

B. SMETANA, M. KAWULOKOVÁ, S. ZLÁ, A. KALUP, M. STROUHALOVÁ, L. ŘEHÁČKOVÁ,
S. ROSYPALOVÁ, M. TKADLEČKOVÁ, K. MICHALEK, J. DOBROVSKÁ

COMPARISON OF SOLIDUS AND LIQUIDUS TEMPERATURES OF REAL LOW CARBON STEEL GRADE OBTAINED BY USE OF THERMAL ANALYSIS METHODS

The paper deals with the study of phase transition temperatures (solidus and liquidus temperatures) with the use of different thermal analysis methods. Currently, the key thermal analysis methods are DTA (Differential Thermal Analysis), DSC (Differential Scanning Calorimetry) and 'direct' thermal analysis (TA). The study presents the basic principles of these methods, their characteristics, advantages, disadvantages and results obtained with these three very often used methods. The paper presents results from the high temperature region (above 1000°C) with the focus on the melting and solidifying region of real steel grade – multicomponent alloy. The paper discusses results obtained with the three mentioned methods at heating/cooling process, with different loads of analysed samples and other factors that can influence the obtained results. The evaluation of heating/cooling curves, DTA and DSC – curves at heating and cooling is demonstrated. The obtained solidus and liquidus temperatures are compared and discussed.

Keywords: liquidus, solidus, steel, thermal analysis, conditions, methods

PORÓWNANIE TEMPERATUR SOLIDUS I LIKWIDUS STALI NISKOWĘGLOWEJ UZYSKANYCH ZA POMOCĄ METOD ANALIZY TERMICZNEJ

Praca dotyczy badania temperatur przemian fazowych (temperatur solidus i likwidus) z użyciem różnych metod analizy termicznej. Obecnie kluczowymi metodami analizy termicznej są: różnicowa analiza termiczna DTA, skanująca kalorymetria różnicowa oraz „bezpośrednia” analiza termiczna TA. Praca przedstawia podstawowe zasady, charakterystykę, zalety, wady i wyniki uzyskane przy użyciu tych trzech, bardzo często stosowanych metod. Przedstawiono wyniki z zakresu wysokiej temperatury (powyżej 1000°C) z naciskiem na zakres topnienia i krzepnięcia stali. Omówiono wyniki uzyskane przy zastosowaniu wspomnianych metod podczas procesu nagrzewania/chłodzenia, z uwzględnieniem różnych obciążeń analizowanych próbek i innych czynników, które mogą wpływać na uzyskane wyniki. Podano ocenę krzywych nagrzewanie/chłodzenie DTA i DSC. Porównano i omówiono uzyskane temperatury solidus i likwidus.

Słowa kluczowe: likwidus, solidus, stal, analiza termiczna, warunki, metody

1. INTRODUCTION

Better control of the entire steel production cycle – from selection of quality raw materials, through proper control of primary and secondary metallurgy processes, and finally, the optimum setting of casting and solidification conditions, is necessary for modern competitive steelworks. It is very important to solve problems relating to refining processes, optimising slag regimes [1, 2] thermal and chemical homogenisation of the melt [3–6] or filtration of steel.

It is necessary, for each steel mill, to improve and optimise production processes continuously to compare

favourably with other competitors. To improve and optimise technological processes of steel production, it is necessary to know, among others, proper material data. One of many important data for the steel production process are phase transition temperatures. In the low temperature region phase transition temperatures of e.g. eutectoid transformation, $\alpha \leftrightarrow \gamma$ transition etc., which are important for subsequent heat and mechanical treatment [7], are of a great significance. In the high temperature region the most important data are temperatures of solidus, liquidus, $\gamma \leftrightarrow \delta$ transition, peritectic transformation [8–10]; e.g. knowledge of liquidus temperature is crucial for optimal setting of cast-

B. Smetana (bedrich.smetana@vsb.cz), M. Kawuloková, S. Zlá, A. Kalup, L. Řeháčková, S. Rosypalová, J. Dobrovská – VŠB-Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Physical Chemistry and Theory of Technological Processes, and Regional Materials Science and Technology Centre, Czech Republic

M. Strouhalová, M. Tkadlečková, K. Michalek – VŠB-Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Department of Metallurgy and Foundry, and Regional Materials Science and Technology Centre, Czech Republic

ing conditions. Other very important thermophysical and thermodynamical data, that can be used indirectly (via simulation SWs, e.g. PROCAST, MAGMASOFT, etc.) for optimisation of real casting process, are heat capacity [11], enthalpy [12] and their dependence on temperature, latent heat of phase transitions [13] and many others [12].

