TEMPERATURES OF LIQUIDUS, SOLIDUS AND PERITECTIC TRANSFORMATION OF Fe-C-Cr BASED ALLOYS

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Abstract

Three alloys based on Fe-C-Cr were studied. These alloys contained carbon in a range of 0.31 - 0.38 wt.% and chrome 1.06 - 4.99 wt.%. Temperatures of solidus (T_S), liquidus (T_L) and peritectic transformation (T_P) were studied in high temperature region. These temperatures were obtained using two thermal analysis methods: "Direct" Thermal Analysis (TA) and Differential Thermal Analysis (DTA). The Setaram Setsys 18TM was used for experiments with use of DTA method. Measurements were done in inert atmosphere of pure argon by heating rate of 10 °C.min^{-1}. The Netzsch STA 449 F3 Jupiter was used for experiments with use of "direct" TA method. Measurements were done in inert atmosphere of pure argon by heating and cooling rate of 5 °C.min^{-1}. Phase transformation temperatures were obtained by heating and cooling process. Experimental data were compared and discussed with calculation results using IDS (Solidification analysis package) and SW Thermo-Calc with use of the TCFE8 (Thermo-Calc Fe-based alloys) database. Temperatures of solidus (T_S), liquidus (T_L) and peritectic transformation (T_P) were obtained. Difference between experimental and theoretical values temperatures of liquidus was relatively low. With increasing content of carbon and chrome grew the difference between theoretical and experimental values by temperature of solidus and peritectic transformation.

Keywords: DTA, “direct” TA, temperature of phase transformation, Thermo-Calc, Fe-C-Cr alloys

1. INTRODUCTION

One of the most important binary systems of engineering practice is Fe-C system (the bases of many steels) [1, 2]. At present days empirical relationships [3] and thermodynamic calculations [4] are most often used for obtaining of thermophysical and thermodynamic properties of steels (phase transition temperatures, heat effects of phase transformations, heat capacity and others). Experimental measurements are used much less. The confrontation of theoretical and experimental data show that there are differences between them, often significant [5].

In high temperature region (for alloys based on Fe-C) temperatures of solidus, liquidus and peritectic transformation are the most important. These temperatures are important for example for adjusting of casting conditions and for simulations of real technological production processes of steels [6]. In low temperature area many authors deal with study of temperatures of the eutectoid transformation, temperature of the end of the ferrite to austenite transformation and temperature of the start of the pearlite formation [5].

To obtain thermophysical and thermodynamic properties, thermal analysis methods are often used [7]. This paper presents results obtained by two thermal analysis methods: "Direct" Thermal Analysis (TA) and Differential Thermal Analysis (DTA). "Direct" thermal analysis (TA) is based on direct measurement of temperature of the sample. Temperature is carried out in dependence on time during the sample is heating or cooling in controlled atmosphere [8]. By Differential Thermal Analysis (DTA) temperature effects during continuous linear heating or cooling in controlled atmosphere are studied. The temperature of the analysed sample is measured relative to the temperature of reference sample [7].

Temperatures of solidus (T_S), liquidus (T_L) and peritectic transformation were experimentally obtained. These were discussed and compared with results calculated using SW Thermo-Calc (ver. 2015b) and database TCFE8 and with results obtained using kinetic SW IDS.

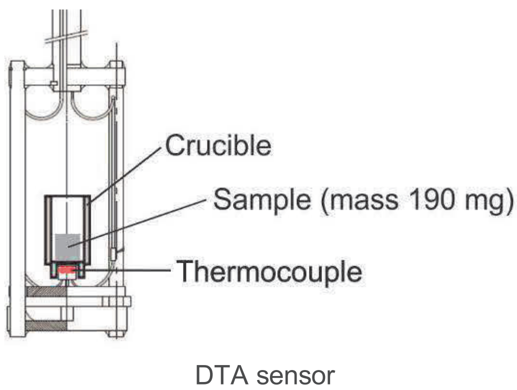
2. EXPERIMENT

Three alloys based on Fe-C-Cr were studied. Carbon and chrome content of these alloys shows **Table 1**. Temperature calibration was performed using Ni (4N5) or Pd (5N). Corrections were performed with respect to influence of heating rate and sample mass.

