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Recenzované vědecké články

Thermal Analysis of Alloys Based on Fe-C-Cr in High-Temperature Area

Termická analýza zliatin na báze Fe-C-Cr vo vysokoteplotnej oblasti

Ing. Ľubomíra Drozdová; **doc. Ing. Bedřich Smetana, Ph.D.**; **Ing. Simona Zlá, Ph.D.**; **Ing. Mario Machů**; **prof. Ing. Jana Dobrovská, CSc.**; **doc. Ing. Lenka Řeháčková, Ph.D.**; **prof. Ing. Karel Michalek, CSc.**; **doc. Ing. Karel Gryc, Ph.D.**

VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Regional Materials Science and Technology Centre, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic

Three alloys based on Fe-C-Cr were studied. These alloys contained carbon in a range of 0.28 – 0.38 wt.% and chromium 1.06 – 4.99 wt.%. Temperatures of solidus (T_S), liquidus (T_L) and peritectic transformation (T_P) were studied in the high-temperature region. These temperatures were obtained using two thermal analysis methods: Differential Thermal Analysis (DTA) and direct Thermal Analysis (TA). The Setaram Setsys 18_{TM} was used for experiments with the use of DTA method. Measurements were done in an inert atmosphere of pure argon at a heating rate of 10 °C·min^{-1}. The instrument Netzsch STA 449 F3 Jupiter was used for experiments with the use of direct TA method. Measurements were done in an inert atmosphere of pure argon by a heating and cooling rate of 5 °C·min^{-1}. Phase transformation temperatures were obtained by heating and cooling process and they were also approximated to "equilibrium conditions". The experimental data were compared and discussed with the calculation results using IDS (solidification analysis package), SW Thermo-Calc with the use of the TCFE8 (Thermo-Calc Fe-based alloys) database. Two alloys were compared with the published data on similar steels.

***Key words**: Fe-C-Cr alloys; DTA; "direct" TA; temperatures of phase transformations; Thermo-Calc; IDS*

Študované boli tri zliatiny na báze Fe-C-Cr. Tieto zliatiny obsahovali uhlík v rozmedzí 0,28 – 0,38 hm. % a chróm 1,06 – 4,99 hm. %. Vo vysokoteplotnej oblasti bola sledovaná teplota solidu (T_S), likvidu (T_L) a peritektickej transformácie (T_P). Tieto teploty boli získané pomocou dvoch metód termickej analýzy: diferenčnej termickej analýzy (DTA) a priamej termickej analýzy (TA). Zariadenie Setaram Setsys 18_{TM} bol použitý pre experimenty s DTA metódou. Merania boli prevádzané v inertnej atmosfére čistého argónu s rýchlosťou ohrevu 10 °C·min^{-1}. Zariadenie Netzsch STA 449 F3 Jupiter bol použitý pre experimenty s použitím priamej TA metódy. Merania boli prevádzané v inertnej atmosfére čistého argónu s rýchlosťou ohrevu a ochladzovania 5 °C·min^{-1}. Teploty fázových transformácií boli získané pri ohreve a ochladzovaní. Hodnoty získané pri ohreve boli aproximované k rovnovážnym podmienkam. Experimentálne dáta boli porovnávané a diskutované s výsledkami vypočítanými SW IDS (solidification analysis package), SW Thermo-Calc s použitím databázy TCFE8 (Thermo-Calc, zliatiny na báze Fe). Dve zliatiny boli porovnávané s publikovanými podobnými oceľami. S rastúcim obsahom uhlíka (v rozmedzí od 0,308 do 0,380 hm. %) a chrómu (rozmedzie 1,058 až 4,990 hm. %) sa teplota solidu, likvidu a peritektickej transformácie znižuje. Najväčší rozdiel medzi výsledkami experimentálnych metód bol pozorovaný pre teplotu solidu pre zliatinu s najvyšším obsahom C, Si, Cr a Mo medzi DTA a TA (ochladzovanie), teplotný rozsah 1397 – 1410 °C. Najmenší rozdiel medzi výsledkami experimentálnych metód bol v prípade teploty peritektickej transformácie pre zliatinu s najnižším obsahom C, Cr a Ni (teplotný rozsah 1484 – 1486 °C) a zliatinu s obsahom legujúcich prvkov v rozmedzí medzi dvomi vyššie uvedenými zliatinami (teplotný rozsah 1471 – 1473 °C). Rozdiel medzi experimentálnymi a teoretickými hodnotami teploty likvidu bol relatívne nízky. S rastúcim obsahom uhlíka a chrómu vzrástol rozdiel medzi teoretickými a experimentálnymi hodnotami teploty solidu a peritektickej transformácie Obe vyššie menované zliatiny boli porovnávané s podobnými oceľami publikovanými inými autormi. Publikované výsledky sú nižšie ako experimentálne získané. Výsledky ukazujú, že kvôli svojej jednoduchosti sú výpočty efektívnym nástrojom na získanie požadovaných údajov, ale môžu sa považovať iba za orientačné. Vypočítané výsledky by mali byť vždy overované experimentálnymi meraniami. Pri experimentálnych meraniach boli presnejšie špecifikované teploty fázových transformácií vo vysokoteplotnej oblasti. Tento postup je okrem iného prínosný pre reálne technologické procesy (napr. odlievanie a tuhnutie) prostredníctvom optimalizácie procesov pomocou simulačného SW (Procast, Magmasoft); mohla by sa dosiahnuť väčšia homogenita výrobkov a zníženie tolerancií medzi výslednými hodnotami vypočítanými a experimentálne zistenými.

