INFLUENCE OF HEATING RATE ON THE LIQUIDUS TEMPERATURE MEASURED BY DTA METHOD FOR Fe-C-Cr BASED SYSTEMS

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Abstract

This paper deals with the influence of the experimental conditions settings of the chosen DTA method on obtained data. The article is focused on the study of heating rate effect on shifting of liquidus temperature (T_L) of Fe-C-Cr based systems (steels). Heating rate belongs to the frequently and easily changing parameter and its influence on the obtained data is substantial. DTA measurements were realised using the SETARAM Setsys 18_{TM} laboratory system. The samples (steels) were analysed at selected controlled heating rates (1, 2, 5, 10 and 20 K / min). It has been found that the value of liquidus temperature shifted with the increasing heating rate towards to the higher values and this dependence was expressed. Application of obtained results can substantially contribute to minimising the influence of the used heating rate mode on the liquidus and enables an extrapolation to the so called "zero" heating rate. It is thus possible to obtain for the investigated systems the liquidus temperatures close to the equilibrium temperatures without necessity of making set of experimental measurements, which is highly time-consuming.

Keywords: DTA, heating rate, liquidus temperature, steel

1. INTRODUCTION

Differential Thermal Analysis (DTA) is a method suitable for obtaining of thermo-physical data about metallic systems. This method makes it possible to obtain some thermo-dynamical and thermo-physical data, such as temperatures (e.g. liquidus and solidus temperature) and latent heats of phase transformations. Experimental conditions may have a substantial influence on thermo-dynamical and thermo-physical data obtained by this method. It is possible to include among experimental conditions for example temperature mode (heating / cooling), heating / cooling rate, mass of the analysed sample, type and purity of atmosphere surrounding the sample during analysis, reference sample, kind of crucible [1]. Heating rate is the most frequently changing experimental condition. The heating rate should be chosen with regard to the specific behaviour of the sample during the thermal analysis. It is necessary to take into account namely the possible change of the chemical composition during the analysis [2, 3] and the shape of the DTA curves (size and position of the peaks) [4, 5].

Thermo-physical and thermo-dynamical properties of Fe-C based metallic systems (steels) are still a subject of extensive research [2]. In spite of that the number of experimental data about these systems is still insufficient. From the technological point of view, the most critical parameters are the solidus (T_S) and liquidus (T_L) temperatures. Precise knowledge of T_L is particularly important with regard to the temperature setting of the steel overheating prior to casting. The T_S is related in particular to the process of solidification, where there are segregation phenomena in the two-phase region between T_L and T_S. Although it is possible to find in available literature the values of some of the above physical quantities, there are quite differences in these data. These differences may be caused also instead of others, by use of different experimental conditions of measurements at one method. The paper deals with possibilities of elimination of some influences at experiments [6, 7].

The purpose of this investigation was the study of heating rate effect on shifting of liquidus temperature (T_L) obtained by the DTA method for Fe-C-Cr based systems (steels).

2. EXPERIMENT

2.1. Differential thermal analysis (DTA)

Method of Differential thermal analysis (DTA) [8] was used for the purposes of measurement of temperatures of liquidus temperatures (T_L) of the Fe-C-Cr based systems (steels). 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.

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. With use of this method it is possible to obtain temperatures and latent heats of phase transformations.

2.2. Experimental conditions

Three real grades of steels were taken from continuous cast billets (generally labelled steel A, B and C).For each steel a stick with diameter of approx. 3.5 mm was mechanically cut from the billet and cylinders with the height of approx. 3 mm were cut from it. The samples were then polished and cleaned by ultrasonic effect in acetone. The mass of the cylinders needed for DTA was approximately 190 mg. Chemical composition of analysed samples is given in **Table 1**.

Table 1 Chemical composition of real steel grades (steels A, B and C)

Steel	C	Cr	Mn	Si	P	S	Cu	Ni	Al	Mo	V	Ti	Sn
	(wt. %)												
A	**0.094**	0.034	1.170	0.199	0.013	0.003	0.031	0.011	0.028	0.003	0.060	-	0.002
B	**0.148**	0.059	1.224	0.341	0.010	0.004	0.086	0.030	0.030	0.005	0.055	0.002	0.007
C	**0.270**	0.738	1.148	0.233	0.012	0.004	0.075	0.032	0.024	0.101	0.003	0.001	0.005

Method of differential thermal analysis (DTA) was used for the purposes of measurement of liquidus temperatures of steel samples. Data, i.e. temperatures of phase transformations were acquired with use of experimental laboratory equipment for thermal analysis Setsys 18_{TM} (**Figure 1a**) made by SETARAM and measuring rod 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 [9].