Table 1 Carbon and chrome content of studied alloys, (wt. %)

Alloy	C	Cr
A	0.308	1.058
B	0.320	1.540
C	0.380	4.990

For obtaining the values of temperatures of phase transformations by use of "Direct" Thermal Analysis (TA) **Netzsch STA 449 F3 Jupiter** (TA, S - type, thermocouple, see **Figure 1** and compare with DTA sensor) was used. The measurements were carried out in alumina crucibles in inert atmosphere of argon (6N), sample weight was cca 23 g and the heating and cooling rate was 5 °C.min^{-1}. Each type of alloy was observed by two measurements at the same conditions at controlled cycling experiments - two heating runs and two cooling runs.



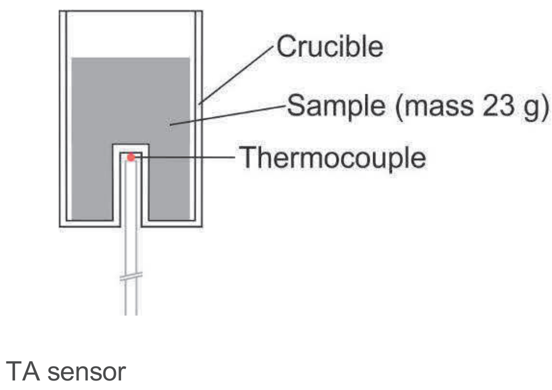


Figure 1 Arrangement of DTA and TA sensor

For obtaining the phase transformations temperatures Differential Thermal Analysis (DTA) **Setaram Setsys 18$_{TM}$** (with DTA sensor, S-type, tri-couple, **Figure 1**) was used. The measurements were carried out in alumina crucibles in inert atmosphere of argon (6N), sample weight was cca 190 mg and the heating rate was 10 °C.min^{-1}. Each type of alloy was analysed by three measurements at the same conditions at heating process. DTA sensor has one thermocouple with three thermocouple “ends” in series and TA sensor has one thermocouple, see arrangement at **Figure 1**.

3. CALCULATIONS

Theoretical calculations were performed using kinetic SW IDS (InterDendritic Solidification) and thermodynamic SW Thermo-Calc, version 2015b and database TCFE8. IDS module simulates the solidification phenomena from liquid down to 1000 °C [9]. The calculation did not include elements Sn, B, As, Sb, Pb, Bi. The CALPHAD method is used for calculation by SW Thermo-Calc [10]. For calculation are not included elements Sn, As, Sb, Pb, Bi (this element is not defined in software database), also diamond and graphite phases are excluded.

4. RESULTS AND DISCUSSION

DTA curves, heating and cooling curves, were obtained from experimental measurements, **Figures 2 - 4**. Temperatures of phase transformations are marked on curves. Experimental phase transition temperatures and theoretical values are presented in **Table 2.**

Table 2 Experimental and theoretical temperatures of phase transformations of alloys, (°C)

Temperature	Experimental			Theoretical	
	DTA	TA (heating)	TA (cooling)	Thermo-Calc*	IDS**
Alloy A					
T_S	1447	1449	1451	1449	1446
T_P	1486	1484	1458	1486	1482
T_L	1498	1503	1499	1503	1502
Alloy B					
T_S	1445	1447	1437	1451	1438
T_P	1471	1473	1449	1458	1461
T_L	1498	1501	1495	1504	1500
Alloy C					
T_S	1397	1405	1410	1395	1386
T_P	1438	1441	1416	1449	1432
T_L	1474	1480	1476	1480	1475
*elements not included for calculation: Sn, As, Sb, Pb, Bi					
**elements not included for calculation: Sn, B, As, Sb, Pb, Bi					

4.1. Temperature of solidus, T_S

Temperature of solidus obtained by DTA for **alloy A** is 1447 °C, by TA (heating) 1449 °C and by TA (cooling) regime 1451 °C. Solidus temperature calculated using SW Thermo-Calc is 1449 °C and by SW IDS 1446 °C. Temperature interval of detected solidus temperature is 1447 - 1451 °C. Theoretical interval for solidus temperature is 1446 - 1451 °C. These intervals almost overlap.

