SOLIDUS, LIQUIDUS AND PERITECTIC TRANSFORMATION TEMPERATURES OF Fe-C-Cr-Ni-Mo BASED ALLOYS

SMETANA Bedřich[1,2], ZLÁ Simona[1,2], KAWULOKOVÁ Monika[1,2], DROZDOVÁ Ľubomíra[1], DOBROVSKÁ Jana[1,2], KALUP Aleš[1,2], ŘEHÁČKOVÁ Lenka[1,2], ROSYPALOVÁ Silvie[1,2], STROUHALOVÁ Michaela[2,3], MICHALEK Karel[2,3], JONŠTA Petr[4], SUŠOVSKÝ Michal[4]

[1] *Department of Physical Chemistry and Theory of Technological Processes, VSB - Technical University of Ostrava, Czech Republic, EU, bedrich.smetana@vsb.cz*

[2] *Regional materials science and technology centre, VSB - Technical University of Ostrava, Czech Republic, EU*

[3] *Department of Metallurgy and Foundry, VSB - Technical University of Ostrava, Czech Republic, EU*

[4] *Vítkovice Heavy Machinery a.s., Ostrava, Czech Republic, EU, jonsta@vitkovice.cz*

Abstract

The paper deals with the study of key thermophysical properties - phase transition temperatures (liquidus, peritectic transformation and solidus) with use of DTA (Differential Thermal Analysis) and “direct” thermal analysis (TA). Results obtained with these two very often used methods at heating and cooling process are presented. There are presented results from the high temperature region with focus on the melting and solidifying region of Fe-C-Cr-Ni-Mo based metallic alloys. The paper discusses obtained results at heating/cooling process, with different loads of analyzed samples and other factors that can influence the obtained results. The evaluation of DTA - curves and heating/cooling curves is demonstrated. The obtained experimental phase transition temperatures are mutually compared and discussed. Temperatures of liquidus, peritectic transformation and solidus are discussed with values theoretically calculated by selected SWs, such as Thermo-Calc and IDS (solidification analysis package) and with values delivered by steel company producer. Differences between liquidus, peritectic transformation and solidus temperatures were encountered (in some cases substantial) between theoretical and experimental values.

Keywords: Temperatures, liquidus, peritectic transformation, solidus, Fe-C-Cr-Ni-Mo alloys

1. INTRODUCTION

It is necessary, for each steel production company, to improve and optimize production processes continuously to compare favourably with other competitors. The better control of the entire steel production cycle - from selection of quality raw materials, through proper control of primary and secondary metallurgy processes [1], and finally, the optimum setting of casting and solidification conditions [2], is necessary for modern competitive steel making company.

To improve and optimize the technological processes of steel production, it is necessary to know, among others, the proper material data. One of many important data for steel production process are phase transition temperatures (from low [3, 4] and also high temperature region [5-7] up to 1600 °C). In the high temperature region, there are the most important temperatures of liquidus, peritectic transformation and solidus, which are important mainly for setting of casting conditions and for a simulation of casting and solidification of real technological processes related to steel production - modelling of casting processes using e.g. PROCAST SW [1] etc.

This paper presents results obtained by two methods of thermal analysis. Presented results (temperature of liquidus T_L, peritectic transformation T_P and solidus T_S) were obtained using TA - “direct” thermal analysis and DTA - Differential Thermal Analysis. Experimentally obtained data were discussed and compared with results calculated using SW Thermo-Calc (ver. 2017a, TC SW) and database TCFE8 and also with results obtained using kinetic SW IDS and delivered liquidus temperature values by steel plant producer.

2. EXPERIMENT

Ten alloys with graded elements content based on Fe-C-Cr-Ni-Mo were studied. Chemical composition (selected main elements) is presented in **Table 1**.

