel S320GD

Changes of specific heat as a function of temperature are similar for both tested steels due to their similar chemical compositions. Within the range without phase transitions, the specific heat grows with an increase in temperature, which is consistent with the classic Debay's theory for specific heat of solid bodies. The occurrence of a phase transformation is manifested with a peak on the curve of dependence $c_p(T)$. The peaks corresponding to individual transformations are shifted in relation to the peaks recorded during the DSC tests because of the higher heating rate of the samples. The magnetic transformation is a second-order transition, with a continuous change in specific heat with temperature. The other phase transitions occurring in steels, including melting, are first-order transitions. During these transitions a discrete change in the

specific heat occurs at the temperature of thermodynamic equi-librium – related to the emission or absorption of the latent heat of phase transitions. Due to the test methodology the peaks occurring on the curve of dependence of specific heat on temperature do not correspond to the latent heat. Therefore, the dependence of specific heat on temperature originating directly from the measurement must not be used in the con-tinuous casting modelling. It is necessary to approximate the values of specific heat within the range of phase transitions. Fig. 3 and 4 show the simplest method of approximation of the value c_p in the phase transition range. To determine the value $c_p'(T)$ a linear interpolation was applied in accordance with the equation 5 [10]:

$$c_p'(T) = c_p^S + \frac{c_p^E - c_p^S}{T_E - T_S}(T - T_S) \qquad (5)$$

where:

$c_p'(T)$ – interpolated dependence of specific heat on tem-perature, [J·g^{-1}·K^{-1}]

c_p^S, c_p^E – specific heat of respectively the beginning and end of the peak of the first order phase transition, [J·g^{-1}·K^{-1}]

T_S, T_E – Temperature respectively the beginning and end of the peak of the first order phase transition, [K].
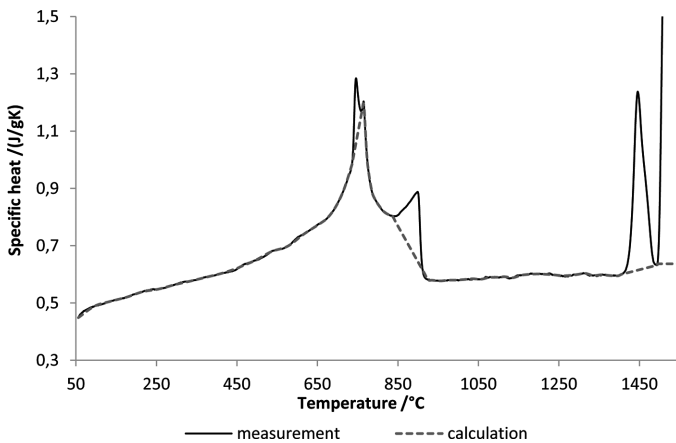

Fig. 4. Dependence of specific heat on temperature for steel S235JR

The calculated results of dependence of specific heat on temperature presented on Fig. 3 and Fig. 4 as a dotted line omit disturbances arising from phase transitions occurring in steel and may be used directly in a numerical simulation of the continuous steel casting process.

4. Conclusion

The presented results of thermal analysis tests concern two steel grades cast with a continuous casting machine. The analysis of the obtained results allowed determination of the phase transition temperatures and thermal effects of transi-tions. The enthalpy of melting (DH$_D$) together with solidus

(T$_{D\ Solidus}$) and liquidus temperature, determined for the ana-lyzed grades of steel are shown in Table 2.

Changes in temperature during the continuous casting of steel process cause a change in the characteristic thermophysical properties of steel. The value of the specific heat of steel varies with temperature, which should be taken into account in the numerical modelingof the process. Results of this study allowed to determine the specific heat depending on the tem-perature for the two grades of steel. In order to eliminate the disturbances appearing in the cp(T) curve, resulting from phase transitions, approximation curve of the specific heat in the range of phase transformation was calculated. The calcu-lated specific heat curve upon temperature, should be used in the numerical calculation.

REFERENCES

[1] A. Buczek, A. Burbelko, P. Drożdż, M. Dziarmagowski, J. Falkus, M. Karbowniczek, T. Kargul, K. Miłkowska-Piszczek, M. Rywotycki, K. Sołek, W. Ślęzak, T. Telejko, L. Trębacz, E. Wielgosz, Modelowanie procesu ciągłego odlewania stali, monografia, Radom 2012.

[2] K. Sołek, L. Trębacz, Thermo-Mechanical Model of Steel Con-tinuous Casting Process, Archives of Metallurgy and Materials **57**, 1 (2012).

[3] A. Burbelko, J. Falkus, W. Kapturkiewicz, K. Sołek, P. Drożdż, M. Wróbel, Modeling of the Grain Structure Formation in the Steel Continuous Ingot by Cafe Method, Archives of Metallurgy and Materials **57**, 1 (2012).

[4] Malinowski Z., Telejko T., Hadała B., Influence of heat transfer boundary conditions on the temperature field of the continu-ous casting ingot, Archives of Metallurgy and Materials **57**, 1 (2012), Doi: 10.2478/v10172-012-0030-7.

[5] E. Wielgosz, T. Kargul, J. Falkus, Comparison of experimental and numerically calculated thermal properties of steels. In: Pro-ceedings paper, METAL 2014: 23rd International Conference on Metallurgy and Materials, Brno 2014.

[6] P.K. Gallagher, Handbook of thermal analysis and calorimetry: principles and practice. 2nd ed. Oxford: Elsevier; 2003.

[7] H. Saari, D. Y. Seo, J. Blumm, J. Beddoes, Thermophisical property determination of high temperature alloys by thermal analysis, J. Therm. Anal. Cal., **73**, 381-388 (2003)

[8] E. Wielgosz, T. Kargul, Differential scanning calorimetry study of peritectic steel grades, J. Therm. Anal. Cal., **119**, 1547-1553 (2015).

[9] B. Smetana, S. Zlá, J. Dobrovská, P. Kozelsky, Phase transfor-mation temperatures of pure iron and low alloyed steels in the low temperature region using DTA, Int. J. Mat. Res. (formerly Z. Metallkd.) 101, 3 (2010).

[10] NETZSCH Proteus Thermal Analysis, program manual v. 5.2.0.