Temperature of solidus obtained by DTA for **alloy B** is 1445 °C, by TA (heating) 1447 °C and by TA (cooling) regime 1437 °C. Solidus temperature calculated using SW Thermo-Calc is 1451 °C and by SW IDS 1438 °C. Temperature interval of detected solidus temperature is 1437 - 1447 °C. Theoretical interval for solidus temperature is 1438 - 1451 °C. These intervals overlap with small deviations.

Temperature of solidus obtained by DTA for **alloy C** is 1397 °C, by TA (heating) 1405 °C and by TA (cooling) regime 1410 °C. Solidus temperature calculated using SW Thermo-Calc is 1395 °C and by SW IDS 1386 °C.

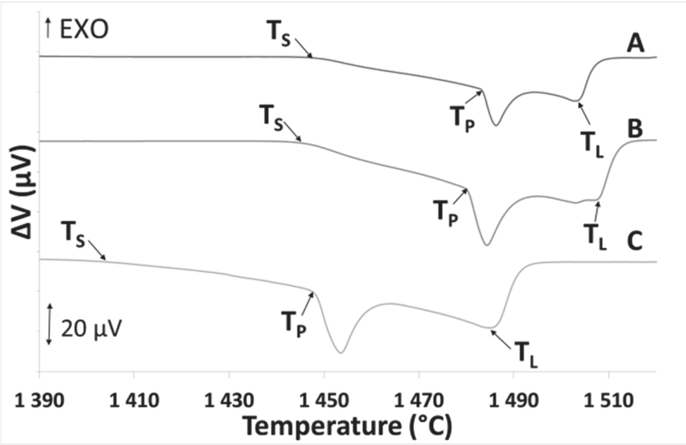


Figure 2 DTA curves of analyzed alloys, heating rate 10 °C/min, melting

Solidus temperature is 1397 - 1410 °C. Theoretical interval for solidus temperature is 1386 - 1395 °C. These intervals do not overlap. Experimental temperatures of solidus are higher than theoretical.

With increasing C (range 0.308 - 0.380 wt. %) and Cr (range 1.058 - 4.990 wt. %) temperature of solidus decreases, what is in agreement with the general knowledge. The highest is T_S for alloy A, lower for alloy B and the lowest is T_S for alloy C, experimental and theoretical temperature interval do not cover each other. It applies for all methods. Temperature intervals between detected and theoretical values have the best agreement for alloy A, lower for alloy B and the lowest for alloy C. Differences of temperature of solidus between thermal analysis methods could be (are) very often caused by problems with proper determination of start of melting process, especially by “direct” thermal analysis (TA). For temperature of solidus obtained by TA (cooling) unequivocal trend of temperature shift (T_S) in depending on the chemical composition was not observed. It could be caused due to different undercooling of analyzed samples. Similar problems connected with cooling can be encountered in case of T_P. Due to a different degree of cooling (without unequivocal trend) of alloys, when secondary phase nucleates (austenite). T_P temperatures obtained at cooling were not included for discussion (are not representative).

4.2. Temperature of peritectic transformation, T_P

The start of peritectic transformation temperature for **alloy A** is at 1486 °C (DTA), 1484 °C (TA, heating), calculated using SW Thermo-Calc is 1486 °C and by SW IDS 1482 °C. Temperature interval of detected temperature of peritectic transformation is 1484 - 1486 °C. Theoretical interval for temperature of peritectic transformation is 1482 - 1486 °C. These intervals overlap.

