STUDY OF THE INFLUENCE OF EXPERIMENTAL CONDITIONS ON THE TEMPERATURES OF PHASE TRANSFORMATIONS IN HIGH-TEMPERATURE AREA FOR Fe-C-Cr AND Fe-C-Ni BASED SYSTEMS

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Abstract

One model alloy based on Fe-C-Cr and one model alloy based on Fe-C-Ni were studied. Fe-C-Cr based alloy contained carbon of 0.34 wt. % and chromium of 0.92 wt. %. Fe-C-Ni based alloy contained carbon of 0.38 wt. % and nickel of 1.08 wt. %. Temperatures of phase transformations (temperature of the solidus, liquidus and peritectic transformation) were studied in the high-temperature area by a heating rate of 1, 2, 5, 10 and 20 °C/min., the influence of heating rate was investigated. The influence of the sample mass was also studied by the heating rate of 10 °C/min. Samples with mass 50, 100, 190, 280 and 370 mg were studied. Samples with the mass 190 mg were studied by various heating rates. The Setaram Setsys 18_{TM} device was used for experiments with the use of the DTA method. No influence of the heating rate was detected for the temperature of solidus for both alloys. The most significant influence of heating rate was observed for the temperature of liquidus (temperature difference 6 - 8 °C). More noticeable impact of heating rate on the temperature of peritectic transformation shift was observed by Fe-C-Cr based alloy investigation. The influence of sample mass is negligible regarding the temperature of solidus and significant in case of liquids (for both alloys) and peritectic transformation (for Fe-C-Cr alloy) temperature.

Keywords: DTA, heating rate, sample mass, temperatures of phase transformations, Fe-C-Cr and Fe-C-Ni based alloys

1. INTRODUCTION

Thermo-physical and thermodynamic properties of systems based on Fe were and still are a subject of extensive research [1-3]. To predict thermo-physical and thermodynamic material properties of complex systems is necessary to have a high quality of experimental data of simpler systems such as Fe-C-O, Fe-C-O-Cr or Fe-C-O-Ni [1,2,4,5]. The key material data required for the thermodynamic and thermos-physical description of materials include the heat capacities, the phase transformation temperatures, latent heat and others [2].

Temperatures of phase transformations of Fe- based systems (steels) have technological importance and are commonly used as the input data in software packages (e. g. Procast, Magmasoft, ANSYS Fluent). This paper presents results obtained by one of the thermal analysis methods: Differential thermal analysis (DTA) which makes it possible to obtain temperatures of phase transformations [6]. Experimental conditions influence on experimental data obtained by this method. To those belongs heating/cooling rate, the mass of the sample, type and purity of atmosphere during analysis, reference sample [7]. The paper deals with possibilities of elimination of some influences at experiments.

This paper presents the influence of the heating rate and the mass on the sample on temperatures of phase transformations in the high-temperature area (temperature of solidus, liquidus and peritectic transformation). Influence of heating rate of the temperature on liquidus was studied in [8], and influence of the heating rate and mass of the sample of temperatures of phase transformations in the low and high-temperature area was studied in [9].

2. EXPERIMENT

2.1. Sample characterization

One model alloy based on Fe-C-Cr and one model alloy based on Fe-C-Ni were studied. The first alloy contained carbon of 0.34 wt. % and chromium of 0.92 wt. %. The second alloy contained carbon of 0.38 wt. % and nickel of 1.08 wt. %. Chemical composition that was determined directly on samples for thermal analysis is presented in **Table 1**.

Table 1 Chemical composition of studied alloys /wt. %

Alloy	C	Cr	Ni	O	P	S	Mn	Al
Fe-C-Cr	0.344	0.924	0.001	0.002	0.004	0.007	0.056	0.010
Fe-C-Ni	0.382	0.010	1.084	0.002	0.004	0.005	0.030	0.010

The samples for DTA analysis were processed into the form of cylinders with a diameter 3.5 mm and high of 3 mm. The mass of the cylinders was 190 mg for analysis of the influence of the heating rate and 50, 100, 190, 280 and 370 mg for analysis of the influence of the mass of the samples. The samples were polished (the possible oxidation layer was removed) and cleaned ultrasonically in acetone before analysis. Temperature calibration was performed using Pd for all alloys.

