

APPLICATION OF HIGH TEMPERATURE DTA TO MICRO-ALLOYED STEELS

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Paper deals with investigation of phase transitions temperatures for selected real grades of micro-alloyed steels. Temperatures of characteristic phase transitions were obtained using Setaram SETSYS 18_{TM}. The DTA technique was selected for the study of micro-alloyed steels. Temperatures of phase transitions (liquidus, solidus etc.) were obtained. Influence of admixed and alloyed elements on shift of temperatures was investigated. Resulting data were compared with temperatures of phase transitions of Fe-C, Fe-Mn systems and with temperatures calculated according to relations published in available literature. Thermodynamic-kinetic solidification model IDS was used to calculate characteristic equilibrium temperatures of investigated systems.

Key words: steel, DTA, temperatures, phase transitions

Primjena visokotemperaturne DTA za mikrolegirane čelike. Članak se bavi studijom faznih transformacija odabranih mikrolegiranih čelika. Temperaturne karakteristike faznih transformacija su istraživane rabljenjem laboratorijskog sustava Setaram SETSYS-18_{TM}. DTA tehnika je odabrana za studij mikrolegiranih čelika. Temperature faznih transformacija (likvidus, solidus itd.) su dobivene. Istraživan je utjecaj primjesa i legirajućih elemenata na promjene temperatura faznih transformacija. Dobiveni eksperimentalni rezultati su bili uspoređeni s temperaturama faznih transformacija sistema Fe-C, Fe-Mn a i s temperaturama izračunatih iz dostupne literature. Termodinamičko-kinetički model skrućivanja IDS je rabljen za izračun karakterističnih ravnotežnih temperatura faznih transformacija istraživanih sustava.

Ključne riječi: čelik, DTA, temperature, fazne transformacije

INTRODUCTION

Structure and properties of complex metallic systems, on the basis of Fe-C, are still object of extensive research [1, 2]. To this date a lack of experimental material data of about these systems (of real steel grades) still persists and moreover the presented data mentioned e.g. in works [1, 2] differ.

In recent years considerable number of mathematical models [3] enabling calculation of thermo-physical and thermo-dynamical data.

Obtaining of credible results requires, however, necessarily also exact experimental data characterising thermo-physical material properties. Typical necessary data are temperatures of phase transitions [2, 4-7], latent heats of phase transitions [4, 6], specific heats [8], surface tensions [9, 10] and other important data (thermal conductance, etc.).

It is possible to find some data in literature, but only very rarely all the necessary data are available. The material data were measured primarily for many binary and ternary systems. Smaller amount of data was obtained for more complex systems on the basis of Fe-C. Many of the obtained data are valid for certain temperature interval only. Many systems were investigated in

low-temperature region (20-1000 °C) [4, 6, 7] and seldom in high-temperature (above 1000 °C) [1, 2, 5].

The paper reports about study of real multi-component systems in the high-temperature region. The temperatures of liquidus, solidus and other phase transitions were investigated. Due to a lack of exact experimental data in this area, and also due to necessity to use these data as input data for many simulation programs, numerical [3, 11, 12], physical [13, 14] models and requirements of practice (casting conditions), the investigation of multi-component metallic alloys based on Fe-C, is still highly topical theme.

THEORETICAL BACKGROUND OF PHASE TRANSITIONS OF IRON BASED SYSTEMS

Fe-C system

The transitions in liquidus-solidus region are highly important in Fe-C based systems [1, 15]. At cooling process of a melt in the Fe-C system [16], Figure 1, in concentration interval 0-0,53 wt.% of carbon, the system starts to solidify according to the AB curve.