This paper presents the obtained solidus and liquidus temperatures and differences between them, which arise from the equipment arrangement and method used for analysis. The methods for determination of solidus and liquidus temperatures used in this work are: DTA – Differential Thermal Analysis, DSC – Differential Scanning Calorimetry and TA – ‘direct’ thermal analysis. The utilisation of different methods, equipment arrangement and other factors can substantially influence the resulting data [14, 15]. So, the short critical insight into aspects of thermal analysis methods in connection with temperatures of solidus and liquidus of real low carbon steel is the main objective of this paper. Selected characteristics of thermal analysis methods are presented. Some advantages and disadvantages of them are discussed.

2. THERMAL ANALYSIS METHODS

For many dozens of years, methods of thermal analysis have been used in many branches for characterisation of thermal behaviour of materials at the heating/cooling process and as well as at isothermal conditions. Many important material properties are investigated: temperatures of phase transitions, their latent heats, heat capacities, kinetic parameters of phase transitions [12], thermal stability of materials, diffusion processes and other [12].

There are many factors that can influence the resulting data. The whole experimental arrangement of the tangible equipment (not modifiable by user) has an influence: furnace type, type of sensors, count of thermocouples, etc. On the other hand, there are conditions of performed experiments which can be very easily modified by the user: heating/cooling rate, atmosphere, sample weight, crucible, etc. All the mentioned factors can substantially influence the resulting data [12, 15].

Tangible equipment (its own arrangement), concrete experimental method and experimental conditions can be the decisive factors for obtaining reliable data (if the operator is not taken into account – the role of the evaluator can also be crucial). With the three currently most frequently used methods (TA, DTA and DSC) with three experimental systems it is possible to perform thermal analysis measurements at our working site.

2.1. DIRECT THERMAL ANALYSIS (TA)

‘Direct’ thermal analysis [12] is based on the direct measurement of the temperature of the sample during its continuous linear heating/cooling or isothermal dwell. Figure 1 presents the arrangement of the ‘direct’ thermal analysis method with the use of NETZSCH STA 449 F3 JUPITER at our working site (crucible, sample in crucible – grey coloured, placement of the thermocouple – not directly in contact with the sample, red marks the thermocouple junction).

The result of TA is the so-called heating/cooling curve, if heating/cooling is performed. With the focus on phase transitions, there is a deviation on the heating/cooling curve from the otherwise linear curve progression during the running phase transformation in the samples. It is possible to obtain temperatures of phase transformations based on the curve deviations (e.g. liquidus and/or solidus temperatures, peritectic transformation) if the heat effect of phase transition and sensor sensitivity is large enough.

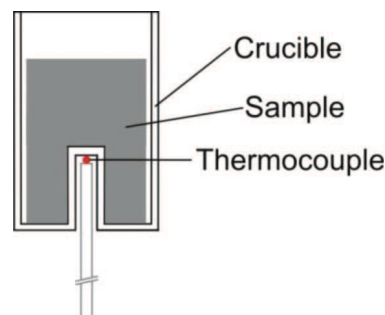


Fig. 1. Sketch of TA arrangement, corundum crucible, steel sample, thermocouple (S-type)

Rys. 1. Układ TA, tygiel korundowy, próbka stali, termoelement (typ S)

2.2. DIFFERENTIAL THERMAL ANALYSIS (DTA)

Differential Thermal Analysis (DTA) [12] is a method based on the measurement of temperature difference between the measured sample and reference. Figure 2 shows a sketch of DTA arrangement used in our laboratory. DTA tri-couple sensor is presented (only the sample side; crucible, sample – grey coloured and three thermocouple junctions – red), which is used in Setaram SETSYS 18_{TM} equipment. The reference can be an empty reference crucible or reference crucible with a standard material (e.g. pure metal, etc.). The sample and the reference are subjected to the same settings of the temperature programme of the continuous linear heating/cooling (in special cases – isothermal dwell).

