LATENT HEATS OF PHASE TRANSITIONS OF Fe-C BASED METALLIC SYSTEMS IN HIGH TEMPERATURE REGION

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Abstract

The paper deals with the study of latent heats of phase transformations of model Fe-C based metallic alloys and real grades of steels in high-temperature region (above 1000°C). The investigation was focused on the study of latent heats of $\gamma\leftrightarrow\delta$ transformation and melting (solidification). Six model alloys were prepared and studied. Nine real grades of steels were studied as well. Latent heats of phase transformations were obtained using DTA method (differential thermal analysis). Setaram Setsys 18_{TM} (TG/DTA/DSC/TMA) modular experimental system was used for measurements. Controlled heating/cooling of alloys was conducted at the rate of 7 K/min. The influence of carbon, manganese and other alloyed and admixed elements on magnitude of latent heats of phase transformations was investigated. Experimental values of latent heats of $\gamma\rightarrow\delta$ phase transformation range 10-18 J/g and for transformation $\delta\rightarrow\gamma$ range 11-18 J/g. Latent heat of melting is within the range of 165-261 J/g and that of solidifying is within 162-294 J/g. Comparison of the obtained experimental data with the data presented in the literature was also carried out. Comparison of calculated latent heats (IDS software) with experimental values was made. It follows from comparison of the obtained results with the data accessible in the literature that there is a lack of experimental data.

Keywords: latent heat, Fe-C, steel, thermal analysis, DTA, gamma-delta, melting, solidifying

1. INTRODUCTION

Material properties, thermo-physical and thermo-dynamical data belong to the most important data [1-11]. Many of these data, temperatures of phase transitions [7-11], latent heats of phase transitions [8, 10], specific heats [12], surface tensions [13-15] and other important data (thermal conductance, etc.), can be calculated using many simulation programs, e.g. IDS/software (Solidification Analysis Package). 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) [8, 10, 11] and seldom in high-temperature region (above 1000°C) [1, 9]. Obtaining of credible results requires, however, necessarily also exact experimental data characterising thermo-physical material properties. It is suitable to support these data by structural and phase analysis. 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 about these systems still persists and moreover the presented data mentioned e.g. in the works [1, 2] differ. The paper reports about study of six model alloys based on Fe-C and nine real multi-component alloys in the high-temperature region. The latent heats of $\gamma\leftrightarrow\delta$, melting and solidifying 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 [16-18], physical [19, 20] models and requirements of practice (casting conditions), an investigation of Fe-C based metallic alloys is still highly topical theme.

2. EXPERIMENT

Experimental measurements were made using DTA (Differential Thermal Analysis) and performed with use of the laboratory system Setaram SETSYS 18_{TM}. In order to ensure a high-purity (dynamic) inert atmosphere the protective gas (Ar, 6N) was also cleaned in the getter. Controlled rate of heating/cooling (7 K/min) of alloys was conducted. A high-purity atmosphere was ensured for analysis, but in spite of that some oxidation and decarburisation might have occurred in some samples [8]. It can, however, be presumed on the basis of experience and previous measurements of loss of carbon in the prepared alloys at our working site after DTA-analyses that loss of carbon can be quite considerable. DTA-analyses of the samples were made in corundum crucibles. Temperature and enthalpic calibration was performed using standard metals: In, Sn, Bi, Pb, Zn, Al, Ag, Au, Cu, Ni and Pd, purity 5N.

Six model alloys with graded carbon content were prepared by vacuum melting of plasma iron ingots with addition of graphitic carbon. It is probable that during this melting a reaction between the added carbon and oxygen has occurred, which created CO. The more carbon was added during vacuum melting, the more oxygen reacted with carbon and created CO (which was proven also by an increased pressure in vacuum furnace). Nine real grades of steel were taken from continuously cast slabs. The mass of the cylinders needed for DTA was approximately 150 mg. Chemical composition of the analysed samples is given in **Table 1**.