2.2. Experimental conditions

For obtaining the temperatures of phase transformations with the help of Differential Thermal Analysis (DTA) was used Setaram Setsys 18_{TM}. The measurements were carried out in alumina crucibles with a volume of 80 μl. An empty corundum crucible served as a reference sample. The dynamic atmosphere of argon was maintained in the furnace during analysis to protect the sample against oxidation. The purity of argon was higher than 99.9999 %. Samples for the influence of heating rate were analysed at the heating rate of 1, 2, 5, 10 and 20 °C/min. The samples for the influence of mass were analysed with the heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

Temperatures of phase transformations in the high-temperature area were obtained based on the evaluation of DTA curves. Temperatures of solidus (T_S), liquidus (T_L) and peritectic transformation (T_P) were detected. Measured DTA curves of five experimental measurements for the influence of heating rate on shifting of temperatures of phase transformations are in **Figure 1** and **Figure 2**. Experimental values with the correction to Pd for this influence are in **Table 2** and **Table 3**. Measured DTA curves of five experimental measurements for the influence of the mass of the sample on shifting of temperatures of phase transformations are in **Figure 3** and **Figure 4**. Experimental values with the correction to Pd for this influence are in **Table 4** and **Table 5**. Tables also present the statistical data (average, standard deviation and coefficient of variation CV) obtained from the measured values [10].

3.1. Influence of heating rate on shifting of temperatures of phase transformations

From **Table 2** and **Table 3** can be seen the influence of heating rate on all temperatures measured by DTA method. All temperatures are shifted with the increased heating rate to the higher values except for the temperature of solidus. For Fe-C-Cr alloy the smallest influence of heating rate is for temperature of solidus (**Table 2**; T_{MAX}-T_{MIN}= 5 °C, CV = 0.11 %). The greater influence of heating rate is for temperature of liquidus (**Table 2**; T_{MAX}-T_{MIN}= 6 °C, CV = 0.15 %). The biggest influence is clear for temperature of peritectic transformation (**Table 2**; T_{MAX}-T_{MIN}= 7 °C, CV = 0.17 %). For Fe-C-Ni alloy was not detected the temperature of peritectic transformation for all heating rates because the difference between T_P and T_L is very small and by higher heating rates effect of peritectic transformation merged with melting. Influence of heating rate for heating rates 1 - 5 °C/min is not detected for temperature of solidus (**Table 3**; T_{MAX}-T_{MIN}= 1 °C). By heating rates 10 and 20 °C/min with increasing heating rate increase temperature of solidus (**Table 3**; T_{MAX}-T_{MIN}= 4 °C). The biggest influence is clear for temperature of liquidus (**Table 3**; T_{MAX}-T_{MIN}= 8 °C, CV= 0.21 %).

Table 2 Influence of heating rate to temperatures of phase transformations of Fe-C-Cr alloy

Heating rate (°C/min)	T_S (°C)	T_P (°C)	T_L (°C)
1	1439	1494	1510
2	1439	1495	1510
5	1436	1496	1512
10	1441	1499	1513
20	1438	1501	1516
0	**1439**	**1493**	**1510**
Statistic			
Average	1439	1497	1512
T_{MIN}	1436	1494	1510
T_{MAX}	1441	1501	1516
ΔT_{MAX}-T_{MIN}	5	7	6
St. deviation	1.62	2.61	2.23
CV (%)	0.11	0.17	0.15

Table 3 Influence of heating rate to temperatures of phase transformations of Fe-C-Ni alloy

Heating rate (°C/min)	T_S (°C)	T_P (°C)	T_L (°C)
1	1441	1502	1506
2	1440	1503	1506
5	1441	1505	1508
10	1443	-	1511
20	1447	-	1514
0	**1440**	**1501**	**1505**
Statistic			
Average	1442	1503	1509
T_{MIN}	1440	1502	1506
T_{MAX}	1447	1505	1514
ΔT_{MAX}-T_{MIN}	7	3	8
St. deviation	2.50	1.25	3.10
CV (%)	0.17	0.08	0.21

Based on DTA results, a regression dependence of the heating rate influence for all temperatures of phase transformations was developed (**Figure 1** and **Figure 2**). In the charts, the reliability value R2 is shown for completeness. The obtained values of T_S, T_P and T_L were extrapolated to the “zero” heating rate, and these values are also given in **Table 2** and **Table 3**. Based on the obtained dependences, it is possible to correct the data (T_S, T_P, 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.