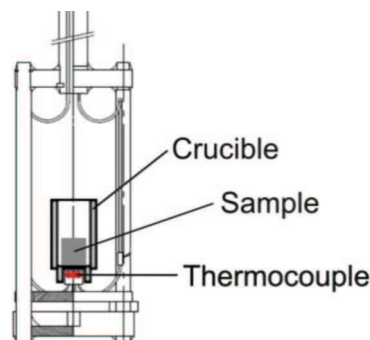


Fig. 2. Sketch of DTA arrangement, corundum crucible, steel sample, thermocouple (S-type)

Rys. 2. Układ DTA, tygiel korundowy, próbka stali, termoelement (typ S)

The result is the so called DTA curve expressing the dependence of the temperature difference between the measured sample and reference (reference sample). If there is any ongoing phase transformation in the sample, there is a deviation from the baseline (a peak is formed). It is possible to consequently obtain the

temperatures of phase transformations by interpretation of such peaks for given experimental conditions and many other parameters as well.

2.3. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Differential Scanning Calorimetry (DSC) [12] is a method based on the same principle as DTA. DSC is also based on measurement of the temperature difference between the measured sample and reference. The reference can be also an empty reference crucible or reference crucible with a standard material.

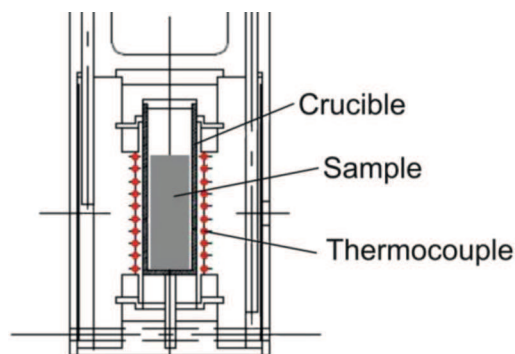


Fig. 3. Sketch of 3D DSC arrangement, corundum crucible, steel sample, thermocouple (B-type)

Rys. 3. Układ 3D DSC, tygiel korundowy, próbka stali, termoelement (typ B)

The sample and reference are subjected to the same settings of temperature programme of the continuous linear heating/cooling (in special cases – isothermal dwell). If the calibration with respect to the heat is performed, the heat fluxes difference between the sample and the reference is the result of the DSC method. Figure 3 shows a sketch of 3D DSC sensor (only the sample side) used by Setaram MHTC (Multi High Temperature Calorimeter Line 96); corundum crucibles are used for analyses, B-type sensor – 20 thermophiles surround the crucible, grey is the sample).

2.4. EXPERIMENTAL BASE USED AT OUR WORKING SITE

There are many experimental systems used for determination of solidus and liquidus temperatures of many materials, steels included: Setaram, Netzsch, Mettler, TA Instruments and other.

There are three commercially produced devices placed at our working site, partially presented above, that can be used for obtaining solidus and liquidus temperatures. These apparatuses are from two different manufacturers and are used in three modifications as mentioned above: Netzsch STA 449 F3 Jupiter is used for direct thermal analysis, Setaram SETSYS 18_{TM} is used with the DTA sensor and Setaram MHTC (Multi

High Temperature Calorimeter) is equipped with a 3D DSC sensor (B – type). More specific information about configuration of the presented apparatuses can be found e.g. in [14].

3. EXPERIMENT

For each method samples of a specific shape were prepared. Samples from real steel grade (low carbon steel) were prepared for this study. Chemical composition (wt. %) is presented in Table 1.

The weight of the prepared samples was: 23÷25 g for TA, around 1.2 g for 3D DSC and approximately 180 mg for DTA. Experiments were performed at five different heating/cooling rates by TA (1, 5, 10, 15 and 20°C·min⁻¹), at one heating rate using MHTC (5°C·min⁻¹) and DTA (10°C·min⁻¹). Temperature calibration was performed using pure nickel (5N) and its standard melting temperature of 1455°C. Selected results: heating/cooling curves, DTA and DSC curves, are presented in Figures 4–9. Experiments were performed in corundum crucibles in inert atmosphere of Ar (6N). Different heating/cooling conditions were not used with these steel samples using DTA and DSC. Experiments demonstrating the influence of heating/cooling rate on shift of temperatures of liquidus and solidus (with samples analysed by 3D DSC and DTA) were partially published in [15]. In addition to that, the study of the influence of the weight of sample using 3D DSC and DTA was performed earlier [14]. Temperatures of solidus and liquidus obtained using 3D DSC and DTA were corrected besides correction with respect to the melting point of pure nickel influenced by heating rate and sample weight.