***Kľúčové slová**: zliatiny Fe-C-Cr; DTA; „priama" TA; teploty fázových transformácií; Thermo-Calc; IDS*

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

The Fig. 1, shows section of metastable diagram of Fe-Fe_3C (full line) and Fe-Cr-C (dashed line), content of chromium is 5 wt. %. In the high-temperature region, several important phase transformations take place. During cooling, at the first solidification of melt, it takes place according to the curve AB (a curve of liquidus). During solidification, δ ferrite is formed in the limited region. The whole system is in a solid state on the curve AHB (a curve of solidus). A peritectic reaction can be expressed schematically by the following equation: LIQUID + δ ⇒ γ. Liquid and δ ferrite transform to solid austenite in point J (peritectic point) by an isothermal reversible reaction which applies for the area under the HJB curve [6].

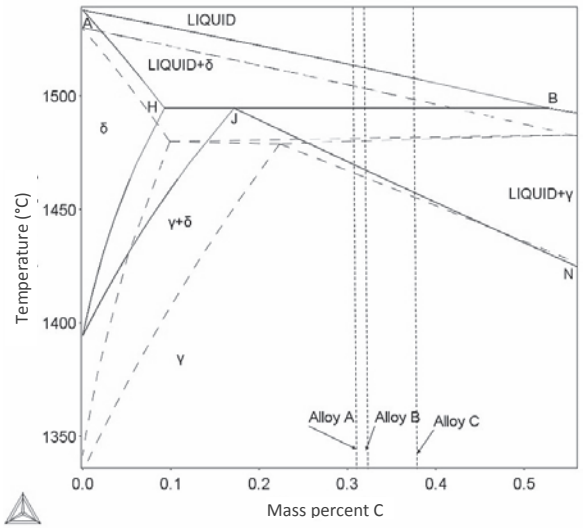

Fig. 1 Fe-C (full line) and Fe-Cr-C (dashed line) metastable equilibrium diagram

Obr. 1 Metastabilný rovnovážny diagram Fe-C (plná čiara) a Fe-C-Cr (přerušovaná čiara)

In the high-temperature region (for alloys based on Fe-C), there are the most important temperatures of the solidus, liquidus, and peritectic transformation. These temperatures are important, for example, for adjustment of casting conditions and for simulations of real technological production processes of steels [7, 8]. In the low-temperature area, many authors deal with studies 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 [9] are often used. This paper presents results obtained by two thermal analysis methods: Differential Thermal Analysis (DTA) and "direct" Thermal Analysis (TA). By Differential Thermal Analysis (DTA) temperature effects during continuous linear heating or cooling in the controlled atmosphere are studied. The temperature of the analyzed sample is measured in respect to the temperature of the reference sample [9]. The direct thermal analysis (TA) is based on direct measurement of the temperature of the sample. Influence of temperature is studied in the dependence on time during the heating or cooling of the sample in the controlled atmosphere [10].