Table 1 Chemical composition of analyzed Fe-C-Cr-Ni-Mo alloys, (wt.%)

Steel	C	Cr	Ni	Mo
	(wt. %)			
1	0.25	0.94	0.03	0.75
2	0.28	0.61	0.03	0.17
3	0.31	1.06	0.04	0.24
4	0.32	1.54	0.89	0.19
5	0.37	1.09	0.03	0.23
6	0.38	1.99	1.07	0.21
7	0.38	5.00	0.30	0.15
8	0.38	4.99	0.26	1.16
9	0.41	1.08	0.03	0.21
10	0.43	4.98	0.09	1.22

Direct thermal analysis (TA) and Differential thermal analysis (DTA) were used for obtaining of phase transition temperatures. More specific information about these two methods can be found e.g. in [8]. Two experimental systems were used for phase transition temperatures determination: Netzsch STA 449 F3 Jupiter for direct thermal analysis (TA, S - type thermocouple) and Setaram SETSYS 18$_{TM}$ with DTA sensor (S - type, tri-couple) for Differential thermal analysis. Phase transition temperatures were obtained by use of DTA (sample mass about 150 mg) at heating process - heating rate was 10 °C.min^{-1} and also TA method (sample mass about 24 g) at controlled cycling experiments - two heating runs and two cooling runs were performed; heating and cooling process at 5 °C.min^{-1}. Samples were analysed in corundum crucibles in inert atmosphere of Ar (6N). Temperature calibration was performed using Ni (4N5) or Pd (5N). Corrections respected influence of heating rate and influence of mass of sample were performed.

3. CALCULATIONS

Theoretical calculations were performed using kinetic SW IDS (InterDendritic Solidification) and thermodynamic SW Thermo-Calc. IDS SW simulates the solidification phenomena from liquid down to 1000 °C [9]. The calculation did not include elements Sn, B, As, Sb, Pb, Bi. The CALPHAD method is implemented for calculation with SW Thermo-Calc [10]. For calculation with TC SW, following elements: Fe, C, Mn, Si, P, Cu, Ni, Cr, Al, Mo, V, Nb (diamond and graphite were excluded from calculation) were included. Theoretical temperatures of liquidus, used in real casting process, were delivered by our industrial partner.

4. RESULTS AND DISCUSSION

DTA curves, heating and cooling curves, were obtained from experimental measurements (only sample 7 is presented), **Figures 1 - 3**. Phase transition temperatures are denoted for each of the presented curve (temperature of liquidus - red, temperature of peritectic transformation - blue and temperature of solidus - green).