4. RESULTS AND DISCUSSION

Based on the curves evaluation, the temperatures of solidus T_s and liquidus T_L were derived for all the performed experiments. Only the selected curves: for heating and cooling rate 5°C·min⁻¹ (10°C·min⁻¹ for DTA) are presented in Figures 4–9. Figures 4–9 show the ‘raw’ data; temperatures are not corrected with respect to the melting point of the standard (Ni, 5N) and experimental conditions.

As a representative, solidus T_s and liquidus T_L temperatures were taken from temperatures obtained for heating and cooling with the use of the TA method (large samples, 23÷25 g). From DTA and DSC analyses only values obtained for heating were taken. The reason for that is as follows. Due to difficulties with origination of the first critical nuclei at the cooling process the relatively high degree of undercooling and different degree of undercooling can be encountered,

Table 1. Chemical composition of studies samples, wt. %

Tabela 1. Skład chemiczny badanych próbek, % mas.

C _{spal.}	Mn	Si	P	S _{spal}	Cu	Ni	Cr	Al	Ak	O
0.077	0.635	0.291	0.021	0.008	0.064	0.027	0.049	0.026	0.024	0.002
N	Mo	V	Ti	Nb	Ca	Sn	B	O _{spal.}	N _{spal.}	
0.004	0.003	<0.003	<0.003	<0.003	0.002	0.004	<0.0005	0.002	0.004	

C_{spal.}, S_{spal.}, O_{spal.}, N_{spal.} – elements determined by combustion analysers, Ak – aluminium in solution. Fe balance

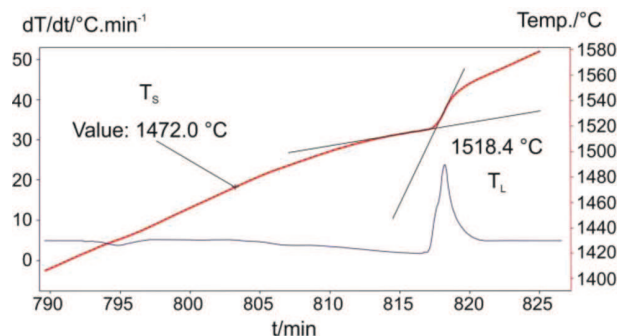


Fig. 4. Heating curve, TA, 5°C·min⁻¹, Netzsch STA 449 F3 Jupiter

Rys. 4. Krzywa grzewcza, TA, 5°C·min⁻¹, Netzsch STA 449 F3 Jupiter

mainly by using small samples (from milligrams up to few grams), the values of solidus and liquidus could be therefore sometimes not representative (e.g. it is possible to obtain, for the same conditions of cooling, different values of T_s and T_L , in some cases the differences are a dozen of degrees or more).

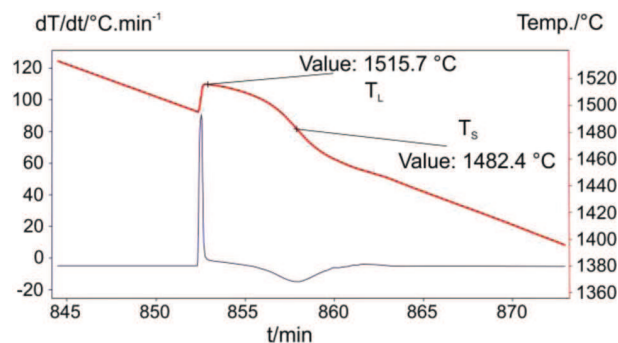


Fig. 5. Cooling curve, TA, 5°C·min⁻¹, Netzsch STA 449 F3 Jupiter

Rys. 5. Krzywa chłodzenia, TA, 5°C·min⁻¹, Netzsch STA 449 F3 Jupiter

So, if focused on the representative temperature values (heating and cooling as well), it is possible to state that the maximum difference between T_s obtained with the use of TA, DTA and DSC is 22°C (1494÷1472°C), and for T_L also 22°C (1538÷1516°C). Mainly from the