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

1. Theoretical calculation

Temperatures of phase transformation can be calculated by thermodynamic software, such as Thermo-Calc [4], MT DATA [11], Pandat [12], FACT Sage [13]. They differ in the user interface, graphical level and optimization [14]. In the simulation, this software usually use the CALPHAD method. The accuracy of the numerical simulation depends on the accuracy of thermodynamic databases, thermophysical and thermodynamic properties depending on temperature [15].

Theoretical calculations were performed using thermodynamic SW Thermo-Calc, version 2015b and database TCFE8 for alloys of steels and cast irons and kinetic SW IDS (InterDendritic Solidification). The CALPHAD method is used for calculation by SW Thermo-Calc [16]. Elements Sn, As, Sb, Pb, Bi (this element is not defined in software database) are not included in the calculation; diamond and graphite phases are also excluded. The IDS module simulates the solidification phenomena from liquid down to 1000 °C [17]. The calculation did not include elements Sn, B, As, Sb, Pb, Bi.

1.1 Thermo-Calc

The software uses the CALPHAD method (thermodynamic properties are described through with the use of the Gibbs free energy) and it is used for calculations of stable and meta-stable heterogeneous phase equilibria, amounts of phases and their compositions, thermochemical data, such as enthalpies, heat capacity and activities, transformation temperatures, such as liquidus and solidus, driving force for phase transformations, phase diagrams (binary, ternary and multi-component) and more [4].

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1.2 IDS

SW IDS (InterDendritic Solidification) is a thermo-dynamic-kinetic-empirical tool for simulation of the solidification including phase transformations from the melt down to the room temperature of low-alloyed steels and stainless steels containing chromium up to 26 wt.%. Temperatures of phase transformations are dependent on a steel composition, a cooling rate, and a dendrite arm diameter. The calculations are made in one volume element set on the side of a dendrite arm. The SW is used for calculation of important thermophysical material properties (enthalpy, thermal conductivity, density, etc.) [17].

Theoretical calculations present a quick and relatively inexpensive form of obtaining results, but they can often be inaccurate or totally misleading. For this reason, it is necessary to verify, supplement and refine them with original experimental results for a particular studied alloy.

2. Experimental

In the experimental part, the samples and experimental conditions are characterized. The experimental and theoretical results and their discussions are given below.

2.1 Samples characterization

Three alloys based on Fe-C-Cr were studied. These alloys contained carbon in a range of 0.308 – 0.380 wt. % and chromium 1.058 – 4.990 wt.%. Alloys are marked in the Fe-Fe_3C system at Fig. 1. The content of these alloys is presented in Tab. 1. Samples for analysis were mechanically cut from the heavy steel forging ingot.

Tab. 1 Content of studied alloys (wt.%)
Tab. 1 Zloženie skúmaných zliatin (hm. %)

Alloy	C	Cr	Mn	Si	P	Mo	Ni
A	0.308	1.058	0.750	0.265	0.016	0.243	0.040
B	0.320	1.540	0.460	0.270	0.008	0.190	0.890
C	0.380	4.990	0.380	0.940	0.008	1.160	0.260

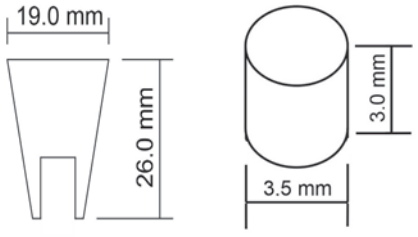

Fig. 2 Characterization of analysed samples; left- for DTA method; right – for TA method
Obr. 2 Charakteristika analyzovaných vzoriek; vľavo – pre DTA metódu; vpravo – pre TA metódu

The samples for DTA analysis were processed into the form of cylinders with a diameter of 3.5 mm and a height of approx. 3 mm (Fig. 2 left). The mass of the cylinders was 190 ± 5 mg. The samples for TA analysis were processed into the form of a cone with a conical shape; their dimensions are presented in Fig. 2 on the right**.** The samples were polished (in order to remove a possible oxidation layer) and cleaned by ultrasonic impact in acetone before analysis.

