PHASE TRANSFORMATIONS TEMPERATURES OF REAL STEEL GRADE

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Abstract

The paper deals with the study of phase transformations temperatures of real peritectic micro alloyed steel grade. Phase transformations temperatures were obtained using Differential Thermal Analysis (DTA) and Setaram Setsys 18TM laboratory system. There are presented results from the low temperature region (below 1000 °C) and high temperature region (above 1000 °C). Extrapolation of obtained phase transformation temperatures to “zero” mass and “zero” heating rate is performed. The following temperatures of phase transformation were determined: eutectoid transformation (740 C), end of alpha-gamma transformation (845 °C), start of gamma-delta transformation (1472 °C), peritectic transformation (1486 °C) and liquidus temperature (1511 °C).The obtained phase transformations temperatures are discussed. Phase transformations temperatures are calculated using thermodynamic and kinetic software ThermoCalc and IDS also. Experimentally obtained data of phase transformations temperatures are compared with calculated data and discussed. Experimentally obtained data are essential for thermodynamic calculations and they are used also as input data for numerical mathematical and physical models.

Keywords: Differential thermal analysis, Steel, Phase transformations temperatures, ThermoCalc, IDS

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 steel making company. It is very important to solve (continuously improve) the refining processes, optimize the slag modes [1, 2] thermal and chemical homogenization of the melt [3] or filtration of steel.

It is necessary (for each steel making company) to continuously improve and optimize production processes in order to be competitive in respect to other competitors. For improvement and optimization of technological processes of steel production it is necessary to know, among others, the proper material data. Very important data are for example temperatures [4, 5] and latent heats of phase transformations, specific heat, surface tensions [6]. Although it is possible to find in available literature values of some of the above mentioned physical quantities, we can see differences even between these available data. One of the possibilities of obtaining the necessary data is use of simulation (calculation) programs, such as IDS software for calculation of temperatures of phase transformations and other material properties of steels. The calculated values should be verified by experimentally obtained data. Differential thermal analysis (DTA) is one of the methods that are suitable for obtaining thermo-physical data of steels. In the presented paper the differential thermal analysis was used for obtaining the temperatures of phase transformations. The experiments were supported by theoretical calculations using the software ThermoCalc (CALPHAD method) and IDS. Experimental data obtained in the low temperature region are very important for subsequent heat and mechanical treatment. Temperatures of solidus and liquidus [7, 8] are in the high temperature region and they are important mainly for setting of casting conditions.

2. DIFFERENTIAL THERMAL ANALYSIS (DTA)

Differential thermal analysis is a dynamic thermal analytic method used for investigation of temperature effects of an investigated sample connected with its physical, chemical or physical-chemical changes during its continuous linear heating or cooling [9]. This method is used for measurement of temperature differences between investigated and reference samples. Temperature of the reference sample follows the selected temperature program, temperature of the investigated sample is subject to changes, which reflect physical and chemical transformations occurring in the sample. This method makes it possible to express all physical, chemical of physical-chemical changes that are accompanied by sufficiently big change of enthalpy.

3. THERMOCALC

This thermodynamic software is based on CALPHAD method. CALPHAD method enables prediction of phase composition of multicomponent system by utilizing thermodynamical parameters of subsystem (experimentally obtained phase and thermodynamical data of the lower order system). CALPHAD method enables (besides calculation of equilibrium) calculation of numerous thermodynamical parameters [10]. In this work ThermoCalc (version 4.1) was used for calculation of phase transformation temperatures of real steel grade. Calculations were performed with use of the database TCFE7 Steels/Fe-alloys database version 7 [11]. Only selected phases (BCC, FCC, CEMENTITE and LIQUID) were considered for calculation.

4. IDS

The IDS model simulates the solidification of low-alloyed steels and stainless steel containing Cr up to 26 wt% and Ni up to 16 wt %. The solutes considered are C, Si, Mn, P, S. Cr, Mo, Ni, Cu, Al, N, Nb, Ti, V B, Ca, O and H. The model applies thermodynamic chemical-potential-equality equations, interfacial mass balance equations of solutes and FD application of Fick`s second law of solute diffusion. Depending on steel composition, cooling rate and dendrite arm diameter (default value provided), the model determines the stable solution phases and their fractions and compositions as a function of temperature [12]. The IDS software was also used for calculations of phase transformation temperatures of real steel grade.