Subsequent cooling leads to solidification of remaining amount of melt (δ -ferrite is formed). In the concentration interval from 0-0,08 wt.% of carbon the δ -ferrite creation is finished according to the AH curve (solidus). In the concentration interval 0,08-0,16 wt.% of carbon

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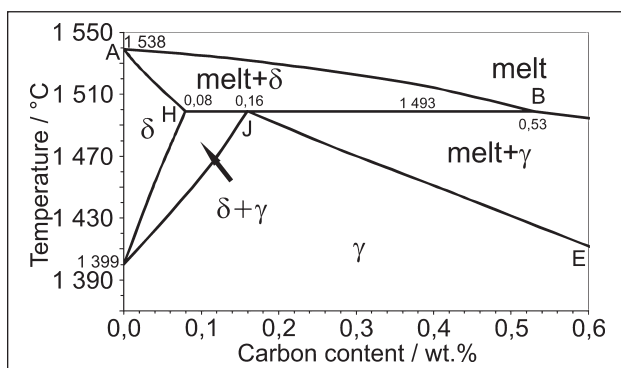


Figure 1 Equilibrium Fe-C phase diagram

(HJ-curve) the hypo-peritectic, and in the concentration interval 0,160-0,53 wt.% the hyper-peritectic reaction (curve JB) takes place. It is possible to describe the peritectic reaction of Fe-C based system by the following scheme: melt + δ -ferrite \rightarrow austenite (γ). Austenite is formed from melt and δ -ferrite. Peritectic reaction takes place at 1493 °C. The solidus curve of Fe-C diagram is denoted by letters AHJE.

Fe-Mn system

The melt of Fe-Mn system [17], Figure 2, starts to solidify according to the KL curve, δ -ferrite is formed. Points KMPO denote δ -region. Austenite (γ) starts to precipitate according to the OR curve. The main constituents of our analysed samples were carbon and manganese. Therefore the comparison of the obtained data with polythermic sections of Fe-C-Mn system would be more appropriate. However, only very little information about Fe-C-Mn system in the area of polythermic phase diagrams were found. Only isothermal sections of Fe-C-Mn system were found [18].

The shift of temperatures of phase transitions and their mechanism is influenced mainly by individual admixed and alloying elements.

Table 1 shows the influence of some elements on shifting of the characteristic A_4 -temperature [16].

Theoretical calculations, IDS

Experimentally obtained temperatures of phase transitions are compared with theoretical temperatures calculated according to the relations published in [19-23]. These relations make it possible to calculate temperatures of liquidus (T_L) and solidus (T_S). These relations are mostly assumed as equilibrium.

Apart from these relations the IDS software [3] was also used for calculation of temperatures of phase transitions. This software enables calculation of equilibrium and non-equilibrium (for cooling process) temperatures of phase transitions. Calculation of temperatures of phase

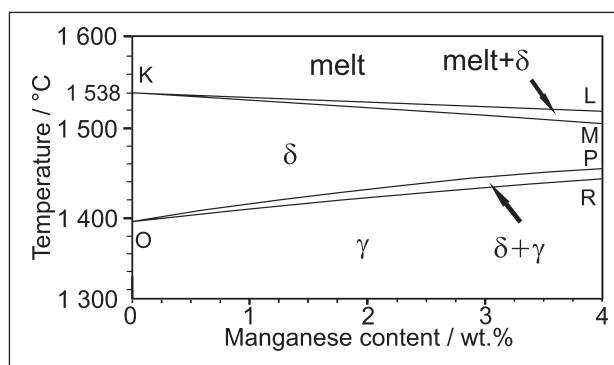


Figure 2 Equilibrium Fe-Mn phase diagram

Table 1 Influence of selected elements on shift of A_4 , the γ - δ (δ - γ) transition temperature position of Fe-C based alloys [16]

Shift of A_4 temperature	Element
$A_4 \downarrow$	Si, Al, Mo, P, V, Ti, Sn, S, Cr
$A_4 \uparrow$	Mn, Ni, Cu, C, Co

transitions assumes some simplifications [3]. Temperatures of phase transitions of alloys 1-4 (equilibrium conditions), Table 2, were calculated.

Experiment

Experimental measurements were made using the laboratory system Setaram SETSYS 18TM and DTA (Differential thermal analysis). High-purity dynamic inert atmosphere around the sample was held (He, purity > 99,9999 %).