Temperature calibration was performed using Ni (4N5) or Pd (5N). Corrections were performed with respect to the influence of the heating rate and the sample mass.

2.2 Experimental conditions

For obtaining the phase transformations temperatures with help of Differential Thermal Analysis (DTA) using the instrument **Setaram Setsys 18$_{TM}$** (with DTA sensor, S-type, tri-couple, Fig. 3), the measurements were carried out in alumina crucibles with a volume of 100 µl. An empty corundum crucible served as a reference sample. Dynamic atmosphere of argon was maintained in the furnace during analysis in order to protect the sample against oxidation. The purity of argon was higher than 99.9999 %. The heating rate was 10 °C·min^{-1}. Each type of alloy was analyzed by three measurements at the same conditions at the heating process. DTA sensor have one thermocouple with three thermocouple "ends" in series and TA sensor has one thermocouple, see the arrangement in Fig. 4.

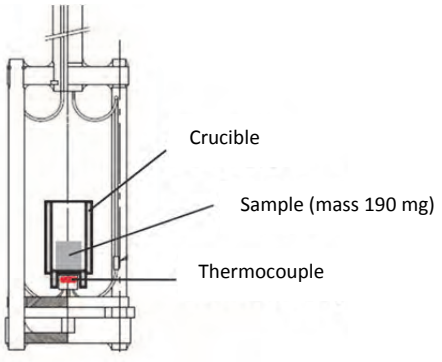

Fig. 3 Arrangement of DTA sensor
Obr. 3 Usporiadanie DTA senzoru

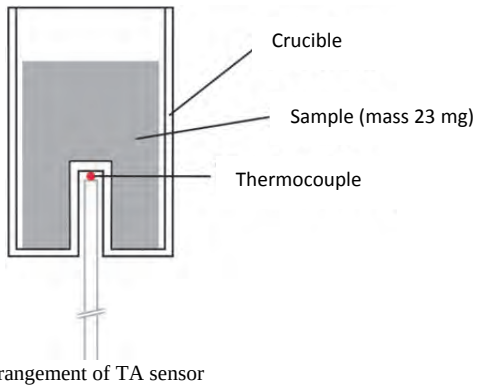

Fig. 4 Arrangement of TA sensor
Obr. 4 Usporiadanie TA senzoru

For obtaining the values of temperatures of phase transformations by use of "Direct" Thermal Analysis (TA) the instrument **Netzsch STA 449 F3 Jupiter** (TA, S - type, thermocouple, Fig. 4) was used. The

measurements were carried out in alumina crucibles with the volume of 14 ml. Dynamic atmosphere of argon was maintained in the furnace during analysis in order to protect the sample against oxidation. The purity of argon was higher than 99.9999 %. The heating and cooling rate was 5 °C min^{-1}. Each type of alloy was observed by two measurements under the same conditions at the controlled cycling experiments – two heating runs and two cooling runs.

Temperatures of phase transformations were obtained on the basis of DTA curves (Fig. 5), and evaluation of the heating (Fig. 6) and cooling (Fig. 7) curves. Fig. 5 shows the DTA curves obtained for the analyzed alloys at the heating rate of 10 °C·min^{-1}. On the DTA curve, two thermal effects (peaks) are observed in each alloy.