5. EXPERIMENTAL EQUIPMENT AND CONDITIONS

Steel samples (peritectic micro alloyed steel) were prepared from billets continuously cast on billet caster in ArcelorMittal Ostrava a.s. Produced billets are used for production of seamless line pipes. A stick with diameter of approx. 3.5 mm was mechanically cut from the billet of the alloy and cylinders with the height of approx. 3 mm and mass from 150 to 220 mg were cut from it. The samples were then polished and cleaned by ultrasonic impact in acetone. Ten samples were analysed in the low temperature region and ten samples in the high temperature region.

Method of differential thermal analysis (DTA) [9] was used for the purposes of measurement of temperatures of phase transformations of real steel grade. Data, i.e. temperatures of phase transformations were acquired with use of experimental laboratory equipment for thermal analysis Setsys 18_{TM} (**Fig. 1a**) made by Setaram and measuring rods TG/DTA of the type „S“ (S - type rod Pt/PtRh 10%), which enable measurement within the temperature range from +20 °C up to +1600 °C. Steel samples were analysed in corundum (Al_2O_3) crucibles with volume of 100 µl, **Fig. 1b**. An empty corundum crucible served as reference sample, **Fig. 1b** - left crucible. During heating/cooling a permanent dynamic atmosphere was maintained – flow of Ar

(> 99.9999 %) was 2 litres/hour. Steel samples were during experiment control heated at the rate of 10 °C/min in the low and also in the high temperature region.

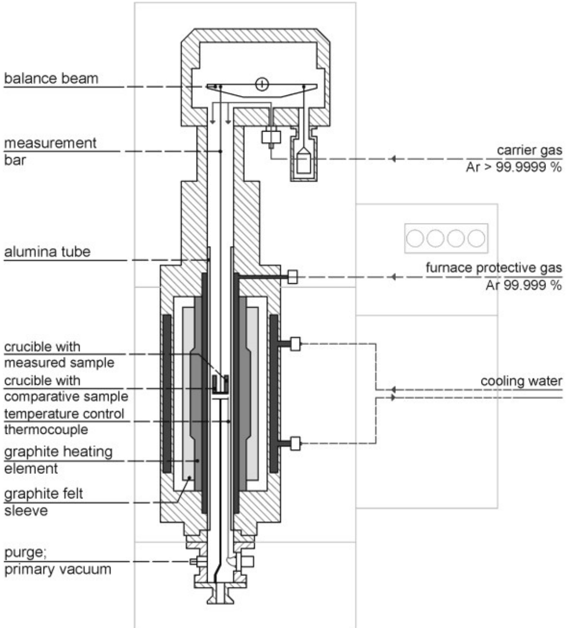

Fig. 1a SETARAM Setsys 18TM

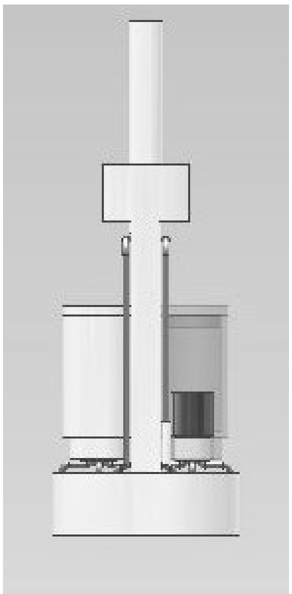

Fig. 1b Measurement bar with corundum crucibles

6. RESULTS AND DISCUSSION

Temperatures of phase transformations were obtained on the basis of evaluation of DTA curves for heating, Figs. 2 and 3. During cooling an under-cooling of samples occurred, that's why the values obtained at cooling were not evaluated. The difference between the temperatures obtained at heating and cooling exceeded in some cases even 20 °C.