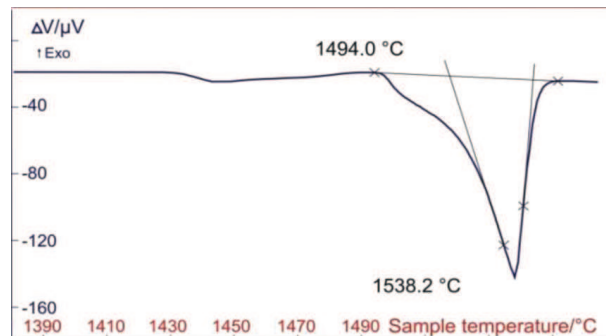


Fig. 6. DTA curve, heating 10°C·min⁻¹, Setaram SETSYS 18TM

Rys. 6. Krzywa DTA, ogrzewanie 10°C·min⁻¹, Setaram SETSYS 18TM

technological point of view, this difference is relatively substantial. But this difference must not be considered, because of the raw data. With a proper temperature calibration and correction of experimental influence (mainly sample weight and heating rate), it is possible to obtain comparable results.

The 'corrected' experimental solidus and liquidus temperatures (Table 2) are also compared with the calculated temperatures obtained with the use of SWs Thermo-Calc, Computherm and IDS, Table 3.

From experimental values of temperatures of solidus and liquidus selected statistic values (from at least four values) were calculated: mean value, mean deviation and variation coefficient, Table 2. The relatively higher value of mean deviation and variation coefficient was encountered by T_s obtained with the use of TA at cooling. This fact can be explained by a relatively strong dependence of T_s on cooling rate (the higher the cooling rate, the lower the solidus temperature, the difference is up to 39°C for lowest and highest cooling rates). For lower cooling rates T_s is higher at the cooling process (below 10°C·min⁻¹). For 10°C·min⁻¹, it is the same. For higher cooling rates, T_s is lower than the one obtained at heating (above 10°C·min⁻¹), Table 2.

The shift of T_s is with high probability caused by the mechanism of solidification in the sample, but also, on the other hand, the shift of T_s to a lower temperature could be caused by the experimental conditions (delay of signal detection, etc.) and probably could be partially

Table 2. Experimental temperatures of solidus T_s and liquidus T_L

Tabela 2. Temperatury solidus T_s i likwidus T_L z doświadczenia

Steel	TA						DTA			3D DSC		
	Heating			Cooling			Heating					
	Rate *	T _s	T _L	Rate *	T _s	T _L	Rate *	T _s	T _L	Rate *	T _s	T _L
		[°C]			[°C]			[°C]			[°C]	
	1	1478	1524	1	1509	1523	10	1493	1523	5	1487	1523
	5	1479	1525	5	1489	1523		1491	1522		1486	1522
	10	1479	1525	10	1479	1521		1494	1524		1486	1523
15	1479	1525	15	1474	1521	1492		1524	1486		1522	
20	1480	1525	20	1470	1520		1491	1523		—	—	
Mean value		1479	1525		1484	1522		1492	1523		1486	1523
Mean deviation		0.7	0.5		13.8	1.2		1.2	0.7		0.4	0.5
Variation coeff. [%]		0.05	0.03		0.93	0.08		0.08	0.05		0.03	0.03

* heating or cooling rate in °C·min⁻¹

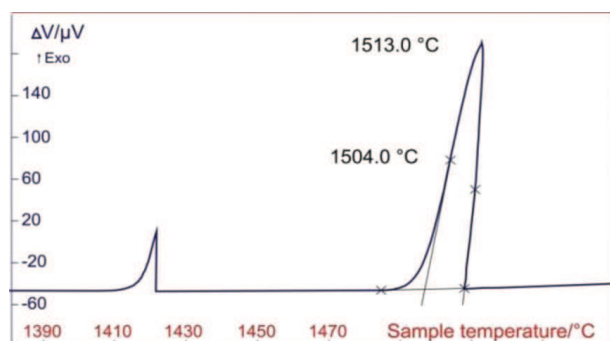


Fig. 7. DTA curve, cooling $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, Setaram SETSYS 18_{TM}