3. Results and discussion

The peaks correspond to melting. The temperature of solidus (T_S) corresponds to the start of the first peak. The temperature of liquidus (T_L) corresponds to the end of two peaks. Between temperatures of solidus and liquidus, there is visible peritectic transformation, which is represented by a temperature of peritectic transformation (T_p). Temperatures T_S, T_P and T_L were also obtained on the basis of heating and cooling curves (Fig. 6, 7) by TA method at the heating and cooling rate of 5 °C·min^{-1}. Experimental phase transition temperatures and theoretical values are presented in Tab 2**.**

Tab. 2 Experimental and theoretical temperatures of phase transformations of alloys, °C

Tab. 2 Experimentálne a teoretické teploty fázových transformácií, °C

Temperature	Experimental			Theoretical	
	DTA	TA[1]	TA[2]	Thermo-Calc[3]	IDS[4]
Alloy A					
T_S	1447	1449	1451	1442	1446
T_P	1486	1484	1458	1486	1482
T_L	1498	1503	1499	1503	1502
Alloy B					
T_S	1445	1447	1437	1452	1438
T_P	1471	1473	1449	1487	1461
T_L	1498	1501	1495	1504	1500
Alloy C					
T_S	1397	1405	1410	1396	1386
T_P	1438	1441	1416	1449	1432
T_L	1474	1480	1476	1480	1475
[1]heating					
[2]cooling					
[3]elements not included for calculation: Sn, As, Sb, Pb, Bi					
[4]elements not included for calculation: Sn, B, As, Sb, Pb, Bi					

In the T_A cooling curve, the undercooling effect is evident. The equivocal trend of undercooling (also under the identical experimental conditions), in the case of nucleation of the secondary phase (austenite), was observed from T_A curves obtained at the cooling process. For that reason T_P temperatures obtained at cooling were not included for discussion (they are not representative).

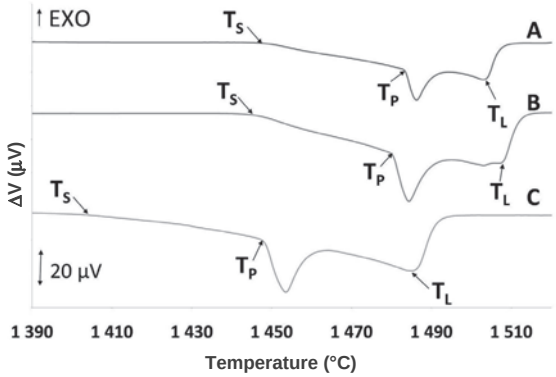

Fig. 5 DTA curves of analyzed alloys, heating rate 10 °C·min^{-1}, melting

Obr. 5 DTA krivky skúmaných zliatin, rýchlosť ohrevu 10 °C·min^{-1}, taveni

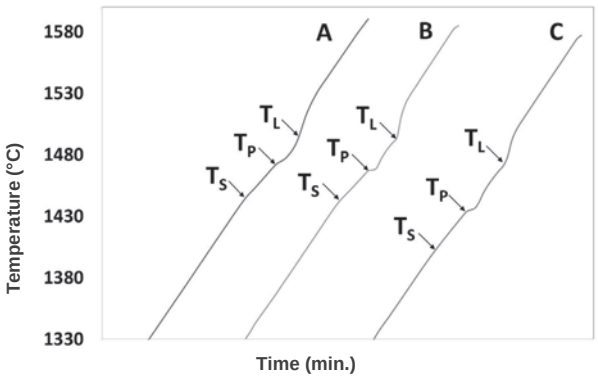

Fig. 6 Heating curves of analyzed alloys, heating rate 5 °C·min^{-1}, melting

Obr. 6 Krivky ohrevu skúmaných zliatin, rýchlosť ohrevu 5 °C·min^{-1}

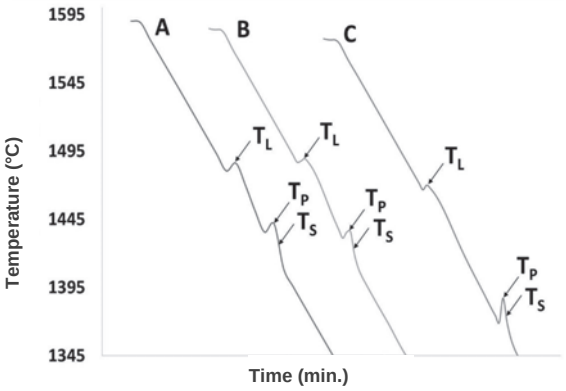

Fig. 7 Cooling curves of analyzed alloys, cooling rate 5°C·min^{-1}, melting

Obr. 7 Krivky ochladzovania skúmaných zliatin, rýchlosť ochladzovania 5 °C·min^{-1}, tuhnutie