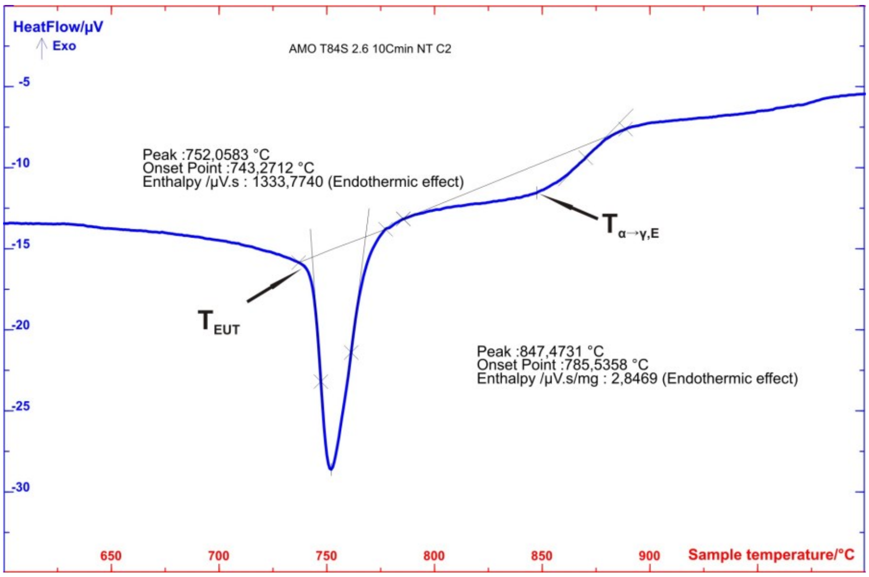

Fig. 2 DTA curve of the analysed steel in the low temperature region

Figure 2 shows a DTA curve of steel in the low temperature region (below 1000 °C). The first peak corresponds to eutectoid phase transformation and temperature of the peak start corresponds to the temperature of eutectoid phase transformation, **Fig. 2**. Temperature of eutectoid phase transformations is marked as T_{EUT}. On the basis of characteristic form of the curve before start of the peak it is possible to assume that part of the peak was the peak, corresponding rather to the Curie transformation (a complete overlapping of these two peaks took place). Due to overlapping of the peaks it is, however, impossible to determine exactly the temperature of the Curie transformation. For this reason the temperature was not evaluated. The second peak corresponds to the alpha-gamma phase transformation. Alpha-gamma phase transformation starts at the temperature of eutectoid phase transformations. The temperature of the second peak top corresponds to the temperature of the end of the alpha-gamma phase transformation. Temperature of the end of the alpha-gamma transformation is marked as $T_{\alpha\rightarrow\gamma,E}$.

Figure 3 shows DTA curve of steel in the high temperature region (above 1000 °C). The temperature of the first peak start corresponds to the temperature of start of the gamma-delta transformation. Temperature of transformation start is marked as $T_{\gamma\rightarrow\delta,S}$. Peritectic transformation temperature was evaluated as the temperature of second peak start. Peritectic transformation temperature is marked as T_P. Temperature of the third peak top corresponds to the liquidus temperature. Liquidus temperature is marked as T_L.

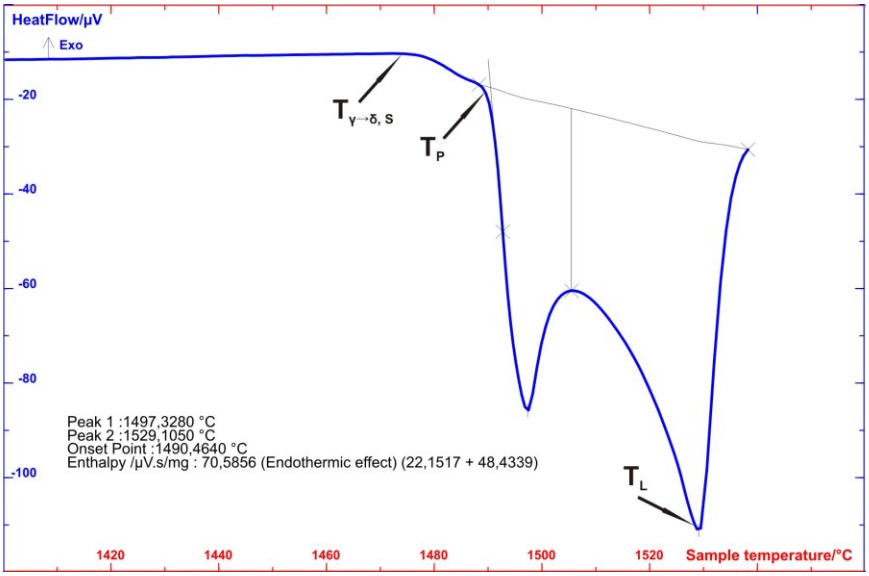

Fig. 3 DTA curve of the analysed steel in the high temperature region

The temperatures of phase transformations, obtained on the basis of DTA curves evaluation, were extrapolated to the „zero" heating rate and „zero" sample mass [13]. The obtained temperatures were corrected also on the basis of the temperature calibration (temperature of melting of pure metals). Experimentally obtained phase transition temperatures (corrected) are presented in **Table 1**.