Steel samples were analysed in corundum (Al_2O_3) crucibles with volume of 100 µl, **Figure 1b**. An empty corundum crucible served as reference sample, **Figure 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 rates of 1, 2, 5, 10 and 20 K / min within the temperature range from 20 to 1600 °C.

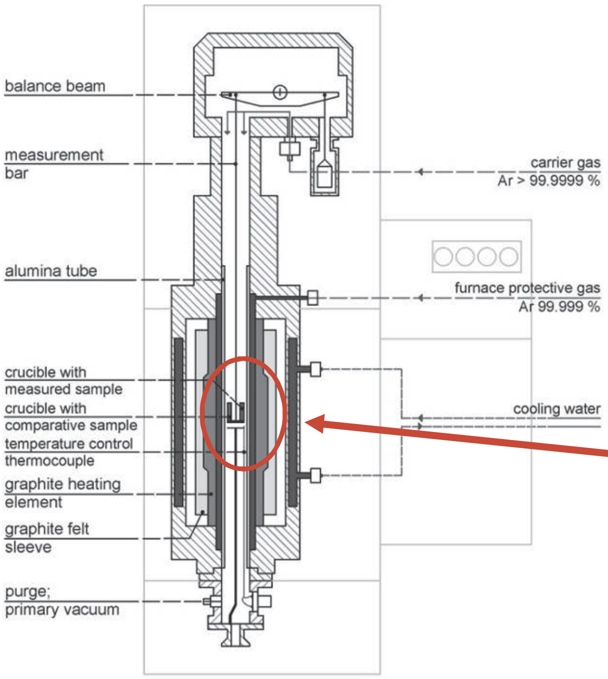

Figure 1a SETARAM Setsys 18TM

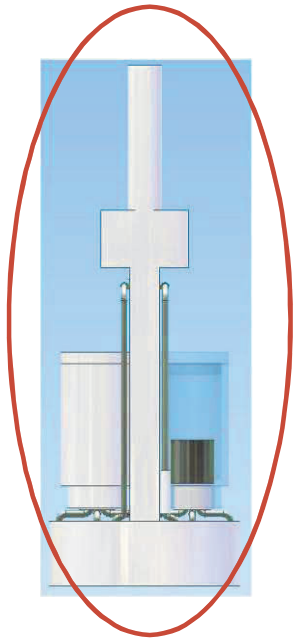

Figure 1b Measurement bar with corundum crucibles and sample of steel

3. RESULTS AND DISSCUSION

It is possible to obtain the investigated liquidus temperatures (T_L) from the so called DTA-curves, which demonstrate heat phenomena during linear heating of samples. For clearness and for better assessment of the effect of varying heating rate on shifting of temperatures all the obtained DTA-curves of the steels A, B and C were brought into one common image (**Figure 2** - steel A; **Figure 3** - steel B and **Figure 4** - steel C).

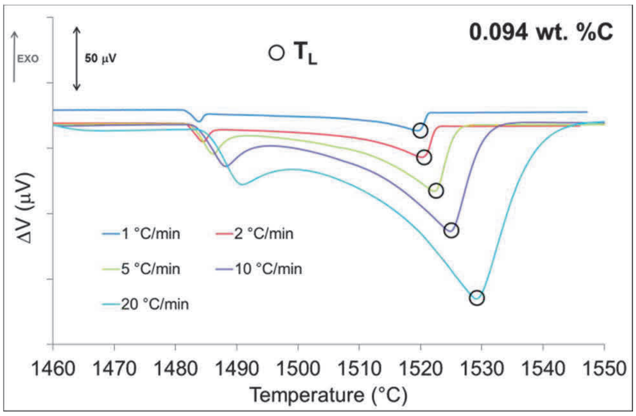

Figure 2 Evaluated DTA - curves of the steel A (heating rates 1, 2, 5, 10 and 20 °C / min)