3.1 Alloy A

The temperature of solidus obtained by DTA for the alloy A is 1447 °C, by TA (heating) it is 1449 °C and by

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TA (cooling) regime it is 1451 °C. Solidus temperature calculated using SW Thermo-Calc is 1449 °C and using SW IDS it is 1446 °C. The temperature interval of detected solidus temperature is 1447 – 1451 °C. The theoretical interval for solidus temperature is 1446 – 1451 °C. These intervals almost overlap. In the case of the temperature T_S a good agreement between the temperatures determined by both methods was achieved. The maximal temperature difference is 4 °C.

The start of peritectic transformation temperature for the alloy A is at 1486 °C (DTA), 1484 °C (TA, heating), when calculated using SW Thermo-Calc it is 1486 °C and using SW IDS it is 1482 °C. A temperature interval of the detected temperature of peritectic transformation is 1484 – 1486 °C. The theoretical interval for the temperature of peritectic transformation is 1482 – 1486 °C. These intervals overlap. In the case of the temperature T_P, a very good compliance between the temperatures determined by both methods was achieved. The temperature difference is 2 °C.

The temperature of liquidus for the alloy A obtained by DTA is 1498 °C, by TA (heating) it is 1503 °C and by TA (cooling) it is 1499 °C. The theoretical value obtained by SW Thermo-Calc is 1503 °C and by SW IDS it is 1502 °C. The temperature interval of the detected temperature of liquidus is 1498 – 1503 °C. The theoretical interval for the temperature of liquidus is 1502 – 1503 °C. These intervals overlap. In the case of the temperature T_L, a good compliance between the temperatures determined by both methods was achieved. The maximal temperature difference is 5 °C.

In the accessible literature, some values of phase transition temperatures were found. In the work [10], there was published the temperature of solidus and liquidus for similar steel with the carbon content of 0.29 wt.% and the chromium content of 1.02 wt.%. The analysis was performed by direct thermal analysis for a sample with the mass of approximately 35 g at the cooling process with the cooling rate of 2 °C s^{-1}. The temperature of solidus was 1415 °C, and the temperature of liquidus was 1486 °C. The smallest difference between the experimentally obtained data and the published values of T_L is for the DTA method. The difference is 12 °C. The largest difference between the experimental and published values of T_S is for the TA cooling. The difference is 36 °C. The temperatures stated by the authors in [9] are lower than the experimentally determined temperatures.

3.2 Alloy B

The temperature of solidus obtained by DTA for the alloy B is 1445 °C, by TA (heating) it is 1447 °C and by TA (cooling) regime it is 1437 °C. The solidus temperature calculated using SW Thermo-Calc is 1451 °C and using SW IDS it is 1438 °C. The temperature interval of detected solidus temperature is 1437 – 1447 °C. The theoretical interval for the solidus temperature is 1438 – 1451 °C. These intervals are overlapped with small deviations. In the case of the temperature T_S, a lower compliance between the temperatures determined by both methods was achieved. The maximal temperature difference is 10 °C.

The start of peritectic transformation temperature for the alloy B is at 1471 °C (DTA) and at 1473 °C (TA, heating). Temperature calculated using SW Thermo-Calc is 1458 °C and using SW IDS it is 1461 °C. The temperature interval of the detected temperature of peritectic transformation is 1471 – 1473 °C. The theoretical interval for the temperature of peritectic transformation is 1458 – 1461 °C. These intervals do not overlap. The detected temperatures are higher than theoretical ones. In the case of the temperature T_P, a very good compliance between the temperatures determined by both methods was achieved. The temperature difference is 2 °C.

The temperature of liquidus for the alloy B obtained by DTA is 1498 °C, by TA (heating) it is 1501 °C and by TA (cooling) it is 1495 °C. The theoretical value obtained by SW Thermo-Calc is 1504 °C and by SW IDS it is 1500 °C. The temperature interval of the detected temperature of liquidus is 1495 – 1501 °C. The theoretical interval for the temperature of liquidus is 1501 – 1504 °C. These intervals do partially overlap. In the case of the temperature T_L, a good compliance between the temperatures determined by both methods was achieved. The maximal temperature difference is 6 °C. For the alloy B, similar steel with phase transformation values was not found in the available literature.