The start of peritectic transformation temperature for **alloy B** is at 1471 °C (DTA) and 1473 °C (TA, heating). Temperature calculated using SW Thermo-Calc is 1458 °C and by SW IDS 1461 °C. Temperature interval of detected temperature of peritectic transformation is 1471 - 1473 °C. Theoretical interval for temperature of peritectic transformation is 1458 - 1461 °C. These intervals do not overlap. Detected temperatures are higher than theoretical.

The start of peritectic transformation temperature for **alloy C** is at 1438 °C (DTA) and 1441 °C (TA, heating). Temperature calculated using SW Thermo-Calc is 1449 °C and by SW IDS 1432 °C. Temperature interval of detected temperature of peritectic transformation is 1438 - 1441 °C. Theoretical interval for temperature of peritectic transformation is 1432 - 1449 °C. These intervals partially overlap.

With increasing C (range 0.308 - 0.380 wt. %) and Cr (range 1.058 - 4.990 wt. %) temperature of peritectic transformation decreases. The highest is T_P for alloy A, lower for alloy B and the lowest is T_P for alloy C. It applies for all methods. Temperature intervals between detected and theoretical values have the best compliance for alloy A, lower for alloy C and by alloy B are not overlapped. Detected temperature of peritectic transformation obtained TA (cooling) is unrepresentative and is influenced by undercooling and secondary nucleation of austenite phase, therefore we do not include this value in results.

4.3. Temperature of liquidus, T_L

Temperature of liquidus for **alloy A** obtained by DTA is 1498 °C, TA (heating) 1503 °C and by TA (cooling) 1499 °C. Theoretical value obtained by SW Thermo-Calc is 1503 °C and by SW IDS 1502 °C. Temperature interval of detected temperature of liquidus is 1498 - 1503 °C. Theoretical interval for temperature of liquidus is 1502 – 1503 °C. These intervals overlap.

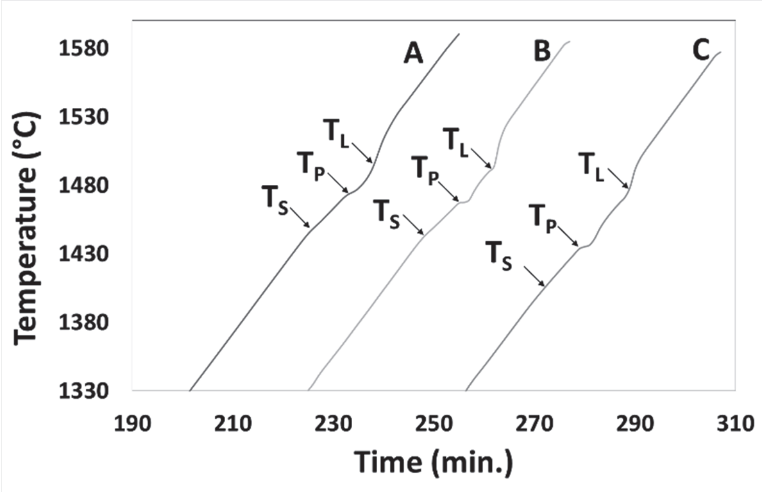


Figure 3 Heating curves of analyzed alloys, heating rate 5 °C.min^{-1}, melting

Temperature of liquidus for **alloy B** obtained by DTA is 1498 °C, TA (heating) 1501 °C and by TA (cooling) 1495 °C. Theoretical value obtained by SW Thermo-Calc is 1504 °C and by SW IDS 1500 °C. Temperature interval of detected temperature of liquidus is 1495 - 1501 °C. Theoretical interval for temperature of liquidus is 1501 – 1504 °C. These intervals partially overlap.

