INFLUENCE OF EXPERIMENTAL CONDITIONS OF THE DIRECT THERMAL ANALYSIS METHOD ON THE COURSE OF COOLING FOR SELECTED METALLIC SYSTEMS

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Abstract

The paper is devoted to the study of the influence of experimental conditions of the direct thermal analysis method for use in high-temperature thermal analysis equipment Netzsch STA 449 F3 JUPITER during controlled cooling mode.

The first part of the article is focused on monitoring of the effect of experimental conditions on the solidification point of the standard material nickel (a purity of 99.995 %) and the total shape of cooling curve. On the basis of experimental measurements, a deviation obtained by interpreting the cooling curves for various cooling rates (5; 10; 15 and 20 °C min^{-1}) for nickel samples of various weights (5; 10; 15 and 20 g) from the generally recognized melting / solidification point of nickel (1455 °C) can be quantified.

Besides the identification of the influence of experimental conditions on the temperature of solidification and the total cooling curve of nickel shape during solidification, the paper focuses attention on the mapping and interpreting the response found during the solidification of steel sample and the resulting to liquidus (T_L) and solidus (T_S) temperature of this steel. Findings from the discussion about the influence of experimental conditions on the solidification point of nickel and shape of cooling curve are implemented in a contribution to the method of identifying the solidus and liquidus temperature at selected real steel grades.

Keywords: Nickel, steel, direct thermal analysis, cooling curve, solidification

1. INTRODUCTION

Experimental conditions have essential effect on data which describe thermo-physical and thermo-dynamic properties of the investigated system [1-4]. Especially in this context, rate of the process of heating/cooling, the size (mass) of the sample, purity of internal furnace atmosphere may be mentioned. The authors already have a lot of experience using various methods of thermal analysis, e.g. [5-7]. Previous paper [8] was focused on detail study of the effect of mass and heating and cooling rate of the studied samples on shift of phase transformation temperatures on pure nickel samples under conditions of direct thermal analysis method (DirTA). The influence of boundary conditions of the experiment, whose can increase or decrease the phase transformation temperature and to verify the stability and reproducibility of these results was determined. Since, more experiments on nickel samples and also on steel samples were done. So, this paper is devoted only to cooling mode. But, it expands the discussion and implements obtained knowledge into results got for real steel grade. Determination of T_L and T_S of real steel grades is very important for next optimization of casting of steel in steelwork practice and also for proper setting of numerical simulations, e.g. [9, 10].

2. EXPERIMENTAL METHOD AND CONDITIONS

Method of direct thermal analysis (DirTA) is based on direct measurement of the temperature of the studied sample during its continuous linear heating/cooling. Experimental measurements based on a defined goal (high temperature phase transformation) were performed on a sample of pure metal with a high melting point (nickel with purity 99.995 %) and on selected real steel grade with approximately 0.08 wt.% C and 0.6 wt.% Mn. Sample of nickel standard with melting point 1455 °C [11] was used. Device for simultaneous thermal analysis Netzsch STA 449 F3 Jupiter was used.

Nickel samples were prepared in form of stick with a diameter of 3.5 mm and a variable length up to 4 mm. Steel samples was prepared in one piece with diameter of 14 mm and approx. 20 mm length. Before the laboratory analysis samples have always been grinded, debarred of eventually oxidise layer and subsequently purified in acetone under the treatment with ultrasound.

Analysis of pure nickel, the conditions of measurements was: cooling rates (5, 10, 15, 20 °C.min^{-1}). Samples with different mass (5, 10, 15, 20 g) were analysed. Each sample was analysed in a corundum crucible with a volume of about 4 ml. The analyses of nickel were realised after melting and next solidifying of nickel samples into uniform volume in the crucible. The mass of steel samples in interval from 23 to 26 g and only one cooling rate (5 °C.min^{-1}) was used.

Constant dynamic inert atmosphere (Ar, 6N), which should minimize the possible oxidation of the analysed samples, was kept in the interior of furnace apparatus. Additionally, for this purpose, a system OTS (Oxygen Trap System) has been installed.

3. RESULTS AND DISCUSSION

With the use of the above mentioned experimental apparatus and method the temperatures of solidification point of "pure" nickel have been measured and the influence of experimental conditions was observed. Moreover, the measurements for selected steel grade were realised too.

3.1. Solidification point temperatures of nickel standard

Solidification points of nickel samples were determined as maximum of the peak (local maximum temperature) on cooling curve [8].

Table 1 summarize obtained results like an influence of the mass of the sample and the chosen cooling rates on solidification point temperature of studied standard material (nickel).