Rys. 7. Krzywa DTA, chłodzenie $10^{\circ}\text{C}\cdot\text{min}^{-1}$, Setaram SETSYS 18_{TM}

during melting, contact of sample with sensor-crucible, change of chemical composition – possible decarburisation [11], oxidation, etc.). Furthermore, the evaluation

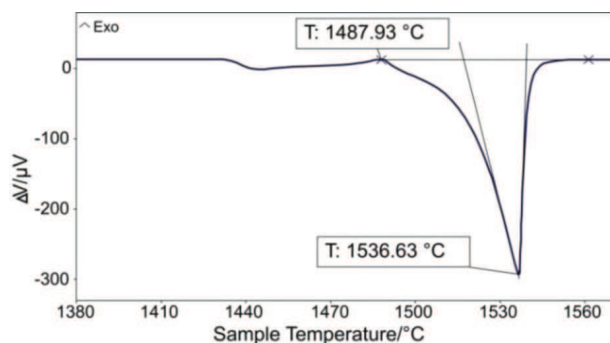


Fig. 8. DSC curve, heating $5^{\circ}\text{C}\cdot\text{min}^{-1}$, Setaram MHTC

Rys. 8. Krzywa DSC, ogrzewanie $5^{\circ}\text{C}\cdot\text{min}^{-1}$, Setaram MHTC

corrected if the shift dependence of inflection point – T'_S of standard material was known – not performed in this work).

Temperatures of solidus, the mean values, are: for TA (heating) 1479°C , for DTA 1492°C and DSC 1486°C . Solidus temperatures obtained in the frame of each method only slightly differs from each other (the maximum deviation is 3°C). Temperatures of solidus T_S obtained at heating with the use of TA are almost the same for each heating rate. Differences between T_S acquired with the use of TA, DTA and DSC are higher. The maximum difference is 13°C (TA and DTA values). That fact could be caused mainly by the arrangement of the experimental systems alone, sample weight, sensitivity of used sensors and other aspects (inhomogeneous temperature field, releasing/absorption of latent heat

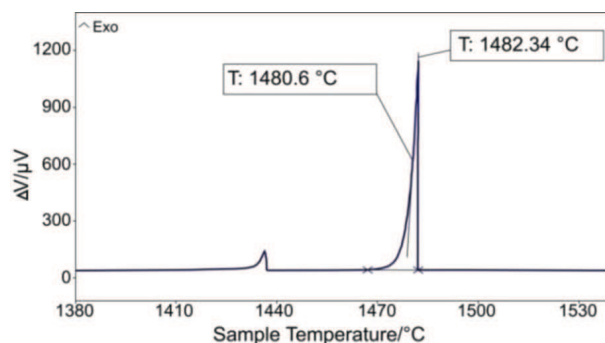


Fig. 9. DSC curve, cooling $5^{\circ}\text{C}\cdot\text{min}^{-1}$, Setaram MHTC

Rys. 9. Krzywa DSC, chłodzenie $5^{\circ}\text{C}\cdot\text{min}^{-1}$, Setaram MHTC

of the obtained curves (overlapping of heat effects, not sharp deviation from base line, etc.) can be in some cases very difficult and relatively substantial differences can arise from this fact (even more than dozens of degrees can be encountered), see Figures 4–9.

The calculated values of solidus are very close to the experimental values, the maximum deviation is 11°C ($1490\div 1479^{\circ}\text{C}$); temperatures of solidus very often differ if compared to results from different experiments, if experimental results and calculations are compared – differences can be in dozens of degrees). Temperature of solidus obtained with the use of TA is only about 1 Celsius degree lower than T_S calculated with the use of Thermo-Calc and at the same it is possible to say if the compared T_S (DTA) and calculated T_S are according to the SW Computherm. It is possible to state that the experimentally obtained values of solidus correspond to the temperature interval of $1480\text{--}1490^{\circ}\text{C}$ (the lowest and highest calc. value of solidus, Table 3).

Temperatures of liquidus, the mean values, are: for TA 1525°C (heating) and 1522°C (cooling), and for DTA 1523°C and DSC 1523°C . The liquidus temperature obtained in the frame of each method only slightly differs from each other (the maximum deviation is 3°C). Temperatures of liquidus T_L obtained at heating with the use of TA are the same (almost the same) for each heating rate. Cooling shows that T_L is very slightly dependent on the cooling rate. Differences between T_L acquired with the use of TA, DTA and DSC are minimal. The maximum difference is no more than 3°C . When comparing T_L obtained at heating and cooling (TA), it is visible that T_L slightly shifts to the lower values (undercooling was observed but very low and with a certain trend – the higher the cooling rate, the lower T_L , very slightly contrary to the small samples). This fact was observed also by [16].