Temperature of liquidus for **alloy C** obtained by DTA is 1474 °C, TA (heating) 1480 °C and by TA (cooling) 1476 °C. Theoretical value obtained by SW Thermo-Calc is 1480 °C and by SW IDS 1475 °C. Temperature interval of detected temperature of liquidus is 1474 - 1480 °C. Theoretical interval for temperature of liquidus is 1475 - 1480 °C. These intervals overlap.

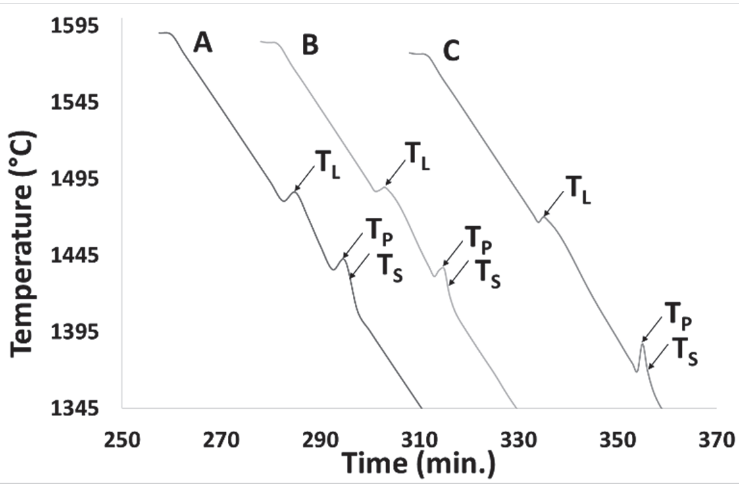


Figure 4 Cooling curves of analyzed alloys, cooling rate 5 °C.min^{-1}, solidification

With increasing C (range 0.308 - 0.380 wt. %) and Cr (range 1.058 - 4.990 wt. %) temperature of liquidus decreases. T_L for alloy A and alloy B is missing to each other. T_L for alloy C is lower than for alloy A and B. Temperature intervals between detected and theoretical values have the best agreement for alloy A and C and for alloy B partially overlap. Values of standard deviations were the smallest for DTA method (interval 0 - 2), middle for TA heating (interval 0 - 6) and the highest for TA cooling (interval 0 - 16). The highest difference for TA cooling was by temperature of peritectic transformation, therefore was this temperature excluded from the results. The differences between experimental results obtained by each method can be caused by different heating rate (DTA - 10 °C.min^{-1}, TA - 5 °C.min^{-1}), sample mass (alloy samples for TA analysis were 100 times larger than samples for DTA analysis), by cooling effect (undercooling) and by different arrangement of sensors (**Figure 1**).

The differences between experimental and theoretical values may be caused by software (calculation method, simplifying assumptions, elements not included in to the calculation and other) and databases that are used the software. The difference between theoretical and experimental temperatures can be caused in some cases by chemical, phase and structural heterogeneity.

5. CONCLUSION

Liquidus (T_L) and solidus (T_S) temperatures and temperature of start of peritectic transformation (T_P) were obtained experimentally and theoretically. They were discussed and compared. Experimentally obtained transition temperatures are close to calcucalted values. With increasing C (range 0.308 - 0.380 wt. %) and Cr (range 1.058 - 4.990 wt. %) temperature of solidus, liquidus and peritectic transformation decreases. The largest difference between experimental methods was observed for temperature of solidus for alloy C between DTA and TA (cooling), temperature range 1397 - 1410 °C. The smallest difference between experimental methods was in the case of temperature of peritectic transformation for alloy A (temperature range 1484 - 1486 °C) and alloy B (temperature range 1471 - 1473 °C). Difference between experimental and theoretical values of liquidus temperatures was relatively low. With increasing content of carbon and chrome grew the difference between theoretical and experimental values of solidus temperature and peritectic transformation. By experimental measurements more precisely temperatures of phase transformations in high temperature region were specifed. This fact, among others, could bring a benefit for real technological processes (e.g. casting and solidification) via optimization of processes using simulation SW (Procast, Magmasoft); larger homogeneity of products and reduction of defects could be reached.

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