Table 1. Chemical composition of analysed samples, wt.%

Sample		C	Mn	Si	P	S	Cr	Ni	Mo	V	Al	Cu	O
Fe-C	1	0.002	0.021	0.005	0.004	0.008	0.003	0.026	0.002	0.012	0.001	0.006	0.0430
	2	0.004	0.009	0.004	0.004	0.007	0.002	0.023	0.002	0.007	0.001	0.006	0.0880
	3	0.005	0.026	0.006	0.004	0.008	0.003	0.024	0.002	0.013	0.001	0.006	0.0380
	4	0.038	0.025	0.014	0.004	0.008	0.004	0.026	0.002	0.015	0.002	0.006	0.0020
	5	0.167	0.020	0.007	0.004	0.008	0.003	0.025	0.002	0.013	0.003	0.006	0.0005
	6	0.197	0.022	0.019	0.004	0.008	0.004	0.024	0.002	0.017	0.005	0.006	0.0004
Steel	1	0.050	1.160	0.162	0.011	0.011	0.050	0.030	0.002	0.004	0.027	0.080	-
	2	0.060	1.345	0.191	0.012	0.010	0.050	0.028	0.000	0.016	0.028	0.070	-
	3	0.067	1.050	0.194	0.007	0.005	0.690	0.256	0.001	0.007	0.033	0.500	-
	4	0.075	1.355	0.195	0.017	0.012	0.050	0.050	0.000	0.035	0.019	0.090	-
	5	0.078	1.165	0.213	0.015	0.011	0.060	0.375	0.003	0.039	0.036	0.105	-
	6	0.164	0.357	0.201	0.019	0.007	0.050	0.014	0.000	0.001	0.029	0.060	-
	7	0.183	1.340	0.287	0.011	0.009	0.050	0.036	0.000	0.003	0.031	0.130	-
	8	0.185	1.280	0.264	0.015	0.011	0.090	0.216	0.029	0.005	0.029	0.170	-
	9	0.186	1.310	0.264	0.012	0.016	0.050	0.043	0.000	0.002	0.033	0.080	-

3. RESULTS AND DISCUSSION

After a proper temperature and enthalpic calibration analyses of the samples were performed. The result of DTA analysis is the so called DTA-curve. DTA-curves of the analysed samples of Fe-C based alloys are presented in Figures 1 and 2. These figures present DTA-curves obtained at heating (7 K/min). Peaks of $\gamma \rightarrow \delta$ and melting were observed.

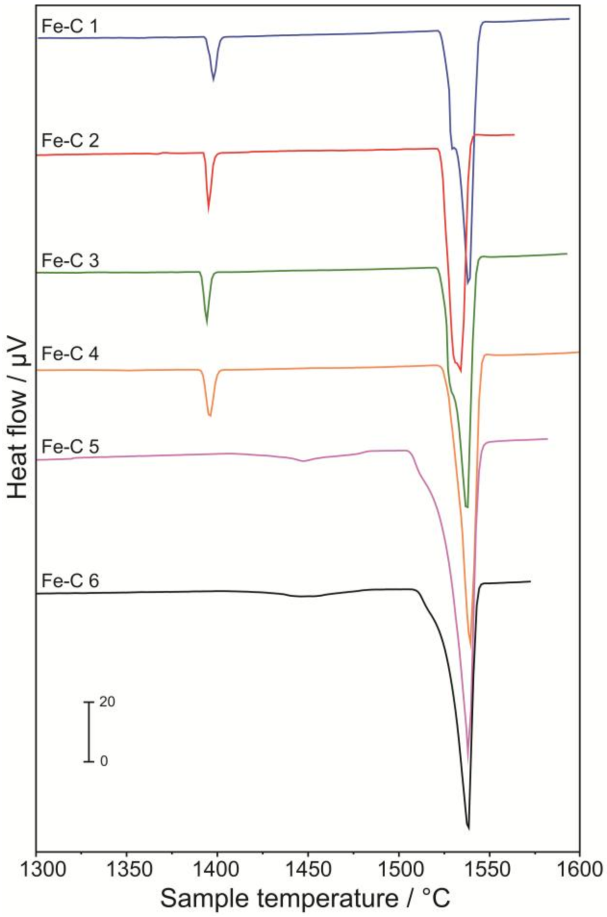

Fig. 1. DTA–curves of model alloys Fe-C, heating 7 K/min.

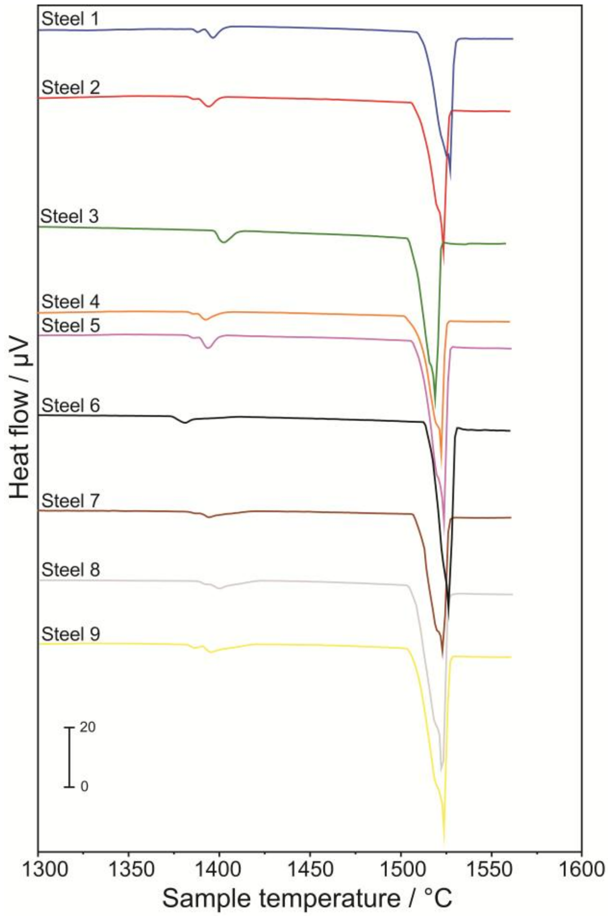

Fig. 2. DTA–curves of real grades of steels, heating 7 K /min.