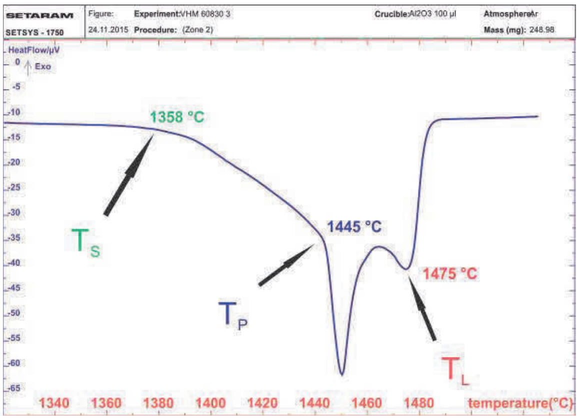

Figure 1 DTA curve of analyzed steel (7), heating 10 °C.min^{-1}, melting

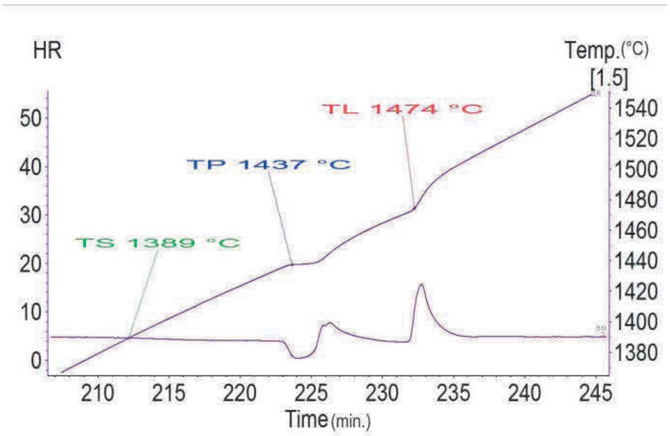

Figure 2 Heating curve of analyzed steel (7), heating 5 °C.min^{-1}, melting

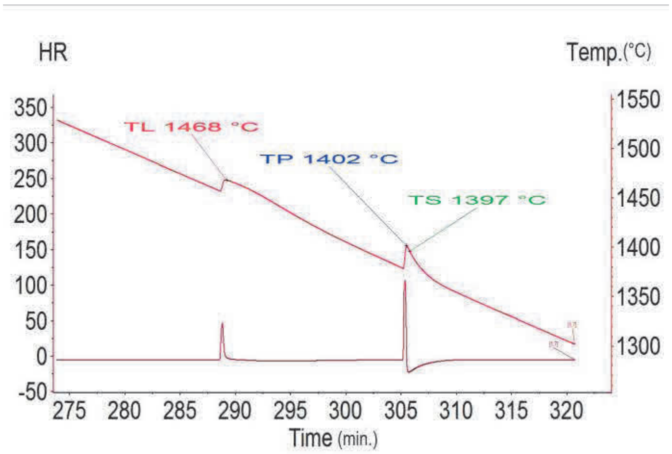

Figure 3 Cooling curve of analyzed steel (7), cooling 5 °C.min^{-1}, solidification

All obtained data were compared to each other. Evaluated temperatures of liquidus are presented also by **Table 2**. Phase transition temperatures are compared with calculated isoplethal equilibrium phase diagram (Fe, C, Mn, Si, P, Cu, Ni, Cr, Al, Mo, V, Nb are incl. for calcs, Fe and C content is changing), see **Figures 4 - 7**.

Experimental temperatures of liquidus summarized in **Table 2** are in good agreement in the case of samples 1-6, 8 and 10 (the difference is no more than 6 °C). The largest deviation was revealed by samples 7 and 9. If compared experimental temperature values with delivered temperature values by industrial partner and calculated using IDS, so the differences are in maximum 7 °C in case of samples 1-3. Higher differences were encountered by samples 4-6 and 9, up to 12 °C. The smallest agreement is between temperatures of liquidus for samples 7, 8 and 10. The results indicate, that mainly the higher the content of carbon and chromium cause the larger temperature differences (see samples 7, 8 and 10).

Liquidus temperatures and solidus temperatures are also presented with phase diagrams calculated by SW TC, **Figures 4-7**. Good agreement between experimental and theoretical values is observable for temperatures of liquidus and solidus for samples 1-6, differences no more than 5 °C. The substantial higher differences were observed for samples 7-10. The maximum difference does not exceed 14 °C in the case of T_L. The largest difference was encountered by temperature of solidus: 61 °C (sample 8).

Table 2 Temperatures of liquidus, experimental (DTA and TA) and theoretical, (°C)

Steel	DTA	TA		Max. difference	Indust. partner	IDS	Max. difference
		Heating	Cooling				
	T_L			ΔT	T_L		ΔT
1	1502	1502	1502	0	1503	1508	6
2	1500	n.m.	n.m.	0	1500	1507	7
3	1498	1503	1499	5	1497	1503	6
4	1498	1501	1495	6	1506	1500	11
5	1492	1493	1487	6	1492	1497	10
6	1486	1486	1484	2	1496	1487	12
7	1465	1473	1468	8	1493	1474	**28**
8	1474	1480	1476	6	1491	1475	**17**
9	1485	1496	1490	11	1488	1494	9
10	1470	1475	1471	5	1488	1470	**18**
Note: n.m. means not measured.							

Peritectic transformation was observed by all the samples and the start of peritectic transformation was evaluated at heating process (by DTA). These temperatures are also included in **Figures 4-7**. It is possible to state that the differences between calculated and experimental values are not so large like in the case of solidus temperature but also are not in so good agreement like selected liquidus temperatures. The differences between TC SW calculation and experimental values is up to 12 °C, only by the sample 7, 8 and 10 is the difference up to 22 °C.