Table 1 Solidification point of the standard material in mode of the linear cooling, °C

≈ Mass, g	Cooling rate, °C.min^{-1}			
	5	10	15	20
	1425	1425	1425	1367
10	1440	1439	1441	1443
15	1448	1446	1447	1444
20	1448	1448	1447	1448

Experimentally determined solidification point temperatures of "pure" nickel under cooling mode were found in the range of temperatures from 1367 to 1448 °C.

The dependency of the shift of solidification point for the cooling mode on the mass of the sample was identified (**Fig. 1**).

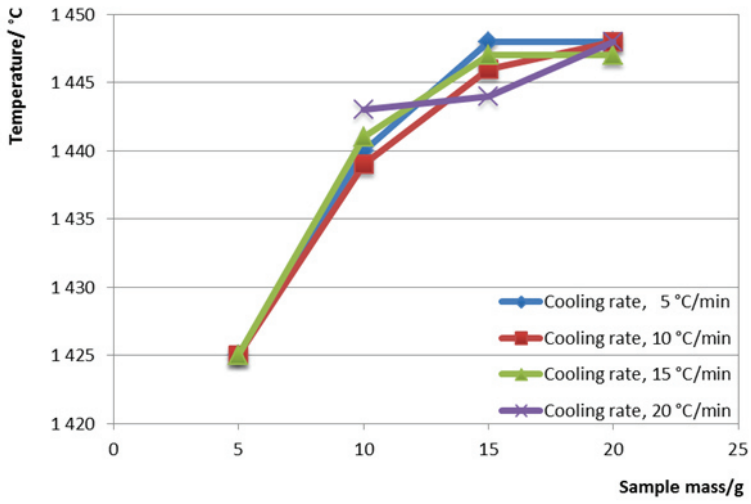

Fig. 1 Nickel mass influence on the shift of solidification point temperature in mode of the linear cooling

With the increasing mass of the sample more significant shift of solidification point temperature to higher values occurs. This verdict is evidently for small masses (10 g, especially for 5 g), where it was significantly lower solidification point temperatures, caused by a large supercooling of the sample due to its small mass [12]. The results show a relatively large difference between the minimum and maximum measured temperature of solidification process. A temperature difference between these two extreme temperatures is 81°C. It is obvious that with increasing mass of the samples occurs the solidification point at higher temperatures - the supercooling of the samples is less. This trend can be also observed across the various cooling rates.

It is evident that stable values independent on cooling rate were read for largest samples (20 g). On the basis of obtained results it seems that it is necessary to use samples of mass larger than 20 g to prevent the negative influence of experimental conditions during direct thermal analysis. Based on the difference between measured solidification point value (1448 °C) and generally accepted melting point for nickel (1455 °C) [11] can be set the correction value usable for measuring the phase transformation temperature during linear cooling in this high temperature area. The "real" temperature of such transformations should be 7 °C higher than read ones.

Moreover, there were realised two experiments for large nickel samples (cca 20 g) and cooling rate 5 °C.min^{-1} to prove the reproducibility of used methodology, see **Fig. 2**.

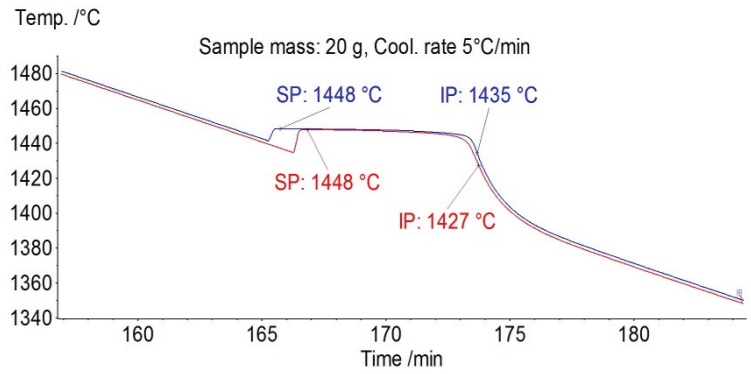

Fig. 2 Similar shape of cooling curves from two experiments under the same conditions for nickel

Very similar shape of both cooling curves is visible and the same solidification points (SP) values were read. The change of cooling curve slope at this point (IP) should be related to time when the phase transformation (solidification process) ends including its exothermal effect. Next shape of cooling curve is connected especially with temperature gradient between sample and environment in furnace. It is evident (**Fig. 2**) that the temperatures corresponding to IP on these two cooling curves differ (8 °C) for standard material. This difference should be related to different supercooling during both measurements. It can be assumed that this negative impact of experimental conditions will occur also for steel samples where IP temperature is often used for determination of T_S.

3.2. Determination of T_L and T_S for selected steel grade

Next part of evaluation was focused on implementation of above acquired knowledge into methodology of T_L and T_S determination for real steel grade by DirTA method. T_L and T_S read from individual cooling curves

from realised experiments (experiment ID) and then corrected based on above identified temperature correction (+ 7°C) are summarised in **Table 2**.