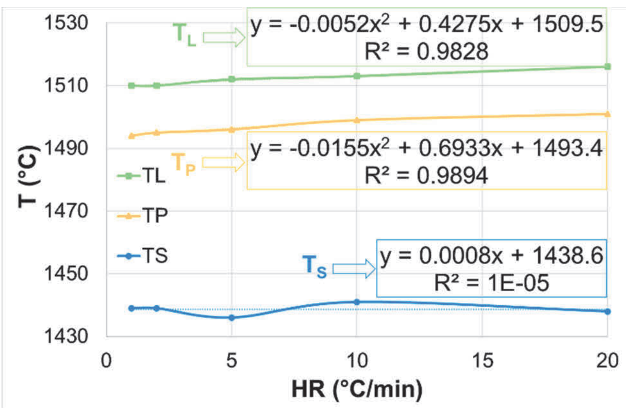

Figure 1 Regression dependence of heating rate for Fe-C-Cr alloy

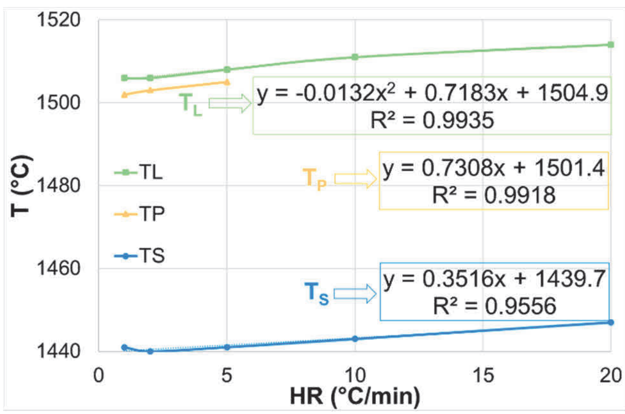

Figure 2 Regression dependence of heating rate for Fe-C-Ni alloy

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 the kinetics of phase transformations (transition mechanism) [8,9].

3.2. Influence of the mass of the sample on shifting of temperatures of phase transformations

From **Table 4** and **Table 5** can be seen the influence of the mass of the sample on shifting all temperatures measured by DTA method. The smallest influence of the mass is detected for temperature of solidus for both alloys (T_{MAX}-T_{MIN}= 4 - 5 °C, CV= 0.09 - 0.13 %). The temperature of the peritectic transformation was not detected for mass 50 - 190 mg. The influence of the mass for the temperature of peritectic transformation of Fe-C-Cr alloy and liquidus temperature of both alloy is very close (T_{MAX}-T_{MIN}= 7 - 8 °C, CV = 0.17 - 0.19 %).

Table 4 Influence of the mass to temperatures of phase transformations of Fe-C-Cr alloy

Mass	T_S	T_P	T_L
(mg)		**(°C)**	
50	1440	1495	1509
100	1440	1497	1511
190	1441	1499	1513
280	1439	1501	1515
370	1443	1502	1517
0	**1441**	**1493**	**1508**
	Statistic		
Average	1441	1499	1513
T_{MIN}	1439	1495	1509
T_{MAX}	1443	1502	1517
ΔT_{MAX}-T_{MIN}	4	7	8
St. deviation	1.36	2.56	2.83
CV (%)	0.09	0.17	0.19

Table 5 Influence of the mass to temperatures of phase transformations of Fe-C-Ni alloy

Mass	T_S	T_P	T_L
(mg)		**(°C)**	
50	1440	-	1506
100	1440	-	1509
190	1443	-	1511
280	1443	1511	1513
370	1445	1511	1514
0	**1439**	**-**	**1504**
	Statistic		
Average	1442	1511	1511
T_{MIN}	1440	1511	1506
T_{MAX}	1445	1511	1514
ΔT_{MAX}-T_{MIN}	5	0	8
St. deviation	1.94	0.00	2.87
CV (%)	0.13	0.00	0.19