Samples were taken from real castings of steels and machined into the form of cylinders. The mass of the cylinders was approximately 150 mg. Chemical compositions of the analysed samples are given in Table 2.

Analyses of the samples were made in corundum crucibles. Temperature calibration was performed using Ni (5N). Prepared samples were analysed at heating and cooling rates of 7 °C·min⁻¹. From each real grade of steel three pieces of samples were analysed (temperatures of phase transitions were taken as average of three obtained temperatures for each sample). Mean root-square error was evaluated (for temperatures of γ - δ transition \pm 6 °C, solidus temperature \pm 2 °C and temperature of liquidus \pm 1 °C). Relatively high degree of super-cooling was observed at cooling process.

RESULTS AND DISCUSSION

Temperatures of liquidus, solidus and temperatures in γ - δ region were obtained. These temperatures were obtained on the basis of evaluation of DTA-curves. Figure 3 shows DTA curves obtained for the analysed alloys (samples) 1-4 at the heating rate of 7 °C·min⁻¹.

Table 2 Chemical composition of analysed samples of steels / wt.%

Sample	Composition / wt.%														
	C	Mn	Si	P	S	Cu	Ni	Cr	V	Al	Ca	Ti	Mo	Sn	Nb
1	0,050	1,160	0,162	0,011	0,011	0,080	0,030	0,050	0,004	0,03	0,002	0,002	0,002	0,00	0,03
2	0,067	1,050	0,195	0,008	0,006	0,500	0,256	0,690	0,007	0,03	0,002	0,003	0,001	0,01	0,00
3	0,164	0,357	0,201	0,019	0,007	0,060	0,014	0,050	0,001	0,03	0,002	0,000	0,000	0,01	0,00
4	0,186	1,310	0,264	0,012	0,016	0,080	0,043	0,050	0,002	0,03	0,002	0,001	0,000	0,01	0,00

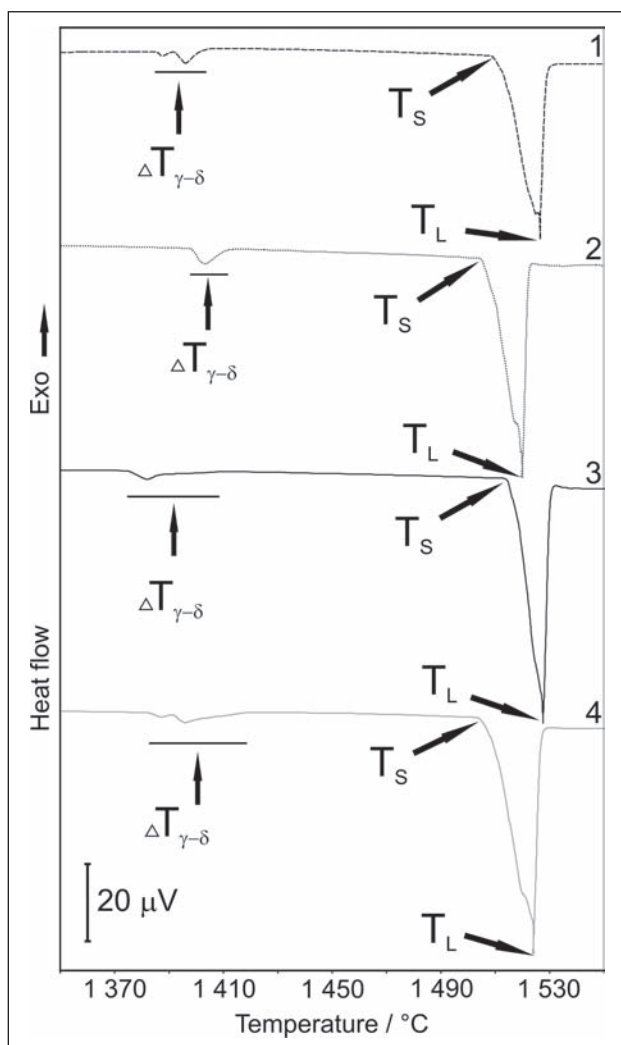


Figure 3 DTA curves of the analysed alloys, heating rate $7\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

Peaks on DTA curves denote running phase transitions. Small jumps close to T_L (few degrees below T_L ; before peak top temperature) are probably caused by movement of the sample in a crucible. Cylindrical samples changed during melting their shape to the small droplet. The droplet moved and covered partially crucible bottom and partially crucible wall. The movement of sample caused this spurious effect.

