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INFLUENCE OF DIRECT THERMAL ANALYSIS EXPERIMENTAL CONDITIONS ON DETERMINATION OF THE HIGH TEMPERATURE PHASE TRANSFORMATION TEMPERATURES

WPLYW WARUNKÓW PROWADZENIA BEZPOŚREDNIEJ ANALIZY TERMICZNEJ NA OKREŚLENIE TEMPERATUR WYSOKO TEMPERATUROWYCH PRZEMIAN FAZOWYCH

Thermo-physical and thermodynamic properties of metallic systems represent some of the most important data that allows to describe their behaviour under strictly specified conditions. These data are the basic, input data for simulative programs, which can model this behaviour and they can be applied to real conditions. Method of direct thermal analysis is the one of the methods of enabling to obtain such data. This paper deals with application of this method on particular sample of pure standard material. The experimental laboratory system for thermal analysis Netzsch STA 449 F3 Jupiter was used for experimental measurements. This paper is studying the influence of experimental conditions on the obtained temperature of phase transformations and on shift of phase transformation temperatures with respect to the monitored experimental conditions, accuracy and credibility of the measured data. Acquired values of this data could be significantly influenced by experimental conditions, size (mass) of samples, purity of inert atmosphere and also by regimes of controlled heating and cooling rates.

Keywords: nickel, melting/solidification point temperature, direct thermal analysis, heating/cooling rate, sample mass

Właściwości fizyczne i termodynamiczne układów metalicznych stanowią jedne z najważniejszych danych, które pozwalają opisać ich zachowanie w ściśle określonych warunkach. Dane te są podstawowymi danymi wejściowymi dla programu, który może symulować model tych zachowań i które mogą być zastosowane do rzeczywistych warunków. Metoda prostej (bezpośredniej) analizy termicznej jest jedną z metod pozwalających na uzyskanie takich danych. Niniejszy artykuł dotyczy zastosowania tej metody, w szczególności próbki czystego materiału standardowego. Do pomiarów eksperymentalnych było używane urządzenie dla analizy termicznej Netzsch STA 449 F3 Jupiter. W artykule analizowano wpływ warunków doświadczalnych na uzyskane temperatury przemian fazowych oraz na zmiany temperatur przemian fazowych z uwzględnieniem monitorowanych warunków doświadczalnych, dokładności i wiarygodności danych pomiarowych. Warunki doświadczalne, wielkości (masa) próbek, czystość atmosfery obojętnej, a przedziały kontrolowanej szybkości ogrzewania i chłodzenia mogą w znaczący sposób wpływać na otrzymane wartości tych danych.

1. Introduction

Experimental conditions have essential effect on data which describe thermo-physical and thermodynamic 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]. This paper is focused on the next study of the effect of mass and heating and cooling rate of the studied samples on shift of phase transformation temperatures. Main aim is to monitor the influence of mentioned boundary conditions of the experiment, which can increase or decrease the phase transformation temperature and to verify the stability and reproducibility of these results. Obtained data

will be implemented into the evaluation process of thermo-analytical experiments devoted to high-temperature phase transformations for real steel grades and will be used to verify of the methodology as correct method for determining the high temperature phase transformation temperatures.

2. Direct thermal analysis method

Method of direct thermal analysis is based on direct measurement of the temperature of the studied sample during its continuous linear heating/cooling. The temperature of the sample is measured at its centre by a thermocouple depending on time. A heating/cooling curves of the experiment are plotted.

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During the process of phase transformation running (in our case, the melting point temperature of the sample) changes on the temperature curve can be registered. The deflection of temperature curve from its linearity, respectively linear progression is observed. From the diversions on the curve the temperatures of phase transformation can be obtained. The temperature at which a solid melts and becomes a liquid is the melting point. On the other hand, during cooling regime a liquid metal becomes solid at the temperature called solidification point.

Pure crystalline substances have a clear, sharply defined melting point. During the melting process, all of the energy added to a substance is consumed as heat of melting, and the temperature remains constant under ideal conditions. Theoretically the melting point and solidification point should have the same value.

The procedure to determine the melting point of studied standard is based on the methodology of the extrapolation technique. Melting point temperature by using tangents as extrapolated temperature of registered changes on the temperature curve is identified. The solidification point can be read from a cooling curve as a local peak value.

3. Experimental methodology

Experimental measurements based on a defined goal (high temperature phase transformation) were performed on a sample of pure metal with a high melting point. Sample of nickel standard with melting point 1455°C was used. The purity of the nickel responds to 99.995%. Chemical composition of “pure” nickel is shown in Tab. 1.