Table 3. Calculated temperatures of solidus T_S and liquidus T_L

Tabela 3. Obliczone temperatury solidus T_S i likwidus T_L

Steel	Thermocalc ¹		IDS ²				Computherm ³	
	Equilibrium		Equilibrium		Cooling $0.01^{\circ}\text{C}/\text{min}$		Equilibrium	
	T_S	T_L	T_S	T_L	T_S	T_L	T_S	T_L
	[$^{\circ}\text{C}$]							
	1480	1525	1485	1525	1485	1525	1490	1527

¹ SW Thermocalc ver. 3.1, database TCFE7

² SW Solidification analysis package, the following elements are not included: V, Ti, B, Nb, Sn, Al_{rozp.}, N_{spal.}, O_{spal.}

³ SW Computherm, the following elements are not included: B, Sn, Al_{rozp.}, N, O

Theoretical values of T_L are presented in Table 3. Theoretical values of T_L calculated according to the SWs Thermo-Calc and IDS are the same (1525°C) and T_L calculated according to the SW Computherm is 1527°C.

An excellent agreement between experimental values and also between experimental and calculated values was achieved. The maximum difference between the presented values is 5°C.

Obtaining reliable phase transition temperatures is a difficult task. Many authors do that, but do not consider the whole arrangement of the equipment and conditions, from which differences can arise, others do that reliably but have only one method and equipment.

It is possible to conclude (on the basis of our long-term experiences) that differences between solidus temperatures obtained using different equipment and methods or with calculation and modelling, results can differ substantially in comparison to temperatures of liquidus. When comparing temperatures of solidus, the differences are often in dozens of degrees (sometimes even more). When comparing temperatures of liquidus, the differences are often in degrees (relatively high differences are not usual).

These differences can arise mainly from the above-mentioned factors: apparatus arrangement, experimental conditions (sample weight, heating/cooling regime and their rate; it is also necessary to consider that the heating and cooling processes are the reversed processes, but not mirror processes. So, the melting and solidification are not the mirror processes. The progress of melting/solidifying is not the same in the reversed manner and therefore the results can differ due to a physical basis of the processes.

It is necessary to think also about temperature fields in samples (large-inhomogeneous vs. small samples – homogeneous; the colder parts of samples are heated by warmer and vice versa; these effects arise mainly if larger samples are used [17]), it is necessary to consider detection limits of sensors, it is necessary to consider that different alloys – especially multicomponent like steels – can behave in a different manner in comparison with lower order systems (binary, ternary, etc.), it is necessary to consider possible change of chemical composition in some cases – mainly decarburisation and also oxidation [11]. Decarburisation and also oxidation have to be minimised with the use of an inert atmosphere and by the corresponding heating/cooling rate. The risk of possible decarburisation and oxidation is substantially higher when small samples (milligrams or few grams) are subjected to study with meth-

ods of thermal analysis; more about decarburisation can be found e.g. in [11]). The amount of latent heat absorbed (released) during phase transition (melting/solidification) has also a significant influence on the possible detection of phase transition temperatures. Furthermore, the evaluator (operator) can play the key role for the results of evaluation – human factor can play a decisive role.

5. CONCLUSIONS

In this work, possibilities of measurement of solidus and liquidus temperatures using three measurement systems, Netzsch STA 449 F3 Jupiter (“direct” thermal analysis), Setaram SETSYS 18TM (DTA) and Setaram MHTC (3D DSC), were presented. A short review of experimental equipment and used methods was performed. Results obtained with different arrangement of apparatuses and methods were presented. The real sample, low carbon steel, was used for the demonstration of results. A short discussion of the obtained results, temperatures of solidus T_S and liquidus T_L was carried out. For solidus temperature, higher differences were observed, in the case of temperatures of liquidus an excellent agreement was achieved. The paper presents also some advantages and disadvantages of the used methods and some other factors that can influence the results (not discussed in detail). The main factors that can influence the results are: the apparatus itself – its arrangement, used method and sensor, sample weight, heating/cooling rate. The paper shows that each of the three presented methods is usable for investigation of temperatures of solidus and liquidus. The paper also shows the fact, that if appropriate correction with respect to the melting point of standard and experimental conditions is performed, the obtained results can be comparable (are the same or almost the same).