Characteristic transition temperatures are shown in Figure 3, Table 3 (T_L denotes liquidus temperature; T_S solidus temperature; $T_{S,\gamma-\delta}$ temperature of start of $\gamma-\delta$ transition; $T_{1,\gamma-\delta}$ onset temperature of the second peak of $\gamma-\delta$ transition; $T_{2,\gamma-\delta}$ termination temperature of the second peak of $\gamma-\delta$ transition, only sample 4; $T_{E,\gamma-\delta}$ termination temperature of $\gamma-\delta$ transition; $\Delta T_{\gamma-\delta}$ denotes temperature interval, in which the $\gamma-\delta$ transition runs).

Temperature interval $\Delta T_{\gamma-\delta}$ varies from 21–48 $^{\circ}\text{C}$. The widest temperature interval was observed for the sample 3 and sample 4. Relatively narrow temperature interval was observed for the samples 1 and 2. Table 4 shows transition temperatures calculated according to IDS [3], equilibrium calculations (T_L denotes liquidus temperature; T_S solidus temperature; aus+ start of austenite creation; MnS start of MnS creation; Fer- disappearance of delta ferrite; NbC start of niobium carbide creation).

Table 3 Experimental temperatures of phase transitions, heating

Exp.	Temperature / $^{\circ}\text{C}$					
	$\Delta T_{\gamma-\delta}$				T_S	T_L
Sample	$T_{S,\gamma-\delta}$	$T_{1,\gamma-\delta}$	$T_{2,\gamma-\delta}$	$T_{E,\gamma-\delta}$		
1	1383	1392	-	1409	1508	1526
2	1398	-	-	1419	1506	1521
3	1375	1393	-	1423	1514	1528
4	1385	1392	1403	1426	1503	1524

Tables 5 and 6 present temperatures of solidus (T_S) and liquidus (T_L) temperatures calculated using relations published in [19–23].

Table 4 Calculated temperatures of phase transitions, IDS

IDS	Temperature / $^{\circ}\text{C}$					
	T_L	aus+	T_S	MnS	Fer-	NbC
1	1525	1464	1493	1440	1430	1035
2	1521	1485	1484	1370	1452	-
3	1520	1487	1480	1320	1479	-
4	1512	1485	1464	1466	1483	-

Significant differences could be caused by the dynamics of DTA experiments. Primarily, the peak temperatures are shifted to higher temperatures in dependence on the heating rate [4, 5, 25]. Experimentally obtained solidus temperatures of samples 1 and 2 agree with the values calculated according to [19, 22]. Considerable differences are between other calculated and experimental values of solidus temperature.

Table 5 Calculated solidus temperatures

Calc.	Temperature / $^{\circ}\text{C}$				
	T_S				
Sample	[19]	[20]	[21]	[22]	average
1	1512	1477	1510	1510	1502
2	1508	1479	1506	1506	1500
3	1494	1483	1486	1486	1487
4	1481	1470	1472	1472	1474

Experimentally obtained liquidus temperatures are for the samples 1 and 2 in very good agreement with the temperatures of liquidus calculated using IDS [3] and relations in [19–23]. Higher differences were observed for the samples 3 and 4. Differences could have been partially caused by possible decarburization of samples [4, 24].

Table 6 Calculated liquidus temperatures

Calc.	Temperature / $^{\circ}\text{C}$				
	T_L				
Sample	[19]	[20]	[21]	[23]	average
1	1524	1521	1525	1525	1524
2	1519	1518	1521	1519	1519
3	1518	1516	1519	1518	1518
4	1511	1507	1513	1511	1511

Temperatures of phase transitions were plotted in Figures 4 and 5. Figure 4 compares experimental temperatures with Fe-C equilibrium diagram and Figure 5 with Fe-Mn equilibrium diagram. Admixed and alloyed elements shift significantly the temperatures of phase transitions.