TABLE 1
Chemical composition of analysed sample of “pure” nickel, wt. %

Cu	Fe	Ti	Co	Mn
0.0001	0.0002	0.0002	0.0001	0.0002
Zr	Cr	V	Mg	Si
0.0002	0.0002	0.0005	0.0002	0.0002

To determine the melting point of “pure” nickel device for simultaneous thermal analysis Netzsch STA 449 F3 Jupiter was used.

Experimental system Netzsch (see Fig. 1) allows to measure the thermo-physical and thermodynamic properties of materials at high temperatures.



Fig. 1 Netzsch STA 449 F3 Jupiter

Characteristic properties and experimental possibilities of this high sophisticated system are shown in Tab. 2.

TABLE 2
Experimental options of the high temperature experimental system
Netzsch STA 449 F3 Jupiter

Experimental options	Netzsch STA 449 F3 Jupiter
Experimental methods	c-DTA – „calculate DTA curve”; TG/DTA; TG/DSC; TG
Temperature range	+ 20°C to + 2000°C
The rate of heating/cooling	0.01 to 50°C.min ⁻¹
Temperature programs	linear heating/cooling; isothermal holding time; cycling
Sample mass	up to 30 g (35 g)
Atmosphere	vacuum; inert; reactionary
Cp sensor type	DSC flat sensor

In all cases of analysis, the same conditions of measurements: heating and cooling rates (5, 10, 15, 20°C.min⁻¹) were respected. Samples with different mass (5, 10, 15, 20 g) were analysed. Nickel samples were prepared in form of stick with a diameter of 3.5 mm and a length of about 4 mm. Before the laboratory analysis, samples of nickel standard have always been grinded, debarred of eventually oxidise layer and subsequently purified in acetone under the treatment with ultrasound.

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. Each sample was analysed in a corundum crucible with a volume of about 4 ml. Summary overview of the measurement setup is shown in Tab. 3.

TABLE 3
Experimental setup

Sample	Mass, g	Experimental conditions	
Ni	5, 10, 15, 20	Atmosphere: inert (Ar, 6N); 50 ml.min ⁻¹	Temperature program: linear heating
Heating rate, °C.min ⁻¹			Thermocouple: Pt/PtRh 10%
Cooling rate, °C.min ⁻¹		TG measuring rod: type „S”	

4. Results and discussion

With the use of the above mentioned experimental apparatus and method a temperatures of high temperature phase transformation (melting/solidification point) of “pure”

nickel have been measured and the influence of experimental conditions was observed.

4.1. Melting point temperatures of nickel standard in the heating mode

The first series of experiments were focused on the determination of experimental environment on nickel standard melting point during the sample heating. The results obtained under different heating rate and mass conditions are summarized in Tab. 4.

TABLE 4
Melting point of the standard material in mode of the linear heating, °C

≈ Mass, g	Heating rate, °C.min ⁻¹			
	5	10	15	20
5	1451	1452	1454	1455
10	1451	1450	1451	1451
15	1450	1450	1450	1450
20	1450	1450	1451	1451

An example of analysed heating curve is shown on Fig. 2.

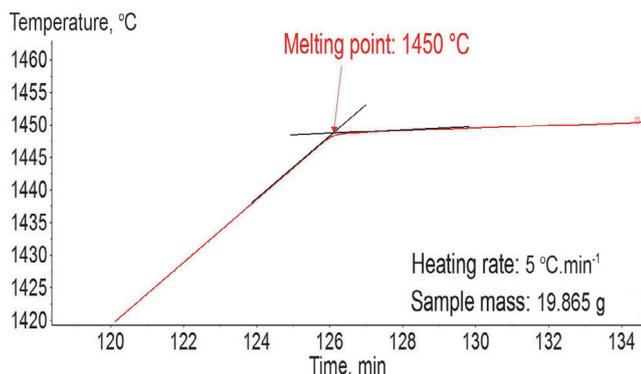


Fig. 2. Example of heating curve obtained during linear heating of nickel sample

Figure 2 shows in detail the determination of the melting point of “pure” nickel from the measured heating curve. It is evident, original linear increasing of temperature is stopped when the phase transformation (melting point of nickel here) starts. Next, a melting process should be connected with other line. Melting point was determined as the temperature extrapolated from these two locally linear interval of heating curve.

4.1.1 An influence of sample mass on determined temperature of melting point

Melting point obtained with selected heating rates for the different mass of the nickel samples are shown in Fig. 3.