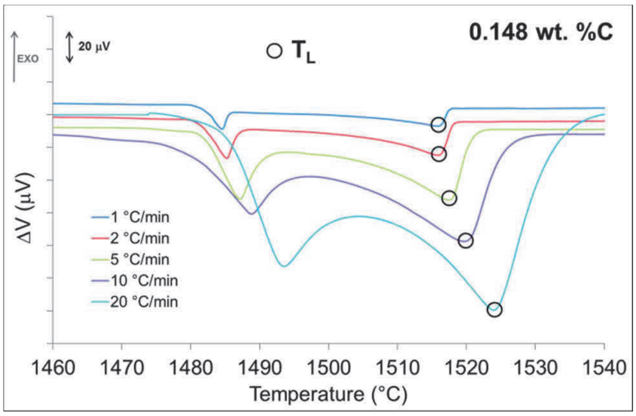

Figure 3 Evaluated DTA - curves of the steel B (heating rates 1, 2, 5, 10 and 20 °C / min)

The obtained values of liquidus temperatures of all three steels are given in the **Table 2**. This table also presents the statistical data (average, standard deviation σ and variation coefficient V) obtained from the measured values [10].

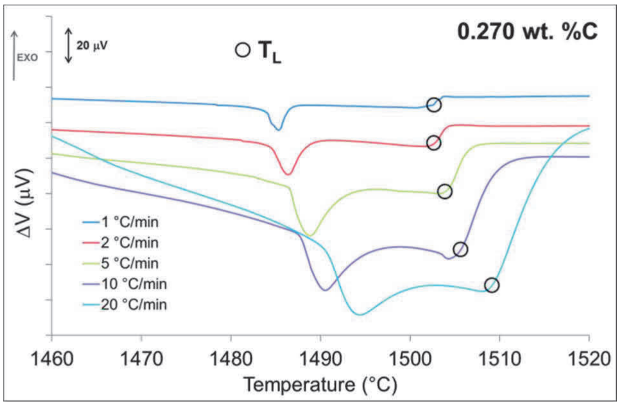

Figure 4 Evaluated DTA - curves of the steel C (heating rates 1, 2, 5, 10 and 20 °C / min)

From the **Figures 2-4** and **Table 2** can be seen the influence of heating rate on all liquidus temperatures measured by DTA. The temperatures are shifted with the increasing heating rate to the higher values. The greatest difference between the liquidus temperature obtained at 20 ° C / min and 1 ° C / min (**Table 2**, $\Delta T_{(max-min)}$) is evident in the steel with the lowest carbon content (steel A, 10 °C). With the increasing carbon content (steel B and C), the difference decreases, the effect of the heating rate on the liquidus temperature is lower The shift of temperatures to higher values with the increasing rate can be explained in method DTA by dynamics of the process and by detection capabilities of instruments. Different heating rates can also have a significant effect on kinetics of phase transformations (transition mechanism).

Table 2 Liquidus temperatures of real steel grades (steels A, B and C)

steel A (0.094 wt. % C)		steel B (0.148 wt. % C)		steel C (0.270 wt. % C)	
Heating rate	T_L	Heating rate	T_L	Heating rate	T_L
(°C / min)	(°C)	(°C / min)	(°C)	(°C / min)	(°C)
20	1529	20	1524	20	1509
10	1525	10	1520	10	1506
5	1522	5	1517	5	1504
2	1520	2	1516	2	1503
1	1519	1	1516	1	1503
0	**1519**	**0**	**1515**	**0**	**1503**
Statistic					
average	1523		1519		1505
σ	4		3		2
V (%)	0.24		0.20		0.15
ΔT (max-min)	10		8		6

Based on DTA results, a regressional dependence of the heating rate influence on the liquidus temperature was developed for all steels (**Figure 5**). In the charts, the reliability value R^2 is shown for completeness. The obtained values of T_L of all investigated steels were extrapolated to the "zero" heating rate and these values are also given in **Table 2**. On the basis of the obtained dependences it is possible to correct the data (T_L) obtained for other investigated Fe-based metallic systems, such as steels, to the "zero" heating rate. We can thus obtain for the investigated systems the temperatures close to equilibrium temperatures, without time-consuming experimental measurements.