Table 2 Measured and corrected T_L and T_S for studied steel grade, °C

Experiment ID	Measured temperature		Corrected temperature	
	T_L	T_S	$T_{L\ cor.}$	$T_{S\ cor.}$
1	1514	1478	1521	1485
2	1514	1477	1521	1484
3	1513	1477	1520	1484
4	1513	1478	1520	1485
5	1513	1480	1520	1487
6	1511	1473	1518	1480
7	1514	1477	1521	1484
8	1514	1476	1521	1483

Although results are for a steel (a very heterogeneous material), it is clear that read T_L are very close. The average T_L after temperature correction is 1520 °C. This is only 1 °C lower value than T_L determined for this steel grade based on DirTA method when heating mode was used [12, 13].

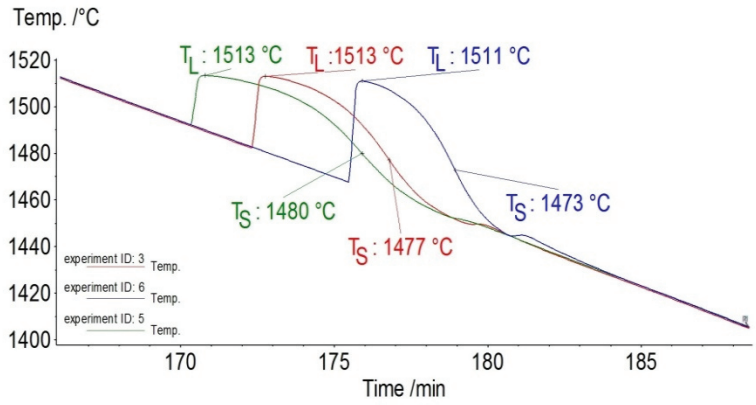

Fig. 3 T_S (maximal, medium and lowest) read from individual cooling curves for studied steel grade

More different values were obtained for T_S (**Table 2**). Selected cooling curves obtained during DirTA for studied steel grade are plotted in **Fig. 3**. The difference between maximal and minimal T_S is 7 °C. On the other hand, this deviation is lower than deviation for above discussed results from measurements realised on pure nickel samples (8 °C), see **Fig. 2**.

These deviations are affected bz properties and different supercooling of measured steel samples and probably also with used methodology and its physical limitations. However, all measurements was realised based on relevant conditions and as mentioned, the deviation is lower than for nickel standard. So, an average value 1484 °C is fully relevant T_S for this low carbon steel grade. This is only 4 °C higher value than T_S determined for this steel grade based on DirTA method when heating mode was used [12, 13].

4. CONCLUSION

Thermo-physical and thermodynamic properties of metallic systems represent some of the most important data that allow us to describe their behaviour under strictly specified conditions. The experimental laboratory system for thermal analysis Netzsch STA 449 F3 Jupiter was used. In this paper, the influence of selected experimental conditions (sample mass, cooling rate) on a temperature of solidification point of "pure" nickel T_L

and T_S of real steel grade was studied. Experimental measurements based on defined goal by method of direct thermal analysis have led to the following findings for standard material (nickel):

1) Temperature interval for solidification point based on direct thermal analysis under linear cooling conditions is wide. The solidification point for most of sample mass was found in interval between 1440 and 1448 °C. Thermal analysis of the smallest samples (5 g) led to lowest solidification point of nickel with an extreme value (1367 °C) if the highest heating rate (20 °C.min^{-1}) was applied.
2) Different trends were obtained if the solidification point for medium mass samples (10 g, 15 g) were determined for changing of cooling rates. Only, the solidification point for the largest samples (20 g) was stable despite of different cooling modes. So, it is necessary to use samples of mass larger than 20 g to prevent the negative influence of experimental conditions during direct thermal analysis. Moreover, the shift of inflection points on cooling curves was observed.
3) The difference of measured solidification point against generally accepted melting point (7 °C) of nickel is used for correction of high temperature phase transformation temperatures readings from direct thermal analysis experiments of real steel.

Above described knowledge was implemented to evaluation of DirTA results obtained for samples of low carbon steel grade:

4) Based on set temperature correction (+7 °C), final T_L and T_S are very close (-1 °C/ +4 °C) to previous results based on heating mode. There was also observed a shift of T_S for individual measurements, but deviations are not bigger than for standard material (nickel).

Presented results led to new knowledge about thermal analysis method and used methodology, even though is robustness, will be analysed for better understanding to its limitation in further works. Nevertheless, obtained T_L and T_S are applicable into steelwork practice and into numerical modelling.

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