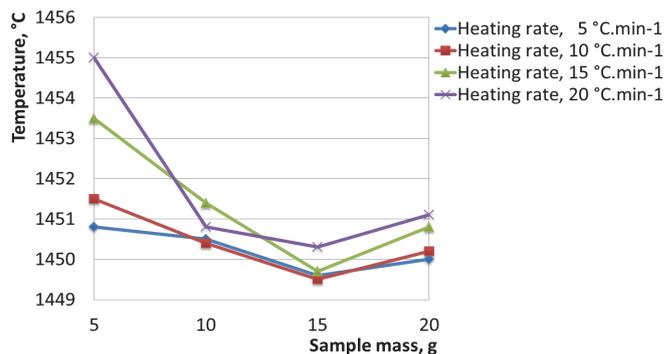


Fig. 3. Sample mass influences on the shift of melting point temperature in regime of the linear heating

It can be registered that the measured temperature melting point was experimentally determined in the range from 1450 to 1455°C. Across the selected heating rates the dominant trend was observed only for sample with a mass of 5 g. It is evident that melting point is higher with increasing heating rate.

This trend is detectable also for the other masses, since the shift that occurs there at different mass is on the order of several Celsius degrees (about 2°C) and it can be neglected.

4.1.2 An influence of heating rate on determined temperature of melting point

In the case of the monitoring of influence of the heating rate on temperatures of melting point (see Fig. 4) can be concluded, that across heating rates rather prevalent trend: for any heating rates the close melting point temperature are visible. First tendency to close temperatures of melting point is evident for heating rates 15 and 20°C.min⁻¹ and for other ones (5 and 10°C.min⁻¹). If the heating rates are higher, the melting points are higher too, especially for heating rates 15 and 20°C.min⁻¹. Except the smallest samples (5 g), this trend can be neglected.

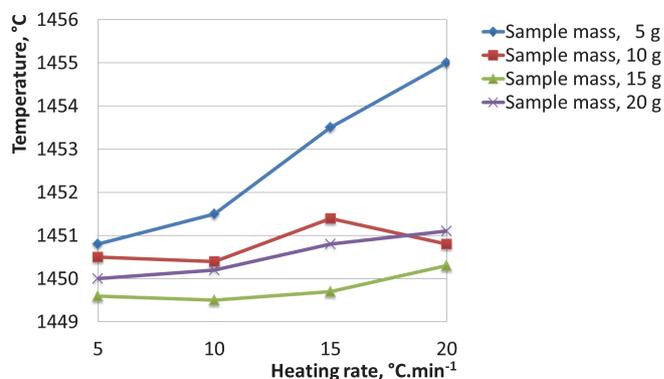


Fig. 4 Influence of heating rate on the shift of melting point temperature in regime of the linear heating

4.2. Solidification point temperatures of nickel standard in the cooling mode

Because, we are generally focused on studying the liquidus and solidus temperatures of real steel grades during their solidification after casting, it is important to describe also the influence of experimental conditions during direct thermal analysis on the cooling process.

An example of analysed cooling curve is shown on Fig. 5.

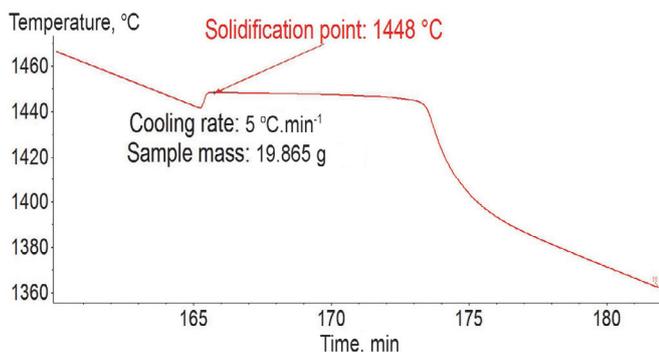


Fig. 5 Example of cooling curve obtained during linear cooling of nickel sample

Solidification point of selected sample (sample mass and experimental conditions mentioned on Fig. 5) as maximum of the peak of cooling curve was determined. Phase transformation is detected at this peak of local maximum temperature in our case of nickel standard.

TABLE 5

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

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

According to Tab. 5, the influence of the mass of the sample and the chosen cooling rates on solidification point temperature of studied standard material will be discussed.

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

4.2.1 An influence of sample mass on determined temperature of solidification point

The dependency of the shift of solidification point for the cooling mode on the mass of the sample was identified (Fig. 6).