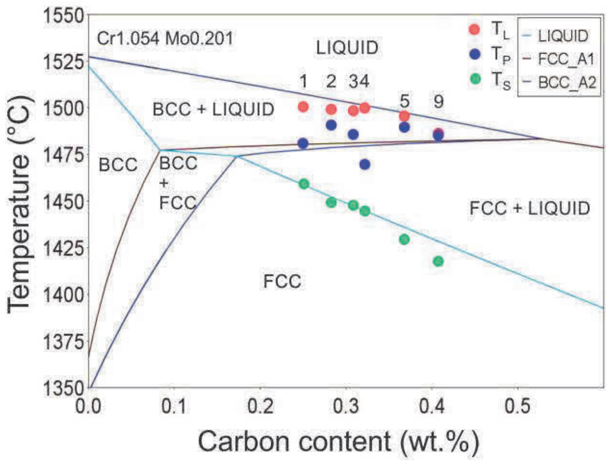

Figure 4 Comparison of T_L, T_P and T_S obtained by DTA with calculated isoplethal phase diagram, steel samples 1-5 and 9

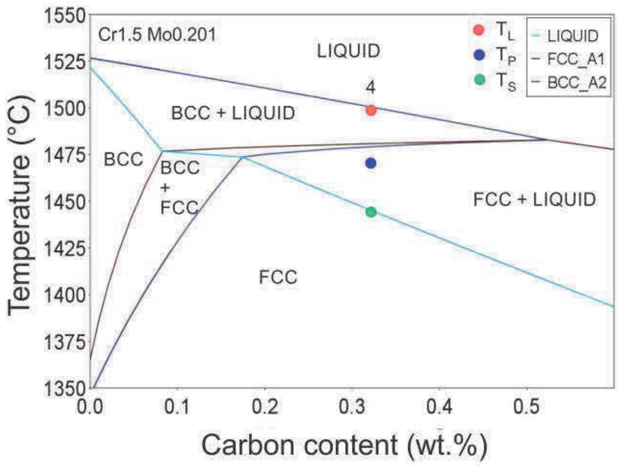

Figure 5 Comparison of T_L, T_P and T_S obtained by DTA with calculated isoplethal phase diagram, steel sample 4

It is possible to conclude, like in the case of comparison of liquidus temperature with IDS values and values delivered by industrial partner, that the main influence on phase transition temperatures will have the carbon and chromium. The largest differences were observed between TC SW calculations and experimental values again by samples 7, 8 and 10. Substantial differences were observed for all three evaluated temperatures (T_L, T_P and T_S).

Similar trends were observed if experimental temperature values were compared with delivered values by industrial partner, calculated by IDS and also by SW TC. It seems that the higher the carbon and chromium content in samples the larger the differences can be encountered. From the technological point of view it is a possibility to shift T_L (mainly by samples 6-8 and 10) to lower values and consequently to lower the costs by casting and solidification - optimize the technological process. The optimization is planned also using SW ProCast via simulation of casting and solidification of steels using presented original experimental data. But implementation to the real process has to be performed very carefully.

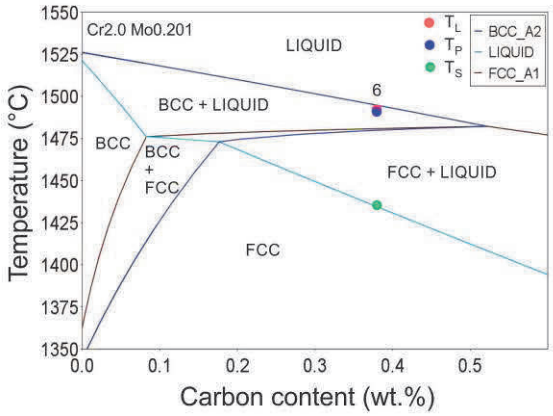

Figure 6 Comparison of T_L, T_P and T_S obtained by DTA with calculated isoplethal phase diagram, steel sample 6