The lowest content of admixed and alloyed elements contains the alloy 3, temperatures of solidus and liquidus are the highest. The lowest solidus was detected for the

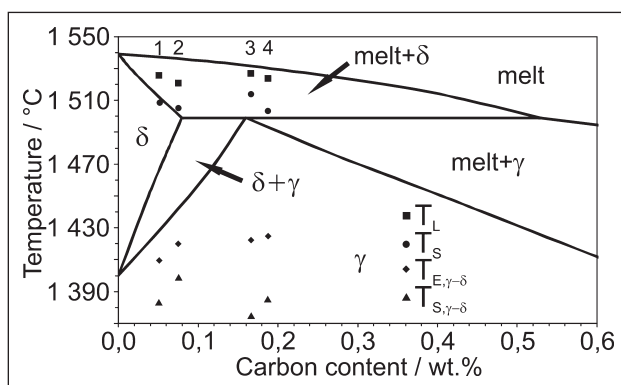


Figure 4 Comparison of experimental phase transition temperatures (heating) with equilibrium diagram Fe-C, small digits 1-4 denote samples 1-4

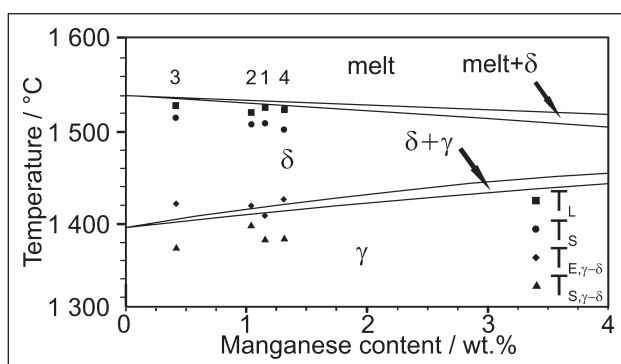


Figure 5 Comparison of experimental phase transition temperatures (heating) with equilibrium diagram Fe-Mn, small digits 1-4 denote samples 1-4

alloy 4. That is first of all due to the highest carbon and manganese content. Liquidus temperatures are lower than liquidus line of Fe-C diagram. Experimental temperatures of solidus and liquidus are lower than liquidus and solidus lines of Fe-Mn system, Figure 5.

Alloys 2 and 3 melt in narrower temperature interval (highest and lowest content of alloyed elements), to the contrary the widest melting interval was observed in the system 1 (18 °C) and system 4 (21 °C). Experimentally obtained phase transition temperatures correspond better with the Fe-Mn diagram, Figure 5.

The narrow temperature interval for γ - δ transition was observed for the samples 1 and 2. Carbon has the main influence on the width of this interval. Temperature interval for the samples 3 and 4 is 48 °C and 41 °C (high content of carbon). The γ - δ transition proceeds probably in one stage (sample 2), two stages (samples 1 and 3) and in three stages in the alloy 4, see Figure 3, DTA curves.

CONCLUSIONS

Paper presents results of investigation in the field of phase transition temperatures of real grades of micro-alloyed steels using DTA. Experimental and calculated temperatures of phase transitions are presented. Obtained experimental data and their comparison with theoretical calculations show in some cases significant differences. Due to a lack of exact experimental data and differences between them, and difference between experimental and theoretical data, the investigation of material properties of metallic alloys based on Fe-C is still highly topical theme. The complexity of multi-

component systems caused by presence of admixed and alloyed elements, interactions of elements, segregation phenomenon, conditions of solidification of real alloys (at production) have great impact on the resulting data. The kinetics of phase transitions, influenced by DTA experiments, may also have corresponding influence.

From the technological point of view the temperatures of solidus and liquidus are very important for the optimal adjustment of casting conditions. Exact and reliable data (serving as input data) are also necessary for many simulation programs and calculations.

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