Table 1 presents also basic statistic functions – average, standard deviation and variation coefficient. Independent parameters show high degree of consistency and low degree of variability. Standard deviation shows higher values for the temperatures $T_{\alpha\rightarrow\gamma,\ E}$ and $T_{\gamma\rightarrow\delta,S}$. This is caused by difficult evaluation of those temperatures on the DTA curves.

Temperatures of phase transformations were calculated also with use of calculation software ThermoCalc and IDS. The calculated temperatures of phase transformations are presented in **Table 2**, which contains for clarity also experimentally obtained temperatures.

Table 1 Experimentally obtained phase transformation temperatures

Sample	T_{EUT} (°C)	$T_{\alpha\rightarrow\gamma, E}$ (°C)	$T_{\gamma\rightarrow\delta,S}$ (°C)	T_P (°C)	T_L (°C)
1	741	844	1474	1486	1510
2	740	847	1473	1486	1510
3	741	846	1471	1486	1511
4	740	844	1472	1485	1511
5	741	849	1465	1486	1512
6	740	844	1470	1485	1511
7	740	844	1474	1486	1511
8	740	844	1474	1486	1511
9	740	844	1474	1486	1510
10	740	845	1475	1485	1510
Average	**740**	**845**	**1472**	**1486**	**1511**
St. deviation.	0	2	3	0	0
Var. coeff. %	0.04	0.19	0.19	0.03	0.03

Table 2 Comparison of experimentally obtained and calculated phase transformation temperatures

	T_{EUT} (°C)	$T_{\alpha\rightarrow\gamma, E}$ (°C)	$T_{\gamma\rightarrow\delta, S}$ (°C)	T_P (°C)	T_L (°C)
ThermoCalc	704	845	1476	1483	1517
IDS	-	830	1476	1480	1517
Experimentally	**740**	**845**	**1472**	**1486**	**1511**

The biggest difference between the experimentally determined and calculated temperature was observed in case of the eutectoid phase transformation. The difference between the experimentally determined temperature and the temperature calculated by the software ThermoCalc was 36 °C. The IDS software does not make it possible to calculate the temperature of the eutectoid transformation. The experimentally determined temperature of the end of the alpha-gamma transformation is the same as the temperature calculated by the ThermoCalc software. The temperature calculated by the IDS software is lower by 15 °C.

The temperature of start of the gamma-delta transformation was calculated by both software programs to be 1476 °C. The experimentally determined temperature is by 4 °C lower than the calculated values. The temperature of the peritectic transformation was calculated to be 1483 °C (ThermoCalc) and 1480 °C (IDS). The experimentally determined temperature was by 3 °C or by 6 °C higher. The liquidus temperature was by both software programs calculated to be 1517 °C. The experimentally obtained temperature was by 6 °C lower.

The differences between the calculated and experimentally obtained temperatures might have been caused by the calculation as such, when the software programs use various simplifications and they thus need not reflect real processes running in the steel during heating.

CONCLUSIONS

Temperatures of phase transformations of the real sample of steel were determined with use of differential thermal analysis. The following temperatures of phase transformations were determined on the basis of experiment: $\mathbf{T_{EUT}}$ (740 °C), $\mathbf{T_{\alpha\rightarrow\gamma, E}}$ (845 °C), $\mathbf{T_{\gamma\rightarrow\delta,S}}$ (1472 °C), $\mathbf{T_P}$ (1486 °C) and $\mathbf{T_L}$ (1511 °C).

Temperatures of phase transformations were calculated with use of the calculation software ThermoCalc and IDS. For the temperatures $\mathbf{T_{\gamma \rightarrow \delta,S}}$, $\mathbf{T_P}$, $\mathbf{T_L}$ very good agreement was obtained between the experimentally determined and calculated temperatures (by both software programs). The maximal difference for these temperatures was 6 °C. The temperature of the end of the alpha-gamma transformation calculated by ThermoCalc was the same as the experimentally determined temperature; the temperature calculated with use of the IDS was lower by 15 °C. The biggest difference (36 °C) was observed in case of the temperature of eutectoid transformation of the experimentally determined temperature and the temperature calculated by the ThermoCalc software.

It is presupposed that experimental values will be discussed in respect of next implementation in to the real technological process directly (e.g.: T_L) or via a simulation and subsequently optimization of real casting process.

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