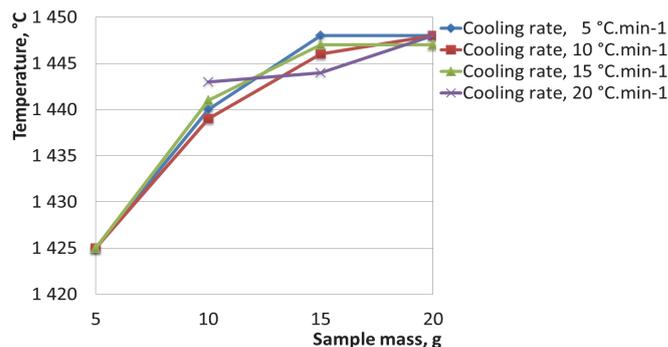


Fig. 6 Sample mass influence on the shift of solidification point temperature in regime of the linear cooling

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 identical small mass (Fig. 7).

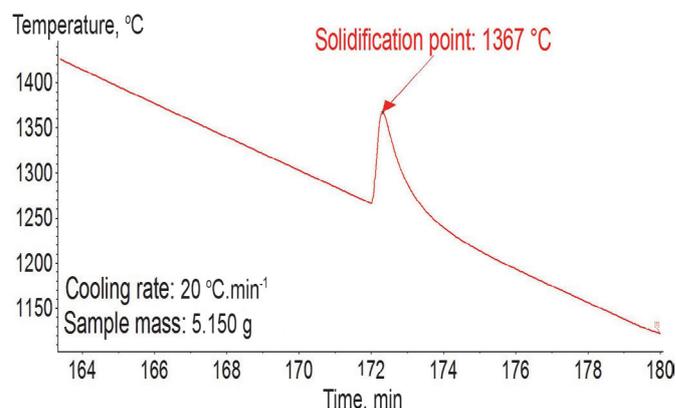


Fig. 7 Cooling curve with high degree of supercooling

The results show a relatively large difference between the minimum and maximum measured temperature of solidification process. A temperature difference between these two extremes 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 rates. For individual sample mass separately, the same trend is not evident through all rates.

4.2.2 An influence of cooling rate on determined temperature of solidification point

From the evaluation the influence of cooling rate on the shift of solidification point, it can be observed that with increasing rate is not obvious influence on the shift on this temperature (Fig. 8).

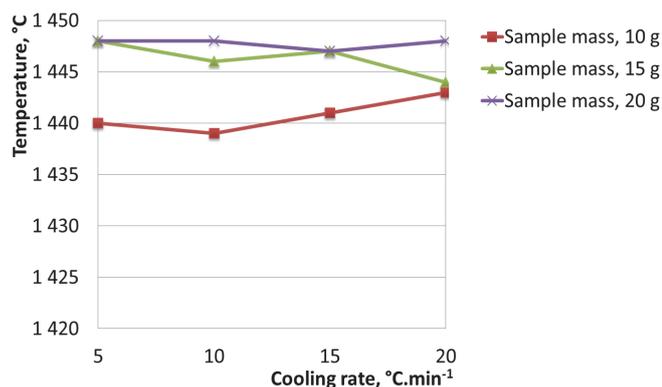


Fig. 8 Influence on cooling rate on the shift of solidification point temperature in regime of linear cooling

It can be argued that has not been experimentally found significant effect of higher or lower rates of cooling to solidification point temperature of nickel standard. Following trend can be registered for each cooling rate: the higher mass of the sample generally led to higher solidification point.

5. Conclusions

Thermo-physical and thermodynamic properties of metallic systems represent some of the most important data that allows 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, heating/cooling rate) on a temperature of melting/solidification point of “pure” nickel standard material with generally accepted melting point (1455°C) was studied. Experimental measurements based on defined goal by method of direct thermal analysis have led to the following findings:

1. The melting point temperature interval under linear heating conditions was from 1450 to 1455°C for all sample masses and heating rates.
2. Generally, there is no significant influence of mass or heating rates for larger samples from 10 to 20 g on measured melting point.
3. However, experiments realised on small samples (5 g) led to any increasing of melting point with higher heating rates.
4. In contrast with heating regime, the temperature interval for solidification point based on direct thermal analysis under linear cooling conditions is wider. The solidification point for most of sample mass was found in interval between 1440 and 1448°C.

5. 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.
6. Different trends were obtained if the solidification point for medium mass samples (10 g, 15 g) were determined for changing of cooling rates.
7. Only, the solidification point for the largest samples (20 g) was stable despite of different cooling regimes.
8. Finally, 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 difference of measured melting point against generally accepted is used for correction of high temperature phase transformation temperatures readings from direct thermal analysis experiments.

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