The following work at our working site will continue in this research area, because of the necessity to obtain proper data and consequently it gives the possibility to optimise real technological processes.

Acknowledgements

This paper was created in the frame of project No. LO1203 “Regional Materials Science and Technology Centre – Feasibility Programme” funded by the Ministry of Education, Youth and Sports of the Czech Republic and the project of the Technology Agency of the Czech Republic No. TA 03011277 and student projects SGS (SP2016/90 and SP2016/103).

REFERENCES

1. Socha L., Bažan J., Gryc K., Machovčák P., Morávka J., Styrnal P.: Evaluation of fluxing agents effect on desulphurization in secondary metallurgy under plant conditions, *Metallurgia*, 2013, 52, pp. 485–488
2. Gryc K., Stránský K., Michalek K., Winkler Z., Morávka J., Tkadlečková M., Socha L., Bažan J., Dobrovská J., Zlá S.: *Mater. Technol.* 2012, 46, pp. 403–406
3. Tkadlečková M., Machovčák P., Gryc K., Michalek K., Socha L., Klus P.: *Arch. Metall. Mater.* 2013, 58, pp. 171–177
4. Michalek K., Gryc K., Morávka J.: *Metallurgia* 2009, 48, pp. 215–218
5. Michalek K., Čamek L., Gryc K., Tkadlečková M., Huczala T., Troszok V.: *Mater. Technol.* 2012, 46, pp. 297–303
6. Gryc K., Michalek K., Hudzieczek Z., Tkadlečková M.: In *METAL 2010: Proceedings of 19th International Metallurgical and Materials Conference*, Brno, Czech Republic, 2010, pp. 42–46
7. Ruzs S., Kubina T., Schindler I., Smetana B., Kawulok P., Cagala M.: *Metallurgia* 2013, 52, pp. 525–528
8. Záludová M., Smetana B., Zlá S., Dobrovská J., Watson A., Vontorová J., Rosypalová S., Kukutschová J., Cagala M.: *J. Therm. Anal. Calorim.* 2013, 112, pp. 465–471

9. Gryc K., Smetana B., Żaludová M., Michalek K., Tkadlečková M., Dobrovská J., Socha L., Válek L., Pachlopnik R.: *Metalurgia* 2013, 52, pp. 445–448
10. Zlá S., Smetana B., Žaludová M., Dobrovská J., Vodárek V., Konečná K., Matějka V., Francová H.: *J. Therm. Anal. Calorim.* 2012, 110, pp. 211–219
11. Smetana B., Žaludová M., Tkadlečková M., Dobrovská J., Zlá S., Gryc K., Klus P., Michalek K., Machovčák P., Řeháček L.: *J. Therm. Anal. Calorim.* 2013, 112, pp. 473–480
12. Gallagher P.K.: *Handbook of thermal analysis and calorimetry: principles and practice.* Oxford: Elsevier 2003
13. Smetana B., Žaludová M., Zlá S., Matějka V., Dobrovská J., Gryc K., Tkadlečková M., Sikora V., Kozelský P., Cagala M.: In *METAL 2011: Proceedings of 20th International Metallurgical and Materials Conference*, Brno, Czech Republic, 2011, pp. 486–491
14. Žaludová M.: *Studium fázových transformací vybraných kovových systémů na bázi Fe a Fe-C.* PhD thesis, VŠB-Technical university of Ostrava, Ostrava, 2013
15. Žaludová M., Smetana B., Zlá S., Dobrovská J., Rosypalová S., Petlák D., Szurman I., Štvrtňová A.: In *METAL 2013: Proceedings of 22th International Metallurgical and Materials Conference*, Brno, Czech Republic, 2013, pp. 585–591
16. Nassar H., Fredriksson H.: *Metall. Mater. Trans. A.* 2010, 41A, pp. 2776–2783
17. Bodin A., Marchal P.D.: *Steel Res.* 1994, 65, pp. 103–109