3.3 Alloy C

The temperature of solidus obtained by DTA for the alloy C is 1397 °C, by TA (heating) it is 1405 °C and by TA (cooling) regime it is 1410 °C. The solidus temperature calculated using SW Thermo-Calc is 1395 °C and using SW IDS it is 1386 °C. The temperature interval of the detected solidus temperature is 1397 – 1410 °C. The theoretical interval for the solidus temperature is 1386 – 1395 °C. These intervals are do not overlap. The experimental temperatures of solidus are higher than theoretical ones. In the case of the temperature T_S, a lower compliance between the temperatures determined by both methods was achieved. The maximal temperature difference is 13 °C.

The start of peritectic transformation temperature for the alloy C is at 1438 °C (DTA) and 1441 °C (TA, heating). Temperature calculated using SW Thermo-Calc is 1449 °C and using SW IDS it is 1432 °C. A temperature interval of the detected temperature of peritectic transformation is 1438 – 1441 °C. The theoretical interval for the temperature of peritectic transformation is 1432 – 1449 °C. These intervals do partially overlap. In the case of the temperature T_P, a very good compliance between the temperatures determined by both methods was achieved. The temperature difference is 3 °C.

The temperature of liquidus for the alloy C obtained by DTA is 1474 °C, by TA (heating) it is 1480 °C and by TA (cooling) it is 1476 °C. The theoretical value obtained by SW Thermo-Calc is 1480 °C and by SW IDS it is 1475 °C. The temperature interval of the detected temperature of liquidus is 1474 – 1480 °C. The theoretical interval for the temperature of liquidus is 1475 – 1480 °C. These intervals do overlap. In the case of the temperature T_L, a good compliance between the temperatures determined by both methods was achieved. The maximal temperature difference is 6 °C.

In the work [10], the temperatures of the solidus, liquidus and peritectic transformation for similar steel with the carbon content of 0.35 wt.% and the chromium content of 5.20 wt.% were published. The analysis was performed by "direct" thermal analysis for a sample with the mass of approximately 35 g at the cooling process with the cooling rate of 2 °C·s^{-1}. The temperature of solidus was 1335 °C, the temperature of peritectic transformation was 1370 °C and the temperature of liquidus was 1471 °C. The smallest difference between the experimentally obtained data and the published values of T_L is for the DTA method. The difference is 12 °C. The largest difference between the experimental and the published values are for the temperatures T_S and T_P. The difference for T_S between the published values and TA cooling is 75 °C. The difference for T_P between the published values and TA heating is 71 °C. An excellent compliance was encountered for the experimental values of T_L obtained in this work with the earlier published values of T_L [10]. The difference between the published values and DTA is 3 °C. The temperatures stated by the authors in [10] are lower than the experimentally determined temperatures. Significant differences between the temperatures specified in [10] and those determined by the differential thermal analysis and the direct thermal analysis might have been caused by different melting conditions, different chemical composition (even small changes in chemical composition can significantly affect the results) or by the difficult reading of the critical temperatures from the diagram. These large differences illustrate how difficult it is to find the thermodynamical data for a specific chemical composition and required conditions.

With an increasing C (range 0.308 – 0.380 wt.%) and Cr (range 1.058 – 4.990 wt.%), the temperature of solidus decreases, which complies with the general knowledge. The T_S is the highest for the alloy A, it is lower for the alloy B and it is the lowest for the alloy C; the experimental and theoretical temperature intervals are not mutually covered. It applies for all methods. The temperature intervals between the detected and theoretical values have the best agreement for the alloy A, lower for the alloy B and the lowest for the alloy C. Differences of the solidus temperature between the thermal analysis methods could be (are) very often caused by the problems with proper determination of the start of the melting process, especially by direct thermal analysis (T_A). For the solidus temperature obtained by TA (cooling), no unequivocal trend of temperature shift (T_S) was observed in dependence on the chemical composition. It could have been caused by different undercooling of the analyzed samples. Similar problems connected with cooling can be encountered in the case of T_P. In the T_A cooling curve, the undercooling effect is evident. The equivocal trend of undercooling (also under the identical experimental conditions), in the case of nucleation of the secondary phase (austenite), was observed from T_A curves obtained at the cooling process. For that reason T_P temperatures obtained at cooling were not included for discussion (they are not representative).