The areas of peaks (peak area corresponds to the heat absorbed/released by the sample during running phase transition in it) were calculated using the SETSOFT program. The temperatures of characteristic phase transitions were evaluated as well. Latent heats of phase transitions were calculated using enthalpic calibration. Values of latent heats are given in **Tables 2** and **3**.

DTA-analysis of sample Fe-C 1 was performed also at the heating rate of 2 K/min, Figure 3. The reason for performing DTA at such a low heating rate was to create clearer area (DTA-curve) between 1350-1425°C. The peak of $\gamma \rightarrow \delta$ transition seemed to be not so sharp at its start (this phenomenon may indicate connection of more than one thermal effect). The DTA-analysis performed at the heating rate of 2 K/min confirmed existence of more than one thermal effect. At the DTA-curve obtained at the heating rate of 2 K/min two peaks were observed contrary to the one at the DTA-curve obtained at the heating rate of 7 K/min. With high probability these two peaks correspond to the phase transitions, which take place in the Fe-O system, see figure 4. No polythermic phase diagrams (cuts) for Fe-C-O system were found in the available literature. It is obvious from DTA-curves obtained for real samples (steels) that they reveal also two similar heat effects. These peaks could be with high probability attributed to the transitions connected with oxygen in the $\gamma \leftrightarrow \delta$

region also. In the future more attention will be paid to this research area. In this paper the peaks (peak) at heating rate of 7 K/min were evaluated. Latent heats from γ↔δ, melting and solidifying were evaluated, see **Tables 2** and **3**.

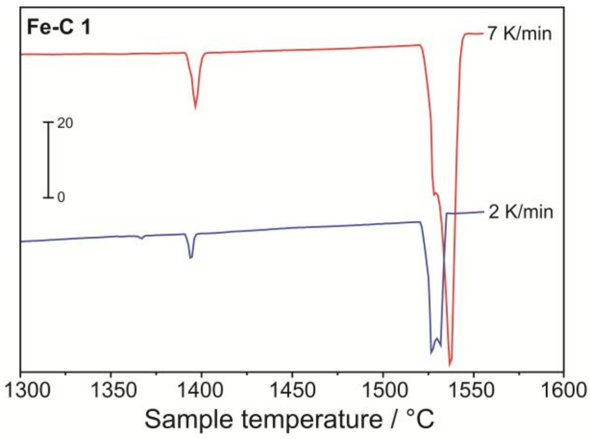

Fig. 3. Comparison of DTA-curve obtained at the heating rate of 7 K /min and DTA-curve obtained at the heating rate of 2 K/min.

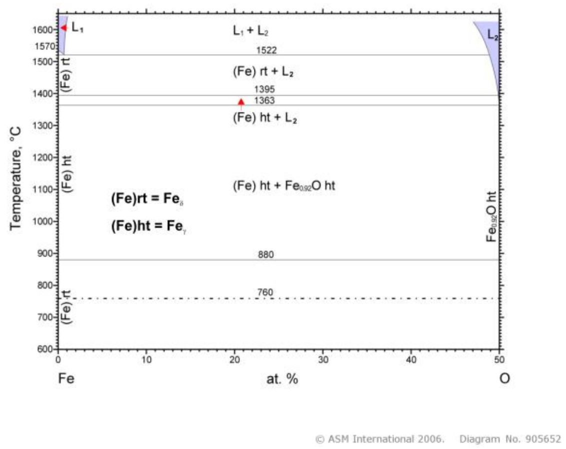

Fig 4. Fe-O equilibrium phase diagram [21]

Table 2 shows latent heats of γ↔δ transition. Only small differences were observed between the values obtained at heating. The dependence of magnitude of latent heats on carbon content is obvious. The higher the carbon content in the sample, the higher the value of heat absorbed or released from the sample. Latent heat for γ→δ transition of the sample Fe-C 2 is slightly higher than the heat of the samples with similar composition. Latent heats differ significantly for the samples Steel 3 and Steel 6. The presence of higher Cr and Ni content and lower Mn content in the sample Steel 3 could have a substantial impact on amount of latent heat. The lower value of latent heat for the sample Steel 6 corresponds with high probability to the low Mn content.