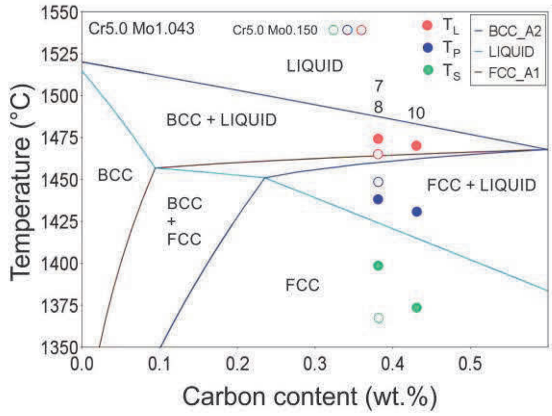

Figure 7 Comparison of T_L, T_P and T_S obtained by DTA with calculated isoplethal phase diagram, steel samples 7, 8 and 10

5. CONCLUSION

Original and new data - values of liquidus (T_L), peritectic transformation (T_P) and solidus (T_S) temperatures were obtained using DTA and Direct thermal analysis using Setaram and Netzsch equipments of Fe-C-Cr-Ni-Mo based alloys. Substantial differences were encountered for all obtained phase transition temperatures mainly by samples with higher carbon and chromium content. New obtained data can be used for databases and SW enhancement. Liquidus temperatures can be used directly for optimum adjusting of casting temperature and all three transition temperatures via e.g. SW Procast (used at our working site) for the whole casting and solidification process. It seems that alloys based on Fe-C-Cr-Ni-Mo with higher carbon and chromium content are still worthy of higher attention.

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 No. TA04010035, GAČR project No. 17-18668S and student project SP2017/59.

REFERENCES

[1] SOCHA, L., HUDZIECZEK, Z., PILKA, V., PIEGZA, Z. Comparison of steel desulphurisation at homogenisation station with physical modelling results. *Metalurgija*. 2015, vol. 54, no. 4, pp. 611-614.

[2] SOCHA, L., BAZAN, J., MORAVKA J., STYRNAL, P., MACHOVCAK, P., OPLER, A., TREFIL, A. Evaluation of the slag regime and desulphurization of steel with synthetic slag containing Cr_2O_3. *Materiali in tehnologije.* 2014, vol. 48, no. 6, pp. 965-970.

[3] KAWULOKOVÁ, M., SMETANA, B., ZLÁ, S., KALUP, A., MAZANCOVÁ, E., VÁŇOVÁ, P., KAWULOK, P., DOBROVSKÁ, J., ROSYPALOVÁ, S. Study of equilibrium and nonequilibrium phase transformations temperatures of steel by thermal analysis methods. *Journal of Thermal Analysis and Calorimetry*. 2017, vol. 127, no. 1, pp. 423-429.

[4] MYSLIVEC, T. *Fyzikálně chemické základy ocelářství*. 2., přeprac. a rozš. vyd. Praha: SNTL - Nakladatelství technické literatury, 1971. 256 s.

[5] KALUP, A., SMETANA, B., KAWULOKOVÁ, M., ZLÁ, S., FRANCOVÁ, H., DOSTÁL, P., WALOSZKOVÁ, K., WALOSZKOVÁ, L., DOBROVSKÁ, J. Liquidus and solidus temperatures and latent heats of melting of steels. *Journal of Thermal Analysis and Calorimetry*. 2017, vol. 127, no. 1, pp 123 - 128.

[6] EDMONDS, D., V., PERELOMA, E. *Phase transformations in steels. Volume 1: Fundamentals and diffusion - controlled transformations*. Cambridge: Woodhead Publishing Limited, 2012. 656 p.

[7] JERNKONTORET. *A Guide to the Solidification of Steels*. Stockholm, 1977. 162 p.

[8] GALLAGHER, P. K. *Handbook of Thermal Analysis and Calorimetry: Principles and Practice. Volume 1.* First edition 1998. Second impression 2003. Amsterdam: Elsevier, 2003. 691 s.

[9] MIETTINEN, J. *Solidification Analysis Package for Steels-User´s Manual of DOS version*. Helsinki: University of Technology, 1999.

[10] ANDERSSON, J. O., HELANDER, T., HOGLUND, L. H., SHI, P. F., SUNDMAN, B. *Calphad*, 2002, vol. 26, no. 2, pp. 273-312.