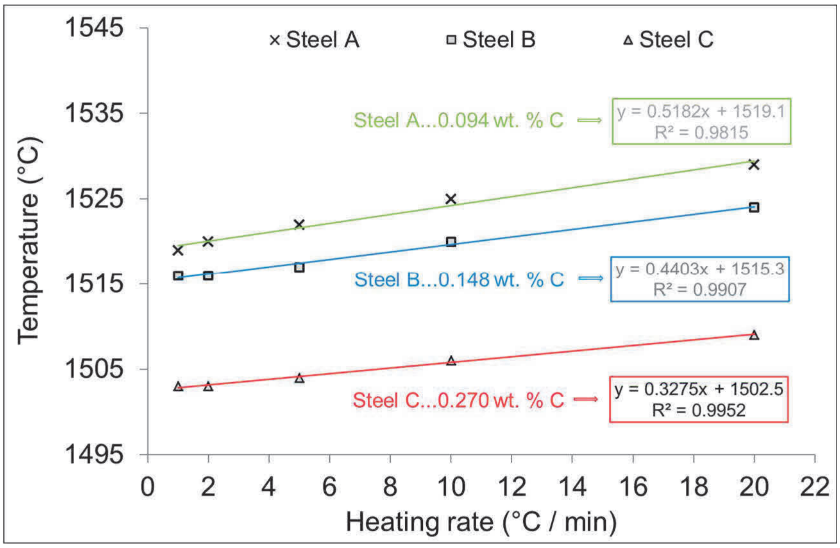

Figure 5 Regressional dependences of steel A, B and C

From the dependences of heating rate influence on the liquidus temperature for three real systems, it was shown that the effect of the heating rate is not the same for steel in general. Depending on the melting of the steel, it varies. For this reason, if we want to subsequently correct the liquidus temperature of the real steel grade, it is necessary to have corrections from the given steel melting area.

For example, if we measure steel with a carbon content of 0.368 wt. % using the same experimental equipment Setsys 18_{TM} and DTA method (heating rate 10 ° C / min), the correction should be made according to the steel C (**Figure 5**, regressional dependence). The measured liquidus temperature of the real steel grade would be corrected (decreased) by 3 ° C (rounded to integers). If we corrected according to the steel A, the correction for T_L would be -5 ° C. According to the steel B, we would also have corrected (decreased) the measured T_L by 5 ° C. In the same way, the influence of the heating rate on the "pure iron" melting temperature was studied in the work [2] (same device Setsys 18_{TM} and the DTA method). It was found that the measured liquidus temperature of the real steel grade would be according to their correction reduced by 7 ° C. Based on the observed differences in corrections, it is necessary to carefully examine the influence of the experimental conditions on the studied liquidus temperatures. These temperatures must be as accurate as possible, because they are used in practice to set the temperature of overheating of the steel during real casting process.

Before the actual measurement of real material (steel) should be performed the influence of experimental conditions (heating rate, mass sample) on the obtained data for each experimental device. Since it has been found that the weight of the analysed sample also has an influence on measured temperature [2], it would also be desirable to supplement the methodology with the influence of the sample mass on the liquidus temperature of the steel. Besides the influence of experimental conditions, calibration measurements must also be carried out for the experimental device. The liquidus temperature must also be corrected to the melting temperature of the pure metal (Ni or Pd).

4. CONCLUSION

In the presented work the influence of experimental conditions - the heating rate - on the liquidus temperature (T_L) was investigated on the steel samples with use of the experimental equipment SETARAM Setsys 18_{TM} and method DTA.

On the basis of obtained dependences that express the influence of the heating rate on the shift of T_L can be seen the influence of heating rate on all liquidus temperatures measured by DTA. The temperatures are shifted with the increasing heating rate to the higher values. The shift of temperatures to higher values with the increasing rate can be explained in method DTA by dynamics of the process and by detection capabilities of instruments. Different heating rates can also have a significant effect on kinetics of phase transformations (transition mechanism).

It follows that the determination of the influence of experimental conditions on the obtained data should be performed on each experimental device before the actual measurement. This may thus help to set the optimum experimental conditions at measurement for obtaining the phase transformation temperatures with minimal influence of experimental conditions.

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