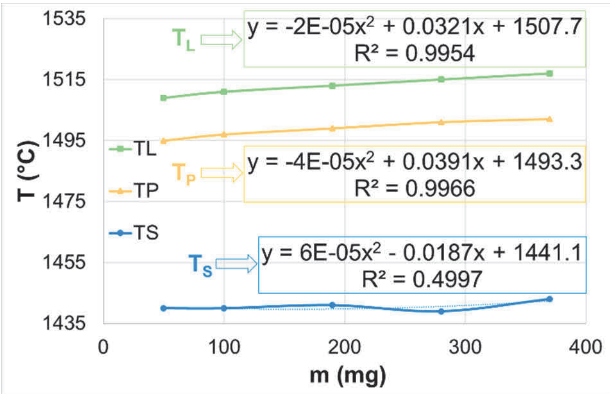

Figure 3 Regression dependence of the mass for Fe-C-Cr alloy

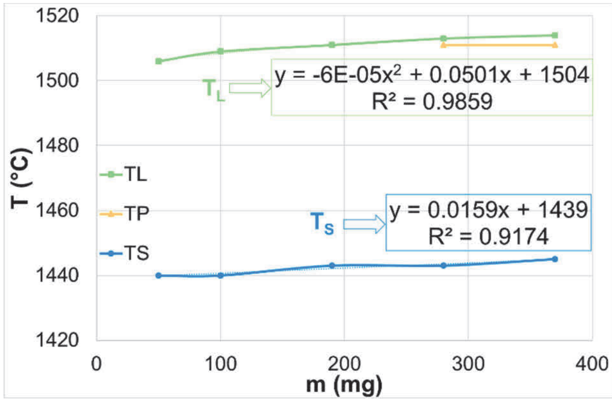

Figure 4 Regression dependence of the mass for Fe-C-Ni alloy

Based on DTA results, a regression dependence of the mass of the sample influence for all temperatures of phase transformations was developer except for the temperature of peritectic transformation for Fe-C-Ni alloy (**Figure 3** and **Figure 4**). In the charts, the reliability value R2 is shown for completeness. The obtained values of T_S, T_P and T_L were extrapolated to the "zero" mass of the sample, and these values are also given in **Table 4** and **Table 5**. On the basis of the obtained dependences, it is possible to correct the data (T_S, T_P, T_L) obtained for other investigated Fe-based metallic systems, such as steels, to the "zero" mass of the sample

The shift to higher temperatures with the increasing mass can be explained by the fact that the larger sample requires more heat for the phase transformation, and that the phase transformation takes place over a longer period of time (i.e. that phase transformation of the larger sample will be terminated only at higher temperature) [9].

Table 6 Comparison of experimental and theoretical temperatures of phase transformations

System	T_S	T_P	T_L
		(°C)	
Fe-Fe_3C (0.34 wt. % C)	1462	1495	1511
Fe-C-Cr (0.34 wt. % C, 0.92 wt. % Cr)	1440	1493	1509
Fe-Fe_3C (0.38 wt. % C)	1457	1495	1508
Fe-C-Ni (0.38 wt. % C, 1.08 wt. % Ni)	1440	1501	1505

The obtained results corrected to the “zero” heating rate and “zero” mass were compared with temperatures of phase transformations of Fe-Fe_3C calculated by SW Thermo-Calc. From the results in **Table 6**, the effect is not detected the impact of chromium and nickel to the shift of solidus temperature. For the temperature of peritectic transformation nickel, which shifts this temperature to higher values, has greater influence. Nickel and chromium have approximately the same influence to shifting of the liquidus temperature to lower values.

4. CONCLUSIONS

The influence of the heating rate and mass of the sample on the temperatures of phase transformations in the high-temperature area was studied by DTA method.

No influence of the heating rate and mass was detected for the temperature of solidus for both alloys. Temperature range of “zero” values is 1439 - 1441 °C. It is clear that chromium and nickel do not influence to shifting of this temperature. “Zero” value of the temperature of peritectic transformation was for Fe-C-Cr alloy the same for the influence of the heating rate and mass of the sample (1493 °C). This temperature was detected for the heating rate of Fe-C-Ni alloy 1501 °C (for the mass was detected only two values; it is not representative). It is clear that chromium decreases T_P and nickel has the opposite effect. “Zero” values of temperature of liquidus for Fe-C-Cr alloy are in the range of 1508 - 1510 °C. Temperature interval for Fe-C-Ni alloy is 1504 - 1505 °C. It is clear that chromium and nickel shift liquidus temperature to lower values.

On the basis of the obtained dependences that express the influence of the mass of the sample and the heating rate, it is possible to correct the data obtained for other investigated Fe-based metallic systems, such as steel, to the "zero" mass and "zero" heating rate. We can thus obtain for the investigated systems the temperatures close to equilibrium temperatures, without time-consuming experimental measurements.

It is necessary to know the influence of experimental conditions for each experimental device for the measurement of temperatures of phase transformations and minimise.

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