Table 2. Latent heats of γ↔δ transformation, J/g

Sample	Fe-C						Steel								
	1	2	3	4	5	6	1	2	3	4	5	6	7	8	9
wt.% C	0.002	0.004	0.005	0.038	0.167	0.197	0.050	0.060	0.067	0.075	0.078	0.164	0.183	0.185	0.186
γ→δ	9.9	13.0	9.6	12.1	16.0	14.1	13.1	12.3	13.8	10.5	12.3	11.0	14.2	14.0	17.5
δ→γ	11.5	-	-	-	11.6	11.3	15.0	15.4	15.2	13.7	16.1	13.5	16.6	17.5	16.0

Latent heats were obtained also for cooling, see **tables 2** and **3**. Latent heats values obtained for cooling could not be taken as authoritative. At cooling process high degree of under-cooling was observed (even by dozens of degrees). Solidification and δ→γ transition were observed at lower temperature and heat released at cooling was substantially higher (accumulation of heat in the samples was observed).

Table 3 shows latent heats of melting. A dependence of the obtained values of latent heats on chemical composition (primarily on carbon content) was assumed. The obtained values, however, do not show unambiguous trend. Experimentally obtained latent heats of melting and solidifying of real steel samples are higher in comparison with latent heats of model alloys. It could be attributed to the higher manganese content in real samples. The values of melting latent heats obtained experimentally are between 165-261 J/g. The values calculated using the IDS software (latent heat of solidification) are within the interval of 238-260 J/g. The values calculated according to the IDS demonstrate ambiguous trend. The latent heat increases with the growing carbon content. The influence of carbon content on magnitude of latent heat was observed. Latent heats were calculated for equilibrium conditions and only carbon was included in calculations. Many factors may exist that influence the resulting values of latent heats of melting. Possible oxidation (even very thin oxide layer on the sample) could prevent good contact with the crucible (smaller amount of heat is detected). Secondly, decarburisation (different degree of decarburisation in the samples during melting) could substantially change properties of the samples and thus the latent heat. Furthermore, movement of the samples during melting could have some impact on the obtained values. The movement of samples in crucible during DTA analysis could cause disturbing effects on the melting peak.

Table 3. Latent heats of melting and solidifying, J/g

Sample	Fe-C						Steel								
	1	2	3	4	5	6	1	2	3	4	5	6	7	8	9
wt.% C	0.002	0.004	0.005	0.038	0.167	0.197	0.050	0.060	0.067	0.075	0.078	0.164	0.183	0.185	0.186
melting	165	205	172	172	261	203	223	210	224	187	208	220	230	246	219
solidifying	192	182	211	178	194	162	254	243	275	187	236	284	279	294	267
IDS	247	247	247	244	259	260	241	240	238	240	243	258	258	258	258

It was almost impossible to find some data for $\gamma\leftrightarrow\delta$ transition in accessible literature. The work [22] presents for latent heat of $\gamma\leftrightarrow\delta$ transition in pure iron 15 J/g. Most of experimentally obtained values of latent heats ($\gamma\leftrightarrow\delta$ transition) are lower than the value for pure iron in the work [22]. For melting process of pure iron the work [22] introduces the value of 247 J/g. A value higher than 247 J/g was calculated only for the sample Fe-C 5.

In the work [23] the values for latent heats of melting within the range of 210-285 J/g (carbon steels, carbon content between 0.03-0.17 wt.%) are presented. The paper [1] presents latent heats of solidifying in the range of 180-200 J/g (carbon content between 0.04-0.16 wt.%). Authors [24] present for steel with the carbon content of 0.22 wt.% the value of 185 J/g. The range of the published values of latent heats of melting and solidifying is considerably wide, 180-285 J/g. Almost all of our evaluated values of latent heats belong to the published interval.

4. CONCLUSIONS

Latent heats of $\gamma\leftrightarrow\delta$ transition, melting and solidifying were obtained by DTA method for Fe-C model alloys and for real samples of steel. The obtained latent heats were compared with the values of latent heats published in literature. Moreover influence of chemical composition on magnitude of latent heats was investigated. Latent heats of phase transitions are dependent on admixed and alloying elements. Primarily, carbon and manganese contents influence the value of latent heat. Results for the Fe-C alloys and probably also for some real poly-component samples of steel may be influenced also by presence of oxygen in the samples. It follows from bibliographic search and from comparison of available data with the data obtained experimentally that lack of experimental data still persists, and moreover differences exist between the data published in literature.

The basic study in the field of latent heats was performed. This area will be studied also in the future. New experimental equipment STA Netzsch F3 Jupiter was bought in the frame of RMSTC project (*Regional Materials Science and Technology Centre*) and it will help to widen the current possibilities of research. Possibilities of this equipment substantially expand the possibilities of research at our working site in the field of acquisition of exact materials data (temperatures and latent heats of phase transformations, specific heats) under precisely defined conditions of heating and cooling processes using large samples.

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