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

Equally, the temperature range between temperatures of solidus and peritectic transformation at heating (DTA and TA[1]) and cooling (TA[2] method) is very different (difference between 26 – 41 °C for heating process, contrary to 6 – 12 °C for cooling process). The relatively large difference between temperatures obtained at heating and cooling process can be attributed mainly to the relatively high undercooling effect. The secondary phase (austenite) nucleates relatively low (at lower temperatures), the undercooling is needed for the start of the nucleation process. Rapid solidification (of remaining melt) follows the start of nucleation. Solidification is terminated (at T_S) very close to the start of nucleation (T_P). So, the temperatures of peritectic transformation and solidus temperatures are very close to each other and the temperature interval of solidification of secondary phase is narrow (kinetics of solidification plays the key role), see differences between T_S and T_P (Figs. 5 – 7 and Tab. 2). There are not taking place such events at heating process.

With an increasing C (range 0.308 – 0.380 wt.%) and Cr (range 1.058 – 4.990 wt.%), the liquidus temperature decreases (except for the value T_L for the alloys A and B obtained by the DTA method, which is invariable) T_L for the alloy C is lower than for the alloys A and B. The temperature intervals between the detected and theoretical values have the best compliance for the alloys A and C and for the alloy B they partially overlap. The values of standard deviations were the smallest for DTA method (interval 0 – 2), average for TA heating (interval 0 – 6) and the highest for T_A cooling (interval 0 – 16). The highest difference for T_A

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cooling was by the temperature of peritectic transformation, therefore, this temperature was excluded from the results. The differences between the experimental results obtained by each method might have been caused by a different heating rate (DTA – 10 °C·min^{-1}, TA – 5 °C·min^{-1}), by a sample mass (alloy samples for TA analysis were 100 times larger than samples for DTA analysis. **The larger sample requires more heat for the phase transformation, and the phase transformation continues for a longer period of time, i.e. the phase transformation of the larger sample will be terminated at higher temperature),** by cooling effect (undercooling) and by a different arrangement of sensors (Fig. 3, 4).

Differences between the experimental and theoretical values might have been caused by software (calculation method, simplifying assumptions, elements not included into the calculation, and so on) and the databases that were used by the software. The difference between the theoretical and experimental temperatures could have been caused in some cases by chemical, phase, and structural heterogeneity.

Conclusions

The liquidus (T_L) and solidus (T_S) temperatures and temperature of the start of peritectic transformation (T_P) were obtained experimentally by DTA and TA methods. They were discussed and compared with theoretical calculations by SWs Thermo-Calc and IDS. The experimentally obtained transition temperatures are closer to the calculated values.

With an increasing C (range 0.308 – 0.380 wt.%) and Cr (range 1.058 – 4.990 wt.%), the temperature of solidus, liquidus and peritectic transformation decreases. The largest difference between the experimental methods was observed for the solidus temperature for the alloy C between DTA and TA (cooling), temperature range of 1397 – 1410 °C. The smallest difference between the experimental methods was in the case of the temperature of peritectic transformation for the alloy A (temperature range 1484 – 1486 °C) and alloy B (temperature range 1471 – 1473 °C). A difference between the experimental and theoretical values of the liquidus temperatures was relatively low. With an increase of the carbon and chromium content, the difference between the theoretical and experimental values of the solidus temperature and peritectic transformation increased.

The alloys A and C were compared with similar steels published in [10]. The published results are lower than the experimentally investigated data.

The results demonstrate that due to their simplicity, the calculations are an effective tool for obtaining the required data, but they can be considered as indicative only. The calculated results should always be verified by the experimental determination.

The temperatures of phase transformations in the high-temperature region were specified more precisely by experimental measurements. 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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